
METAL-ORGANIC FRAMEWORKS AS SUPPORTS FOR FUNCTIONAL MATERIALS

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Declaration

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name, in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission in my name, for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and where applicable, any partner institution responsible for the joint-award of this degree.

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Steven Tsoukatos

3/2/2022

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Abbreviations

AC	Activated carbon
AcOH	Acetic acid
ADP	Atomic displacement parameter
BET	Brunauer-Emmett-Teller
Bipy	2,2'-Bipyridine
BTC	1,3,5-benzenetricarboxylic acid
CCS	Carbon capture and sequestration
CCU	Carbon capture and utilisation
CM	Carbon-based material
CSD	Cambridge Structural Database
DCM	Dichloromethane
DFT	Density functional theory
DMF	N,N-dimethylformamide
DNA	Deoxyribonucleic acid
EDC	Ethylene dichloride
EDX	Energy-dispersive X-ray spectroscopy
esd	Estimated standard deviation
Et ₂ O	Diethyl ether
EtOH	Ethanol
FID	Flame ionising detector
GC	Gas chromatograph
HAADF	High-angle annular dark-field
ICP-MS	Inductively coupled plasma mass spectrometry
IPCC	Intergovernmental Panel on Climate Change
IWI	Incipient wetness impregnation

Abstract

MDC	MOF derived catalyst
MeCN	Acetonitrile
MeOH	Methanol
MOF	Metal-organic framework
MOP	Metal-organic polyhedra
MS	Mass spectrometry
NOAA	National Oceanic and Atmospheric Administration
PPM	Parts per million
PSM	Post-synthetic metathesis
PVC	Polyvinylchloride
PXRD	Powder X-ray diffraction
RGA	Residual gas analyser
SBU	Secondary building unit
SCXRD	Single crystal X-ray diffraction
SEM	Scanning electron microscopy
SMe ₂	Dimethyl sulfide
STEM	Scanning transmission electron microscopy
TCD	Thermal conductivity detector
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
VC	Vinyl chloride
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Abstract

Metal-organic frameworks (MOFs) are intrinsically porous, crystalline materials formed from the assembly of metal nodes and organic linkers. The building-block type synthesis of MOFs has led to the formation of materials with well-defined structures, poised for specific applications. This extends to post-synthetic modification of MOFs, permitting the introduction of added relevance for certain applications. Such materials afforded by this process can be unique and inaccessible via traditional synthetic processes. In this thesis, two avenues for post-synthetic modification of MOFs with metals have been investigated. This includes the post-synthetic metalation of MnMOF-1 with Au(I) and assessment of MOF-derived Ru/TiO₂ for CO₂ methanation. Both areas highlight the exceptional ability MOFs display as support materials, exploiting their intrinsic properties in diverse ways. The work presented herein has the potential to influence further development of flexible materials and assist in progressing strategies for utilisation of captured anthropogenic CO₂ for value-added product formation.

The first chapter introduces MOFs and their conception from supramolecular chemistry. It discusses the dynamic properties MOFs can exhibit and the forms which they take, leading to inherently interesting materials with applicability to a wide range of different areas. It also introduces MOFs as versatile materials for heterogeneous catalysis, capable as acting as both a catalyst itself, and an exceptional support for a catalytic material in both fundamental and applied research.

Work in Chapter 2 details the investigation of ruthenium-loaded titanium MOF-derived catalysts (Ru/TiO₂) for CO₂ methanation. Two Ti MOFs, MIP-207 (Materials of the Institute of Porous Materials from Paris) and the MUV-10(X) (Materials of Universidad de Valencia) heterometallic Ti MOF family, were synthesised, loaded with Ru, and activated under both reaction conditions (*in operando*), and via calcination. The pure Ti MOF yielded catalysts prone to degradation with successive cycles, whereas the heterometallic Ti MOFs yielded highly active catalysts comparable to the most successful Ru/TiO₂ standard.

Chapter 3 explores the metalation of MnMOF-1, a flexible MOF with a free bis-pyrazole coordination site, with Au(I). Single crystal X-ray diffraction (SCXRD) and supporting analyses revealed quantitative metalation of a single pyrazole nitrogen of the bis-pyrazole site in its *anti* conformation, the first example of this coordination geometry in MnMOF-1. This unique post-synthetically metalated material displays retention of the intrinsic flexibility of the framework, otherwise lost for samples chelated to the bis-pyrazole moiety in the syn

Abstract

conformation. The material played a critical role in understanding the conformation and determining of coordination modulated on-off switching of flexibility of a Cu(I) complex in MnMOF-1, a novel mechanism in which to realise reversible structural flexibility in dynamic frameworks.

CHAPTER 1

INTRODUCTION

Chapter 1. Introduction

1.1 Background

1.1.1 Supramolecular Chemistry

At a fundamental level, chemistry is the study of matter, its properties, transformations and interactions.¹ By delving deeper, one can identify bonds, their formation and the resulting materials formed, as a critical cornerstone comprising the field.²⁻⁴ Understanding what drives bond formation and bond behaviour, enables the mysteries of matter to be unravelled, which signifies the importance of its understanding at the most elementary of levels.⁵⁻⁷

The nature of chemical bonds, specifically their types and properties, are derivative of the bonding atoms. The primary interaction, covalent, ionic and metallic, are predominantly the types evoked when considering chemical bonds. The ability to rationalise physical properties displayed by materials constructed from such bonds describes this phenomenon. Indeed, it is on this premise chemical bonding is first introduced and communicated to new students.⁸ However, chemical bonding extends further than the confines of primary bonds, giving rise to unique and dynamic materials.

Supramolecular chemistry, first coined by Jean-Marie Lehn in the latter stages of the 20th century, is often described as the chemistry beyond the molecule.⁹ In short, it is the chemistry of the intermolecular bond.⁹ Recognition and self-assembly processes dictated through these non-covalent, reversible intermolecular interactions, enable construction of supramolecular assemblies, or ‘supermolecules’, from simple, smaller molecular building blocks.^{10,11} Generally, these interactions are weaker than covalent bonds and include hydrogen bonding, dipole-dipole interactions, van der Waals forces, halogen bonding, π - π interactions and metal-ligand interactions.¹²⁻¹⁸

The surge of activity into the field is attributed to pioneering work conducted by Charles J. Pedersen, Jean-Marie Lehn and Donald J. Cram and their respective research into crown ethers and cryptands.^{9,19,20} The highly selective, structure specific, host-guest binding of compounds within the cavities of these materials, jointly earned them the 1987 Nobel Prize in Chemistry, highlighting the importance of molecular recognition in chemical systems. Meeting at the interfaces of chemistry, biology and physics, inspiration in the field of supramolecular chemistry is drawn from many facets. Throughout the past 50 years, research into

supramolecular chemistry has continuously grown and developed, giving rise to diverse advancements throughout these fields.²¹⁻²⁵

Supramolecular chemistry can be separated into two broad categories: self-assembly and host-guest chemistry (depicted in Figure 1.1). In supramolecular chemistry, self-assembly is defined as the formation of complex assemblies through spontaneous, reversible association of molecular building blocks.²⁶ Evidently, the spontaneity drives the *self*-assembly, but, critically, the reversibility afforded by the process enables the formation of complex assemblies. It is this reversibility that allows thermodynamically favoured assemblies to be produced through inherent error-checking and reorganisation during formation.²⁷ Comparatively, introduction of structural complexity to systems has traditionally been approached through organic synthetic pathways, in which covalent bonds are formed and broken through stepwise reactions. Using covalent bonds, however, is challenging, owing to the potential for multiple purifications following consecutive steps and onerous reaction conditions.²⁸ The high effort required to prepare materials this way, coupled with typically low yields, can render it less desirable. Conversely, as discussed previously, the advantages of constructing assemblies through intermolecular interactions lies in the inherent reversibility of the bond.²¹ Due to the weaker nature of intermolecular interactions compared to covalent bonds, bond breaking is achieved much more readily, allowing for reorganisation in the event of incorrect arrangement.

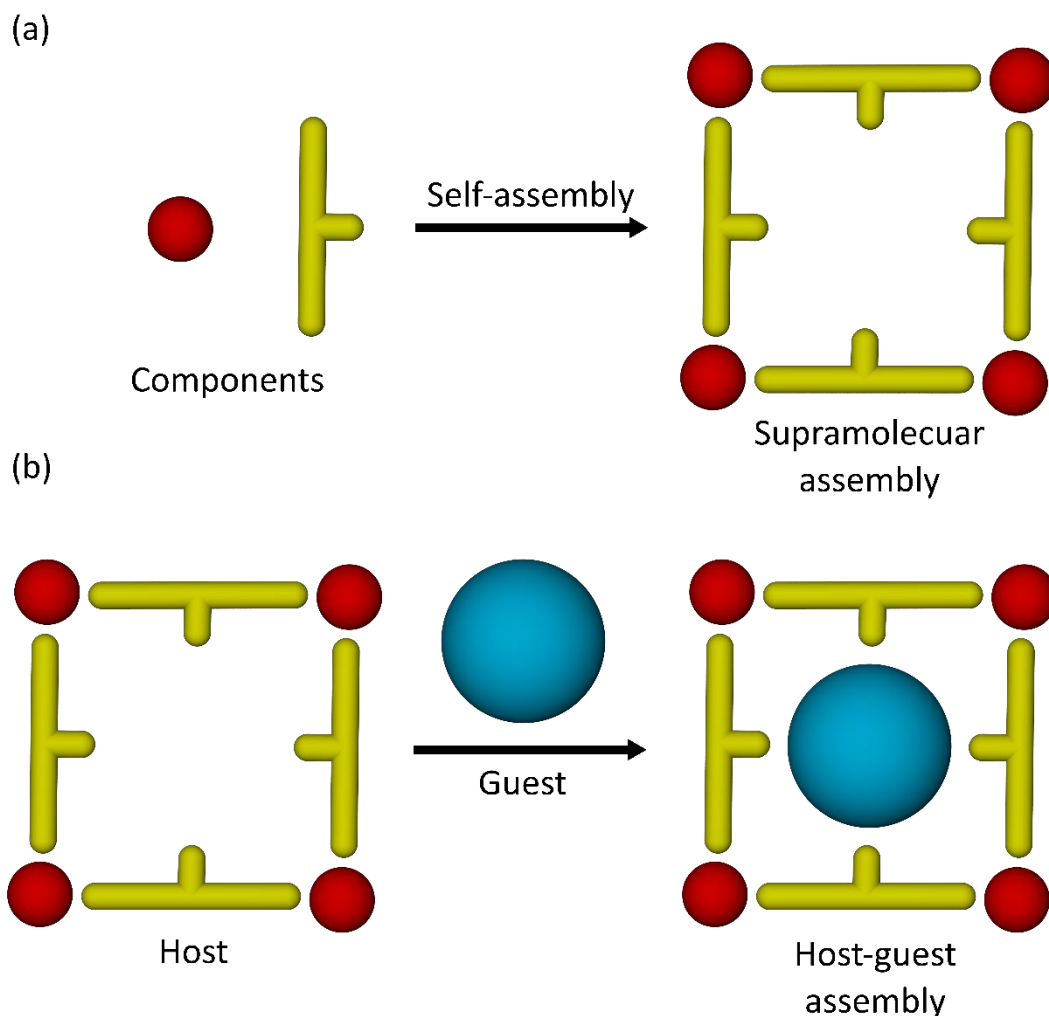


Figure 1.1: Example of supramolecular chemistry exhibiting both **(a)** self-assembly of individual components to form an ordered, complex assembly and **(b)** the formed supramolecular assembly binding a guest within its site-specific cavity via host-guest chemistry.

Host-guest chemistry, on the other hand, refers to the inclusion of small molecular guests within host materials at defined binding sites. The inclusion of guests within hosts proceeds similarly to self-assembly, through non-covalent interactions.

Many examples of both self-assembly and host-guest chemistry exist within nature. This is exemplified within the human body and other living organisms which depend on such interactions to function. The double helix structure adopted by deoxyribonucleic acid (DNA) elegantly illustrates self-assembly. The structure is held together through hydrogen bonds and π - π interactions between complimentary base pairs on polynucleotide chains.²⁹⁻³¹ The reversibility of the bonds offered by forming DNA through non-covalent interactions allows

for DNA replication and repair, without which life would cease to exist. Enzymes are another biological case in which both self-assembly and host-guest chemistry are evident and critical. Composed of polypeptides, enzymes fold into tertiary structures based upon the amino acid sequence.³² Through both covalent and non-covalent interactions, complex assemblies are accessible.³³ Once formed, the structure of enzymes plays a critical role in biological systems by catalysing numerous biochemical reactions.^{34,35} Indeed, the catalytic activity of enzymes is so powerful that they frequently exhibit superior performance in comparison to man-made catalysts.³⁶ Typically, this is a consequence of substrate binding to the enzyme within tailored and flexible binding sites integrated into the tertiary and quaternary structures adopted.³⁷ These natural examples, and the critical roles they play, provide a platform highlighting the importance of supramolecular chemistry and serve as inspiration for future work into the development of new materials.

1.1.2 Metallo-supramolecular Chemistry

Supramolecular chemistry is by no means confined to molecular building blocks. Indeed, the field has inspired inorganic chemists to consider coordination chemistry from a new perspective, specifically in the formation of both discrete and extended coordination assemblies. A subset of supramolecular chemistry, metallo-supramolecular chemistry, is concerned with the self-assembly of inorganic and organic building blocks into complex architectures, built around the metal-ligand bond.^{38,39} The strength of these bonds is dependent on the type of metal centre, and nature of the ligand, and can lead to variations in strength, typically between that of a hydrogen bond and a weak covalent bond.^{18,40} As a result, using metal-ligand bonds enables great control over the form and function of the final material.

Following initial work into the field, increasingly complex discrete architectures are constantly targeted, enabling access to more sophisticated functions.^{41,42} This has led to numerous intriguing structural architectures including molecular knots, helicates, molecular squares, coordination cages and metal-organic polyhedras (MOPs) (depicted in Figure 1.2).⁴³⁻⁵³ The near infinite array of metal and ligand molecular building blocks accessible permits the construction of the aforementioned discrete assemblies and the diverse forms observed.

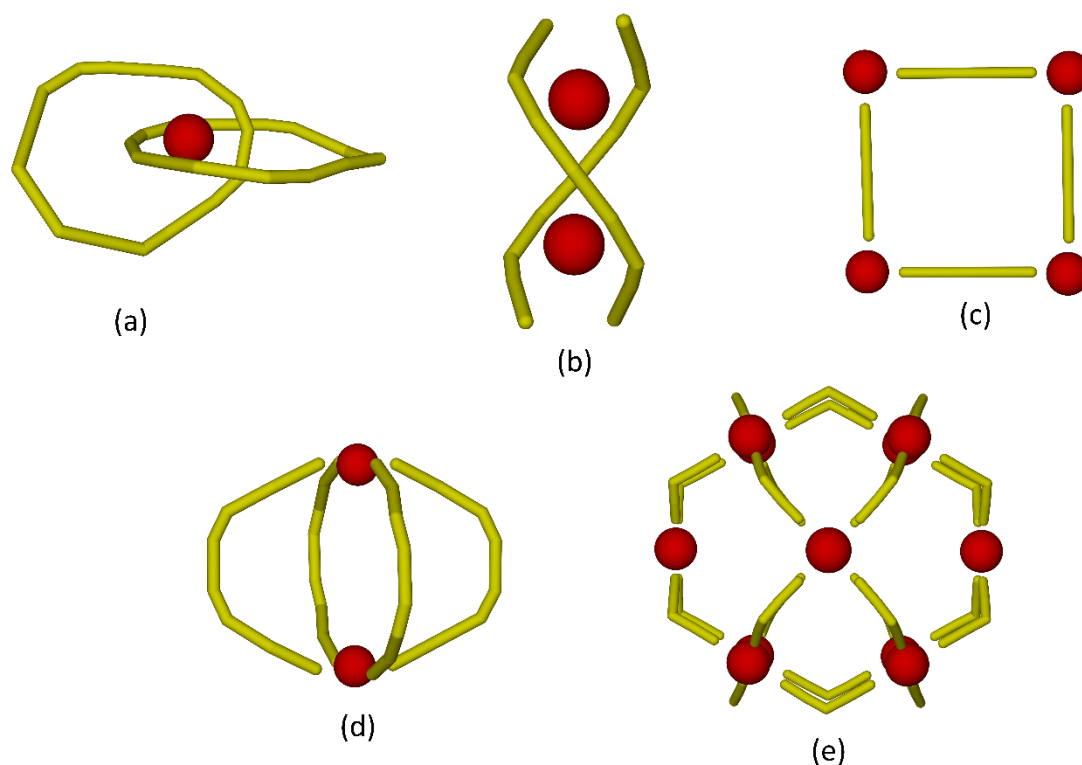


Figure 1.2: Schematic representation of discrete assemblies formed by inorganic (red) and organic (yellow) building blocks through metal-ligand bonds including **(a)** molecular knots, **(b)** helicates, **(c)** molecular squares, **(d)** coordination cages and **(e)** MOPs.

Owing to the modular design of metallo-supramolecular assemblies, information encoded within the complementary modules can be transferred into the final product. This is exhibited in the coordination geometries of metal ions, which are numerous (Figure 1.3), and can be used as orientation centres to direct the overall formation of the resulting assemblies. Additionally, unique optical, electrochemical, and magnetic properties characteristic of the employed metal components can be imbued.^{54,55} This is also evident in the organic components, in which the form and function of the ligand can be integrated.^{56,57} Consideration of anions and solvent systems, other components comprising the supramolecular system, must be given, as both can impact the final form adopted by the ensuing product. Through careful selection of components, materials with desired properties can be reached, either through the convergent combination of materials into discrete metallo-supramolecular assemblies, or through using divergent components leading to infinite metallo-supramolecular assemblies.⁵⁸

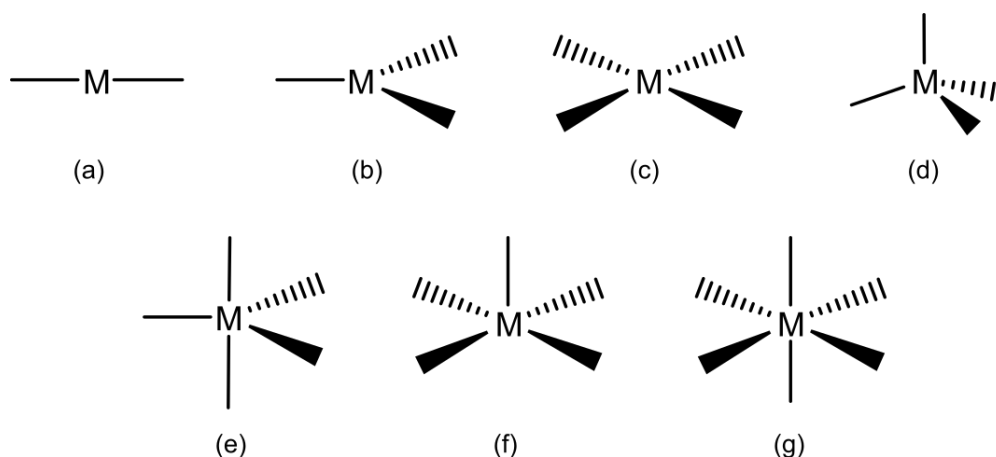


Figure 1.3: Some common coordination geometries exhibited by metal atoms used in metallo-supramolecular chemistry. Those depicted include **(a)** linear, **(b)** trigonal planar, **(c)** square planar, **(d)** tetrahedral, **(e)** trigonal bipyramidal, **(f)** square pyramidal and **(g)** octahedral.

1.2 Metal-Organic Frameworks

1.2.1 Overview

The formation, and potential, of extended metallo-supramolecular assemblies is illustrated by the thriving field of metal-organic frameworks (MOFs). MOFs are crystalline, porous materials constructed from inorganic, metal-based nodes and organic linker building blocks. The first origins of the field can be traced back to the first examples of crystalline, porous materials with pore sizes of approximately 1-2 nm, in the late 1980's and early 1990's respectively.^{59,60} It was not until 1995, however, when Yaghi coined the term metal-organic framework, that the true inception of the field came about.^{61,62} The term MOF is now synonymous with crystalline, permanently porous materials with high surface areas.⁶³ What has followed can only be described as an explosion of research into MOFs. The expansion is evident when considering currently, over 2000 MOF articles are published yearly.⁶⁴ This is further reflected by the MOF subset of the Cambridge Structural Database (CSD) in which more than 100000 different MOF structures have been deposited.⁶³ Of this 100000, 90000 are unique MOFs and, further to this, in excess of 500000 new, synthesised structures have been predicted.⁶⁵ The growth in the field over the past 25 years, and the sustained interest, has generated vast applications ranging from gas storage and separation to catalysis and drug delivery.⁶⁶⁻⁷³

Such diverse applications accessible from using MOFs, can be attributed to the modular building block-type synthesis, the inherent properties, and the propensity for tunability of the framework.^{66,74,75}

1.2.2 MOF Components

As mentioned, MOFs are constructed from metal-based nodes connected through coordination bonds by organic linkers to form 1, 2 and 3 dimensional structures (3D structure formation depicted in Figure 1.4).⁷⁶ As explored previously, using the principles of metallo-supramolecular chemistry allows for inherent error-checking and reorganisation during supramolecular assembly formation, which translates to MOF formation. This enables access to well-ordered materials which in turn gives rise to the intrinsic properties of MOFs, the crystallinity and porosity. The seemingly infinite possible combinations of metal nodes and organic linkers lead to a diverse library of different materials. Unique structures can have profound impacts on the surface areas, even reaching values of up to $7800 \text{ m}^2 \text{ g}^{-1}$.⁷⁷ The changing properties of reported MOFs are also evident in the framework's porosity and the formation of mutable structures, both chemically and physically.⁷⁸

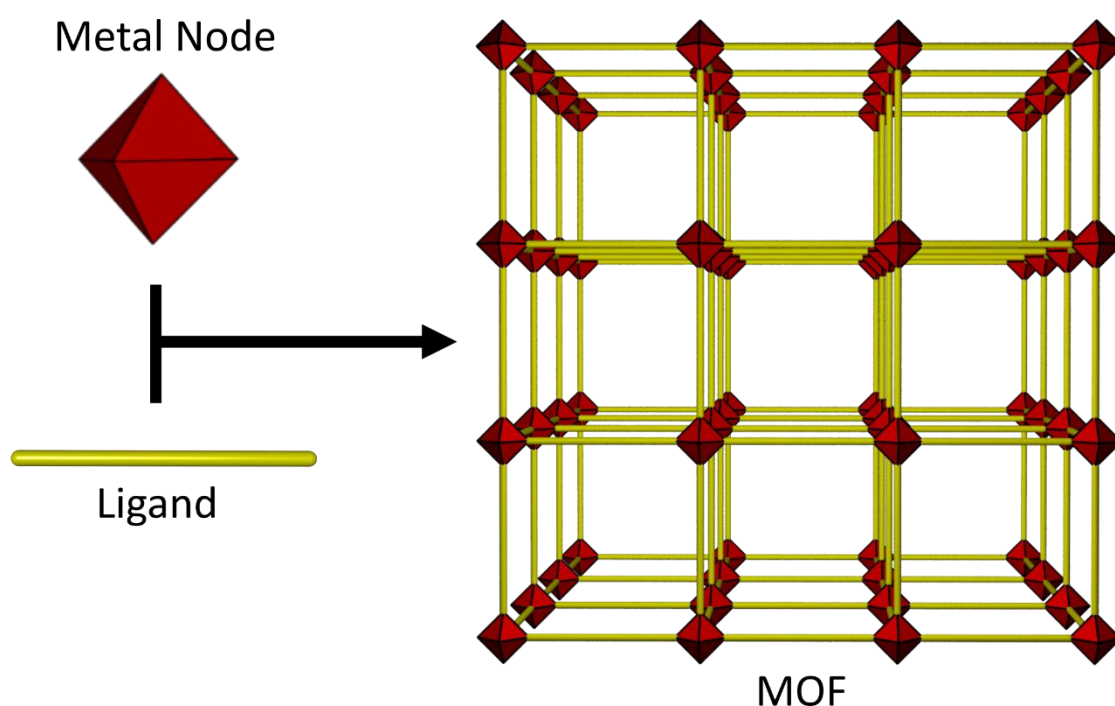


Figure 1.4: Schematic representation of the formation of a three-dimensional metal-organic framework through the self-assembly of metal nodes (red) and organic linkers (yellow).

Although chemists are unable to directly control the self-assembly of the molecular components during the formation of MOFs, avenues exist in ways to provide an element of design to direct the resulting frameworks assembly. Through careful selection of the metal and organic based components, specifically relating to the geometrical features offered, and controlling the reaction conditions, different materials can be targeted. Referred to as reticular chemistry, the judicious selection of MOF building blocks to form predicted structures based on the chosen components has been demonstrated for various periodically extended structures.⁷⁹ In highly connected nets, structure prediction based on the choice of precursors holds, but is shown to break down at low connectivities. Nevertheless, the geometries of the metal and organic based components are known to strongly influence the final structure of a given MOF.⁸⁰

Metals are one half of the major components used to construct a MOF. Typically, transition metals, especially those in the first row are targeted. The well documented coordination numbers and geometries of these metals can be attributed to this. Indeed, when metal atoms act as the sole node of the framework, the diverse range of accessible geometries provide numerous choices for potential framework formation. Typical geometries include linear, trigonal planar, square planar, tetrahedral, trigonal bipyramidal, square pyramidal and octahedral (depicted in Figure 1.3).⁸¹ This is not, however, an exhaustive list, and many other geometries, including distortions exist, providing a swath of potential metals to integrate into a framework.

Using metals as nodes, however, is not limited to single atoms. Incorporation of the metals into multinuclear clusters unlocks access to higher order connecting nodes. The expansion of metal nodes available offers more avenues to realise the desired design of a given framework. In a MOF setting, these multinuclear metal clusters are referred to as secondary building units (SBUs). These clusters have proven critical in advancing the MOF field as they provide two main advantages. Firstly, owing to the strong bonds (typically between the metal and oxygen and the added covalent carbon-carbon and carbon-oxygen bonds in the components of the SBU) introduced, enhanced thermodynamic stability is accessed.⁸² Secondly, SBUs provide enhanced mechanical and architectural stability as unlike for single metal nodes which form weaker bonds with neutral organic linkers with a high degree of conformational freedom, the metals centre within SBUs are locked in position owing to formation of strong, directional bonds.⁸² SBUs can be preformed, isolated and used as a building block, but more often individual clusters are unable to be isolated, and, as such, are typically formed *in situ* during

MOF synthesis.⁵⁸ Some of the most commonly encountered SBUs are the dinuclear paddlewheel square cluster, $[M_2(O_2CR)_4L_2]$, composed of four bridging acetates and two axial ligands, L, the trigonal prismatic cluster, $[M_3O(O_2CR)_6L_3]$, composed of six bridging acetates and three terminal ligands, L, and the tetrametallic cluster, $[M_4O(O_2CR)_6]$, composed of μ_4 -oxo²⁻ centre and six bridging acetates (depicted in Figure 1.5), where R represents the remainder of the molecule attached to the bridging acetates.^{83,84}

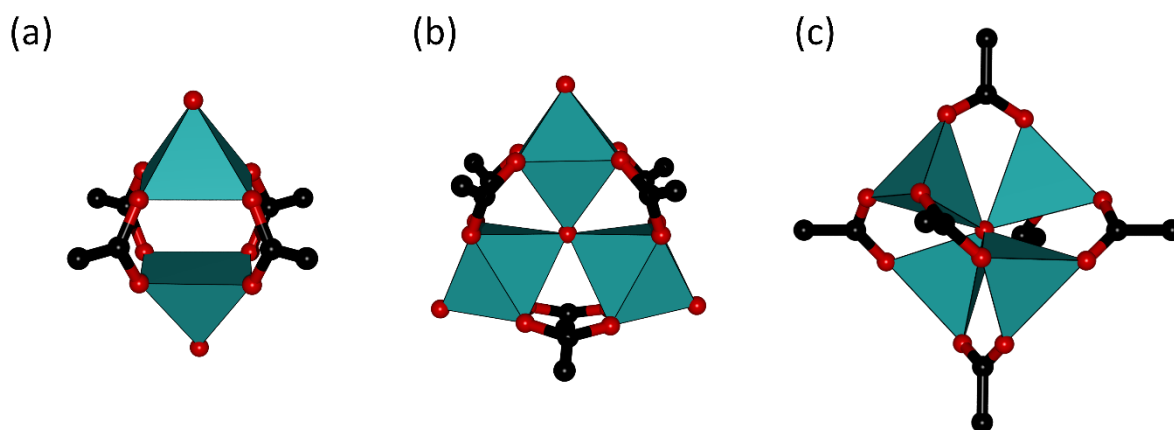


Figure 1.5: Three common SBUs in MOFs (a) the dinuclear paddlewheel square cluster, (b) the trigonal prismatic cluster and (c) the tetrametallic cluster.

Metal geometries are also dictated by the properties of the organic ligands. Ensuring careful selection of metal-ligand combinations that are compatible adds further control over the MOFs final structure. The infinite combinations of donor atoms and geometries offered by ligands gives rise to a diverse array of different MOFs. The number of donor atoms, binding angles, ligand length and ligand flexibility can all strongly influence the final material. Ligands typically fall into one of two categories being either neutral or charged when considering the ligand donors.^{85,86} When using neutral-based ligands, commonly containing N-donor heterocyclic moieties (Figure 1.6), charge balancing counterions to counteract the charge derived from the metal node are typically required.⁸⁷⁻⁸⁹ These will usually sit within the pores of the framework, thus decreasing, or even preventing, guest incorporation within. This is detrimental to host-guest chemistry, but the formation of cationic frameworks in which the anion is uncoordinated to the metal centre itself can have interesting properties and applications.⁸⁵ Conversely, charged ligands, such as carboxylic acid moieties (Figure 1.6), typically form much more robust, porous frameworks.^{89,90} These materials are more suited to applications exploiting the host-guest properties offered by MOFs. By carefully considering the framework properties desired, specific metal nodes and organic ligands that will direct the formation of the material can be selected, allowing for its synthesis.

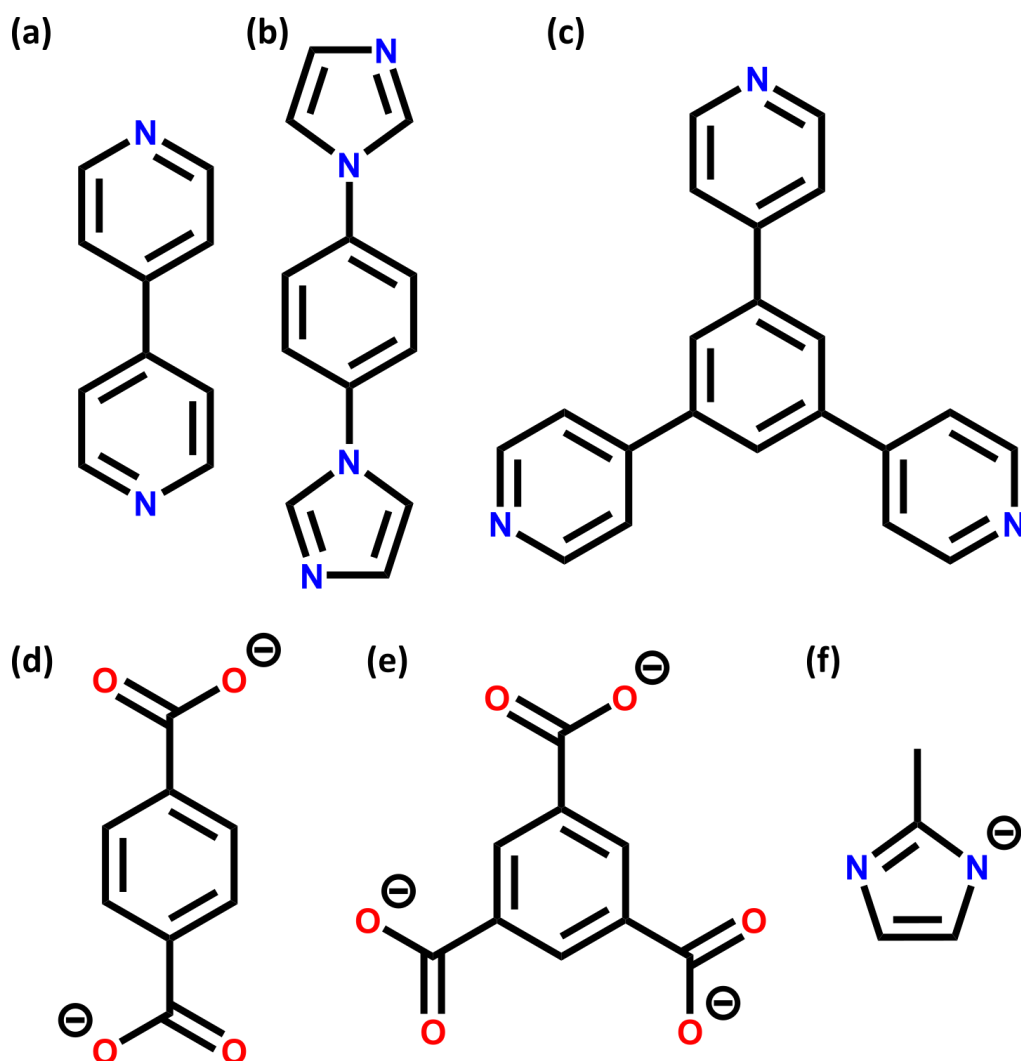


Figure 1.6: Examples of (a-c) neutral and (d-f) charged ligands used during MOF synthesis.

1.2.3 MOF Synthesis and Characterisation

The MOF field is highly interdisciplinary, in which areas of materials, organic, inorganic and physical chemistry are all integrated. Accordingly, the synthesis of MOFs naturally draws from aspects and techniques in each respective discipline. Typical syntheses of MOFs rely on the self-assembly in solvent media. The most common solvent-based synthesis of MOFs is via solvothermal synthesis which refers to the process where a solution containing metal-ligand components is heated under autogenous pressure to affect framework synthesis. The main advantage offered by this technique is the conditions allow for reversibility of bonds formed. This ensures that in instances of incorrect arrangement, the bond can be readily broken and allowed to reorganise to reach the appropriate configuration. This permits the formation of thermodynamically favoured structures through inherent error-checking. In addition, in solvent and at increased temperature, not only are the solubility of ligands commonly increased, but

deprotonation of charged ligands is more accessible.⁹¹ Whilst syntheses are most commonly solvent-based, they are not limited to this medium. Gas-based and solvent-free syntheses for MOFs also exist.⁹²⁻⁹⁵

MOFs can be synthesised via a number of methods such as mechanochemical or slow diffusion, however, solvent-based syntheses provide one of the easiest platform for their preparation.^{96,97} The chosen metal-ligand combination will, of course, define the overall framework properties and structure, but consideration into other components of the synthesis can define its success. Variations of conditions such as the solvent system, temperature, ratio and concentration of reagents, reaction time, and the presence and composition of any modulating agents, can strongly impact crystal form and quality.⁹⁸⁻¹⁰⁰ With such diverse conditions impacting crystal formation, many avenues can be pursued to reach the end product. As such, high through-put characterisation of synthesised materials is required to probe the quality of any prepared MOFs.

Being intrinsically crystalline materials, X-ray diffraction methods are commonly employed in structural characterisation and subsequent studies. Of these, none is more powerful than single crystal X-ray diffraction (SCXRD), permitting complete structural characterisation, provided certain crystallographic requirements are met. Powder X-ray diffraction (PXRD) is also frequently used to identify microcrystalline MOFs due to the characteristic diffraction patterns produced based upon the crystal structure of the material. This high-throughput method is ideal in quick analyses of numerous samples. Recently, PXRD methods have also been applied in the complete structure solution of microcrystalline MOF crystals, which, otherwise, could not be solved by conventional SCXRD means, owing to their size (microcrystalline powders).¹⁰¹

In addition to being crystalline, MOFs often show permanent porosity due to their open architectures. During synthesis, however, solvent molecules and other components fill the internal cavities and prevent direct adsorption analysis. By removing the components within the MOF via an activation process, the adsorption behaviour of the MOF material can be elucidated. This usually involves solvent exchange of the guest within the framework with more volatile solvents, followed by their subsequent removal through either heat or vacuum, or both. Care must be exercised during activation however, as certain frameworks can be unstable to desolvation, leading to the collapse of the framework.¹⁰² Activation success can be confirmed by thermogravimetric analysis (TGA). TGA measures a samples mass over time as it is exposed

to increasing temperatures. It allows the degree of MOF solvation to be calculated and determination of the temperature at which the framework begins to decompose. Upon removal of pore guests within the framework, and confirmation its structure is retained, the material can be considered permanently porous. Further gas-based analysis probing porosity, surface area and pore-sizes can begin.

The permanent porosity of MOFs makes them ideal materials in numerous industrial, commercial and research settings. For one, the gas storage and separation properties offered are highly attractive.^{103,104} The high surface areas of MOFs permit the enhanced gas storage abilities displayed, owing to the stronger surface-gas adsorption as opposed to gas-gas interactions.^{105,106} These high surface areas also permit considerable amounts of surface specific interactions in relatively small MOF amounts, an attractive feature for many applications. Gas separation and selectivity of guest species is dictated by the pore architecture of the framework. Through modification of the pore dimension or via functionalisation of the pore aperture, enhanced separation and encapsulation properties can be imbued.¹⁰⁷ By tuning the material, the desired properties for a given application can be reached, however, structural rigidity is not necessarily required or desired. This has led to the development of a class of MOFs that exhibit structural flexibility, possessing unique properties rigid materials do not display.

1.2.4 Flexible Frameworks

Structural flexibility of materials hold promise in many applications ranging from material science to biology, justifying the significant investigation such materials have gained.¹⁰⁸ In recent years, considerable attention has been given to MOFs possessing dynamic properties, so termed flexible MOFs.¹⁰⁹⁻¹¹² They have been shown to be excellent materials for examining guest responsive activities, that is, the pore size and shape observed is a function of the adsorbates density.¹¹³ This is exemplified by DUT-49 (Dresden University of Technology) which remarkably demonstrates negative gas adsorption, quantified as a reduction in the unit cell volume of 50%, after undergoing a structural transformation during gas adsorption.^{114,115} Whereas some applications favour the employment of structurally rigid MOFs, flexible frameworks possess unique properties well suited to applications typically inaccessible by more conventional materials.¹¹⁶ The applicability of flexible frameworks is evidenced by applications in storage and separation, sensing, and guest capture and release.¹¹⁷⁻¹²³

MOF flexibility proceeds via four main structural modes which are breathing, swelling, linker rotation and subnetwork displacement (Figure 1.7).¹²⁴ The structural modes of flexibility are triggered by external stimuli including gas adsorption and desorption phenomena, temperature, mechanical pressure, and light.¹²⁴⁻¹³⁰ These structural transitions, other than linker rotation, are accompanied by changes to the unit cell volume. Linker rotation exhibits little to no unit cell volume changes as the flexibility relates to the rotation of the linkers in the available pore space.

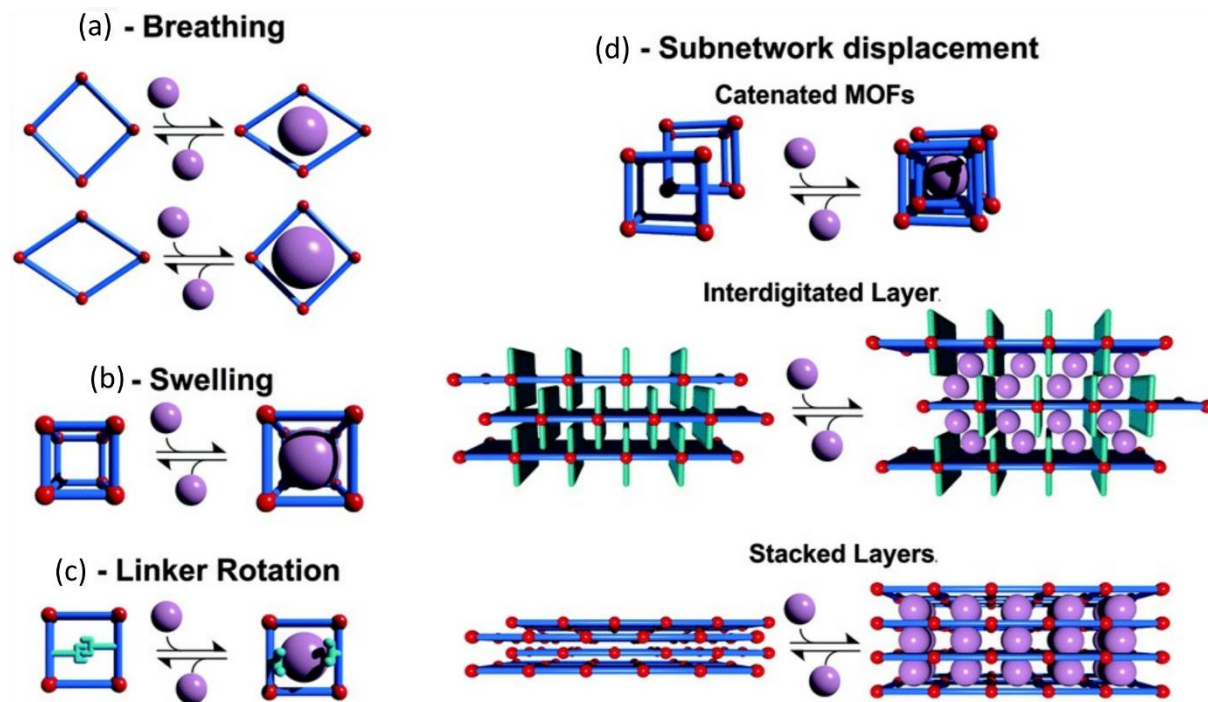


Figure 1.7: The four structural modes of flexibility, **(a)** breathing, **(b)** swelling, **(c)** linker rotation and **(d)** subnetwork displacement (Figure adapted from ref. 124).

The most common of the structural modes of flexibility is breathing. This often takes the form of a narrow or closed-pore phase undergoing a phase transition to a large or open-pore phase. This results in a minimum of two distinct states, but multiple can exist. Swelling is the next most common, in which the unit cell does not change shape but undergoes either an enlargement or contraction. Linker rotation, as previously mentioned, is the odd one out within the group. Unlike the others in which a change in unit cell volume occurs, this structural mode of flexibility is characterised by the unified rotational motion of the linkers. Finally, subnetwork displacement is concerned with the drifting, relocation, or shifting of individual frameworks or layers relative to one another.^{109,124} Specific components integrated into MOF architectures can realise structural flexibility through these classical structural modes of flexibility. Interest into finding new components that operate through novel pathways to realise this flexibility is

continuously ongoing, granting new blueprints in which chemists may go about designing bespoke frameworks for targeted applications.

1.3 MOFs: Heterogenous Catalysts

1.3.1 Challenges in Catalysis

More than 90% of all chemical products require at least one catalytic step during synthesis.¹³¹ Items such as plastics, pharmaceuticals and textiles, common products encountered every day, all require catalytic reaction(s) during preparation.¹³² It is clear catalysts are integral in many items human rely upon daily. One needs to look no further than the human body for this dependence. Taking the form of enzymes regulating biochemical processes, these catalysts enable out continued existence.¹³³ The inherent benefit catalysts provide relates to the processes they can perform. Catalysts can be considered as tools in which starting materials can be converted into more desirable materials through breaking and forming chemical bonds efficiently and selectively.¹³⁴

Currently, many of the main catalytic processes employed in industry were introduced around the 1960's, over 60 years ago.¹³⁵ This includes processes within the refinery and petrochemistry sectors such as cracking, metathesis, propylene oxidation and ammoxidation, the water gas shift, and reforming and hydroreforming reactions.¹³⁵ From the point of inception of these catalysts, many have progressed through different iterations, commonly an evolution of those that came before. This may present as a cause for concern as previous economic growth cycles have shown to be between 60-70 years in the past, requiring new innovation and technologies to combat raw material accessibility and societal requirements.^{135,136} Importantly, this is known to coincide with the chemical industry.^{135,136} As a result, it is becoming ever more apparent that looking to the future, a need to develop new catalysts, specifically with a focus on both disruptive catalysts (catalysts based on new conceptual approaches) and those promoting sustainable production pathways, is required.^{137,138}

Catalysts can typically fit into one of three main types, those being (1) homogeneous, (2) heterogeneous and (3) biochemical.¹³⁹ These are characterised as the (1) reaction mixture and catalyst being of the same phase, (2) reaction mixture and catalyst being of different phases and (3) natural components, namely enzymes, used outside of living cells for chemical reactions.¹³⁹ Herein, only heterogeneous, and briefly homogeneous catalysts, will be considered.

Both heterogeneous and homogeneous catalysts have distinct advantages and disadvantages. The main advantages offered by heterogeneous catalysts is the ease of separation from the reaction medium, owing to the different phases, allowing the simple subsequent reutilisation of the catalyst, and relatively high catalyst stability.^{140,141} Heterogeneous catalysts, however, are hampered by poorly defined active sites, which, in certain cases, can be difficult to fully access and thereby systematically develop.^{140,141} Conversely, homogenous catalysts have well defined active sites, easily accessible by reactants.^{140,141} The difficulty lies in catalyst recovery and reutilisation due to required separation from reaction/product mixtures of the same phase, and low catalyst stabilities.^{140,141} An ideal scenario would see the heterogenization of homogenous catalysts onto a support material, thus enabling access to the strengths of both catalyst classes, whilst excluding the disadvantages. In the past 20 years, research into the area has continued to grow, however, implementation in industry remains elusive.¹⁴²⁻¹⁴⁴

1.3.2 Catalytic activity of MOFs

One of the fundamental applications of MOFs is within catalysis, with many examples emerging since the beginning of the field.^{66,75,145,146} This was first demonstrated in 1994, which also served as a key example highlighting the substrate exclusion properties MOFs offer owing to limiting pore sizes, leading to size-selective catalysis.¹⁴⁷ The properties offered by MOFs, specifically the high surface areas, propensity for tunability and high density of active sites, make them ideal for catalysis. Further coupled with both the advantages afforded by their heterogeneous nature, being solid materials, and the opportunity to impart a degree of homogeneous nature due to the inclusion of defined active sites, MOFs are highly attractive materials to use for catalysis.¹⁴⁶

Catalytic activity of MOFs can either be inherent to the framework, or integrated post-synthetically. In cases where it is inherent to the framework, activity is derived either at the node, taking the form of coordinatively unsaturated metal sites, or within the ligand, taking the form of pendent acid/base sites (Figure 1.8).¹⁴⁶ These active sites can either be integrated within the design of the framework, preceding MOF synthesis, or they can be added in post-synthetically.¹⁴⁷ In addition, catalytically active components can be encapsulated or heterogenized within the MOF acting as a host scaffold framework (Figure 1.8). Large species such as metal nanoparticles, enzymes and molecular catalysts can be encapsulated within the pores of the framework, or for components exceeding pore sizes, the framework can be grown around them.¹⁴⁸⁻¹⁵¹ Smaller species, such as metal complexes, can be regularly incorporated

throughout the framework through post-synthetic metalation.¹⁵² Through this process of encapsulation and heterogenization, the stability and reusability of usually homogenous catalysts can be enhanced whilst retaining high catalytic activity.^{153,154} The diverse methods in which to incorporate and introduce catalytic material, coupled with the extensive selection of frameworks on offer, have led to many types of chemical reactions catalysed within MOFs. These include, but is not limited to oxidations, hydrogenations, Suzuki couplings, Friedel–Crafts, cyclisations and Sonogashira reactions.^{155–160} These examples display the catalytic opportunities offered by MOFs are extensive, warranting further research into the development of new and/or enhanced MOF catalysts.

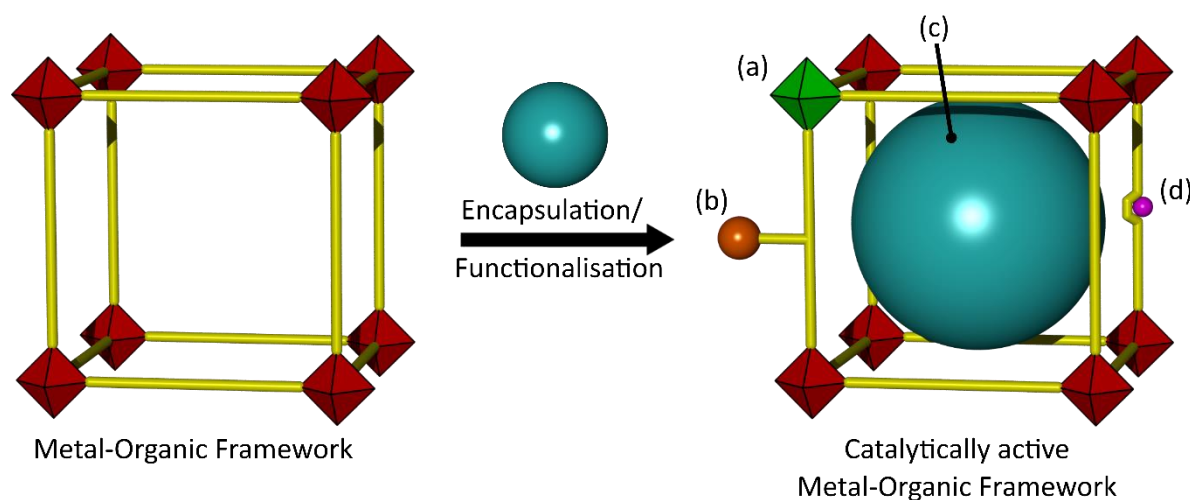


Figure 1.8: Schematic representation of some of the different ways catalytic activity can be integrated into a MOF: **(a)** at the metal nodes, **(b)** at pendant sites, **(c)** encapsulation of larger catalytic species and **(d)** binding of smaller species.

1.4 Thesis Coverage

This thesis presents a study of MOFs as both flexible and catalytically active materials through the integration of metal components both pre- and post-synthetically. The thesis is composed of four standard chapters, inclusive of the introductory (chapter 1) and concluding (chapter 4) chapters. The first chapter has provided a background on supramolecular chemistry and its subsequent utilisation in the development of MOFs. In addition, the properties of MOFs and their applications as dynamic materials and catalysts has been briefly outlined. The final chapter provides a summary of the work presented herein, and potential for future directions.

Chapter 2 details ongoing work into the development of MOF-derived ruthenium on titania catalysts for the hydrogenation of carbon dioxide to form methane. The chapter aims to present the groundwork that has been established in the formation of the catalyst, and its

activity, relative to materials of identical composition prepared under different and conventional conditions. Described in the chapter is the synthesis of two titanium MOF materials, MIP-207 (Materials of the Institute of Porous Materials from Paris) and MUV-10(X) (Materials of Universidad de Valencia), where X is calcium or barium, the subsequent loading of the MOFs with ruthenium, generation of the active phase and the activities for the hydrogenation of carbon dioxide to methane under batch conditions. Significantly, it was observed that a pure titanium MOF precursor led to a catalyst with low CH₄ selectivity and CO₂ conversions, deactivating over subsequent runs. Conversely, the heterometallic titanium frameworks produced highly active, selective, stable catalysts with CH₄ selectivities and CO₂ conversions comparable to exceptional conventional Ru/TiO₂ materials.

Chapter 3 presents the post-synthetic metalation of MnMOF-1 with Au(I) and the first example where the inherent flexibility of the MOF is retained after metalation. In this chapter, the first introduction of Au(I) complexes within MnMOF-1, driven by an interest in harnessing the unique catalytic properties of the metal ion, are targeted. This chapter describes the successful quantitative metalation of MnMOF-1 with Au(I) salts. The resulting MnMOF-1.Au(I) material was characterised via SCXRD and displayed monodentate coordination of the bis-pyrazole moiety in the *anti* conformation, which has not previously been reported for MnMOF-1. Furthermore, the metalated MOF retains its inherent flexibility due to the unique coordination geometry seen for Au. This proved instrumental in establishing an understanding of coordination modulated on-off switching of flexibility that was observed within the same framework metalated with a Cu(I) halide species. The work highlights the development of a previously unseen coordination geometry in MnMOF-1 that assisted in the realisation of a novel mechanism to control flexibility within a MOF. Some results of chapter 3 have been published in a peer reviewed, international journal.¹⁶¹

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CHAPTER 2

MOF DERIVED RUTHENIUM ON TITANIA FOR CO₂ METHANATION

Chapter 2. MOF Derived Ruthenium on Titania for CO₂ Methanation

2.1 Introduction

2.1.1 CO₂ Emissions

Increasing atmospheric concentrations of carbon dioxide (CO₂) have been identified as one of the most significant contributors to global warming and climate change.^{1,2} The global atmospheric concentration of CO₂ has steadily risen since records collected by the National Oceanic and Atmospheric Administration (NOAA) began (Figure 2.1).³ Current levels sit at approximately 410 ppm, substantially increased from pre-industrial revolution levels. The increase is estimated to be approximately 130 ppm, calculated relative to pre-industrial revolution atmospheric concentrations of 280 ppm, determined via paleoclimate evidence, and is predicted to increase further.⁴ Responsibility for such a dramatic increase falls on humans. For over 150 years, our dependence on fossil fuels – raw carbon rich material – has driven unprecedented advancements and development across the world.⁵ This dependence, however, comes at a cost. Anthropogenic CO₂ is the leading contributor to the increase in atmospheric CO₂ concentration, the main culprit being the combustion of fossil fuels.⁶⁻⁸ Indeed the Intergovernmental Panel on Climate Change (IPCC) have reported over 75% of anthropogenic CO₂ emissions are derived from fossil fuels, while land-use changes, such as deforestation, account for the remainder.^{9,10} If anthropogenic CO₂ emissions remain unchecked, the consequences will be disastrous.

The causes, risks and potential impacts that climate change has the power to inflict are broadly known and accepted. This fuelled the inception of the Paris Agreement in 2015, the main aim for which centres around global action against climate change.¹¹ The agreement is an international treaty and legally binding for the 193 parties that have ratified.¹¹ The key target is limiting global warming by no more than 2°C this century relative to pre-industrial levels. To reach this target, peak greenhouse gas emissions for each country should be reached swiftly to achieve a climate neutral world before, subsequently, focus is directed towards developing and implementing low- and zero-carbon solutions.

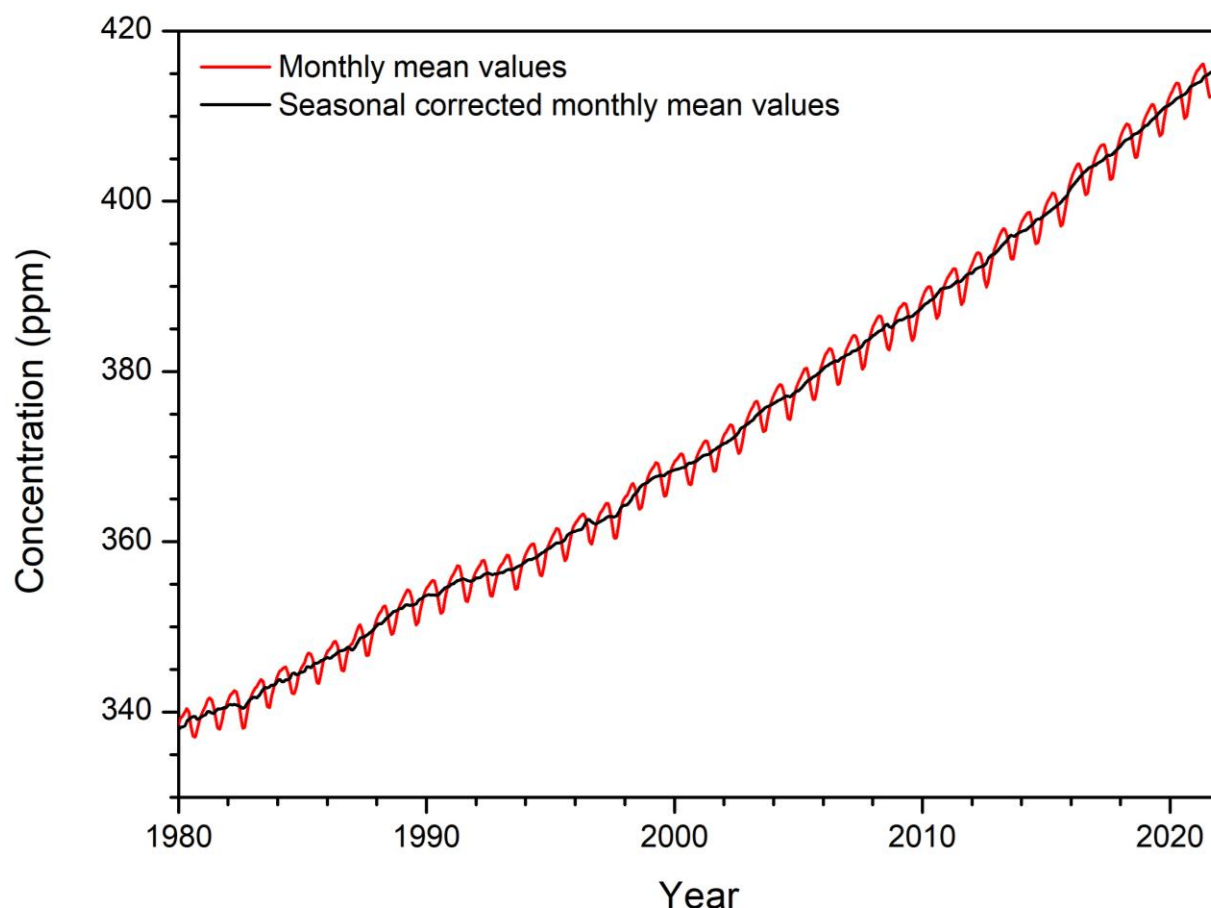


Figure 2.1: Global monthly mean of averaged CO₂ concentration recorded at marine surface sites. Monthly mean values (red) and monthly mean values corrected for the average seasonal cycle (black) are both represented (data provided from ref. 3).

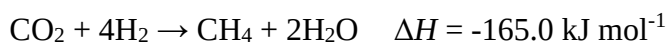
For both countries and scientists, there is a push to not only reduce CO₂ emissions, but to develop methodologies to decrease the concentration of CO₂ in the atmosphere.^{12,13} This, however, is a long and extensive task, and is approached through three main pathways.¹⁴ These include reduction of the CO₂ produced from the source, carbon capture and sequestration (CCS), as well as carbon capture and utilisation (CCU).^{4,15,16} To implement the first strategy, transitioning from fossil fuels to less carbon-intensive sources such as hydrogen (H₂) or renewable energy, and improvements to energy efficiency, are required.¹⁵ Conversely, CCS does not shift away from existing technologies but involves the direct capture of CO₂ produced from a fixed source, before its long-term storage.¹⁷ Potential options include ocean disposal, storage within geological formations and deep forest sequestration.^{15,18-20} CCS, however, will siphon significant energy loads in production systems, driving energy prices higher due to the reduction in net total energy production.²¹ Recently, the direct capture of CO₂ from the air has been gaining momentum.²² The relatively low atmospheric concentrations of CO₂ still make such processes highly costly, but the opportunity for negative emissions is exceedingly

desirable.^{22,23} Of the three, CCU is debatably the most interesting from a chemical point of view, and current research is shifting towards this field.²³

When considering the economical, safety and renewable properties of CO₂, it becomes evident that it is an attractive C₁ building block.²⁴ This is reflected by its use in current industrial processes such as urea production, within the food and beverage industry, water treatment and enhanced oil recovery.^{23,25,26} Unfortunately, the industrial use of CO₂ is still rather limited owing to its thermodynamic stability. The inert nature of the molecule requires high energy inputs coupled with effective and efficient catalysts to achieve suitable conversions.²⁷ Evidently, this drives costs higher than more conventional feedstock material, rendering CO₂ less desirable. Nevertheless, the opportunity offered by recycling and reusing captured CO₂ as feedstock for chemical production to reduce the impact upon global warming, preventing its otherwise emission into the atmosphere, is exceedingly attractive. As such, research is ongoing into CO₂ utilisation in areas such as chemical, fuel and polymer production.²⁵ One such pathway is through the hydrogenation of CO₂ to value added products.²⁸

2.1.2 CO₂ Methanation

In 1902, French chemists Paul Sabatier and Jean-Baptiste Senderens published their findings into the reaction of carbon oxides in the presence of H₂ over nickel.²⁹ Under such conditions, at elevated temperatures, CO₂ and H₂ can be converted into methane (CH₄) and water (H₂O) (Scheme 2.1). Now known as the Sabatier reaction (also CO₂ methanation), the discovery jointly earned Paul Sabatier the Nobel Prize in Chemistry with Victor Grignard. Previously, the reaction has mainly been employed in industry as a purification step to remove trace amounts of carbon monoxide (CO) and CO₂ in H₂-rich feed gases, which, if left unchecked, could result in catalyst-poisoning.³⁰ Interest into its application as a potential alternative to CO₂ methanation for methane production, following the 1970's oil crisis, was also probed, but issues relating to commercial scale up hampered its instalment. In recent times, however, the Sabatier reaction has experienced a fresh surge of activity owing to applications within renewable energy storage, long-term space exploration missions, and importantly, CCU.³⁰



Scheme 2.1: The Sabatier reaction, typically conducted at elevated temperatures and in the presence of a suitable catalyst.

The advantage afforded by CO₂ methanation, centres around the conversion of CO₂ into CH₄, a value-added product. This eventuates as the applications for CH₄ are much more diverse than that of CO₂. The most well-known of these applications is its use as an energy source. Compared to other hydrocarbon-based fuel sources, not only is it the cleanest burning, it possesses the highest energy density of 56 kJ g⁻¹.^{31,32} In addition, CO₂ methanation lends itself remarkably well to integration with power-to-gas technology (Figure 2.2). The process involves the formation of gaseous fuel via electrical power.³³ Most typically, H₂ is formed from the electrolytic splitting of water. Once formed, the H₂ can be used directly, however, issues surrounding the storage and transportation of hydrogen prove problematic for subsequent applications. This relates to the compression/liquefaction processes requiring high energy inputs, often leading to losses of up to 12%, compounded by further losses during transportation due to boil-offs.³⁴⁻³⁶ The conversion of H₂ to CH₄ is considered one of the most promising carriers for H₂, retaining moderately high heat content (relative to H₂) but possessing lower compression energy.^{34,37,38} The conversion is also considered ideal as the only other component required, other than heat and a catalyst, is CO₂, easily accessible and can be integrated within CCU. In addition, CH₄ can easily slot into existing natural gas technologies and infrastructure on the basis natural gas is predominantly composed of CH₄. Conversely, these existing platforms are inaccessible to high concentrations of H₂ on account of hydrogen embrittlement, high autoignition temperature and flame travel distance issues.³⁴

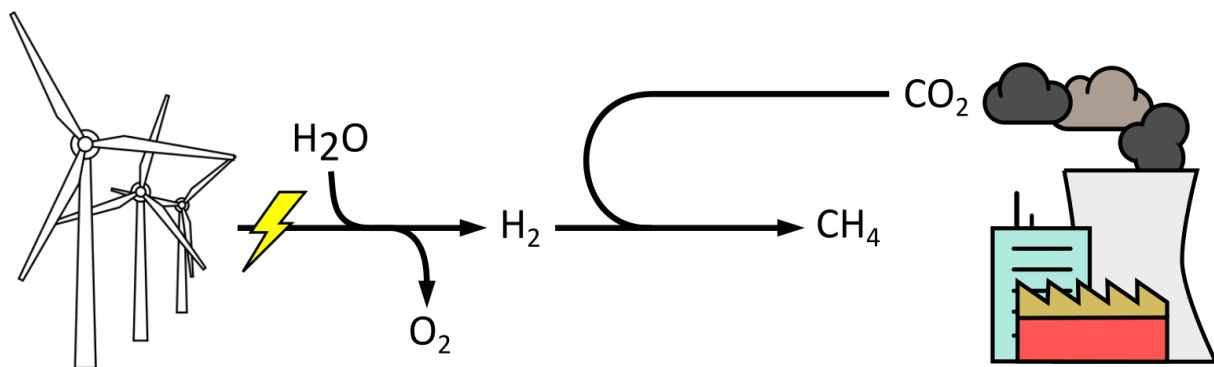


Figure 2.2: Schematic of the power-to-gas pipeline in which H₂, produced from the electrolytic splitting of water powered via energy derived from renewable means, can be integrated with captured CO₂ to form CH₄, reducing atmospheric emission during the formation of a value-added product.

The main challenge for the integration of CO₂ into industry is the improved development of existing catalyst technologies. The reduction of CO₂ can be approached through several pathways including electrochemical, photocatalysis, photosynthesis, biological, and

thermal.³⁹⁻⁴⁴ Herein, only thermal pathways will be considered. Whilst the reaction is thermodynamically favourable ($\Delta G = -130.8 \text{ kJ mol}^{-1}$), the process suffers from significant kinetic limitations owing to the eight-electron process for the reduction of CO₂, fully oxidised carbon, into CH₄, warranting the need for catalysts to achieve competitive conversions and selectivity.^{14,45} This is further compounded when considering that the reverse water-gas shift reaction (Scheme 2.2(3)) is in competition with the methanation of CO₂, and is favoured at higher temperatures ($> 450^\circ\text{C}$).⁴⁶ As such, at these elevated temperatures, CO production is enhanced, reducing selectivity to CH₄, meaning lower temperatures ($< 300^\circ\text{C}$) must instead be targeted, and further justifying the need for effective catalysts to surpass the kinetic energy barrier at these lower temperatures.⁴⁶⁻⁴⁹ The different reactions in competition with CO₂ methanation that can also occur are summarised in Scheme 2.2.



Scheme 2.2: Different reactions that can occur under CO₂ methanation reaction conditions. (1-2) form the desired products and (3-8) undesirable side reactions including (3) the reverse water-gas shift reaction.

It is evident from the potential reactions that could occur, conditions favouring CH₄ production (Scheme 2.2(1) and 2.2(2)) need to be promoted whilst suppressing the formation of side products (Scheme 2.2(3-8)). In a study undertaken by Gao *et al.* the ideal conditions to promote CH₄ formation were probed via simulations performed for Gibbs free energy minimisation.⁵⁰ In terms of reaction temperature, CH₄ was favoured at lower temperatures (200-250°C), whereas CO is favoured at high temperatures ($> 450^\circ\text{C}$). In addition, at these elevated temperatures, CH₄ production decreases as the amount of converted CO₂ and H₂ decrease (Figure 2.3). Pressure also impacts the reaction, in which higher pressures typically result in

greater CO₂ conversions and higher CH₄ selectivity (Figure 2.3). The ratio of reactants was also investigated, indicating at higher H₂:CO₂ ratios, CO₂ conversions and CH₄ selectivity were typically increased (Figure 2.4). These findings were corroborated by thermodynamic studies conducted by Miguel *et al* (Figure 2.5).⁵¹

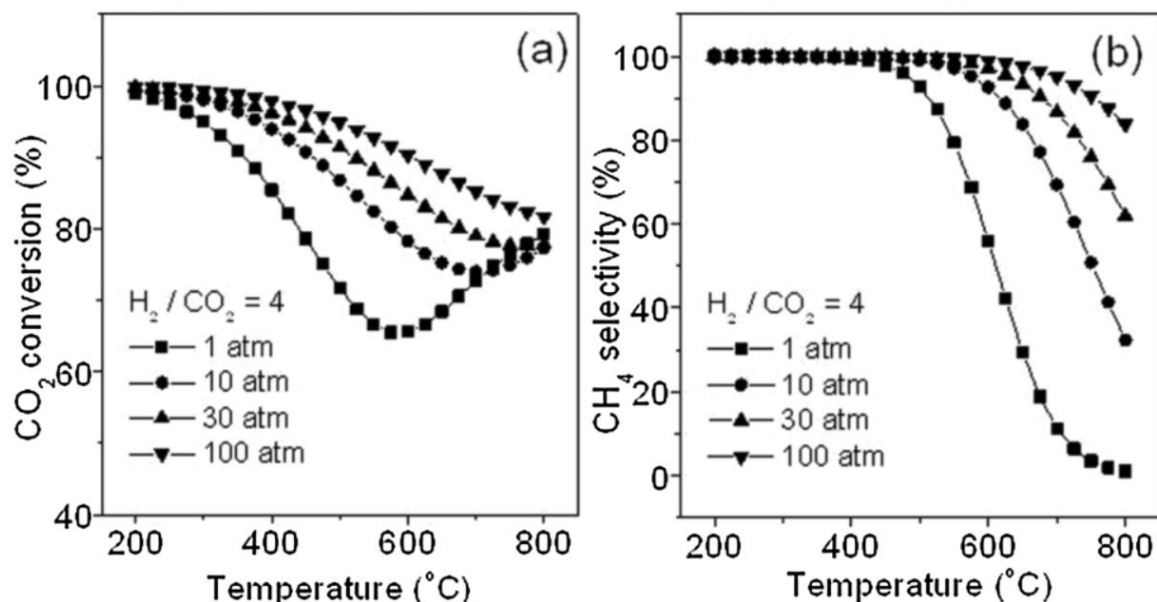


Figure 2.3: Temperature and pressure effect on (a) CO₂ conversion and (b) CH₄ selectivity (Figure adapted from ref. 50).

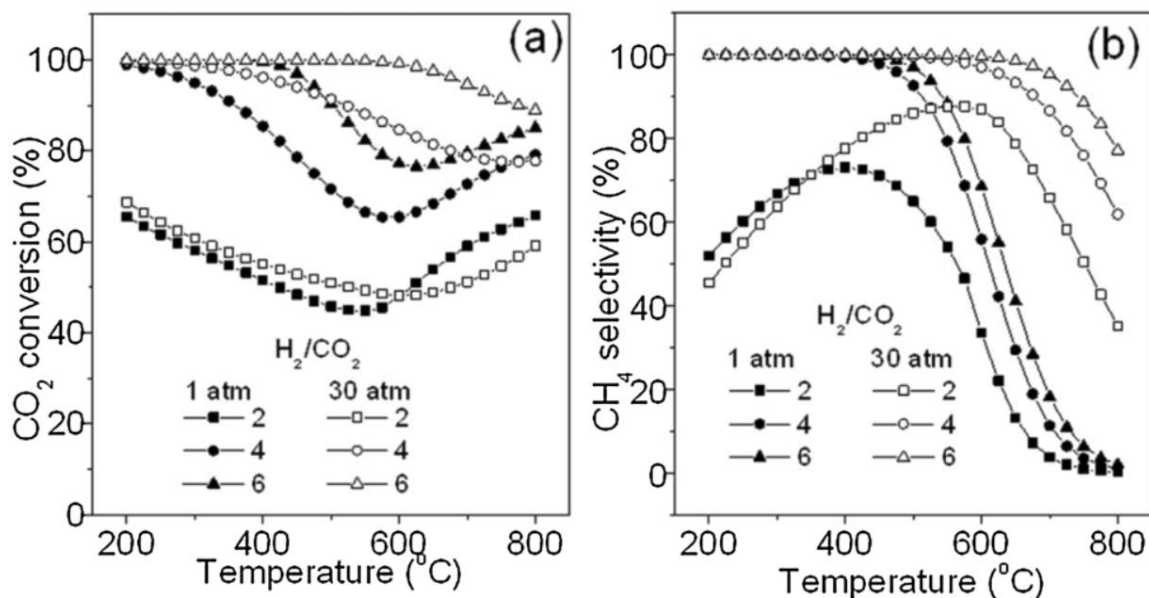


Figure 2.4: Temperature and pressure effect on (a) CO₂ conversion and (b) CH₄ selectivity at different H₂:CO₂ ratios (Figure adapted from ref. 50).

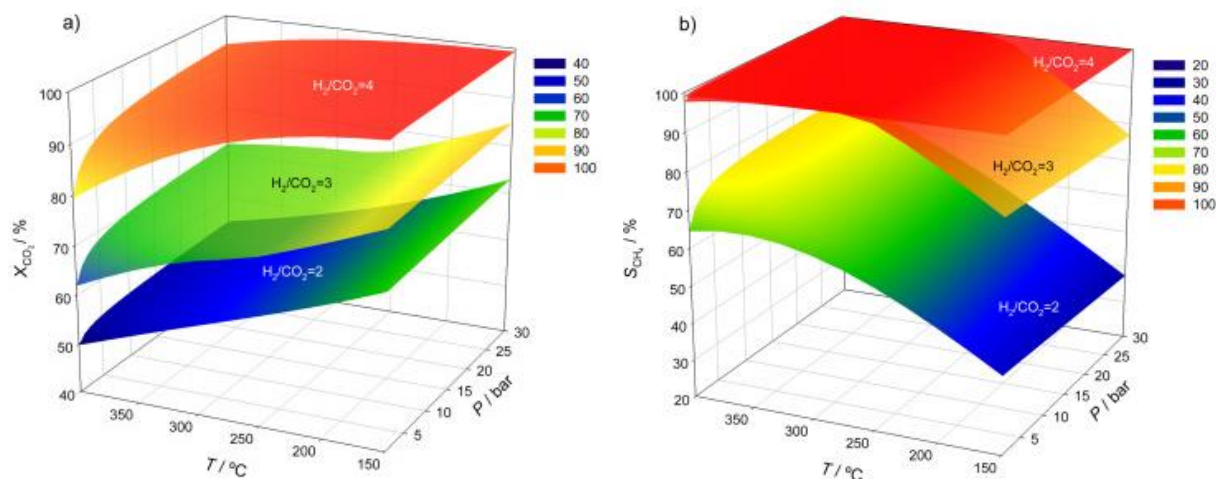


Figure 2.5: Temperature, pressure and H₂:CO₂ ratio effect on **(a)** CO₂ conversion and **(b)** CH₄ selectivity (Figure adapted from ref. 51).

Other than tuning reaction conditions, carefully selecting and developing catalysts is required to favour CH₄ selectivity and promote CO₂ conversion. Recently, a great number of catalysts for CO₂ methanation have been prepared, tested, and analysed.^{14,46,52} Catalysts will typically take the form of metal (nano)particles supported on metal oxides. Common metals used include Ni, Ru, Rh, Fe, Pd, Pt and Ir.⁵³ Typical metal oxide supports for the metal particles include silica (SiO₂), alumina (Al₂O₃), titania (TiO₂), zirconia (ZrO₂), ceria (CeO₂) and silicon carbide (SiC).⁵³ Of those mentioned, Ni is commonly utilised due to the high activities and selectivities exhibited by Ni based catalysts. In addition, the high natural abundance and relatively low cost of Ni makes it extremely desirable, compared against the more expensive options such as Ru and the other platinum group metals. Unfortunately, low temperature methanation is difficult to achieve using Ni-based materials, and higher temperature conditions are required. Subsequently, this results in reduced catalyst lifetimes due to carbon deposition, chemical poisoning, and sintering.⁵³⁻⁵⁵ This behaviour is also reflected for Fe and Co catalysts.⁵² Consequently, attention has turned to other metals such as Ru.

2.1.3 Ru/TiO₂

Ruthenium, a member of the platinum group metals, is considerably more expensive than Ni. Nevertheless, it displays enhanced activity, and selectivity towards CO₂ methanation, and importantly, unlike Ni, it forms highly stable catalysts.^{53,54,56,57} The activity and selectivity of Ru-based catalysts, like most heterogeneous catalysts, are strongly impacted by the support material.^{58,59} This is achieved through enhancing metal-support interactions, electron transfer between the support and metal, metal dispersion and introducing support defect sites.^{53,60,61}

Through implementing different catalyst loading and activation conditions, these modifications can be introduced and refined.

For CO₂ methanation catalysed via Ru, the Ru particle size has the greatest impact on CO₂ conversion and CH₄ selectivity.^{62,63} However, the metal oxide support can still have a profound impact. Ru has been appended on numerous supports, with both TiO₂ and ZrO₂ emerging as the ideal candidates at temperatures below and above 310°C respectively.⁶⁴ In terms of reaction conditions for CO₂ methanation, lower temperatures are preferable, as selectivity is promoted towards CH₄ as opposed to CO. In addition, looking to the future and potential industrial scale-up, lower temperatures require less energy input, which has the benefit of minimising costs. As such, TiO₂ appears as the ideal support for Ru.

By considering the behaviour of TiO₂ on the mechanism for converting CO₂ into CH₄, the reason it is considered the most effective support becomes clear. Typically, basic oxides have the most potential for CO₂ methanation. This is on account of the binding potential the supports provide to adsorb the mildly acidic CO₂. This ensures that not all competitive dissociative adsorption of H₂ and CO₂ has to occur on the Ru surface, as would happen if an inert support was used.⁶⁴ Indeed, if this was the case, as CO is an intermediate formed during the reaction, and considering it binds to the Ru surface much stronger than H₂, catalyst poisoning can eventuate.^{65,66} Additionally, if the support possesses oxygen site vacancies on its surface, like TiO₂ does, the vacancies provide a location for one of the oxygens of the CO₂ to bind to, forming bidentate carbonates, from which CO is derived.⁶⁷ What sets TiO₂ apart is its ability to also accelerate the conversion of CO on the Ru surface through indirect effects.⁶⁴ Electron density can effectively be shifted from the Ru particles to the TiO₂ support, resulting in decreased electron backdonation from Ru to the antibonding π -orbital of CO, consequently weakening the Ru-CO bond.^{64,66} This enables H₂ to more readily adsorb dissociatively on the Ru surface, which otherwise would be saturated with Ru-CO species, and subsequently be used in CH₄ formation.^{64,66} So effective is the catalyst formed by Ru on TiO₂ (Ru/TiO₂), conversion at room temperature and atmospheric pressure is accessible.⁶⁸ The high activities exhibited by Ru/TiO₂ catalysts at low temperatures make them an interesting material to study for CO₂ methanation catalysts, and will be the focus of the work presented herein. By forming these catalysts using porous supports, such as MOFs, gas transport issues that may be encountered on pure TiO₂ supports could potentially be avoided, leading to catalysts with enhanced activities.

2.2 MOF-Derived Catalysts

Metal-organic frameworks (MOFs) are well known for their inherent crystallinity, porosity, and highly tuneable nature. These characteristics lend MOFs well to the field of heterogeneous catalysis as support materials.^{69,70} In fact, some MOFs may have inherent catalytic properties, however, the majority of pristine MOFs typically possesses limited or no active sites, with low thermal, chemical and mechanical stability, restricting their use.^{71,72} To enhance the catalytic potential of MOFs, functionalisation of the backbone of the framework, integration of functional materials into the MOF or conversion of the MOF to functional materials is typically employed.^{69,73-75} In recent times, the latter of these avenues has received elevated interest, providing access to unique materials unobtainable through conventional synthetic approaches.

Utilising MOFs as a sacrificial template is a new method in catalyst preparation, facilitating control over composition and morphology with access to unique nanostructures.⁷⁶⁻⁷⁸ The derived catalyst is most commonly accessed through thermal degradation of the framework, but annealing, including in the presences of elements to be included within the final phase of the MOF derived catalyst (MDC), is possible.^{78,79} The benefits of using MOFs as sacrificial templates in catalyst formation are as follows. Firstly, MOFs themselves possess high surface areas and pore volumes, with a library of unique morphologies available. Following thermal degradation of the framework, as the decomposition occurs simultaneously throughout the material, some, if not all, of the aforementioned properties can be retained in the active catalyst. Secondly, as MOFs possess a high degree of tunability, properties such as composition, morphology and topology can be adjusted, which can subsequently be reflected in the derived material. In addition, owing to the highly porous nature of MOFs, numerous different guests can be encapsulated within the precursor, which will be retained in the derived material. Finally, the pore size, pore chemistry and surface area of the parent MOFs permit significant control over the spatial distribution of introduced catalytic components.

In terms of MOF derived CO₂ methanation catalysts, the activity afforded by such materials had been demonstrated previously. Lin *et al.* have recently prepared a core-shell, nickel-carbon (Ni@C) catalyst from the thermal degradation of a Ni-MOF.⁸⁰ Relative to conventional Ni@C catalysts, the MOF-derived material displayed enhanced conversions (three times greater) whilst maintaining 100% selectivity. Ru-based materials have also been prepared via MOF-derived means. Recently, Lippi *et al.* prepared a Ru/ZrO₂ MOF derived CO₂

methanation catalyst from the *in operando* activation of Ru loaded UiO-66 (Universitetet i Oslo) (Figure 2.6).⁸¹ By definition, and in context of heterogeneous catalysis, *in operando* refers to the activation of some catalytic material under reaction conditions. Lippi *et al.* revealed activation of the MOF-derived catalyst under such conditions is not only completely selective to CH₄ over 250-350°C, but it outperforms materials of the same composition prepared by traditional means, a commercial methanizer catalyst and other control materials in CO₂ conversion over the temperature range.⁸¹ *In situ* X-ray diffraction (XRD) studies, X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS) and Transmission electron microscopy (TEM) revealed under *in operando* conditions, the formation of Ru(0) nanoparticles are promoted by H₂, and the crystallisation of a tetragonal ZrO₂ phase was promoted by the combustion of framework C via CO₂ acting as a mild oxidant, critical for Ru nanoparticle stabilisation.⁸² These examples indicate the potential success catalysts prepared via MOF-derived means may possess.

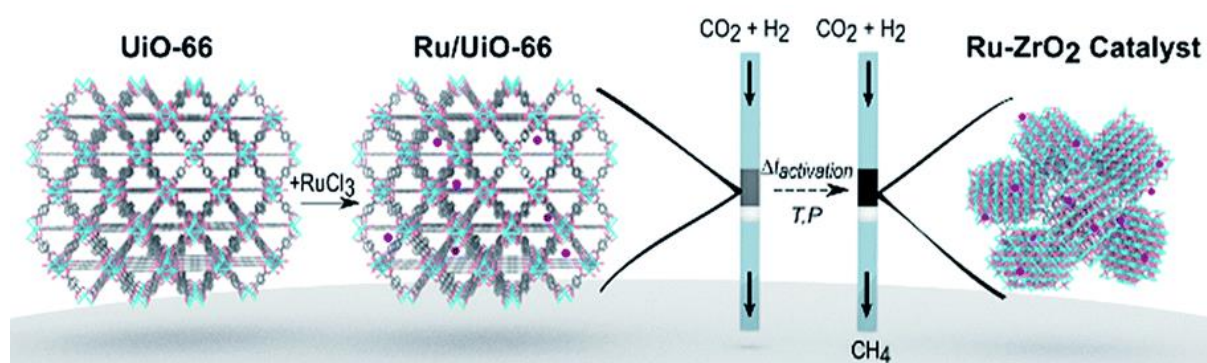


Figure 2.6: Preparation of the CO₂ methanation catalyst Ru/ZrO₂ via *in operando* activation of Ru loaded UiO-66 (Figure adapted from ref. 81).

MDCs are not limited to complete thermal decomposition of the organic linker to access the metal oxide phase but can be controlled in such a way as to produce carbon-based materials (CMs). It has been shown MOF-derived CMs allow great control over resulting composition and porous structure.^{83,84} Inevitably, these materials have received significant interest across diverse fields including within catalysis, forming excellent catalysts for the relevant applications.⁸⁵⁻⁸⁷ The retention of porosity can lead to confinement effects, known to strongly impact guest diffusion throughout the material and phase transformations leading to unique catalytic properties.^{88,89}

Previous MDC studies, in conjunction with investigations of Ru-based CO₂ methanation catalysts supported on TiO₂, led us to hypothesise a MOF-derived Ru/TiO₂ catalyst may yield

a highly active composite towards CO₂ methanation. The proposed work undertaken and presented here was predominantly focused on the generation of MOF-derived Ru/TiO₂ for CO₂ methanation. As investigated, MOF-derived materials can take many forms depending upon the activation pathway selected. For the work presented in this chapter, materials will be activated under reaction conditions (*in operando*) and via calcination (a more conventional activation method). We hypothesise under these activation conditions, three main types of materials will be derived. Firstly, as demonstrated by Lippi *et al.*, *in operando* is expected to yield the MOF-derived Ru(0) loaded TiO₂ metal oxide. Activation via calcination is anticipated to produce the same material, albeit with different properties owing to the contrasting activation conditions. Indeed, as the materials will be calcined in air, RuO₂ may instead form, owing to the oxygen present. However, once under reaction conditions, reduction of RuO₂ to metallic Ru is expected. Secondly, by tuning the parameters *in operando* and calcination activations are performed at, Ru loaded MOF-derived CMs may be reached (the potential pathways are depicted in Figure 2.7). The last potential material that may form is a derivative of the Ru loaded TiO₂ metal oxide. If activation conditions exceed those required to form Ru loaded MOF-derived CMs, resulting in the destruction of the organic-based material, but are not sufficient enough to fully form Ru loaded TiO₂, then a partially formed Ru loaded TiO₂ could result. This material would likely take the form of an amorphous metal oxide material with undeveloped Ru particles. Differences in the properties each activation pathway imbues are expected to impact the catalytic activity of the materials. Analysis of the catalytic potential of the different materials is hoped to reveal a highly active, selective catalyst. The synthesis, characterisation, and catalytic potential of Ru/TiO₂ derived from a pure Ti-MOF loaded with Ru will be in the primary focus of the first section of the chapter, 2.4, whereas the second section, 2.5, will detail an investigation into the synthesis, characterisation, and catalytic potential of Ru/TiO₂ derived from a heterometallic Ti(X)-MOF, where X is calcium or barium, loaded with Ru.

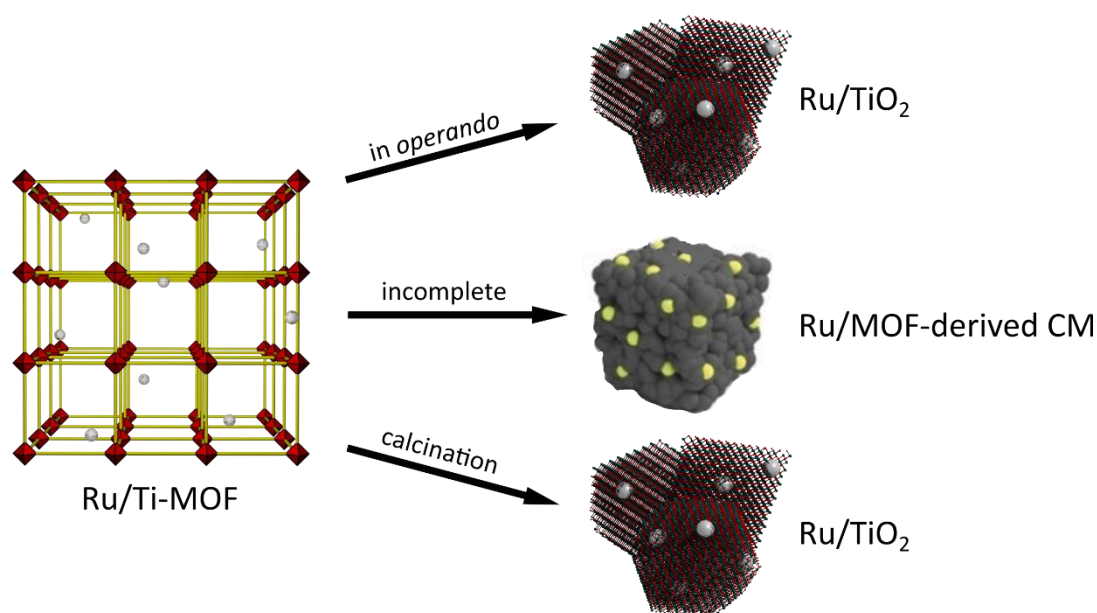


Figure 2.7: Potential pathways (*in operando*, calcination and incomplete activation) for the activation of Ru/Ti-MOF and the materials likely to form. Partially formed Ru loaded TiO₂ could form but is not represented (Figure adapted from ref. 90).

2.3 Titanium MOFs

Since the emergence of the MOF field, the formation of highly stable MOFs has always been desirable, permitting applications in more demanding environments. MOFs synthesised from divalent metals, including Zn²⁺, Co²⁺, Mn²⁺ and Ni²⁺, commonly suffer from poor water stability owing to the metal centre – organic linker interaction being weak.^{91,92} To this end, tetravalent metals are targeted as components for the metal node of the framework. Zr⁴⁺-based MOFs, such as UiO-66, have provided evidence of the stability of frameworks offered by use of these higher valent metals.⁹³ The high charge over ionic radius of high valent metal ions is opposed to that of low valent metals, leading to enhanced reactivities and increased oxophilicity.⁹¹ These properties lend themselves to forming large, rigid, multi-nuclear secondary building blocks (SBUs). Such SBUs promote enhanced framework rigidity, including structural diversity, on account of the high coordination numbers offered.⁹⁴ This is evidenced in the ever-growing library of Zr⁴⁺ MOFs, with diverse SBUs prepared and integrated into the MOF architecture.⁹⁵ Similarly, Ti-MOFs are highly desirable materials. Not only are Ti-MOFs foreseen as materials possessive of high stability (Ti⁴⁺), but Ti-based materials offer unique optoelectronic and photocatalytic properties.^{96,97} In addition, the low toxicity and natural abundance of Ti further promote the investigation into Ti-MOFs.

Whilst the synthesis of Ti-MOFs is attractive, in practice they are unfortunately notoriously difficult to assemble. The enhanced oxygen affinity of Ti⁴⁺ compared to Zr⁴⁺, on account of its smaller ionic radius, leads to stronger Ti-O bonds that can inhibit MOF formation. Ti precursors that would commonly be used are prone to hydrolysis with H₂O under both atmospheric humidity or trace amounts of water in solvent media, resulting in TiO₂ formation.⁹⁸ Indeed, the Ti-O bonds are so strong that solubility is only observed in highly acidic environments (pH ≤ 0) for TiO₂. The consequence of such strong bonds is evident in the difficulty accessing crystalline Ti-MOFs. Not only does the formation of TiO₂ eliminate some Ti precursor from the synthesis, but the affinity of Ti to O results in strong bonds to carboxylate-functionalized linkers. Subsequently, the formation of Ti-O bonds typically prevents bond reversibility that allows MOFs to be produced through inherent error-checking and reorganisation.^{99,100} These properties commonly present as fast, uncontrollable nucleation and irregular growth of the framework, resulting in amorphous materials. Although this is detrimental in the direct synthesis of Ti frameworks, the prospect of including such stable bonds within a MOF remains highly desirable.

Due to the difficulties encountered during Ti-MOF synthesis, it was some 15 years following the inception of the field, in 2009, that the first crystalline and porous Ti-MOF, MIL-125 (Material from Institute Lavoisier), was reported.¹⁰¹ MIL-125 and its derivatives displayed promising photocatalytic properties triggering a surge of activity in the field of Ti-MOFs. It should be noted, however, relative to the overarching MOF field, the number of Ti-based MOFs is limited with only around 20 structures reported at the time of writing, as opposed to the over 90000 unique MOF structures reported.^{91,102} In order to prevent hydrolysis of Ti precursors during Ti-MOF synthesis, several strategies are often employed. The most direct path is via the complete elimination of H₂O from the synthesis environment, involving the handling of reagents under an inert atmosphere in a glovebox and using dry solvents.^{92,99} These conditions are, however, much more involved, and stringent selection of Ti precursors resistant to hydrolysis is more favourable. Commonly, titanium alkoxides (Ti(OR)₄ where R is an alkyl group), are used. The steric hinderance and hydrophobicity of the introduced alkyl groups help prevent the access of H₂O to the Ti centre.^{91,99} Preforming the Ti cluster, as the Ti precursor, is another avenue accessible, providing the benefit of directing the final structure of the MOF, although the original cluster can be prone to reorganisation under reaction conditions, thus in this case the preformed cluster would act solely as a stable source of Ti.^{91,99} The final strategy is via post-synthetic metathesis (PSM) of metal ions, in other words, the post-synthetic

replacement of metal ions with Ti ions within pre-synthesised MOFs.⁹⁹ In addition, solvent selection and controlling pH can be integral in the success of a given synthesis. On this, acetic acid (AcOH) has been shown to strongly assist Ti-MOF synthesis when acting as a solvent or pH controller, or both, in addition to its modulating capabilities.¹⁰³

2.4 Ruthenium Loaded Titanium MOF Derived Ru/TiO₂

2.4.1 Synthesis and Characterisation of MIP-207

To access MOF-derived TiO₂, the activation of a Ti-MOF to generate the metal oxide was targeted. The ease and reproducibility of synthesis under atmospheric conditions of MIP-207 (Materials of the Institute of Porous Materials from Paris) made it an ideal candidate.

MIP-207 is a Ti-MOF constructed from titanium isopropoxide (Ti(O^{*i*}Pr)₄) and 1,3,5-benzenetricarboxylic acid (BTC).¹⁰⁴ The material is formed from the solvothermal synthesis of the two aforementioned compounds in acetic anhydride and AcOH, resulting in tetragonal crystals crystallising in the space group *P4/nbm* with formula [Ti₈(μ₂-O)₈(acetate)₈(BTC)₄]. The unit cell parameters of MIP-207 are $a = b = 24.22 \text{ \AA}$, $c = 7.83 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$. The structure is composed of a Ti₈ metal node cluster bridged via adjacent acetates and BTC carboxylate groups. The bridging groups are orientated in an up-down configuration relative to the symmetrical plane of the cluster core owing to steric hinderance of adjacent BTC molecules. The Ti₈ cluster is linked to four others through the BTC linkers via one of the free BTC *meta* carboxylates relative to the carboxylate composing the Ti₈ cluster, with the remaining free *meta* carboxylate pointing towards the centre of the MOF pore, and remaining uncoordinated. This forms two-dimensional MIP-207 sheets which extend into a three-dimensional material through intermolecular H-bonding occurring between encapsulated guests, and between the guests and the host, where the guests are water molecules positioned between layers. This action stabilises the three-dimensional form of MIP-207 (Figure 2.8).

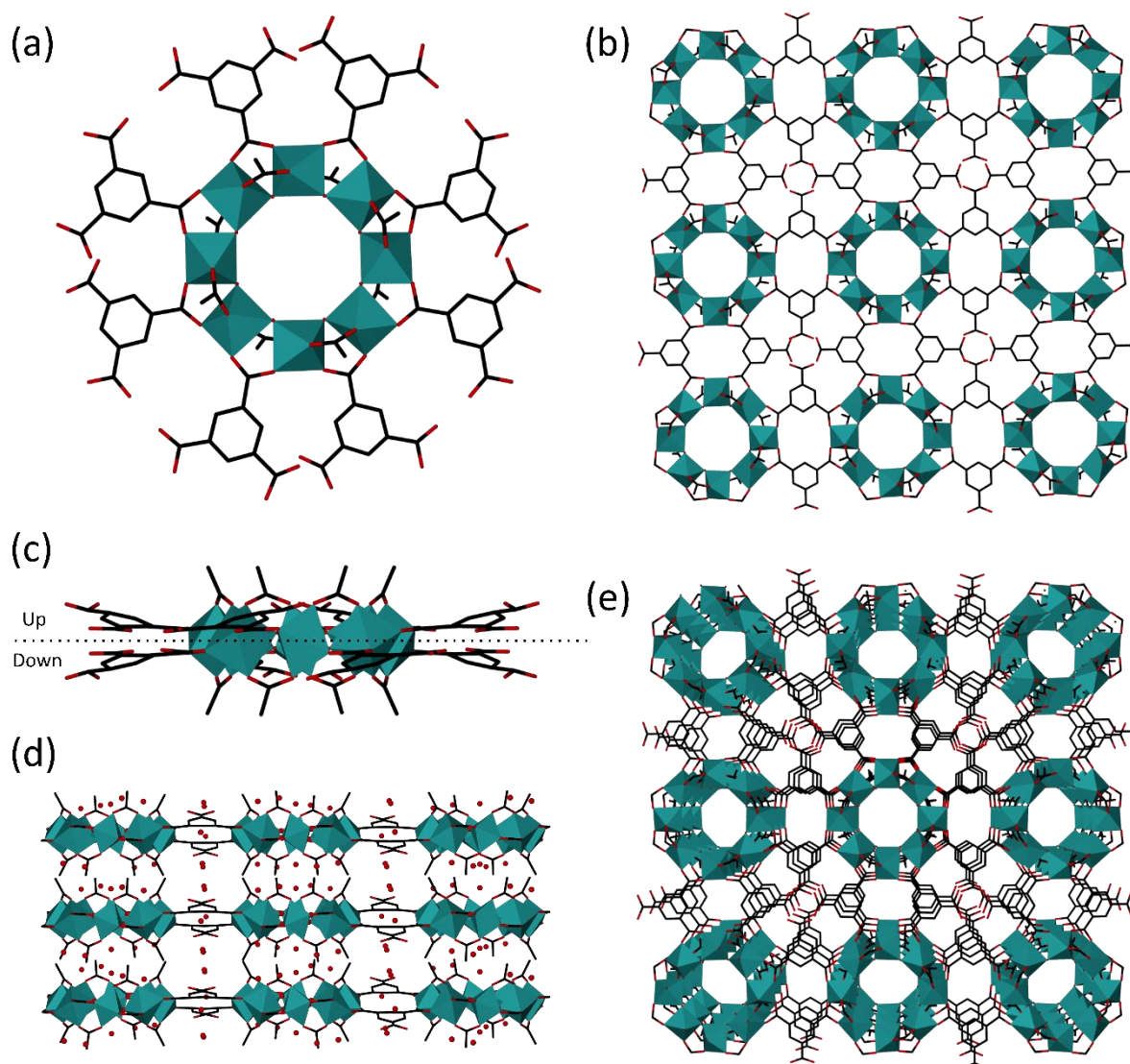


Figure 2.8: Crystal structure of MIP-207 including **(a)** the Ti₈ cluster, **(b)** a single two-dimensional MIP-207 sheet viewed along the *c*-axis, **(c)** the Ti₈ cluster viewed along the *a*-axis exhibiting the up-down configuration of the BTC linkers, **(d)** multiple two-dimensional MIP-207 sheets stacked and viewed along the *a*-axis displaying the guest water molecules (hydrogen omitted for clarity) and **(e)** multiple two-dimensional MIP-207 sheets stacked and viewed along the *c*-axis displaying the micropore system of MIP-207 (C, black; O, red; Ti, blue).

MIP-207 was synthesised using a previously reported method, see experimental 2.7.2.1.¹⁰⁴ To determine the crystal quality (morphology) and size distribution, the synthesised crystals were analysed via TEM and scanning electron microscopy (SEM). Once the samples exhibited a regular form, powder X-ray diffraction (PXRD) was used to analyse the crystallinity of the material and was subsequently compared to the pattern simulated for MIP-207. Following

this, porosity and the surface area of the prepared MIP-207 crystals were determined via gas adsorption analysis.

As-synthesised MIP-207 crystals were collected and thoroughly washed via solvent exchange with acetone, dried, and used for further examination. SEM and TEM analysis of MIP-207 revealed crystals with an average diameter of 117 ± 56 nm (see Appendix 2.9, Figure 2.A.1). The anticipated tetragonal morphology of the crystals was confirmed from the TEM and SEM images (Figure 2.9). The thin, rectangular sheets of MIP-207 evidently vary in size but are on the order of 100 nm. The clear lattice planes visible in the TEM images provide strong evidence of high crystallinity. To confirm this, samples were analysed via PXRD and compared relative to the simulated powder pattern for MIP-207 (Figure 2.10). Good agreement between the patterns indicates the clear formation of MIP-207.

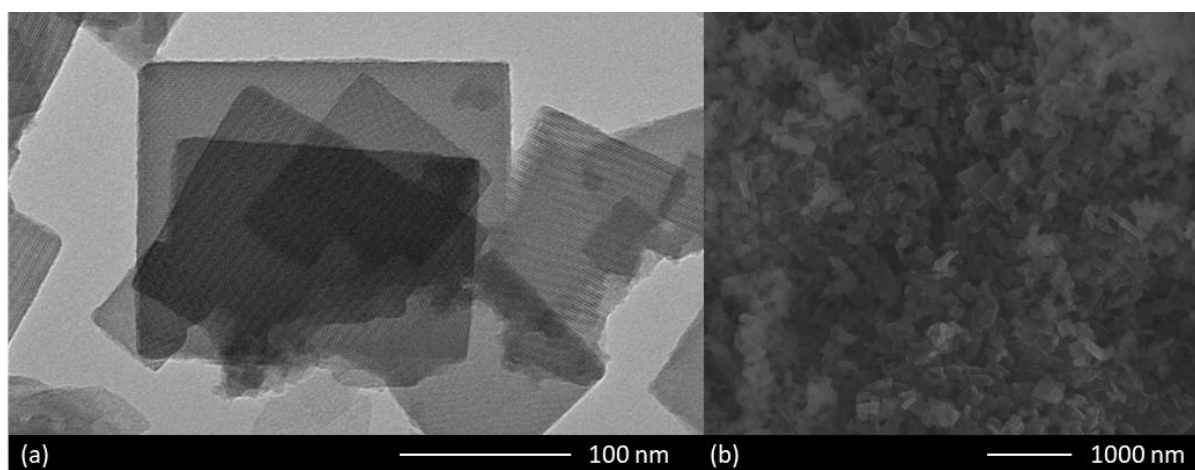


Figure 2.9: (a) TEM and (b) SEM images of as-synthesised MIP-207 which have an average diameter of 117 ± 56 nm.

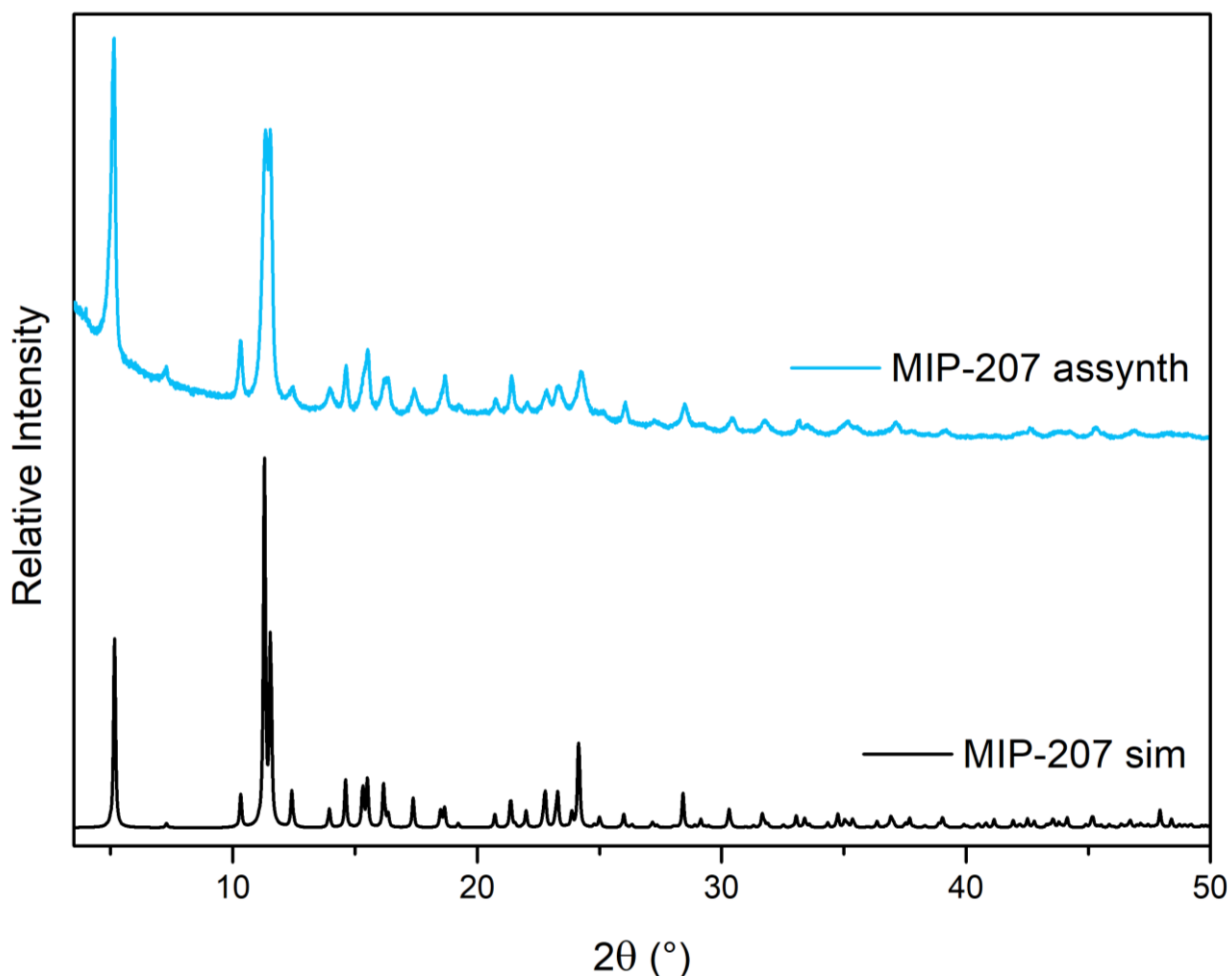


Figure 2.10: PXRD patterns of MIP-207; simulated desolvated MIP-207 (black) and MIP-207 as-synthesised (blue).

With MIP-207 in hand, gas adsorption analysis of the sample was undertaken to establish the pore volume and surface area of the as-synthesised framework possesses before subsequent loading with Ru. A N₂ 77 K adsorption isotherm was collected for MIP-207, post activation from dry acetone (see experimental 2.7.3). The isotherm for MIP-207 is characteristic of a type I isotherm at low partial pressures, exhibiting high uptake of N₂, indicative of microporosity. At higher partial pressures, the gradual increase in the quantity of gas adsorbed with increasing partial pressures suggests the potential of some mesopore characteristics within MIP-207 (Figure 2.11).¹⁰⁵ This is explained through initial covering of the mesopore walls followed by the filling of the pores through multi-layer formation of the adsorbate (N₂). Pore-size distribution (calculated via density functional theory (DFT) N₂ model) confirms the presence of mesopores (see Appendix 2.9, Figure 2.A.2). The Brunauer-Emmett-Teller (BET) surface area and pore volume were calculated from the N₂ isotherm as 530 m² g⁻¹ and 0.28 cm³ g⁻¹ respectively. These values agree with those previously reported for MIP-207.¹⁰⁴

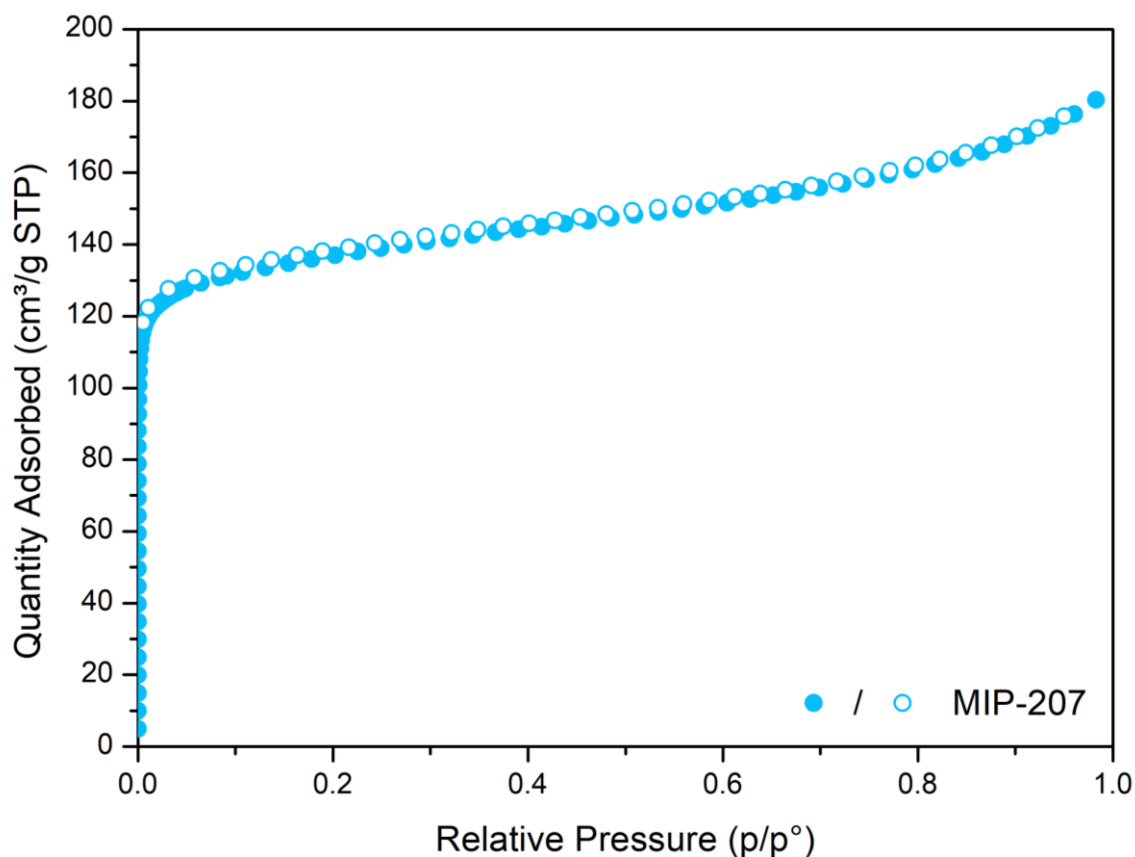


Figure 2.11: 77 K N₂ adsorption isotherm data collected for MIP-207.

2.4.2 Ruthenium Loaded MIP-207

With porous MIP-207 available, synthesis of the catalyst precursor began. Two main pathways were targeted to produce the active catalyst, Ru/TiO₂. Based upon the success of *in operando* MDCs, the first pathway was concerned with the generation of Ru/TiO₂ under reaction conditions.^{80,81} To compliment this, a more conventional method for activation/conversion was sought to compare the *in operando* generated catalyst against. In this instance, calcination was identified as an accessible and suitable procedure.

To prepare MOF derived Ru/TiO₂, MIP-207 was loaded with Ru. This was achieved through aqueous loading of Ru salts directly into the pores of MIP-207 through the incipient wetness impregnation (IWI) method.¹⁰⁶ Porous materials can be considered as ‘molecular sponges’ in the sense that the dry material will be able to adsorb different components (dependent on size) and hold them within its pores, analogous to that of a dry sponge adsorbing water. IWI works on this premise, in that some metal compound is first dissolved into a solvent medium before addition to the porous material to only fill the available pore space. The solvent fills the pores of the material which contains the dissolved metal precursor, effectively loading

the porous material with the desired metal compound with no excess solvent remaining. The solvent can then be removed, typically under elevated temperatures and/or reduced pressure, leaving the now dry porous material loaded with the metal compound.

Being inherently porous materials, MOFs lend themselves to loading of metal salts through IWI, provided retention of long-range crystal order post-loading is not required. In addition, as MOFs are also inherently crystalline, accurate loadings of metal components can be achieved. Based on the molecular formula, quantities of metal to be added can be calculated. The amount of solvent required to fill the pores can then be calculated based on the pore volume accessible in the MOF. The key is to ensure the added solvent is sufficient only to fill the pores. This way, all the solvent will be drawn into the MOF through capillary action, ensuring accurate loadings of metals are introduced and homogenous dispersal of the catalytic material throughout. This process, including the removal of solvent, is depicted in Figure 2.12.

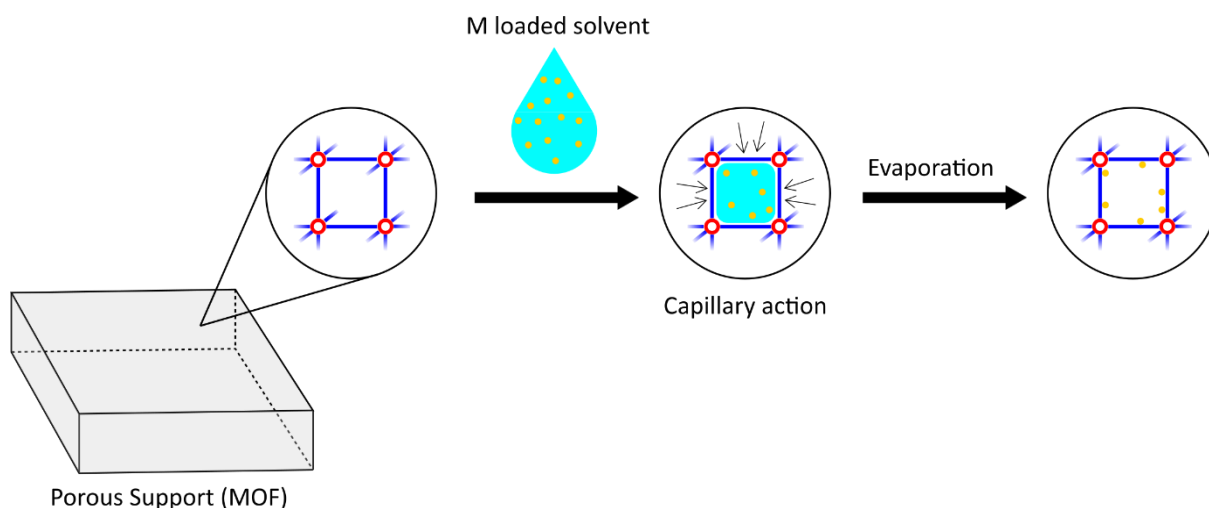


Figure 2.12: Schematic representation of the IWI of a MOF by drawing in the metal (M) loaded solvent via capillary action before removal of the solvent to afford the metal loaded MOF.

To load MIP-207 with Ru, ruthenium(III) chloride (RuCl₃) was selected and dissolved in water. Initially, the total pore volume (0.28 cm³ g⁻¹) of MIP-207 was used to calculate the amount of water required to fill the pores. In practice, however, the amount of water was insufficient and visual inspection indicated a homogenous slurry had not formed. Additional water was added to MIP-207 until a homogenous slurry formed, from which the amount of water required was used to calculate the actual water uptake for IWI. The new value calculated for MIP-207 is 1.34 mL per g of MIP-207. Once the volume of water was known, the amount of RuCl₃ required for a 1 wt. % loading in MIP-207 was calculated and an aqueous solution for typical IWI was made up (see Appendix 2.9, Table 2.A.1) (experimental 2.7.2.2).

PXRD analysis of Ru/MIP-207 showed a reduction in long-range order (see Appendix 2.9, Figure 2.A.3). This is anticipated as the Ru is not loaded into the framework at defined locations but is randomly distributed through the material. Retention of MIP-207 crystallinity is, however, still evident as both the (110) and (310) planes at 5.1° and 11.5° respectively, retain their intensities. To confirm the Ru wt. % loadings in Ru/MIP-207, energy-dispersive X-ray spectroscopy (EDX) was employed. As MOFs are crystalline materials, the abundance of the metals constructing the material in each unit cell will remain constant throughout the crystal. The molecular formula of MIP-207 is [Ti₈(μ₂-O)₈(acetate)₈(BTC)₄], indicating there are 8 titanium atoms present in each unit cell. As such, the average loading of Ru throughout the material within 1 unit cell can be calculated based on the relative Ru:Ti ratios determined via SEM/EDX. This can then be converted into Ru wt. % loadings. Ru/MIP-207 displayed average Ru wt. % loadings of 0.84 ± 0.20 %. Whilst EDX is suitable for quick analyses, at 1 wt. % loadings, the error afforded by such a technique is large. Looking to the future, analysis via techniques such as inductively coupled plasma mass spectrometry (ICP-MS) will yield more accurate data.

2.4.3 Ru/MIP-207 derived Ru/TiO₂ for CO₂ Methanation

When deciding upon reaction conditions, the conditions previously investigated for CO₂ methanation were considered. Temperatures below 300°C promote the formation of CH₄ via CO₂ methanation, as opposed to higher temperatures which favour the reverse water-gas shift reaction, producing CO.^{50,51} As a result, the only temperatures applied in catalytic testing were at, or below, 300°C. H₂:CO₂ ratios also have a strong impact on the success of the reaction. Whilst higher H₂ content will typically increase CO₂ conversions and CH₄ selectivity, H₂ can be considered as a limiting reagent in CO₂ methanation.^{21,50,51} It is important to analyse CO₂ conversion relative to H₂ content in deciding upon an ideal H₂:CO₂ ratio. As H₂ is likely to be the limiting reagent in large scale systems due to its cost, using excessive amounts during CO₂ methanation is cautioned against.²¹ Based upon CO₂ conversion per mole of H₂, no more than a 4:1 ratio of H₂:CO₂ is recommended.²¹ Considering a 3:1 ratio of H₂:CO₂, the CO₂ conversion and low temperature CH₄ selectivity suffer significantly relative to a 4:1 ratio (Figure 2.5).⁵¹ Therefore, a 4:1 ratio of H₂:CO₂ was used for all CO₂ methanation catalytic testing. The final consideration for reaction conditions is the pressure. Although higher pressures typically result in greater CO₂ conversions and higher CH₄ selectivity, this effect is less pronounced at lower temperatures (Figure 2.3).⁵⁰ We were inspired by Ru/TiO₂ catalysts exhibiting conversion at

room temperature and atmospheric pressure to aim for such activity in MOF-derived materials.⁶⁸ For that reason, catalytic testing was run at near atmospheric pressures (~1.2 bar).

The gas phase catalytic reactor accessible for CO₂ methanation catalytic testing was a stainless-steel, high-pressure batch reactor. A schematic representation of the batch reactor is depicted in Figure 2.13. The batch reactor is a small volume (20.45 mL) stainless steel vessel connected to a high-pressure manometer (0-80 bar), a gas manifold (H₂, CO₂, He), a vacuum pump, a gas chromatograph (GC) coupled to both a flame ionising detector (FID) and a thermal conductivity detector (TCD), and a pulse nozzle coupled to a residual gas analyser (RGA). The maximum operating conditions of the batch reactor is from 25-300°C and up to a maximum pressure of 80 bar. During long reactions (> 1 h), real time reaction progression can be followed through continuous pulsing of the reaction gas mixture at low pressures into the RGA (2×10^{-6} Torr). Characteristic m/z mass fragments for the reaction reagents and products can be tracked allowing the consumption and production of each respective component to be determined over the reaction course. Preparing the RGA for analysis, however, requires a minimum of 30 minutes to begin to acquire accurate readings. In addition, if there are overlapping m/z fragments of components within the reaction gas mixture, accurate results for single products are inaccessible, resulting in limited application of the RGA in certain instances. Unlike the RGA, analysis of the reaction gas mixture by GC can only be conducted once per reaction. As the GC has a low-pressure working range (1 bar), the reaction gas mixture requires either evacuation or filling with an inert gas (N₂) to this pressure before injection onto the column of the GC. The FID can detect carbon-containing compounds through their pyrolysis which generates a current between the adjacent electrodes, signalling detection.¹⁰⁷ The detector is, however, only limited to organic/hydrocarbon containing compounds.¹⁰⁷ The TCD is able to detect those components that are not prone to pyrolysis and thus detectable via the FID by analysing the thermal conductivity of matter passing through the detector.¹⁰⁷

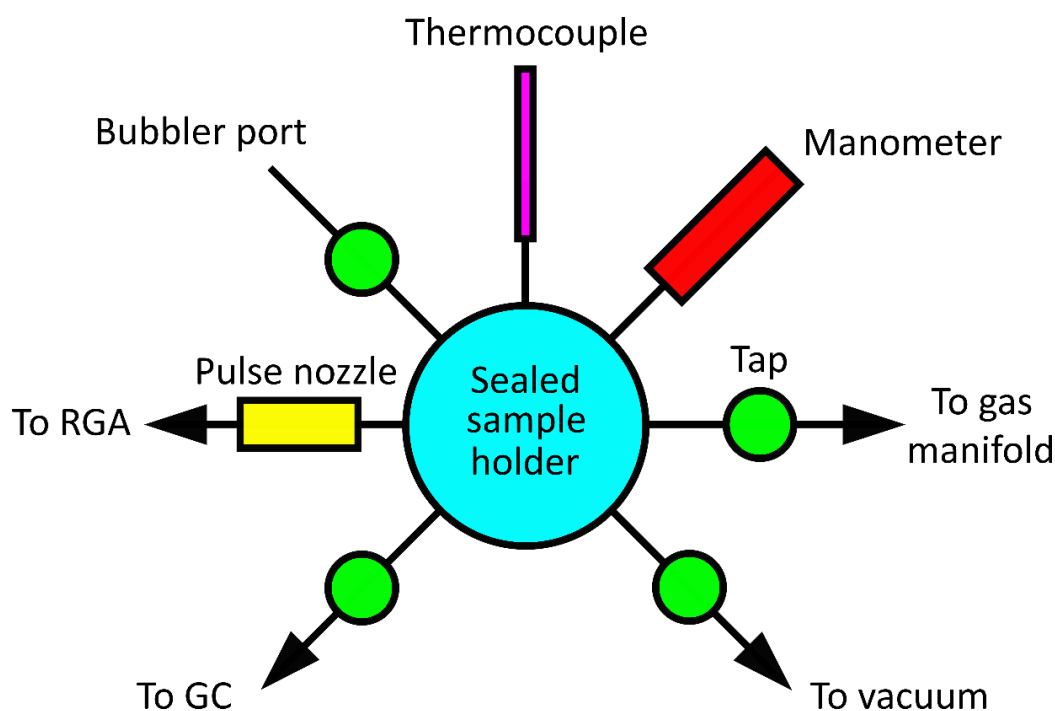


Figure 2.13: Schematic of the batch reactor used during catalytic testing. An image of the reactor itself is accessible in Appendix 2.9, Figure 2.A.4.

With reaction conditions identified, preparation of the catalyst began. As mentioned, two main pathways to produce the Ru/TiO₂, were tested. The *in operando* derived Ru/TiO₂ from Ru/MIP-207 (**Ru/TiO₂(op.)**) would be activated under the reaction conditions and no further preparation was required before catalytic testing. The more conventional calcined material, however, required an initial calcination step before catalytic testing. To determine the point at which the organic component of MIP-207 breaks down resulting in the generation of the metal oxide, TiO₂, thermogravimetric analysis (TGA) of the Ru loaded sample in air (80:20 N₂:O₂) was run (see Appendix 2.9, Figure 2.A.5). The initial gradual loss before 300°C represents the removal of solvent from the pores of the framework. After 300°C, the material undergoes a steep mass decline, characteristic of the decomposition of the organic component of the framework. At 400°C, the organic component is fully degraded and only the metal oxide, in this case TiO₂, remains. Calcination of Ru/MIP-207 was consequently run at 400°C for 4h (experimental 2.7.2.3) to generate MOF derived Ru/TiO₂ via calcination (**(Ru/TiO₂(calc.))**).

Initial CO₂ methanation reactions were carried out with both **Ru/TiO₂(op.)** and **Ru/TiO₂(calc.)** to determine the activities under the reaction conditions over several cycles (experimental 2.7.4.3). To ensure consistent Ru content between samples, the weight loss of calcined samples was calculated and used to determine the mass of **Ru/TiO₂(calc.)** that would equal the original Ru/MIP-207 mass used in the generation of **Ru/TiO₂(op.)**. Once the sample

was weighed, loaded into the sample holder, and sealed in the batch reactor cell, the reagent gases were introduced. CO₂ (200 mbar) and H₂ (1000 mbar) were added to the reactor cell in a 1:4 CO₂:H₂ ratio. The reaction was heated to the appropriate temperature for a given run (250°C and 300°C for **Ru/TiO₂(op.)** and 150°C, 200°C and 300°C for **Ru/TiO₂(calc.)**) for 5 h for the **Ru/TiO₂(op.)** to allow generation of the active catalyst, and for 1 h for **Ru/TiO₂(calc.)** as the active phase had already been generated through the calcination step. The production of CH₄ and consumption of CO₂ was monitored at the end of the reaction via GC in addition to the formation of any by-products (CO, longer chain C products). Longer chain C products are derived from the organic component of the MOF during generation of **Ru/TiO₂(op.)**. The formation of longer chain C products have been observed for other MOF-derived *in operando* generated catalysts.⁸¹ The results for catalysis of **Ru/TiO₂(op.)** and **Ru/TiO₂(calc.)** are depicted in Figures 2.14 and 2.15, the experimental data is accessible in Appendix 2.9, Table 2.A.2. CO₂ conversion percentages are calculated from the detected amount of all products (both CH₄ and by-products) to CO₂ and products. CH₄ selectivity is calculated based on the amount of detected CH₄ relative to all products.

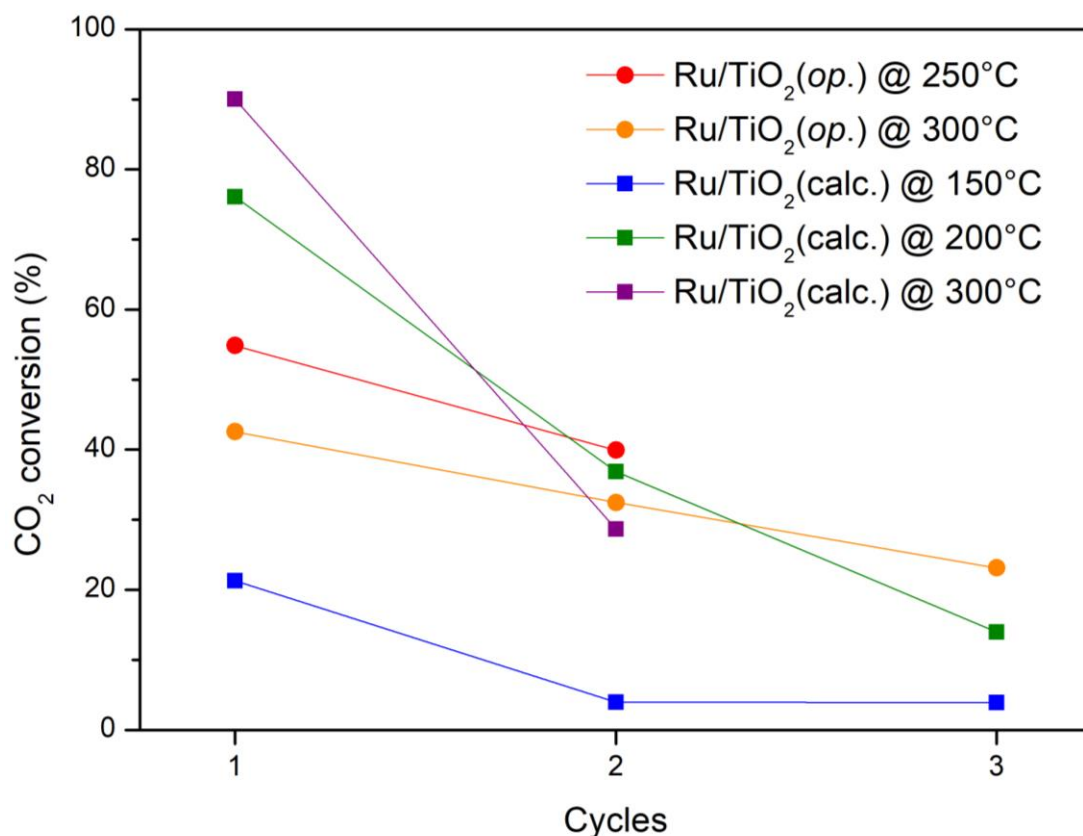


Figure 2.14: CO₂ conversion (%) for CO₂ methanation catalysed via **Ru/TiO₂(op.)** (●) and **Ru/TiO₂(calc.)** (■) at different temperatures on the batch reactor.

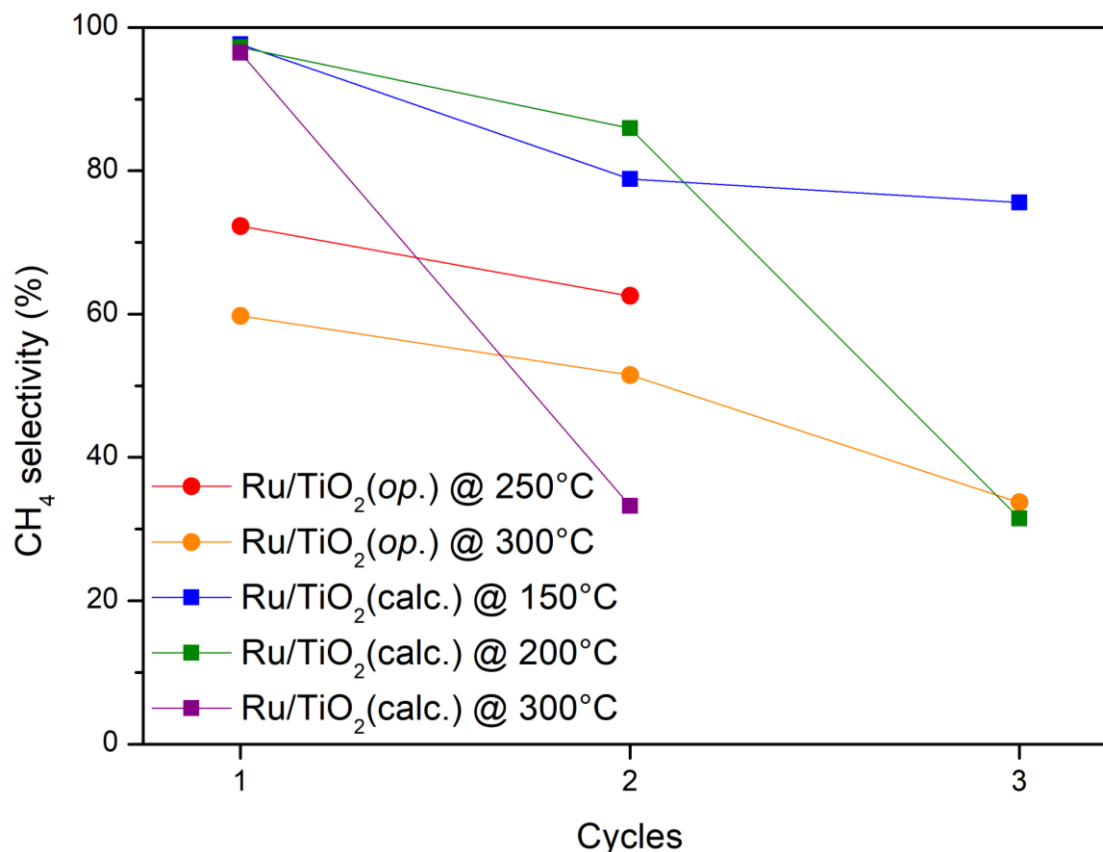


Figure 2.15: CH₄ selectivity (%) for CO₂ methanation catalysed via **Ru/TiO₂(op.)** (●) and **Ru/TiO₂(calc.)** (■) at different temperatures on the batch reactor.

The data observed for the Ru/MIP-207 derived Ru/TiO₂ catalysts for CO₂ methanation demonstrate the effectiveness of the catalyst over several cycles. Upon first analysis, catalysts activated at higher temperatures exhibit enhanced CO₂ conversions. However, CH₄ selectivity reduces with successive cycles, an indication of catalyst deactivation. Delving into the catalytic results deeper, the reasons for the trends become clear.

Considering the reaction temperatures used for the **Ru/TiO₂(op.)** runs, it is evident there is not a great deal of difference between the CO₂ conversions and CH₄ selectivity. The main difference is the sample run at 300°C (**Ru/TiO₂(op.)@300°C**) exhibits slightly higher CO₂ conversions and CH₄ selectivity compared to the sample run at 250°C (**Ru/TiO₂(op.)@250°C**). This contrasts with expectations for higher temperature CO₂ methanation reactions in which a decrease in CO₂ conversions and CH₄ selectivity would be anticipated (Figures 2.3, 2.4 and 2.5).^{50,51} The difference observed is likely a result of better generation of the active catalyst phase at 300°C, leading to enhanced reactivity. Comparatively, at 250°C, the temperature is not high enough to permit the complete activation of the Ru loaded MOF, resulting in a less

effective, partially formed catalyst, accounting for the reduction in activity. PXRD analysis of **Ru/TiO₂(*op.*)@300°C** shows the generation of TiO₂ whereas **Ru/TiO₂(*op.*)@250°C** shows residual MIP-207 material, specifically intensity observed for the (110) peak, however, the reduction in intensity of the other peaks indicates significant degradation of the material (Figure 2.16). This is supported by TEM analysis of **Ru/TiO₂(*op.*)@250°C** and **Ru/TiO₂(*op.*)@300°C** which show the retention of lattice planes consistent with MIP-207 and the formation of a new, small, crystalline phase (titania), respectively (see Appendix 2.9, Figure 2.A.6). For the **Ru/TiO₂(*op.*)@250°C** sample, this can be considered as the beginning of the formation of partially formed Ru/TiO₂ via *in operando* conditions as retention of MOF-characteristics indicates it has not fully formed. Contrastingly, for the **Ru/TiO₂(*op.*)@300°C** sample, Ru/TiO₂ is formed completely via *in operando* conditions. Of note, titania naturally exists in three main crystal polymorphs, those being anatase, rutile and brookite.^{108,109} Titania is composed of distorted TiO₆ octahedra, the difference between the polymorphs relating to the three-dimensional stacking. Both anatase and rutile are tetragonal whereas brookite is orthorhombic.¹⁰⁹ Brookite is the least stable titania phase and consequently is much less common than anatase and rutile. As a result, it has not received the levels of attention the other types have.^{108,109} Under *in operando* conditions, anatase is formed (see Appendix 2.9, Figure 2.A.7).

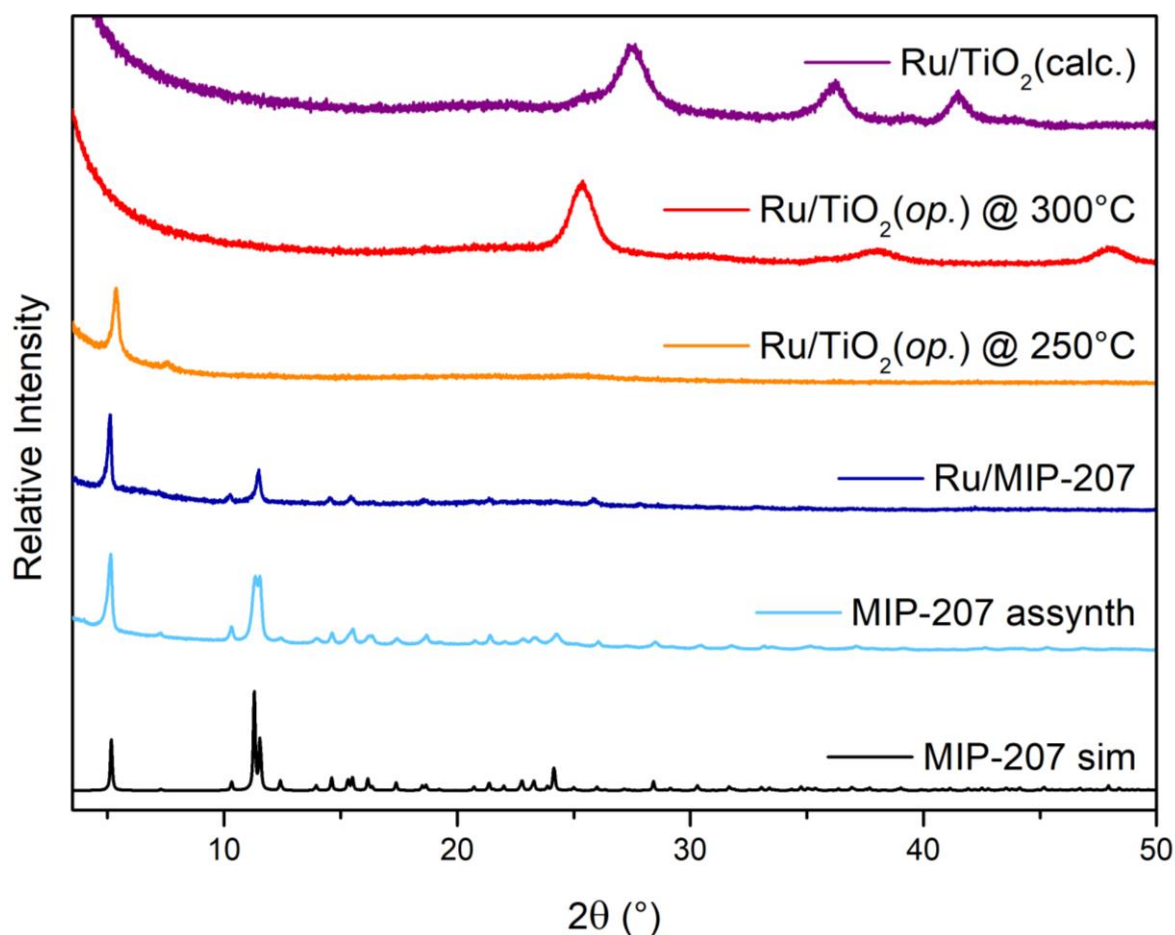


Figure 2.16: PXRD patterns of MIP-207; simulated desolvated MIP-207 (black), MIP-207 as-synthesised (blue), Ru/MIP-207 (dark blue), **Ru/TiO₂(op.)@250°C** after 2 cycles (orange), **Ru/TiO₂(op.)@300°C** after 3 cycles (red) and **Ru/TiO₂(calc.)** (purple).

When considering **Ru/TiO₂(calc.)**, the activities exhibit a similar trend to **Ru/TiO₂(op.)**. At 300°C (**Ru/TiO₂(calc.)@300°C**), the activity is increased compared to the sample run at 200°C (**Ru/TiO₂(calc.)@200°C**), but both are substantially more active than the sample run at 150°C (**Ru/TiO₂(calc.)@150°C**). Again, this contradicts the expected trend. Likely, as Ru/TiO₂ has already been generated in the initial calcination step, the higher temperatures help control the kinetics of the reaction. As these reactions are performed under batch conditions, the confined gas must encounter the catalyst as opposed to flow reaction conditions in which the gas is directly flowed over the catalyst. As there is only ~15 mg of 1% loaded Ru/TiO₂ in a reactor cell with volume of 20.45 mL, at lower temperatures the chance of contact is reduced relative to higher temperatures, owing to collision theory, leading to enhanced conversions at higher temperatures.

Unlike the titania produced under *in operando* conditions, under calcination conditions, rutile is formed predominantly with trace proportions of anatase (Figure 2.16) (see Appendix

2.9, Figure 2.A.7). This result confirms the generation of Ru/TiO₂ via calcination. The formation of both anatase for **Ru/TiO₂(op.)** and rutile for **Ru/TiO₂(calc.)** can rationalise the major reduction in catalyst activity for all runs, evidenced as the drop in CO₂ conversion (Figure 2.14). Whilst metallic Ru is recognised as the active phase responsible for the CO₂ methanation, other forms of Ru such as RuO₂, have been observed to form under similar reaction conditions as those employed here.^{110,111} Kim *et al.* have shown the type of TiO₂ polymorph used in CO₂ methanation can impact drastically on the resulting catalysts performance.¹¹² Under activation conditions, RuO₂ on anatase will form large RuO₂ particles, detached from the anatase surface. Once under reaction conditions, the RuO₂ is deposited back onto the anatase surface as metallic Ru. This process leads to the sintering of Ru, as deposits were agglomerates of small particles with low to no mobility (Figure 2.17). When on rutile, RuO₂ can epitaxially grow on the crystal surface as the same crystal structure is possessed by both rutile and RuO₂, and they share extremely similar lattice parameters (rutile TiO₂: $a/b = 4.5933 \text{ \AA}$, $c = 2.9592 \text{ \AA}$; RuO₂, $a/b = 4.4994 \text{ \AA}$, $c = 3.1071 \text{ \AA}$), epitaxial interactions occur.¹¹² Under activation conditions, layers of RuO₂ typically grow around rutile particles, occasionally acting as a ‘crystalline glue’ between adjacent particles. Under reaction conditions, the sandwiched RuO₂ layers are inaccessible for catalysis and metallic Ru is only present at the tips of the rutile crystals (Figure 2.17). These behaviours mean that using either pure anatase or pure rutile reduces the activity of the catalyst. In order to circumvent this issue, using a mixture of the two (ideally 15-30% rutile content), produces a highly active catalyst, where anatase is essentially used as a dilutant to allow dispersion onto the rutile polymorph.¹¹³ It should be noted that whilst mixed anatase-rutile catalysts are stable at lower temperatures (150°C), treatment at higher temperatures (250°C) can lead to sintering of Ru.¹¹⁴

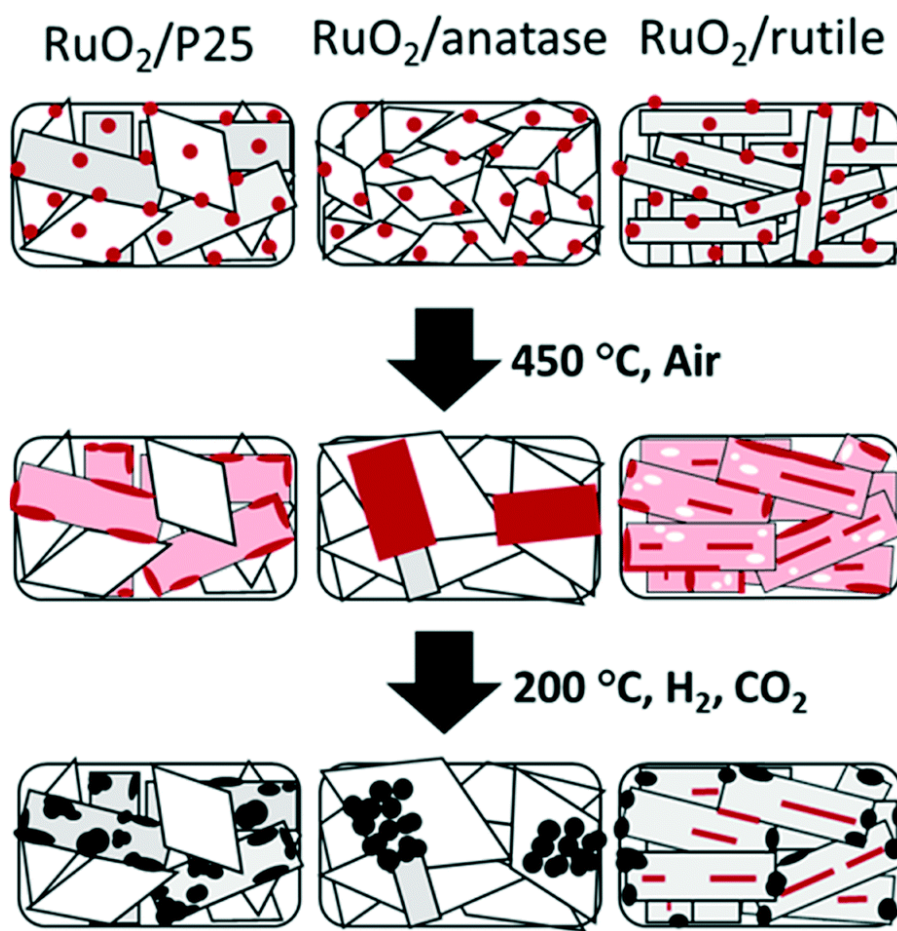


Figure 2.17: Schematic representation of the behaviour of RuO₂ nanoparticles (red) on different polymorphs of titania, rutile (grey) and anatase (white), and P25 (80:20 ratio of Anatase:Rutile), after activation, RuO₂ epitaxially grown sheets (pink), and the subsequent effect of metallic Ru (black) deposition under reaction conditions (Figure reprinted from ref. 112).

Based upon the polymorph of the titania supports for **Ru/TiO₂(op.)** and **Ru/TiO₂(calc.)** catalysts, being both pure anatase and predominantly rutile respectively, we anticipate sintering of the Ru over consecutive cycles lead to loss of activity. It is believed this results from Ru migration and deposition either through the metallic or RuO₂ phase, both of which are able to be produced under reaction conditions. TEM analysis of **Ru/TiO₂(op.)@250°C**, **Ru/TiO₂(op.)@300°C** and **Ru/TiO₂(calc.)@300°C**, compared against the material pre-catalysis, did not yield any quantitative conclusions on Ru sintering (see Appendix 2.9, Figures 2.A.6 and 2.A.8). As a result, scanning transmission electron microscopy (STEM) EDX elemental mapping was pursued to investigate Ru dispersion on the catalytic material pre- and post-catalysis.

As-synthesised MIP-207 revealed a homogenous dispersion of Ti and O throughout the framework (see Appendix 2.9, Figure 2.A.9). This is expected as both Ti and O are the main components constructing the node. Mapping of Ru/MIP-207 did not show any discernible Ru agglomeration or nanoparticles (see Appendix 2.9, Figure 2.A.10). The Ru distribution appears predominantly as noise as at such low loadings (1 wt. %) and assuming homogenous dispersion throughout the framework, detection of single Ru atoms is difficult. It should be noted the L_{α} of Ru (2.558 keV), typically used to detect Ru, has significant overlap with the K_{α} of Cl (2.621 keV). The potential presence of Cl from the RuCl₃ precursor used for IWI of MIP-207 could impact the validity of detected Ru. As such, the K_{α} of Ru (19.233 keV) was used to ensure only Ru would be detected. HAADF (high-angle annular dark-field) imaging of **Ru/TiO₂(op.)@300°C** revealed clear formation of small nanoparticles (see Appendix 2.9, Figure 2.A.11). HAADF imaging depicts regions of higher atomic mass as brighter areas, thus causing the metallic Ru nanoparticles to stand out as bright spots on the darker, but still bright, titania support. Elemental mapping confirmed they are composed of Ru (Figures 2.18 and 2.A.12, see Appendix 2.9). Whilst it can be seen the nanoparticles are somewhat distributed over the support, some regions are free of nanoparticles whereas others exhibit higher densities. It is expected over successive cycles, the Ru nanoparticles will continue to agglomerate, causing reduction in CO₂ conversion. As opposed to **Ru/TiO₂(op.)**, **Ru/TiO₂(calc.)** possesses a much greater reduction in CO₂ conversion. Elemental mapping of **Ru/TiO₂(calc.)** pre-catalysis reveals enhanced levels of Ru agglomeration (Figure 2.19). In the post-catalysis sample, **Ru/TiO₂(calc.)@300°C**, elemental mapping revealed further agglomeration occurred, appearing as large masses of Ru centred around individual particles (Figures 2.20 and 2.A.13, see Appendix 2.9). This likely causes the reduction in catalytic activity observed after consecutive cycles for both catalysts.

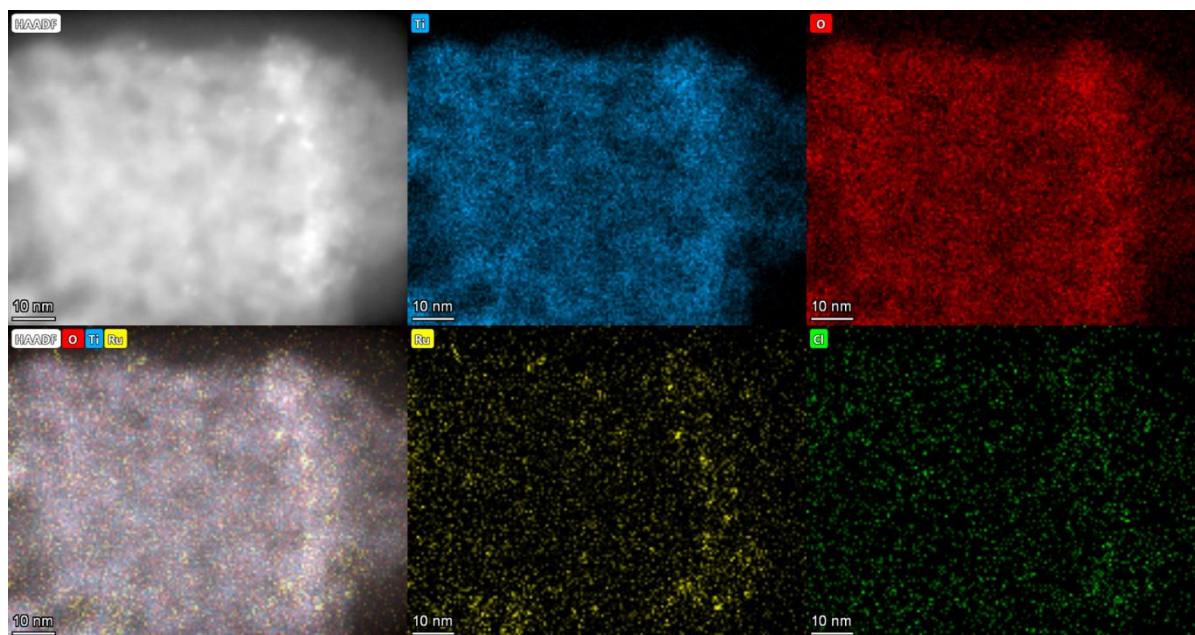


Figure 2.18: STEM-EDX images of **Ru/TiO₂(*op.*)@300°C** revealing an initial agglomeration of Ru nanoparticles throughout the framework (Ti, blue; O, red; Ru, yellow; Cl, green).

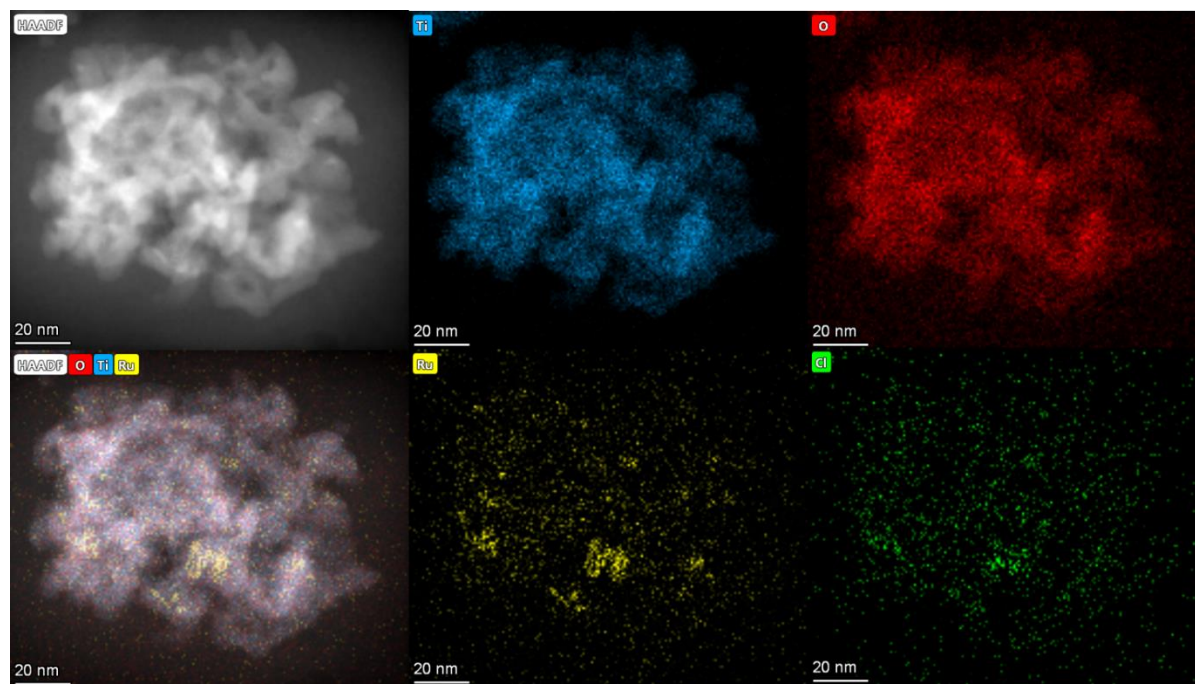


Figure 2.19: STEM-EDX images of **Ru/TiO₂(*calc.*)** pre-catalysis revealing Ru agglomeration (Ti, blue; O, red; Ru, yellow; Cl, green).

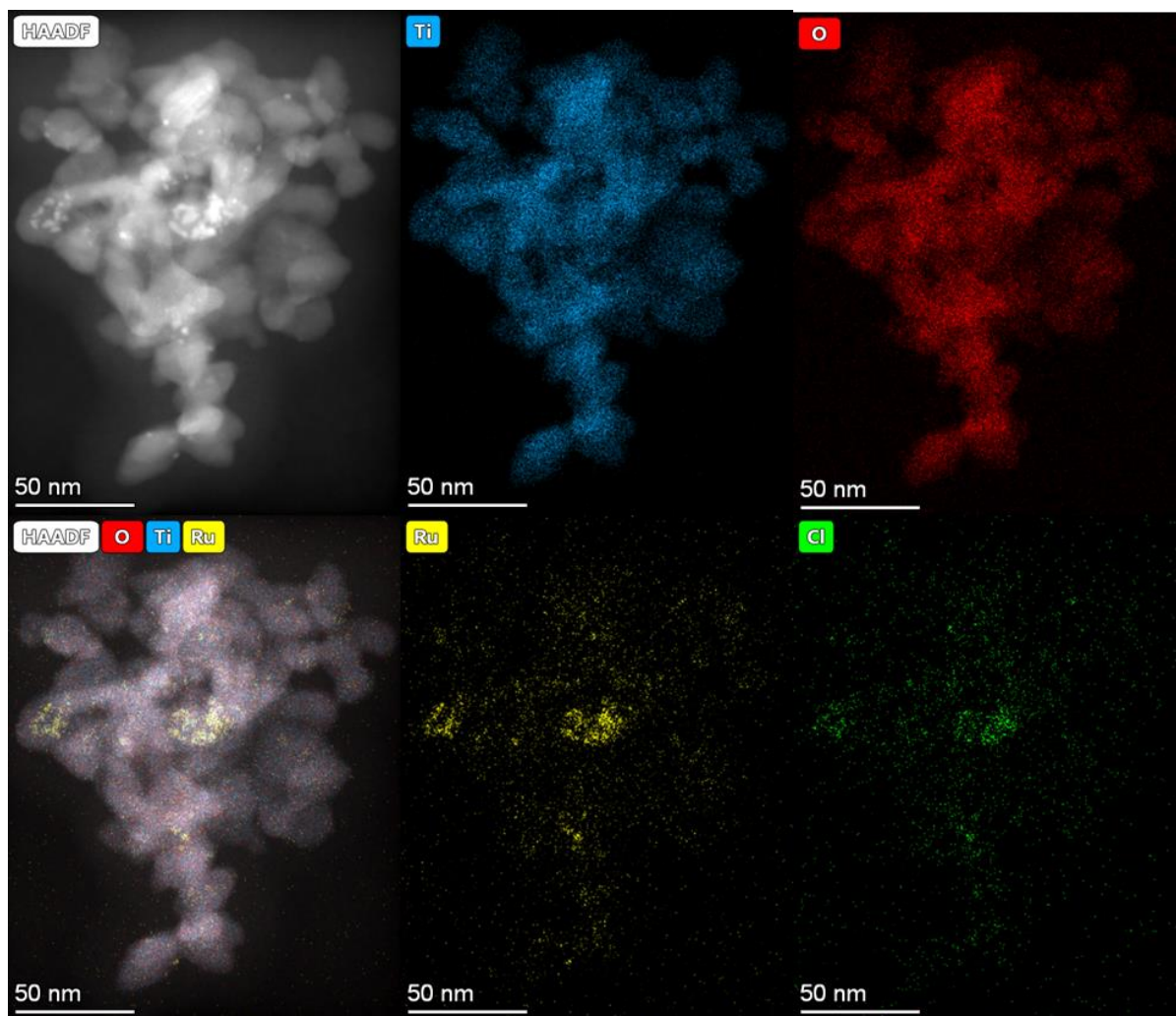


Figure 2.20: STEM-EDX images of **Ru/TiO₂(calc.)@300°C** revealing enhanced levels of Ru agglomeration (Ti, blue; O, red; Ru, yellow; Cl, green).

From the elemental mapping of the **Ru/TiO₂(op.)** and **Ru/TiO₂(calc.)** catalysts, it is evident Ru agglomeration is occurring, consistent with loss of catalytic activity. In addition, through the different stages of activation and generation of the active material, gas adsorption analysis reveals loss of porosity and surface area (see Appendix 2.9, Figures 2.A.14 and 2.A.15). Not only does the titania polymorph produced play a role in Ru agglomeration, but the lack of porosity, surface area and three-dimensionality of the as-synthesised framework may also contribute. Therefore, our focus shifted to titanium-based frameworks with a more defined three-dimensional structure, with consideration into attempting to form mixed-phase supports to prevent Ru agglomeration, and hence, loss of catalytic activity.

2.5 Ruthenium Loaded Heterometallic Titanium MOF Derived Ru/TiO₂

2.5.1 Synthesis and Characterisation of MUV-10(X)

Much like MIP-207, a Ti-MOF easily and reproducibly prepared under atmospheric conditions was pursued. Critically, the ideal candidate would have enhanced porosity and surface area, whilst possessing a three-dimensional network structure. Analysis of the literature on Ti-MOFs revealed the MUV-10(X) (Materials of Universidad de Valencia) family of frameworks exhibit the desired properties but, as heterometallic frameworks, present an opportunity to form mixed phase supports.

MUV-10(X) is a heterometallic Ti-MOF, where X can be Ca, Mn, Ba, etc., and is constructed from Ti(O^{*i*}Pr)₄, a source of the other metal comprising the framework (typically some metal salt), X, and BTC.^{115,116} The material is formed from the solvothermal synthesis of the aforementioned compounds in *N,N*-dimethylformamide (DMF) and AcOH. The synthesis yields octahedral crystals crystallising in the space group *Pm*-3, with formula [Ti₃X₃(μ₃-O)₂(BTC)₄(H₂O)₆]. The cubic unit cell parameters of MUV-10(X) are $a = b = c = 15.84 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$. The structure is composed of Ti₂X₂(μ₃-O)₂(H₂O)₄(CO₂)₈ SBUs connected via fully deprotonated BTC linkers from which the SBU (CO₂) is derived. Within the node, the Ti centres adopt an octahedral geometry whilst the X centres adopt a capped trigonal prismatic geometry (Figure 2.21).

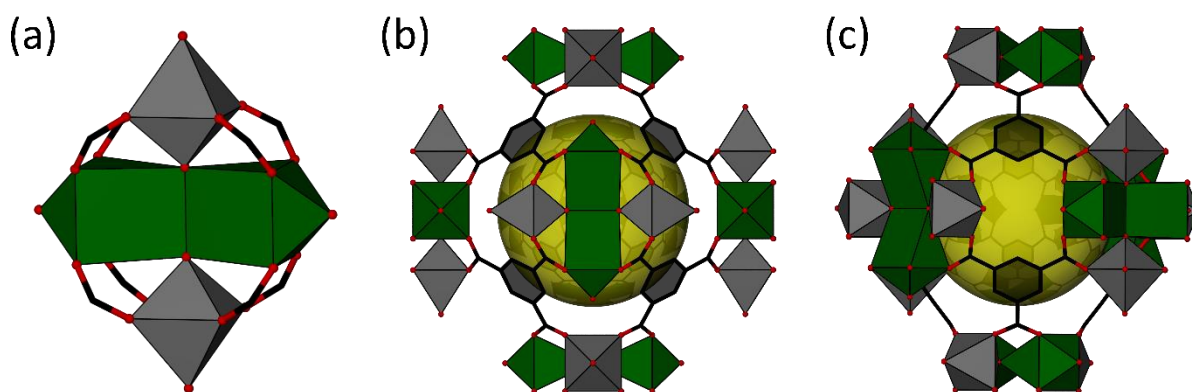


Figure 2.21: Crystal structure of MUV-10(X) including (a) the heterometallic cluster, (b) MUV-10(X) structure viewed along the *a/b/c*-axis including the pore space (yellow sphere) and (c) MUV-10(X) structure viewed between the *a/b/c*-axes including the pore space (yellow sphere) (C, black; O, red; Ti, grey; X, green).

Based on the heterometallic clusters composing the MUV-10(X) MOF family, the metal oxide derived during catalyst activation will presumably be composed of 50% each of Ti and X (excluding O). As the composition of the metal oxide support is known to influence catalytic activity, the mixed phase oxides that may be formed, theoretically, could impact this. When considering elements within the same group, this would permit investigation into the catalytic impact, if any, of subtle changes in Lewis acidity. Ca, Sr and Ba have all been integrated as X in MUV-10(X), as such, this subfamily of MUV-10 emerges as an ideal series to investigate such changes. MUV-10(Ca), MUV-10(Sr) and MUV-10(Ba) were synthesised according to a literature procedure with minor alterations, see experimental section 2.7.2.4. To determine the crystallinity of the material, PXRD powder patterns were collected for the samples and compared to the pattern simulated for MUV-10(Ca). Crystal quality (morphology) and size distribution of the synthesised crystals were also analysed via SEM. Following this analysis, pore volumes and surface areas of the prepared MUV-10 samples were determined via gas adsorption analysis.

As-synthesised MUV-10 crystals were collected and thoroughly washed via solvent exchange with DMF and methanol (MeOH), dried, and used for further examination. Samples were analysed via PXRD and compared to the simulated powder pattern for MUV-10(Ca) (Figure 2.22). Good agreement between the as-synthesised and simulated MUV-10(Ca) indicates the clear formation of MUV-10(Ca). This is additionally the case for MUV-10(Sr), however, the peaks are much broader, suggesting the crystals are smaller in size. The powder pattern of MUV-10(Ba) is similar to that of MUV-10(Ca) simulated, however it possesses extra peaks suggesting the structure may subtly differ from that of MUV-10(Ca). This is likely due to the coordination geometries accessible by Ba(II) which are known to be varied, most frequently exhibiting a coordination number of 9, but can possess coordination numbers from 3 all the way up to 12, potentially changing some connectivity within the node.¹¹⁷ Ca is also known to be varied, but as a result of its smaller size, coordination numbers of 6 to 8 are more frequent.¹¹⁸ As the crystals formed were sufficiently large, structural characterisation of MUV-10(Ba) via single crystal X-ray diffraction (SCXRD) to elucidate the structural differences accounting for the observed powder pattern was undertaken. To collect SCXRD data (experimental 2.7.5), the crystals were mounted on Mitigen mounts in paratone-N oil before exposure to the X-ray source. Solution and refinement of the structure revealed small differences in the structure accounting for the pattern observed. The MUV-10(Ba) crystallises in the space group *P4/mbm*, with formula [Ti₃Ba₃(μ₃-O)₈(BTC)₄(DMF)₂]. The tetragonal unit

cell parameters of MUV-10(X) are $a = b = 24.64 \text{ \AA}$, $c = 14.29 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$. The greatest differences between the MUV-10(Ba) and MUV-10(Ca) structures occur at the SBUs. As theorised, Ba adopts a coordination number of 9, and a tricapped trigonal prismatic coordination geometry. In two of the three SBUs composing the unit cell, disordered DMF molecules coordinate to the Ti centre at the axial position, causing the adoption of an octahedral geometry. At the final SBU, the axial position seems to remain free and instead, a basally distorted square pyramidal geometry (Ti centre is out of the basal plane) is adopted (there is no significant electron density here consistent with coordination to the remaining axial site). The structure of MUV-10(Ba) is depicted in Figure 2.23. The changes in coordination geometry are accompanied by changes to the pore dimensions of the framework. Whilst in MUV-10(Ca) the pore dimensions are equivalent in all directions ($12.93 \text{ \AA}$), in MUV-10(Ba) the pore is elongated along the a axis ($15.06 \text{ \AA}$), remains approximately the same along the b axis ($12.90 \text{ \AA}$) and compressed along the c axis ($11.30 \text{ \AA}$). The subtle changes in the MUV-10(Ba) structure relative to the MUV-10(Ca) structure account for the observed powder pattern; and phase purity is shown by the simulated pattern from the solved MUV-10(Ba) structure closely matching that of the as-synthesised sample (see Appendix 2.9, Figure 2.A.16). The crystallographic information for MUV-10(Ba) is reported in Table 2.A.3, see Appendix 2.9. All of the experimentally collected powder patterns are consistent with the simulated powder patterns of MUV-10(Ca) and MUV-10(Ba), indicating formation of crystalline MUV-10(Ca), MUV-10(Sr) and MUV-10(Ba) respectively.

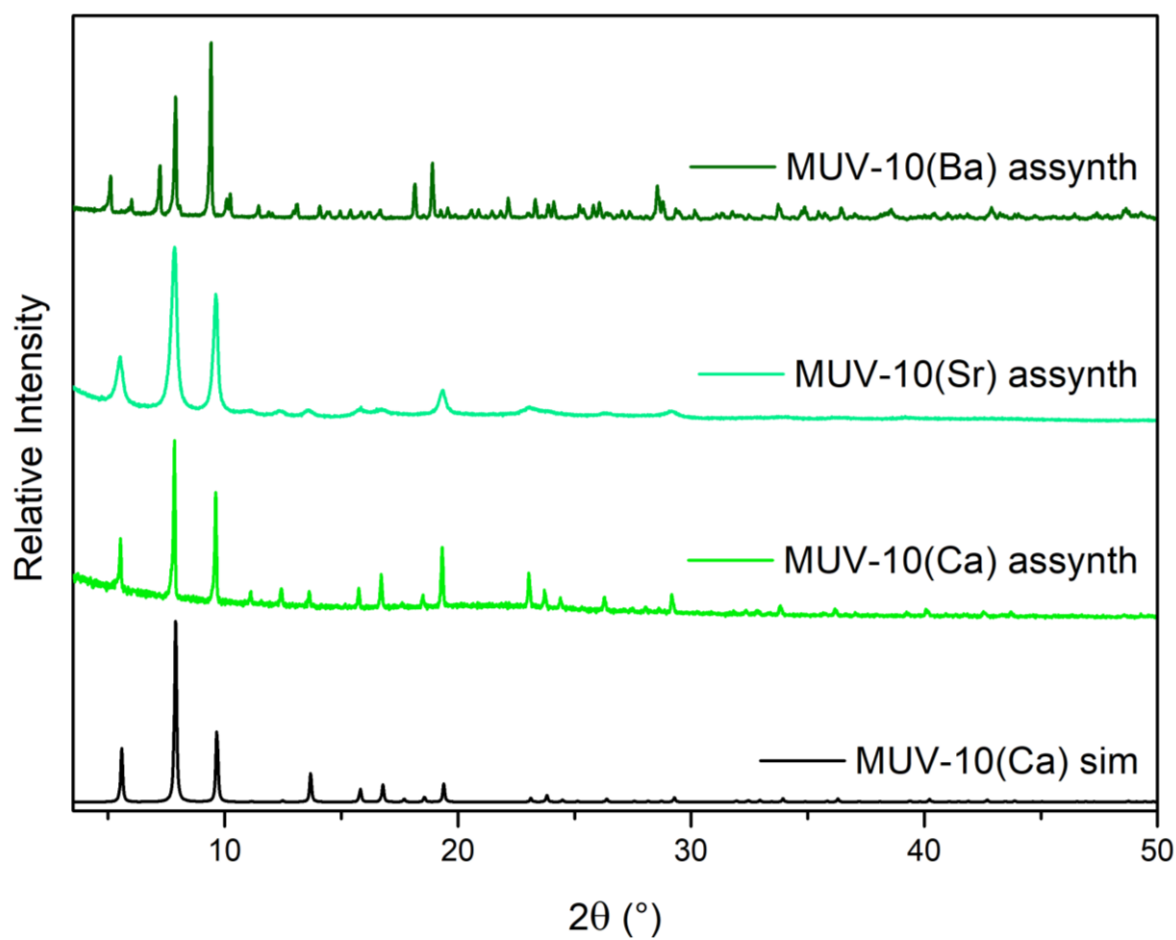


Figure 2.22: PXRD patterns of MUV-10; simulated MUV-10(Ca) (black), MUV-10(Ca) as-synthesised (green), MUV-10(Sr) as-synthesised (aqua) and MUV-10(Ba) as-synthesised (dark green).

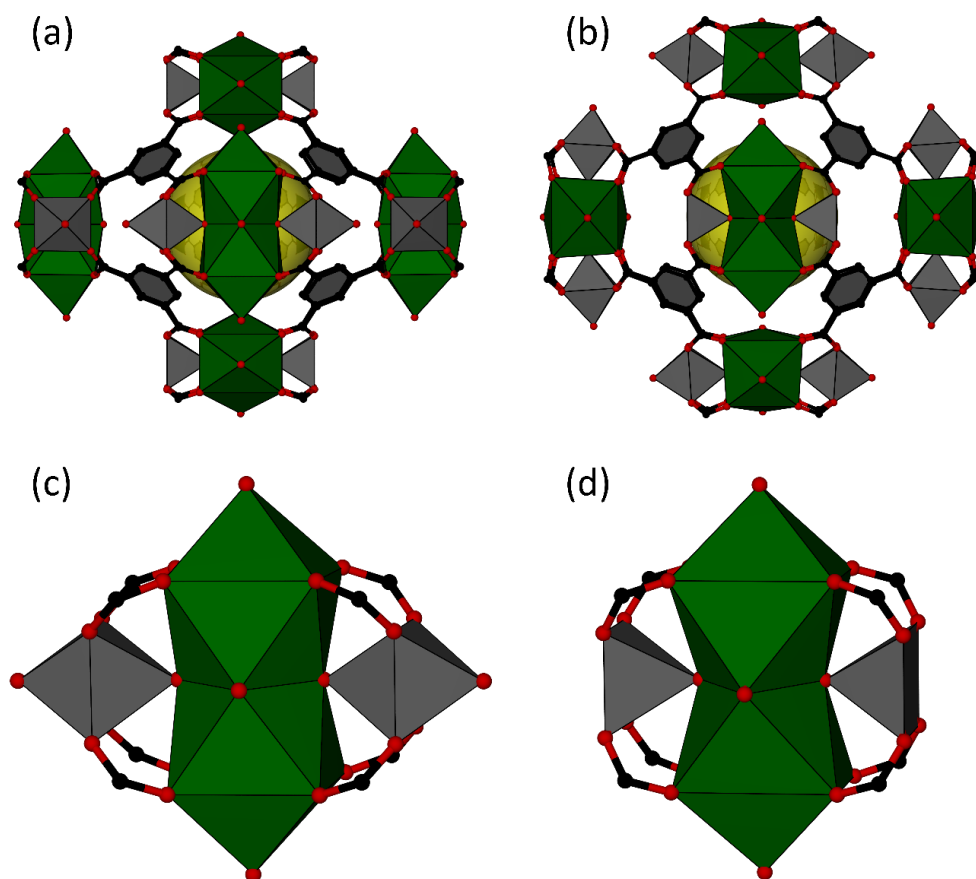


Figure 2.23: Crystal structure of MUV-10(X) including (a) the MUV-10(Ba) structure viewed between the *a/b*-axes, (b) the MUV-10(Ba) structure viewed along the *c*-axis including the pore space (yellow sphere) and (c-d) the two heterometallic clusters composing the structure (hydrogens and disordered DMF has been omitted for clarity) (C, black; O, red; Ti, grey; Ba, green).

SEM analysis of MUV-10(Ca) revealed crystals with an average diameter of 5.0 ± 1.9 μm (see Appendix 2.9, Figure 2.A.17). The anticipated octahedral morphology of the crystals was confirmed from the SEM images (Figure 2.24). SEM analysis of MUV-10(Sr) instead revealed spherical agglomerations of crystalline material (Figure 2.24). This nano-crystalline material is consistent with the broadness of the peaks in the experimental powder pattern for this sample. In an attempt to form crystals of the expected octahedral morphology, numerous different experimental conditions and Sr sources were trialled. Unfortunately, these experiments were unsuccessful and similar nano-crystalline materials were formed. As the nano-crystalline material would prohibit investigation into the impact of the MOF structure on the derived catalysts due to the agglomerated architecture of crystalline material, MUV-10(Sr) was not further investigated. SEM analysis of MUV-10(Ba) revealed crystals with an average

diameter of $176 \pm 28 \text{ }\mu\text{m}$ (see Appendix 2.9, Figure 2.A.18). The anticipated octahedral morphology of the crystals was again confirmed from the SEM images (Figure 2.24).

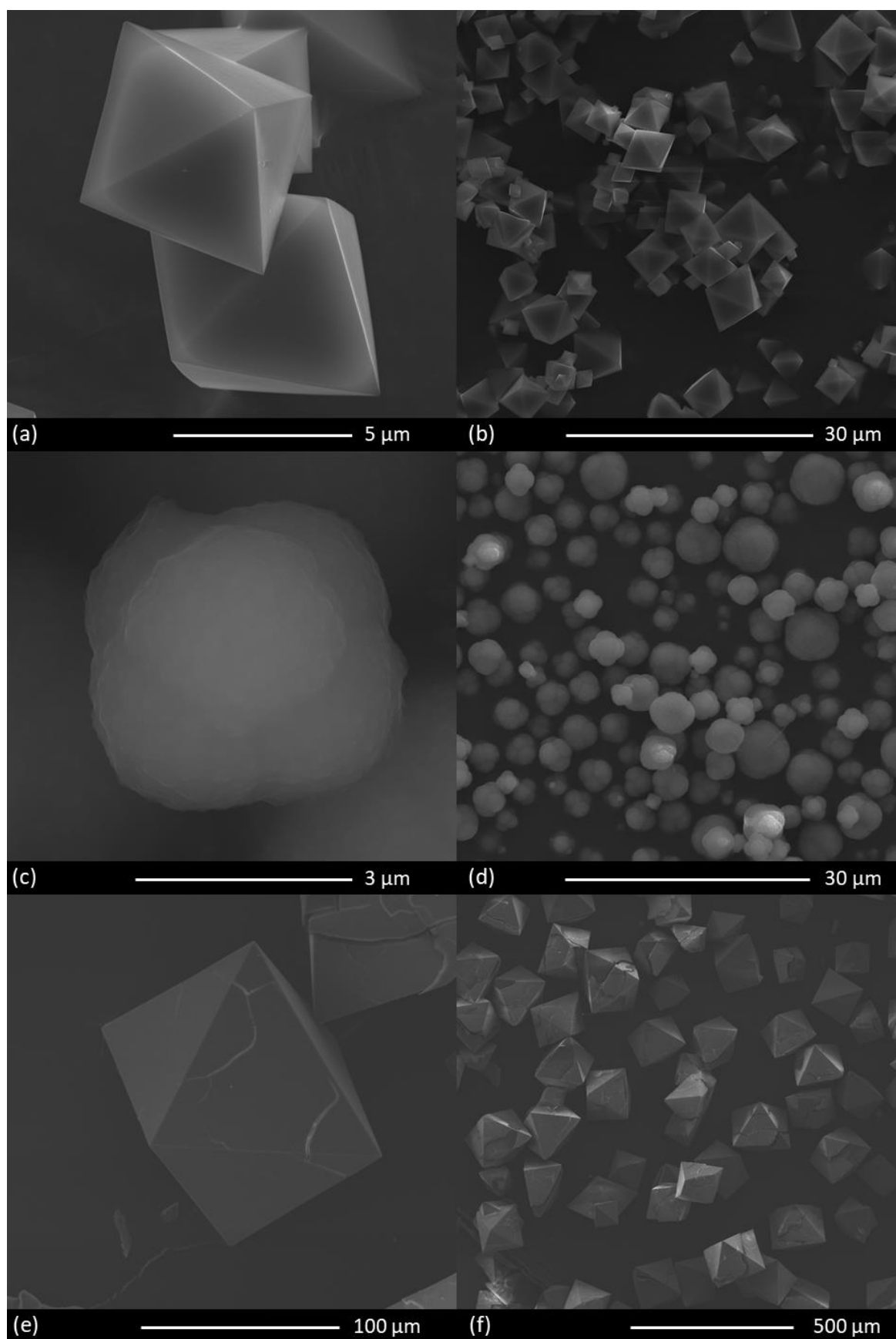


Figure 2.24: SEM images of (a-b) MUV-10(Ca) (c-d) MUV-10(Sr) and (e-f) MUV-10(Ba).

With both MUV-10(Ca) and MUV-10(Ba) successfully synthesised, analysis of the samples via gas adsorption was undertaken to establish the pore volume and surface area before loading with Ru. A N₂ 77 K adsorption isotherm was collected for MUV-10(Ca) and MUV-10(Ba), post activation from dry acetone (see experimental 2.7.3). The isotherms for both MUV-10(Ca) and MUV-10(Ba) are characteristic of a type I isotherm, exhibiting high uptake of N₂ at low partial pressures, indicative of microporosity (Figure 2.25). The BET surface area and pore volume were calculated from the MUV-10(Ca) N₂ isotherm as 820 m² g⁻¹ and 0.39 cm³ g⁻¹ respectively. These values are somewhat reduced relative to those reported for MUV-10(Ca), however they are still relatively high.¹¹⁵ The BET surface area and pore volume calculated for MUV-10(Ba) from the N₂ isotherm were relatively larger at 1210 m² g⁻¹ and 0.50 cm³ g⁻¹ respectively. These values are also somewhat reduced relative to those reported for MUV-10(Ba), however, much like the Ca derivative, they are still relatively high.¹¹⁶ The Ba derivative exhibiting higher values is hypothesised to relate to the larger ionic radius it possesses as opposed to Ca. The effect is two-fold, not only does the larger ionic radius expand pore sizes, but it introduces lattice strain, resulting in high likelihoods of linker vacancies, increasing N₂ uptake through higher quantities of defects and disorder.¹¹⁶ These effects are observed in the collected crystal structure for MUV-10(Ba). Additionally, activation conditions alone may have result in the increased values and must be considered. Differing conditions could have led to potential issues such as pore blockages or a degree of framework collapse. Nevertheless, the increased porosity of MUV-10(Ba) was considered during future experimentation with the framework.

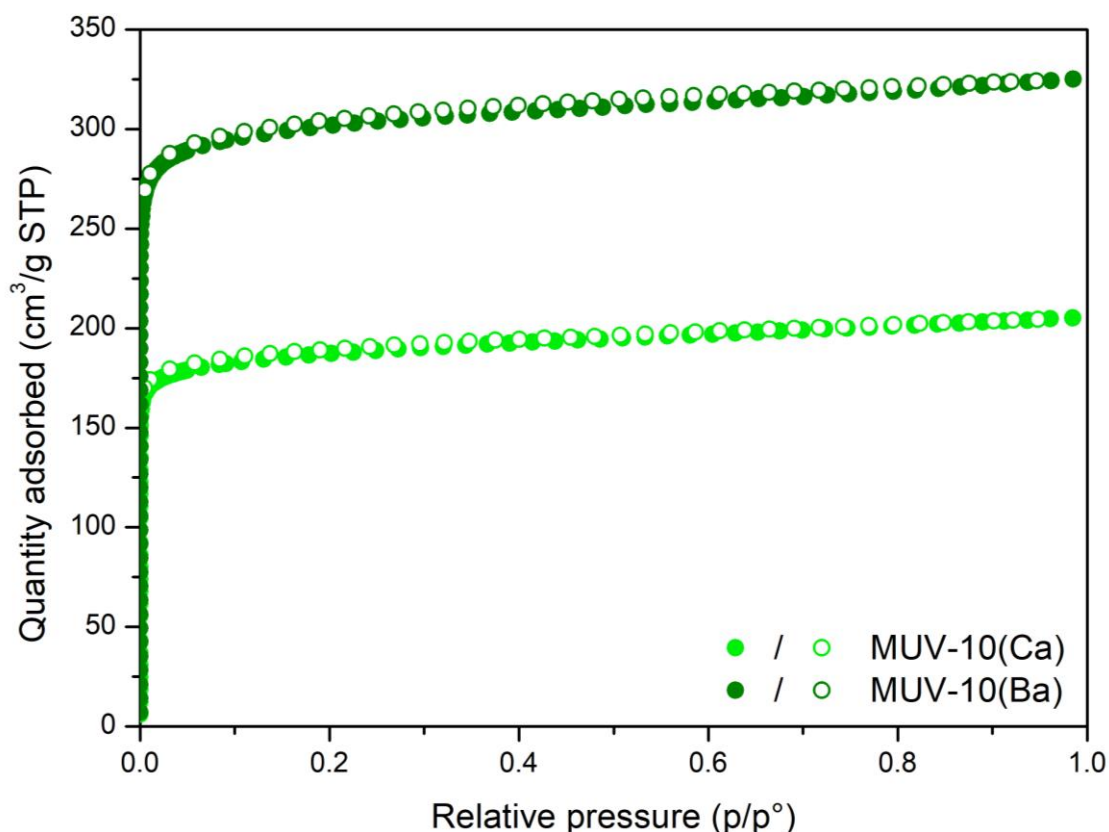


Figure 2.25: 77 K N₂ adsorption isotherm data collected for MUV-10(Ca) (green) and MUV-10(Ba) (dark green).

2.5.2 Ruthenium Loaded MUV-10(Ca,Ba)

With the successful synthesis of permanently porous MUV-10(Ca) and MUV-10(Ba) in hand, synthesis of the catalyst precursor was undertaken. Like the MIP-207 sample preparation, *in operando* and calcination to form the MDCs were the two main pathways employed to produce the active catalyst, Ru/TiO₂. Loading of Ru into the pores of the MOFs was achieved by IWI.

To load MUV-10 with Ru, ruthenium(III) chloride (RuCl₃) was selected and dissolved in water. Initially, the total pore volume of MUV-10(Ca) (0.32 cm³ g⁻¹) and MUV-10(Ba) (0.50 cm³ g⁻¹) were used to calculate the amount of water required to fill the pores. As established for MIP-207, visual analysis revealed this was an insufficient amount to form a homogenous slurry. Additional water was added to MUV-10(Ca) and MUV-10(Ba) until a homogenous slurry formed, from which the amount of water required was used to calculate the actual water uptake for IWI. The new value calculated for MUV-10(Ca) is 0.59 mL per g of MOF and 0.67 mL per g of MOF for MUV-10(Ba). Once the volume of water was known, the amount of RuCl₃ required for a 1 wt. % loading in both MUV-10 MOFs was calculated and an aqueous solution

for typical IWI was made up (see Appendix 2.9, Table 2.A.1) (experimental 2.7.2.2). In addition, the impact of higher wt. % loadings of Ru on the catalytic activity was investigated and a 5 wt. % loading solution was prepared for MUV-10(Ca).

PXRD analysis of Ru/MUV-10(Ca) revealed a small degree in loss of peak intensity but retention of long-range crystal order (see Appendix 2.9, Figure 2.A.19). Conversely, PXRD analysis of Ru/MUV-10(Ba) showed almost a complete loss of long-range structure (see Appendix 2.9, Figure 2.A.20). Such a stark contrast relative to the Ru/MUV-10(Ca) may be a result of partial framework degradation for MUV-10(Ba). This forms an amorphous material, presumably due to the framework being composed of weaker, more susceptible Ba-O bonds as opposed to Ca-O bonds, on account of the Lewis acidities of the relevant metal cations. To confirm the Ru wt. % loadings in the samples, EDX was employed. As with MIP-207, the average Ru loading within the unit cell can be calculated based on the relative Ru:Ti ratios. This can then be converted into Ru wt. % loadings. Ru/MUV-10(Ca) displayed average Ru wt. % loadings of $1.53 \pm 0.38\%$ for the 1 wt.% targeted sample and $3.96 \pm 1.21\%$ for the 5 wt.% targeted sample. Ru/MUV-10(Ba) displayed average Ru wt. % loadings of $1.12 \pm 0.35\%$. Again, further analysis via more accurate techniques such as ICP-MS would reduce the associated error through using EDX and should be performed in the future.

Further analysis of the Ru loaded MUV-10(Ca) and MUV-10(Ba) via gas adsorption analysis was conducted. The 77 K N₂ isotherm collected for Ru/MUV-10(Ca) was interesting, yielding a hysteresis loop fitting the profile of a H4 type isotherm (see Appendix 2.9, Figure 2.A.21). The overall isotherm retains its type I character with the inclusion of a hysteresis loop occurring over a wide p/p° range.^{119,120} This behaviour usually correlates to slit-like pores, a formation that may result due to Ru occupation within the framework, partially occluding the pore apertures.^{119,120} The BET surface area and pore volume were calculated as 810 m² g⁻¹ and 0.38 cm³ g⁻¹. These values are consistent with those calculated from the MUV-10(Ca) N₂ isotherm. With the PXRD results, this supports retention of framework structure. The isotherm collected for Ru/MUV-10(Ba) retains the type I character of the as-synthesised MOF (see Appendix 2.9, Figure 2.A.22). The Brunauer-Emmett-Teller (BET) surface area and pore volume were calculated as 460 m² g⁻¹ and 0.28 cm³ g⁻¹. These values are considerably reduced relative to those calculated for MUV-10(Ba). With the PXRD results, this supports the decomposition and partial collapse of MUV-10(Ba) following loading with Ru.

2.5.3 Ru/MUV-10(Ca,Ba) derived Ru/TiO₂ for CO₂ Methanation

All CO₂ methanation catalytic reactions run for Ru/MUV-10(Ca) and Ru/MUV-10(Ba) derived Ru/TiO₂ were performed in a stainless-steel, high-pressure batch reactor, identical to the one used for Ru/MIP-207 derived Ru/TiO₂ catalytic reactions. The ideal reaction conditions established for CO₂ methanation using Ru/MIP-207 derived Ru/TiO₂ hold for Ru/MUV-10(Ca) and Ru/MUV-10(Ba) derived Ru/TiO₂. Therefore, reactions were run at 300°C with a 4:1 H₂:CO₂ ratio at near atmospheric pressures to promote CH₄ formation through the targeted CO₂ methanation reaction whilst suppressing by-product formation through the other potential side reactions.

With reaction conditions identified, preparation of the catalysts began. As discussed in section 2.4.3, two main pathways of Ru/TiO₂ production from MOF materials were pursued. The *in operando* derived Ru/TiO₂ from Ru/MUV-10(Ca) (**Ru/TiO₂(op.)_Ca**) and Ru/MUV-10(Ba) (**Ru/TiO₂(op.)_Ba**) were activated under the reaction conditions and no further preparation was required before catalytic testing. The calcined material required an initial calcination step before catalytic testing. The point at which the organic component of MUV-10(Ca) and MUV-10(Ba) breaks down resulting in the generation of the metal oxide was determined via TGA of the samples in air (80:20 N₂:O₂) (see Appendix 2.9, Figure 2.A.23). Initial mass loss for both samples from temperatures up to 400°C indicates the removal of solvent from the pores of the framework. After this point, both samples undergo a steep mass decline, characteristic of the decomposition of the organic component of the framework. At 500°C, the organic component is fully degraded and only the metal oxide remains. Calcination of both Ru/MUV-10(Ca) and Ru/MUV-10(Ba) was run at 450°C for 4 h (experimental 2.7.2.3) to generate the MDCs via calcination (**Ru/TiO₂(calc.)_Ca** and **Ru/TiO₂(calc.)_Ba**).

Initial CO₂ methanation reactions were carried out with **Ru/TiO₂(op.)_Ca**, **Ru/TiO₂(op.)_Ba**, **Ru/TiO₂(calc.)_Ca** and **Ru/TiO₂(calc.)_Ba** to determine the activities under the reaction conditions over successive cycles (experimental 2.7.4.3). To ensure consistent Ru content between samples, the weight loss of calcined samples were calculated and used to determine the mass of **Ru/TiO₂(calc.)_Ca** and **Ru/TiO₂(calc.)_Ba** that would equal the original respective Ru/MUV-10 mass used in the generation of **Ru/TiO₂(op.)_Ca** and **Ru/TiO₂(op.)_Ba** respectively. In addition, Ru/TiO₂ was prepared from the IWI of purchased titania (**Ru/TiO₂(std.)**) composed of 80:20 anatase:rutile following the procedures outlined for both MIP-207 and MUV-10 MOFs (experimental 2.7.2.2) (see Appendix 2.9, Table 2.A.1).

This provides an avenue to compare the results of the MDCs to a known, highly active material.¹¹³ The particle size of the titania was determined via TEM analysis returning an average diameter of 28 ± 8 nm (see Appendix 2.9, Figures 2.A.24 and 2.A.25). EDX analysis of the Ru loaded titania confirm loadings of 1.08 ± 0.27 wt. %. Finally, PXRD analysis confirmed the presence of both anatase and rutile titania polymorphs which, as expected, retain crystallinity post Ru loading (see Appendix 2.9, Figure 2.A.26).

Once all samples were prepared, they were weighed, loaded into the sample holder, sealed in the batch reactor cell, and the reagent gases were introduced. CO₂ (200 mbar) and H₂ (1000 mbar) were added to the reactor cell in a 1:4 CO₂:H₂ ratio. The reaction was heated to 300°C for 30 mins. The production of CH₄ and consumption of CO₂ was monitored at the end of the reaction via GC in addition to the formation of any by-products (CO, longer chain C products). Longer chain C products are derived from the organic component of the MOF during generation of **Ru/TiO₂(*op.*)**. The results for catalysis using **Ru/TiO₂(*op.*)_Ca**, **Ru/TiO₂(*op.*)_Ba**, **Ru/TiO₂(*calc.*)_Ca**, **Ru/TiO₂(*calc.*)_Ba** and **Ru/TiO₂(*std.*)** are depicted in Figures 2.26 and 2.27, the experimental data is accessible in Table 2.A.4, see Appendix 2.9. Percentage of CO₂ conversions are calculated from the detected amount of all products (both CH₄ and by-products) to the combined concentration of CO₂ and all products. CH₄ selectivity is calculated based on the amount of detected CH₄ relative to all products.

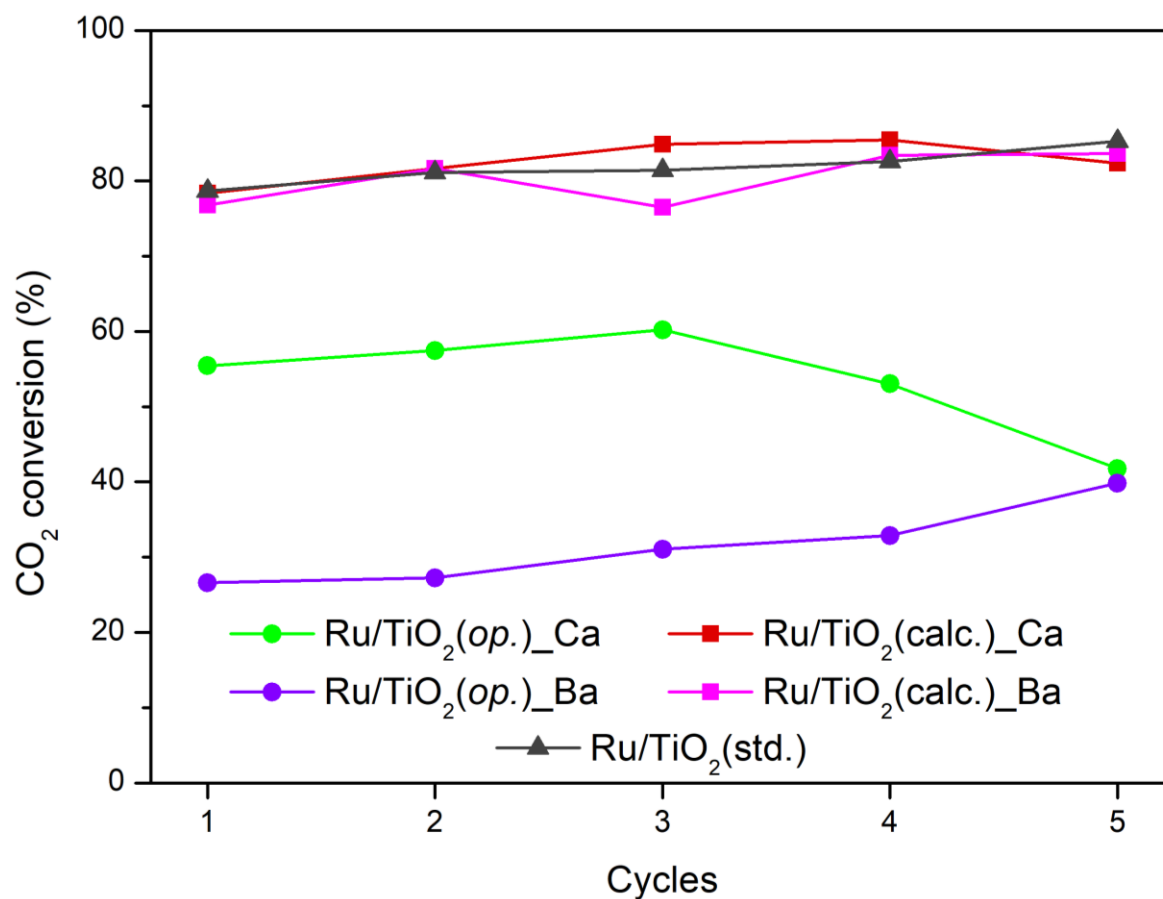


Figure 2.26: CO₂ conversion (%) for CO₂ methanation catalysed via **Ru/TiO₂(op.)** (●), **Ru/TiO₂(calc.)** (■) and **Ru/TiO₂(std.)** (▲) on the batch reactor.

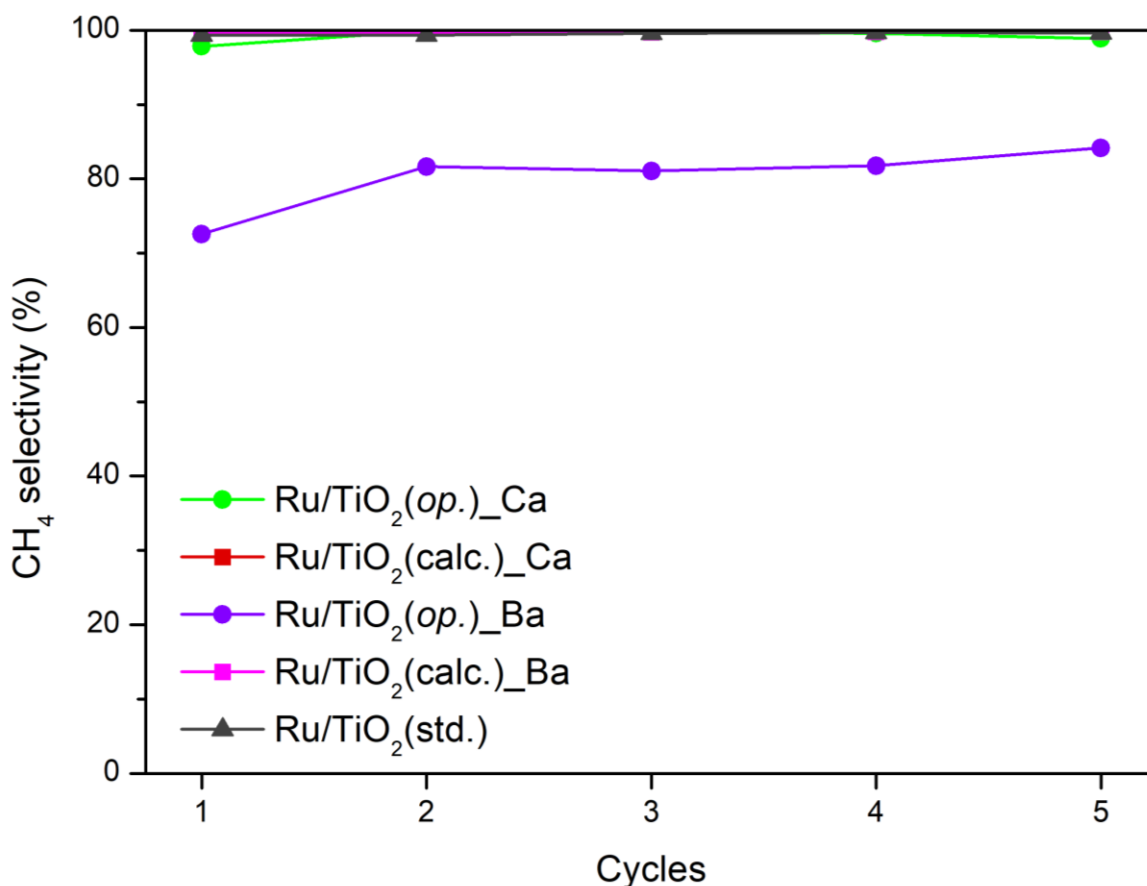


Figure 2.27: CH₄ selectivity (%) for CO₂ methanation catalysed via **Ru/TiO₂(op.)** (●), **Ru/TiO₂(calc.)** (■) and **Ru/TiO₂(std.)** (▲) on the batch reactor.

The conversion and selectivity data obtained for the Ru/MUV-10 derived Ru/TiO₂ catalysts for CO₂ methanation reveal insights into the relative performance of each material. Considering the CO₂ conversions first, it is evident an obvious difference exists. Comparing the *in operando* samples to the calcined, it is clear the calcined material converts more CO₂, however, this is limited at around the 80% mark. Indeed, this maximum conversion is also seen in the **Ru/TiO₂(std.)** sample. This likely stems from the reversibility of the Sabatier reaction.¹²¹ Consequently, the products and reactants will exist in equilibrium. In a batch reactor setup like the one employed for catalytic testing here, the reaction proceeds for a fixed time, in a fixed volume. Over the course of catalytic testing, the reaction gas mixture remains isolated (no gaseous components are added or collected). As a result, if provided enough time, the reaction will reach equilibrium and higher levels of reactant conversion will not be accessible. It is for this reason conversions of CO₂ are not at 100 %. This is supported by the reaction cell pressure monitored over the reaction time (see Appendix 2.9, Figure 2.A.27). Once at temperatures accessible for CO₂ methanation, the consumption of reactants begins, taking the form of a pressure decrease. Over the course of the reaction, equilibrium is reached, represented by the

constant pressure. This behaviour is also observed for both **Ru/TiO₂(op.)_Ca** and **Ru/TiO₂(op.)_Ba**, however the *in operando* samples do not reach the CO₂ conversions seen for **Ru/TiO₂(calc.)_Ca**, **Ru/TiO₂(calc.)_Ba** and **Ru/TiO₂(std.)**. As the *in operando* samples undergo activation under reaction conditions, carbon products are derived from the decomposition of the organic components constituting the framework. CH₄ can be formed in this way, adding to the product concentration in the batch reactor, thus lower levels of CO₂ are required to be converted to reach equilibrium. As reactions reach equilibrium within 30 minutes, it is conceivable not enough time has been provided for complete material activation. Indeed, the MOF-derived Ru/ZrO₂ catalyst produced by Lippi *et al.* required activation times of over 4 h and up to 13 h under flow conditions (fresh reactant gases constantly passed over the material) depending on temperature.⁸¹ Therefore, over a number of consecutive cycles, complete reduction of all the organic material within the framework would occur and the CO₂ conversions for both **Ru/TiO₂(op.)_Ca** and **Ru/TiO₂(op.)_Ba** are expected to increase.

Evidence for the incomplete degradation of MOF organic components is provided by PXRD analysis of **Ru/TiO₂(op.)_Ca** post catalysis (Figure 2.28). Remarkably, after 5 cycles under reaction conditions, the crystallinity of the MUV-10(Ca) is retained. This is further supported by the collected N₂ 77 K isotherm of **Ru/TiO₂(op.)_Ca**, indicating retention of the same profile of Ru/MUV-10(Ca) and calculated surface area and pore volume of 730 m² g⁻¹ and 0.41 cm³ g⁻¹, consistent relative to the material it was derived from (see Appendix 2.9, Figure 2.A.28). The retention of crystallinity is not seen for the **Ru/TiO₂(op.)_Ba** sample as it was lost during Ru loading and compounded post-catalysis (see Appendix 2.9, Figure 2.A.29). The degradation of **Ru/TiO₂(op.)_Ba** is further supported by the collected N₂ 77 K isotherm, resulting in calculated surface area and pore volume of 140 m² g⁻¹ and 0.28 cm³ g⁻¹, significantly reduced relative to Ru/MUV-10(Ba) (see Appendix 2.9, Figure 2.A.30). To reiterate however, remarkably under reducing conditions (H₂), the presence of a Ru catalyst, and at elevated temperatures (300°C), Ru/MUV-10(Ca) retains crystallinity.

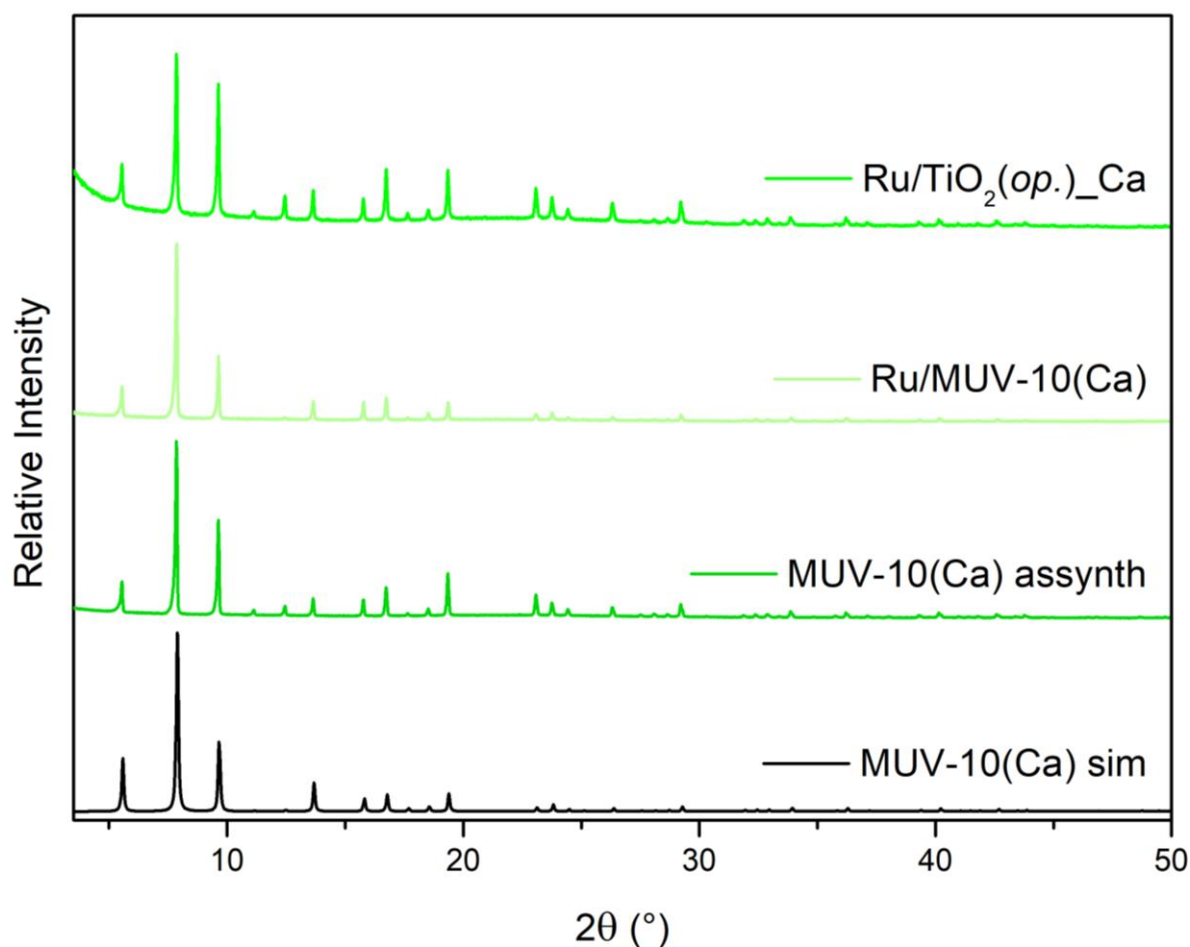


Figure 2.28: PXRD patterns of MUV-10(Ca); simulated MUV-10(Ca) (black), MUV-10(Ca) as-synthesised (green), Ru/MUV-10(Ca) (light green) and **Ru/TiO₂(op.)_Ca** after 5 cycles (lime). Remarkably, **Ru/TiO₂(op.)_Ca** retains crystallinity after catalysis under reducing conditions (H₂), the presence of a Ru catalyst, and at elevated temperatures (300°C) for 5 cycles.

Retention of crystallinity after exposure to such conditions is unprecedented for MOF catalysts and can potentially result from the combination of one or two different reasons. Firstly, the stability of the MOF may be exceedingly high. This stability is already reflected in the pristine MOF, MUV-10(Ca), which displays excellent thermal (up to 450°C), pH (stable between 2 to 12) and chemical (stable in water, concentrated hydrochloric acid and concentrated sodium hydroxide) stability.¹¹⁵ The other potential reason relates to the activity of the catalyst. Analysis of the pressure in the reaction cell (from which reactant consumption can be inferred) shows within 30 minutes, equilibrium is reached. This may indicate that the MOF-derived **Ru/TiO₂(op.)_Ca** catalyst is extremely active and all CO₂ to CH₄ conversions are occurring at the MOF surface, an issue that can be encountered in MOF catalysis due to gas diffusion limitations.¹²² To probe this, TEM analysis of **Ru/TiO₂(op.)_Ca** was undertaken. However, no quantitative conclusions on Ru dispersion could be reached from the images (see Appendix 2.9,

Figure 2.A.31). As a result, STEM-EDX elemental mapping was pursued to investigate Ru dispersion on the catalytic material post-catalysis. Whilst both MUV-10(Ca) and MUV-10(Ba) derivatives experienced degradation under the electron beam, the issue was reduced for the Ca derivatives and imaging of the sample as-prepared was accessible. This issue was intensified for the Ba variants, in that upon exposure to the electron beam, the sample visibly and substantially contracts within 5 seconds. This made imaging extremely difficult, effectively verging on impossible, which is coupled with the knowledge the sample being imaged is not a true representation of the catalyst material due to electron beam facilitated degradation. These issues, along with crystal size ($176 \pm 28 \mu\text{m}$) prevented MUV-10(Ba) from being imaged. To bypass these challenges, microtomy was proposed as a technique highly suited to rectify this problem (see Appendix 2.9, Figure 2.A.32). In the MOF field, microtomy has been demonstrated previously to enable elucidation of the core-shell structure of a MOF@polymer material.¹²³ It is a method in which particles are suspended within a resin and thin sections (100-500 nm) are produced via cutting, affording slices of MOF crystals embedded within the resin. This would allow the analysis of MUV-10(Ba) derivatives, solving the issues relating to the size of the particles.

HAADF imaging of **Ru/TiO₂(*op.*)_Ca** revealed clear formation of small (approximate diameter of 1 – 3 nm), highly distributed nanoparticles (see Appendix 2.9, Figure 2.A.33). Elemental mapping confirmed they are composed of Ru (Figures 2.29 and 2.A.34, see Appendix 2.9). The highly dispersed nanoparticles, in conjunction with the activity of the material, reveal on the heterometallic Ti/Ca framework, sintering of Ru and thus deactivation of the catalyst is avoided. This contrasts with the pure Ti framework (MIP-207) in which increased mobility of Ru leads to sintering. This is potentially attributed to the inclusion of the second metal within the framework, potentially acting as a dilutant of sort, analogous to the role anatase plays in the active forms of Ru/TiO₂. This may also be attributed to the three-dimensionality of the framework, providing more pore space to confine nanoparticles and prevent agglomeration.

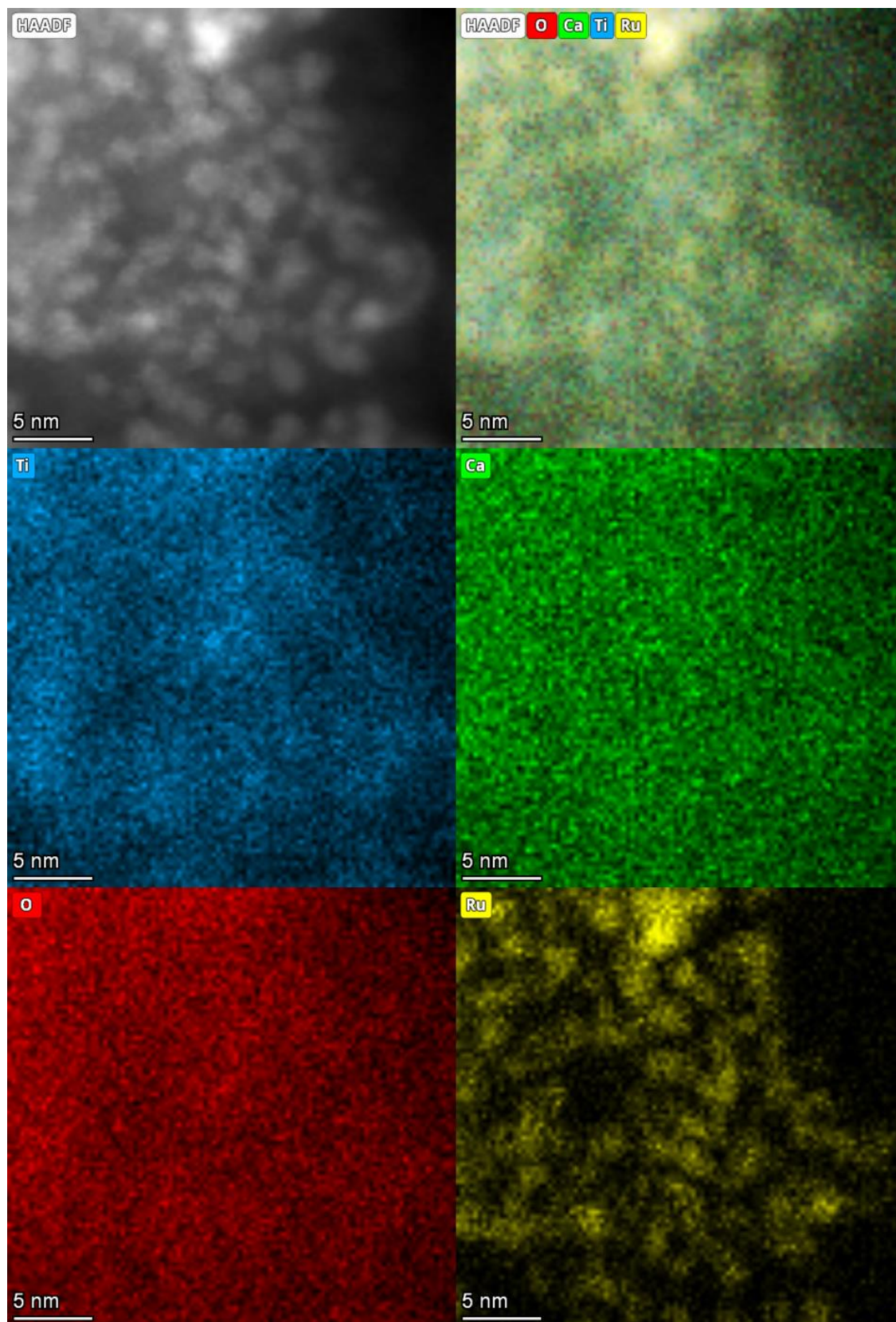


Figure 2.29: STEM-EDX images of **Ru/TiO₂(*op.*)_Ca** post-catalysis after 5 cycles revealing clear formation of small, highly dispersed Ru nanoparticles (Ti, blue; Ca, green; O, red; Ru, yellow).

HAADF imaging of **Ru/TiO₂(*op.*)_Ba** also revealed clear formation of small (approximate diameter of 1 – 3 nm), highly distributed nanoparticles (see Appendix 2.9, Figure 2.A.35). Elemental mapping confirmed they are composed of Ru (see Appendix 2.9, Figure 2.A.36). HAADF imaging confirmed the Ru nanoparticles are only concentrated on the surface of the crystals (Figure 2.30). This indicates gas is not diffusing deeply into the crystals as the catalysis is conducted quickly at the easily accessible external surface of the material. Indeed, so pronounced is this concentration of Ru nanoparticles at the surface, that penetration into the crystal is only observed along cracks formed during activation of the material. These cracks provide easy access to the “core” material of the framework, as gas is not required to diffuse through its pores, but can easily travel along the length of the defect (Figure 2.30). As a result, however, the location of cracks in the MOF can be considered as accessible external surfaces of the framework, resulting in the observed Ru nanoparticles. This surface concentration is further evidenced by elemental mapping showing the distribution of Ru from the surface towards the particle core progresses from highly concentrated to effectively no detected Ru (Figure 2.31). The low selectivity towards CH₄ of **Ru/TiO₂(*op.*)_Ba** can be explained by this phenomenon. Like with the Ca derivative, reactions reach equilibrium within 30 minutes, resulting in insufficient time for complete material activation. Therefore, a large reservoir of organic material used to construct the framework remains within the core of the now degraded framework. Over consecutive reaction cycles, more of this organic material can be converted into C-based products, which is much more pronounced for **Ru/TiO₂(*op.*)_Ba** as opposed to **Ru/TiO₂(*op.*)_Ca** (see Appendix 2.9, Table 2.A.4). Over further reaction cycles, the complete reduction of all the organic material within the framework would occur and CO₂ conversions would be expected to increase.

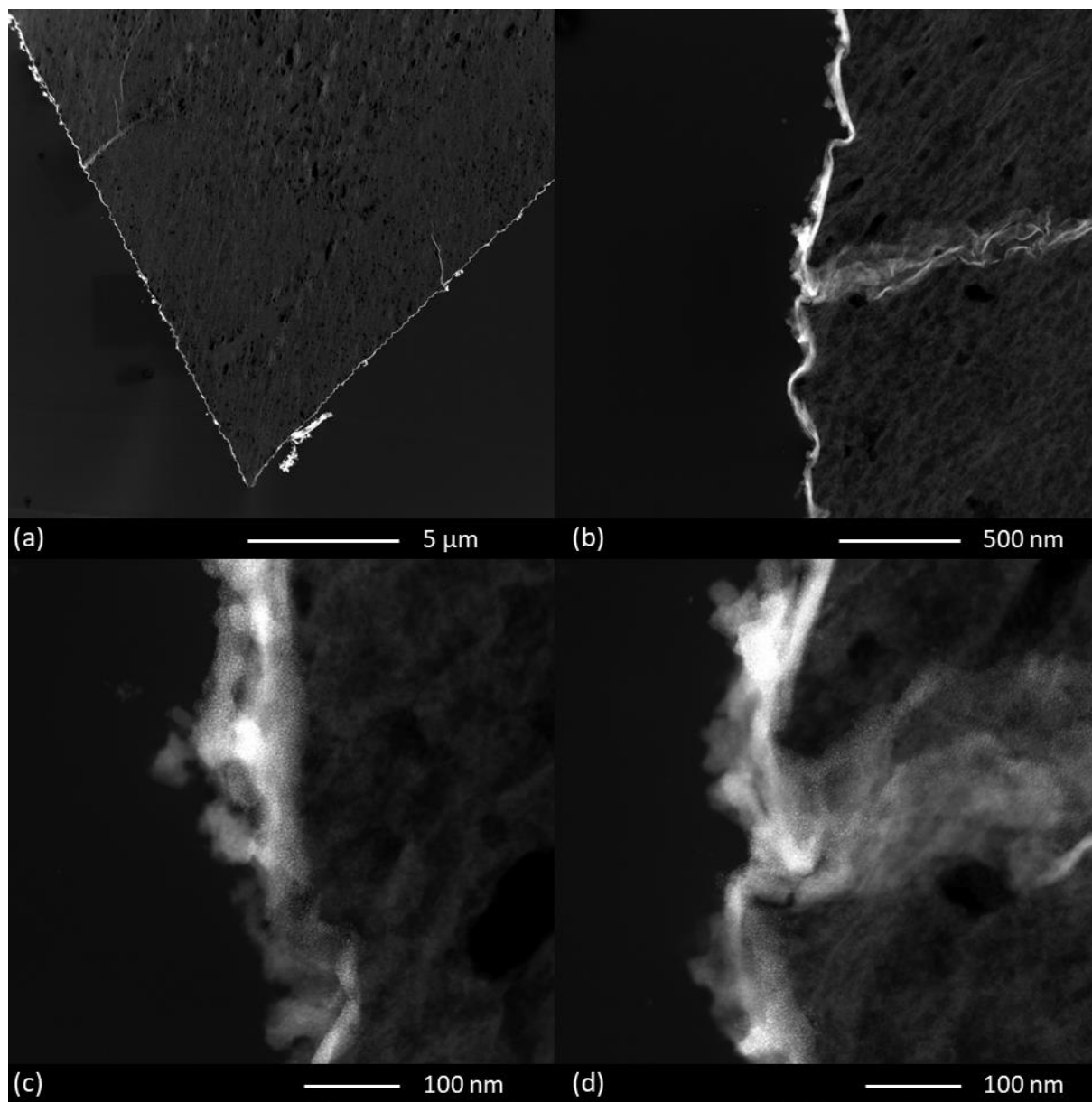


Figure 2.30: (a-d) STEM-HAADF image of **Ru/TiO₂(op.)_Ba** revealing clear formation of small, highly dispersed Ru nanoparticles located at the surface and along defects sites (cracks) whilst the core of the framework remains free of Ru nanoparticles.

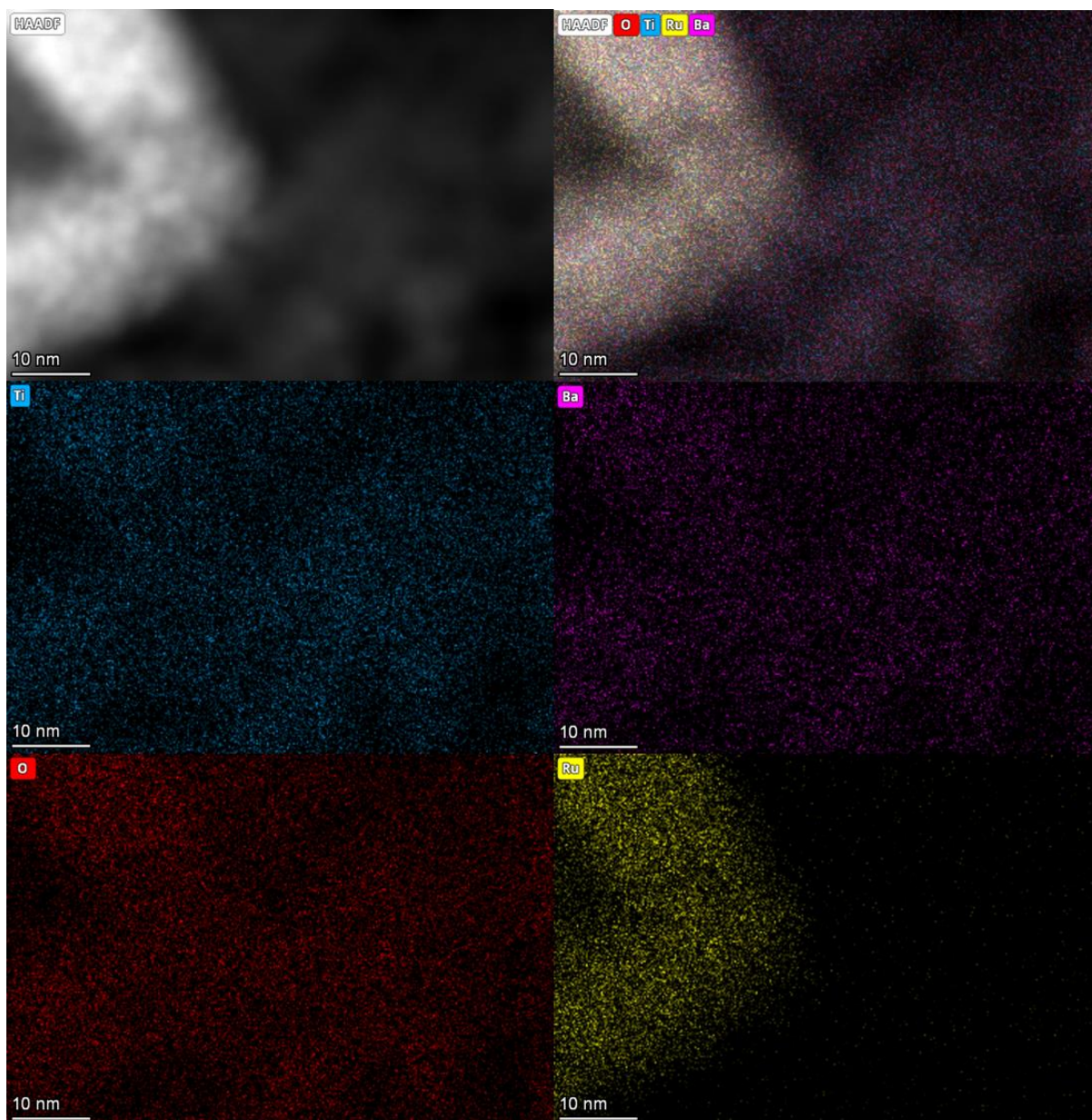


Figure 2.31: STEM-EDX images of **Ru/TiO₂(op.)_Ba** post-catalysis after 5 cycles revealing clear formation of small, highly dispersed Ru nanoparticles located at the surface whilst the core of the framework remains free of Ru nanoparticles (Ti, blue; Ba, magenta; O, red; Ru, yellow).

Considering the CH₄ selectivity, it is evident an obvious difference exists between **Ru/TiO₂(op.)_Ba** and the other samples, **Ru/TiO₂(op.)_Ca**, **Ru/TiO₂(calc.)_Ca**, **Ru/TiO₂(calc.)_Ba** and **Ru/TiO₂(std.)**. The reason for this was previously explored and is likely attributed to the excess organic matter derived from the frameworks organic linker remaining within the core of the material, where this is free to be converted in subsequent cycles. Nevertheless, selectivity towards CH₄ is still high at ~80% and is trending upwards, likely an indication with longer activation times, as the carbon content is completely reduced,

a highly selective material analogous to that of the other Ru/MUV-10 derived catalysts could be formed. **Ru/TiO₂(op.)_Ca**, the other *in operando* sample is much more selective than **Ru/TiO₂(op.)_Ba**. Indeed, relative to the calcined and standard samples, **Ru/TiO₂(calc.)_Ca**, **Ru/TiO₂(calc.)_Ba** and **Ru/TiO₂(std.)**, **Ru/TiO₂(op.)_Ca** is effectively identical in terms of CH₄ selectivity, however, in some instances, higher amounts of C products are formed due to the retention of organic matter derived from the framework's organic linker. This, like for **Ru/TiO₂(op.)_Ba**, is expected to decrease as all the carbon content is completely reduced by affording longer *in operando* activation periods. These differences are marginal though as the selectivity for **Ru/TiO₂(op.)_Ca**, **Ru/TiO₂(calc.)_Ca**, **Ru/TiO₂(calc.)_Ba** and **Ru/TiO₂(std.)** is at, or higher the 99%, detecting only trace levels of CO and other carbon products.

Both calcined samples, **Ru/TiO₂(calc.)_Ca** and **Ru/TiO₂(calc.)_Ba**, show high CH₄ selectivity > 99%, and CO₂ conversion ~80%. These values are consistent with the standard **Ru/TiO₂(std.)**. They are a result of the complete removal of carbon content from the MOF during the calcination step. PXRD analysis of **Ru/TiO₂(calc.)_Ca** and **Ru/TiO₂(calc.)_Ba** and the materials from which they are derived pre-catalysis reveals no clear formation of a crystalline metal oxide (see Appendix 2.9, Figures 2.A.37 and 2.A.38). As calcinations were performed at 450°C, it is likely this resulted in the complete burn off of C-based material but was insufficient to generate a highly crystalline metal oxide, thus an amorphous metal oxide is the expected product. 77 K N₂ isotherms of the calcined pre- and post-catalysis materials indicate transition to a type II profile and a significant drop in porosity reflected in both surface area and pore volume of 78 m² g⁻¹ and 0.17 cm³ g⁻¹, and 51 m² g⁻¹ and 0.13 cm³ g⁻¹, for calcined Ru/MUV-10(Ca) and Ru/MUV-10(Ba) respectively (see Appendix 2.9, Figures 2.A.39 and 2.A.40). This drops slightly further in the post-catalysis materials to 71 m² g⁻¹ and 0.15 cm³ g⁻¹, and 30 m² g⁻¹ and 0.09 cm³ g⁻¹, for **Ru/TiO₂(calc.)_Ca** and **Ru/TiO₂(calc.)_Ba** respectively (see Appendix 2.9, Figures 2.A.39 and 2.A.40). The result indicates the shift from the as-synthesised, highly porous, crystalline MOF, to the MOF-derived metal oxide.

Analysis of the CH₄ selectivity of the calcined samples relative to the standard, suggests the selectivity afforded by **Ru/TiO₂(calc.)_Ca** and **Ru/TiO₂(calc.)_Ba** could potentially be higher than that of **Ru/TiO₂(std.)**. The difference between the samples, however, is less than 0.5% and further testing to truly elucidate if the calcined materials are marginally more selective, whilst maintaining the same conversions, is required. TEM analysis of calcined MUV-10(Ca) and **Ru/TiO₂(calc.)_Ca** was undertaken to investigate the catalytic material formed (see Appendix 2.9, Figure 2.A.41). The data shows highly dispersed Ru nanoparticles

were formed, but to confirm this, HAADF imaging (see Appendix 2.9, Figure 2.A.42) and STEM-EDX elemental mapping was performed (see Appendix 2.9, Figure 2.A.43). This confirmed the formation of small (1-2 nm), highly dispersed Ru nanoparticles, resulting in the high activities displayed. Due to the issues associated with imaging MUV-10(Ba) based materials via TEM, HAADF imaging (see Appendix 2.9, Figure 2.A.44) and STEM-EDX elemental mapping of **Ru/TiO₂(calc.)_Ba** was performed (see Appendix 2.9, Figures 2.A.45 and 2.A.46) on thin sections (100 nm) of the MOF prepared via microtomy. Unlike the previous samples, larger (> 50 nm) Ru particles were formed in addition to the smaller nanoparticles (1 – 3 nm), however these remained highly dispersed on the material surface. This did not negatively impact the activity of the material under batch conditions and was consistent with the CO₂ conversion and CH₄ selectivity of the **Ru/TiO₂(calc.)_Ca** sample. **Ru/TiO₂(std.)** was analysed via TEM, revealing the formation of small (1-2 nm), highly dispersed Ru nanoparticles on the titania surface (see Appendix 2.9, Figure 2.A.47), however further analysis via STEM-EDX elemental mapping is recommended to further characterise the Ru distribution on the material.

The impact of higher wt. % loadings of Ru on the catalytic activity was also investigated. Activation and catalytic testing of the 5 wt. % loaded Ru/MUV-10(Ca) was conducted to give comparable samples to the *in operando* and calcined 1 wt. % loaded Ru/MUV-10(Ca). The results for catalysis using 5 wt. % Ru loaded MUV-10(Ca), **5Ru/TiO₂(op.)_Ca** and **5Ru/TiO₂(calc.)_Ca**, compared to 1 wt. % Ru loaded MUV-10(Ca), **1Ru/TiO₂(op.)_Ca** and **1Ru/TiO₂(calc.)_Ca**, are depicted in Figures 2.A.48 and 2.A.49, the experimental data is accessible in Table 2.A.5, see Appendix 2.9. Analysis of both CO₂ conversions and CH₄ selectivity reveal there is no significant difference between the 5 wt. % and 1 wt. % Ru loaded MUV-10(Ca) MDCs. It should be noted, Lippi *et al.* revealed Ru loadings exceeding 1 wt. % on ZrO₂ do not enhance the catalytic activity.⁸¹ This likely holds for Ru/TiO₂, and consequently all catalytic testing was performed with 1 wt. % Ru loaded MUV-10(Ca) MDCs.

From the catalytic testing of Ru/MUV-10(Ca) and Ru/MUV-10(Ba) MDCs, highly active and selective materials were formed. Confirmation that the catalytic activity is derived from the Ru loading of the MOF was confirmed from control tests using pristine MUV-10(Ca) and MUV-10(Ba), which afforded no C-based products. The calcined variants, **Ru/TiO₂(calc.)_Ca** and **Ru/TiO₂(calc.)_Ba**, displayed CO₂ conversion and CH₄ selectivity in line with the highly active standard, **Ru/TiO₂(std.)**. The *in operando* samples,

Ru/TiO₂(*op.*)_Ca and **Ru/TiO₂(*op.*)_Ba**, displayed reduced CO₂ conversions owing to CH₄ derived from the degradation of the organic linker of the MOF being released under reaction conditions. The CH₄ selectivity of **Ru/TiO₂(*op.*)_Ca**, however, matched that of the calcined variants. Conversely, the **Ru/TiO₂(*op.*)_Ba** sample suffered from reduced CH₄ selectivity, but this is expected to improve as longer activation times permit the complete degradation of the organic linker of the MOF and generation of the active catalyst. The high activities exhibited by the MDCs (reaction under batch conditions at completion within 30 minutes) at atmospheric pressure, led us to postulate the Ru/MUV-10 MDCs may hold potential under more industrially relevant conditions. Moving forward, catalytic testing on a flow reactor to build a more complete picture of the true activities of the MDCs under industrially relevant conditions should be pursued.

2.6 Summary

In summary, two Ti-based MOFs were synthesised. This included a pure Ti-MOF, MIP-207, and two heterometallic Ti-based MOFs, MUV-10(Ca) and MUV-10(Ba). The intrinsic porosity offered by MOFs provided an ideal platform for loading of the frameworks with Ru via IWI. The samples could then be converted to generate MDCs (Ru/TiO₂) for CO₂ methanation. The Ru loaded samples were activated through two different pathways. Firstly, under reaction conditions (*in operando*), and secondly, through the more conventionally applied calcination of the material. The activity of the MDCs was considered in terms of CO₂ methanation and CH₄ selectivity. Under batch reaction conditions, Ru/MIP-207 derived catalysts suffered from sintering and agglomeration of Ru, resulting in catalyst deactivation. Conversely, Ru/MUV-10 derived catalysts displayed high CO₂ conversions and CH₄ selectivity maintained over consecutive cycles. The high conversions and selectivity afforded by Ru/MUV-10 materials towards CO₂ methanation warrants further investigation.

Future research will focus on determining the activity of MOF-derived Ru/MUV-10 samples under flow reaction conditions. Primarily, the CO₂ conversion and CH₄ selectivity of the samples relative to standards, and characterisation of the material post-catalysis is required. This will enable investigation into the properties displayed by the material under flow conditions, and for extended periods, relative to the properties seen under batch reaction conditions. In addition, calcination at higher temperatures and subsequent catalytic testing of such materials, to allow the generation of crystalline metal oxide phases from the heterometallic MUV-10 MOF, is advised. Study of the metal oxide phases produced under these conditions

may provide insight into the enhanced activities and stability afforded from the heterometallic MUV-10 MDCs as opposed to the pure Ti-MOF derived catalysts.

2.7 Experimental

2.7.1 Materials and Measurements

Unless otherwise stated, all chemicals were obtained from commercial sources and used as received. Solvents were dried using literature procedures and degassed with Ar prior to use. Specifically, acetone was distilled over CaSO₄ under N₂. Powder X-ray diffraction data were collected on a Bruker Advanced D8 diffractometer (capillary stage) using Cu K α radiation (λ = 1.54056 Å, 40 kW/ 40 mA, 2θ = 2 – 52.94°, Phi rotation = 20 rotation/min at 1 sec exposure per step, with 5001 steps using 0.3, 0.5 and 0.8 mm glass capillaries). Simulated powder X-ray diffraction patterns were generated from single crystal data using Mercury 4.2.0. Electron dispersive X-ray analysis was collected with an Oxford Instruments Ultim Max 170 EDX attachment on a FEI Quanta 450 FEG environmental scanning electron microscope with a tungsten filament electron source (spot size 3, 20 KeV). Samples for SEM analysis were dry loaded onto adhesive carbon tabs on aluminium stubs and carbon coated (5 nm) prior to analysis. Transmission electron microscopy images were collected using a FEI Tecnai G² Spirit TEM with a LaB₆ filament operating at 120 kV. Images were captured via an in-column Olympus-SIS Veleta CCD camera. High-angle annular dark-field imaging images were collected via a FEI Titan Themis 80-200 and scanning transmission electron microscopy electron dispersive X-ray spectra were recorded using a SuperX detector, analysis was performed on Velox software. Samples for transmission electron microscopy analysis were wet loaded from 70% aqueous EtOH onto copper transmission electron microscopy grids. Ultramicrotomy was conducted on a Leica EM UC7 ultramicrotome. MOF crystals were dispersed and embedded in TAAB Araldite/812 epoxy resin and sliced at a slice thickness of 100 nm. Thermal gravimetric analysis was performed on a Perkin-Elmer STA-6000 instrument under a constant flow of N₂ and O₂ gases (80:20 ratio) at a temperature ramp rate of 5°C/min.

2.7.2 Synthetic Methods

2.7.2.1 MIP-207

MIP-207 was prepared according to a literature procedure.¹⁰⁴

2.7.2.2 General Ru/Support IWI Method

The general Ru/support IWI was prepared according to a literature procedure with minor alterations.⁸¹ Dried support (200 mg) was placed into a 20 mL vial and aqueous RuCl₃ solution

(see Appendix 2.9, Table 2.A.1 for concentrations and volumes) was added. The mixture was stirred to form a homogenous slurry and was dried for 12 h at 80°C to afford Ru/support.

2.7.2.3 General Calcination Method

Dried Ru loaded support (200 mg) was placed into a ceramic crucible. The sample was calcined for 4 h at 400°C (Ru/MIP-207) or 450°C (MUV-10(Ca) and MUV-10(Ba)) in air to afford the calcined Ru/TiO₂.

2.7.2.4 MUV-10(Ca, Sr, Ba)

MUV-10(X) was prepared according to a literature procedure with minor alterations.¹¹⁵ BTC (125 mg, 0.60 mmol) and calcium chloride hexahydrate (26.8 mg, 0.12 mmol) or strontium chloride hexahydrate (48.0 mg, 0.18 mmol) were dissolved in DMF (12 mL) in a 20 mL vial. Glacial AcOH (3.5 mL) and Ti(O^{*i*}Pr)₄ (36 µL, 0.12 mmol) were added and the vial was sealed and heated at 120°C for 48 h. The resulting powder was collected, washed with DMF (3 x 10 mL) and MeOH (5 x 10 mL) and dried under vacuum to afford MUV-10(Ca, Sr). For MUV-10(Ba): BTC (250 mg, 1.20 mmol), barium carbonate (94.8 mg, 0.48 mmol), DMF (12 mL), glacial AcOH (7 mL) and Ti(O^{*i*}Pr)₄ (72 µL, 0.24 mmol) were used instead. The synthesis conditions remain identical.

2.7.3 Gas Adsorption Analysis

2.7.3.1 Activation Protocol

In a typical activation procedure, MOF crystals were loaded wet into sorption analysis tubes from the respective dry solvent under Ar flow. The samples were then dried under a vacuum at 80°C for 3 h to yield activated samples.

2.7.3.2 Gas Adsorption Measurements

Gas adsorption isotherms were measured using volumetric methods on a micromeritics 3-Flex analyser (Micromeritics Instrument Corporation, Norcross, GA, USA) at 77 K (using a cryo-cooler circulator). UHP grade (99.999 %) N₂ was used for all measurements.

2.7.4 Catalysis Experiments

2.7.4.1 Batch Reactor Instrumentation

All batch gas phase catalytic experiments were carried out using a custom-built high-pressure, high temperature sampling equipment (see Figure 2.12). The internal volume of the batch reactor cell is 20.45 ml. The batch reaction cell is in direct contact with a copper block containing two 100 W heater cartridges. This is controlled by a PID (proportional-integral derivative) temperature controller (CAL Controls, Cal 3300) and K-type thermocouple attached to the side of the cell. Batch reaction cell pressure is monitored by a piezoresistive manometer (Keller, 80 bar range). The batch reactor is rated to 300°C at 80 bar internal pressure. The gas phase reaction mixture is analysed using a gas chromatograph (SRI-8610C model) directly connected to the reaction cell.

2.7.4.2 Gas Chromatography

Gas chromatography of the reaction gas mixture was carried out with an SRI-8610C (MG#3) instrument with a thermal conductivity detector (TCD) and a flame ionising detector (FID) equipped with a methanizer. The first chromatographic column was a S.S. molecular sieve 13X packed column (6' length, 1/8" O.D.) followed by a S.S. Haye Sep D packed column (6' length, 1/8" O.D.). He was used as the carrier gas and a H₂ flame was used to combust organic compounds. Initial oven temperature was 30°C and held for 6 min, followed by a ramp at 20°C/min to 250°C. Once at 250°C, the temperature was held for 15 min. Injection port temperature was 60°C, and methanizer was 300°C. Pressure was initially held at 3 PSI for 0.02 min, increased to 20 PSI and held for 2 min, then further increased to 40 PSI and held for 3.8 min before being subsequently decreased to 0 PSI and held for 26 min.

2.7.4.3 CO₂ Methanation Reaction Conditions Under Batch

Ru/support (~15 mg) was loaded into a stainless-steel sample holder capped by a VCR gasket with a 0.5 µm filter and placed in the batch reactor cell. After sealing the reaction cell, the sample was evacuated under high vacuum for 30 mins. At 30°C, CO₂ was introduced to the reaction cell (200 mbar) followed by H₂ (1000 mbar). The reaction was heated to reaction temperature (150-300°C) for the allocated reaction time. The reaction was then stopped, and the gas mixture was analysed via gas chromatography. Reactions were repeated for *n* cycles following this exact procedure.

2.7.5 Single Crystal X-ray Diffraction Data.

2.7.5.1 MUV-10(Ba)

Single crystals of MUV-10(Ba) were mounted in Paratone-N oil on a nylon loop. Single crystal X-ray data were collected at 100(2) K on the MX1 beamline of the Australian Synchrotron using the BluIce software interface, $\lambda = 0.7107 \text{ \AA}$.¹²⁴ Absorption corrections were applied using multiscan methods using XDS, the structures solved using SHELXT, and refined by full-matrix least squares on F^2 by SHELXL, interfaced through the program Olex2.¹²⁵⁻¹²⁹ In general, all atoms were refined anisotropically and hydrogen atoms were included as invariants at geometrically estimated positions. One of the carboxylate donors of the trimesic acid linker is disordered and this was refined with an approximately 50:50 disorder model over the two sites. The coordinated DMF ligand bound to Ti4 is disordered over two sites necessitating use of a series of FREE instructions to allow inclusion of the hydrogen atoms and a DFIX restraint was needed for the N-CH₃ bond. An additional DFIX restraint was used to maintain a chemically sensible Ba-O bond length. The structure clearly shows disordered solvent coordinated to the Ba centres and within the pores but attempts to model this were unsuccessful. The data was treated with the solvent masking feature of Olex2 with the electron density removed equating to an estimated three DMF molecules over two separate voids.

2.8 References

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2.9 Appendix

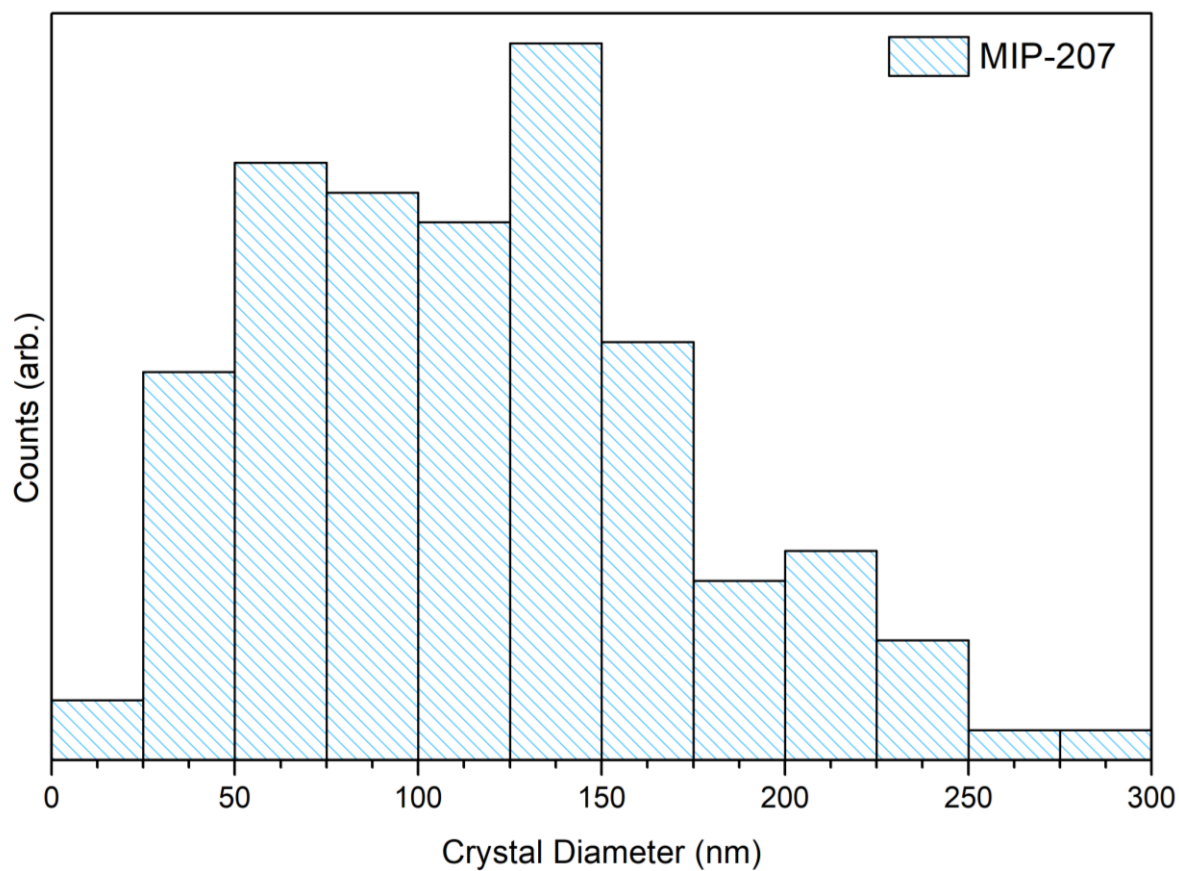


Figure 2.A.1: Size distribution of the crystal diameter for as-synthesised MIP-207. The average diameter is 117 ± 56 nm.

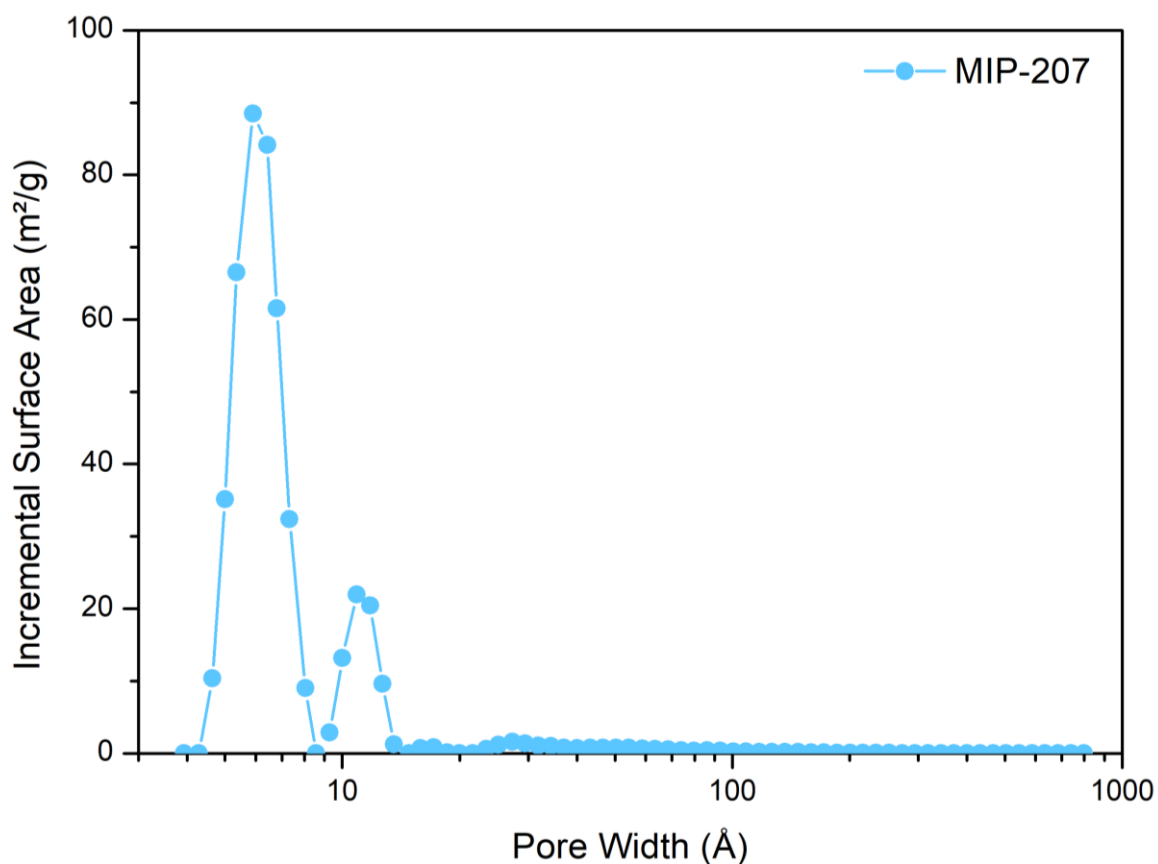


Figure 2.A.2: Pore size distribution calculated via DFT N₂ model for MIP-207.

Table 2.A.1: Water uptake, aqueous RuCl₃ concentration and volumes for the IWI of MIP-207, MUV-10(Ca) and MUV-10(Ba).

Support	Water uptake (mL g ⁻¹)	<i>x</i> wt. %	Aqueous RuCl ₃ concentration (mol L ⁻¹)	Volume of aqueous RuCl ₃ (μL)
MIP-207	1.34	1	0.074	268
MUV-10(Ca)	0.59	1	0.170	118
		5	0.886	118
MUV-10(Ba)	0.67	1	0.150	134
TiO ₂	0.45	1	0.223	90

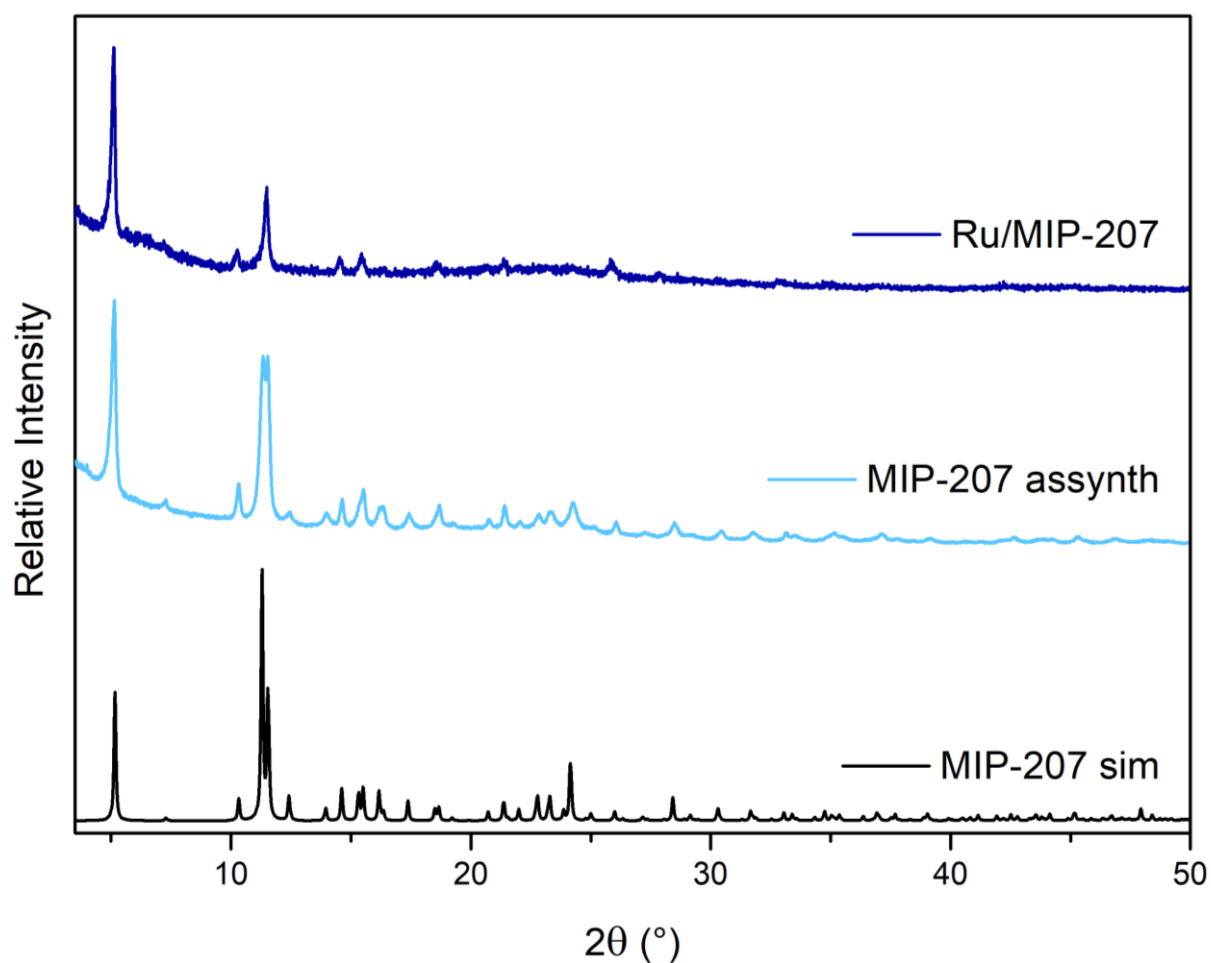


Figure 2.A.3: PXRD patterns of MIP-207; simulated desolvated MIP-207 (black), MIP-207 as-synthesised (blue) and Ru/MIP-207 (dark blue). The Ru/MIP-207 displays a loss in crystallinity on account of the disordered Ru atoms now within the MOF crystals.

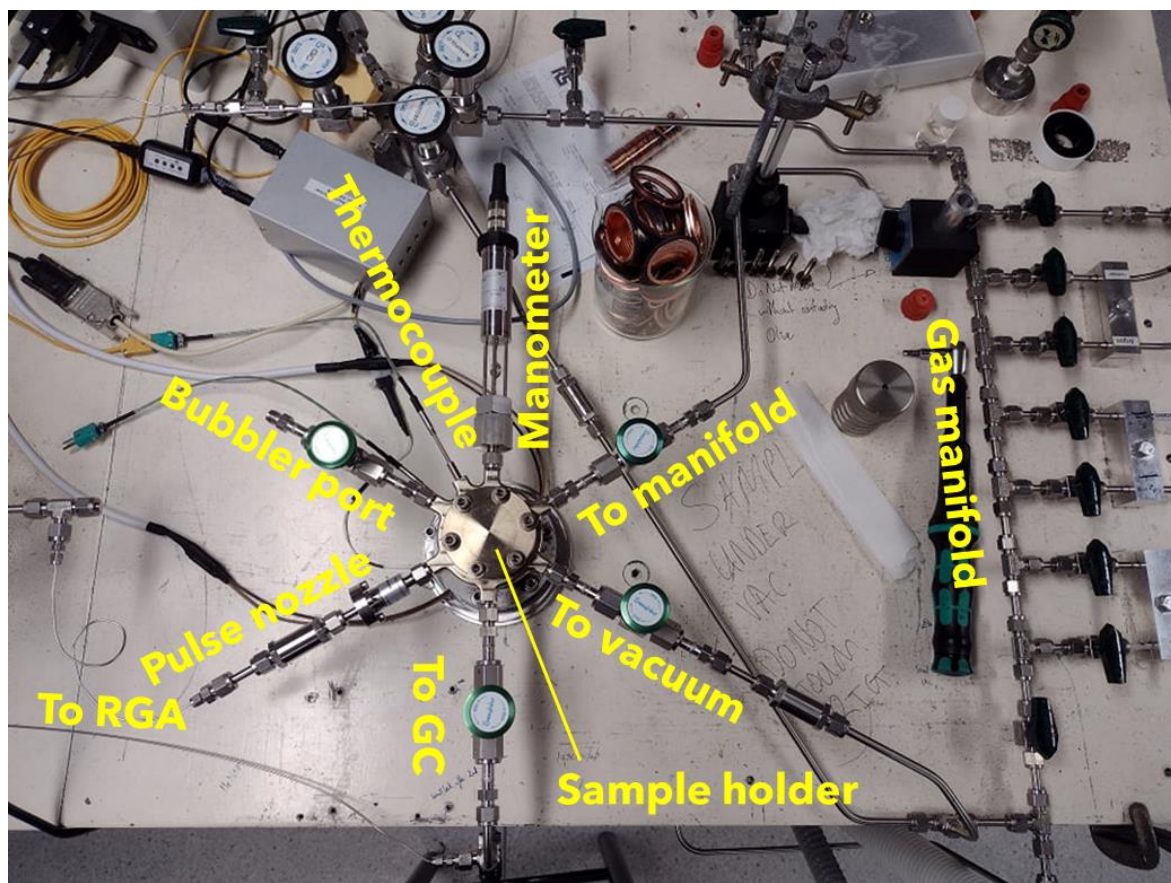


Figure 2.A.4: The batch reactor used during catalytic testing.

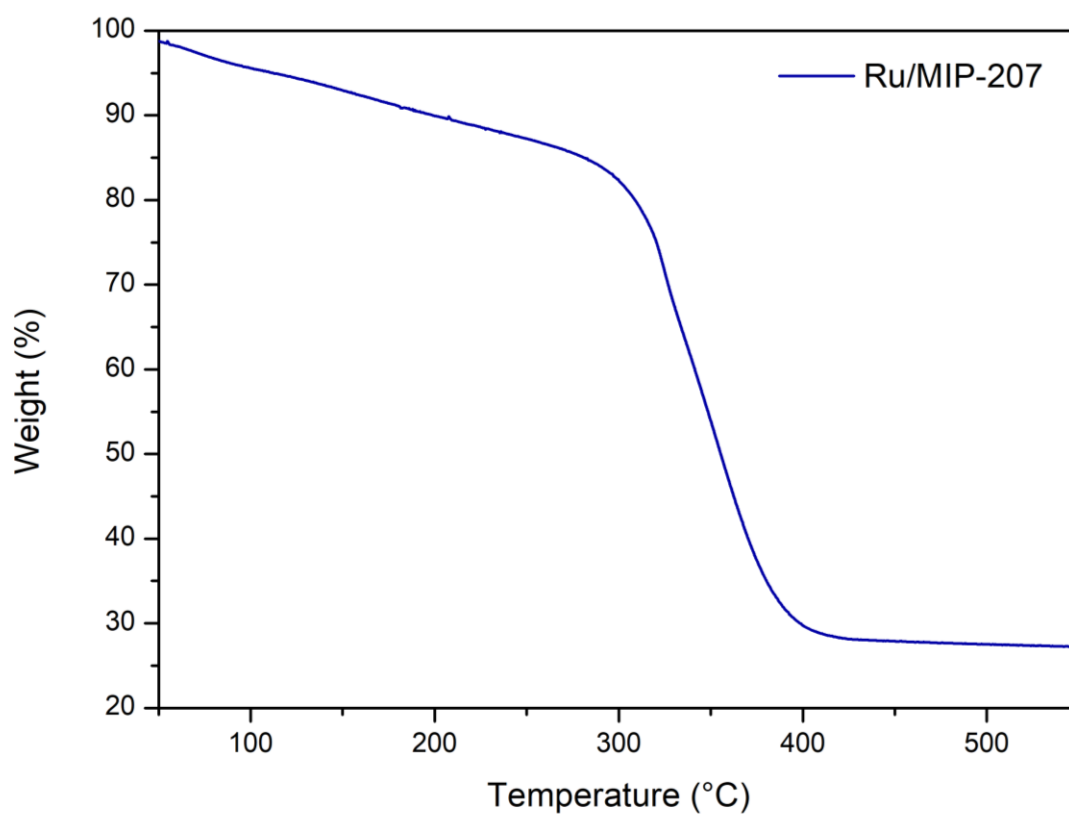


Figure 2.A.5: Thermogravimetric analysis of Ru loaded MIP-207.

Table 2.A.2: Summary of the catalytic reaction data including GC data for CO₂ methanation with **Ru/TiO₂(*op.*)** and **Ru/TiO₂(*calc.*)**.

Catalyst	Cycle	Temperature (°C)	Reaction time (h)	Products (μmol)				% CO ₂ conversion	% CH ₄ selectivity
				CH ₄	CO	Long chain C	CO ₂		
Ru/TiO₂(<i>op.</i>)	1	250	5	48.10	10.68	7.77	54.73	54.88	72.27
	2	250	5	22.53	10.79	2.71	54.26	39.91	62.54
Ru/TiO₂(<i>op.</i>)	1	300	5	56.66	23.71	14.45	127.84	42.58	59.76
	2	300	5	39.12	30.97	5.85	157.98	32.46	51.51
	3	300	5	20.40	37.11	3.03	160.26	27.42	33.70
Ru/TiO₂(<i>calc.</i>)	1	150	1	27.20	0.62	0.04	102.84	21.32	97.62
	2	150	1	4.11	0.81	0.29	126.13	3.97	78.87
	3	150	1	4.09	0.95	0.37	134.00	3.88	75.59
Ru/TiO₂(<i>calc.</i>)	1	200	1	42.27	0.98	0.22	13.64	76.11	97.25
	2	200	1	38.30	6.14	0.12	76.38	36.84	85.96
	3	200	1	5.73	12.48	0.00	111.98	13.98	31.48
Ru/TiO₂(<i>calc.</i>)	1	300	1	47.38	1.53	0.19	5.45	90.01	96.50
	2	300	1	9.55	17.28	0.07	71.47	27.34	35.50

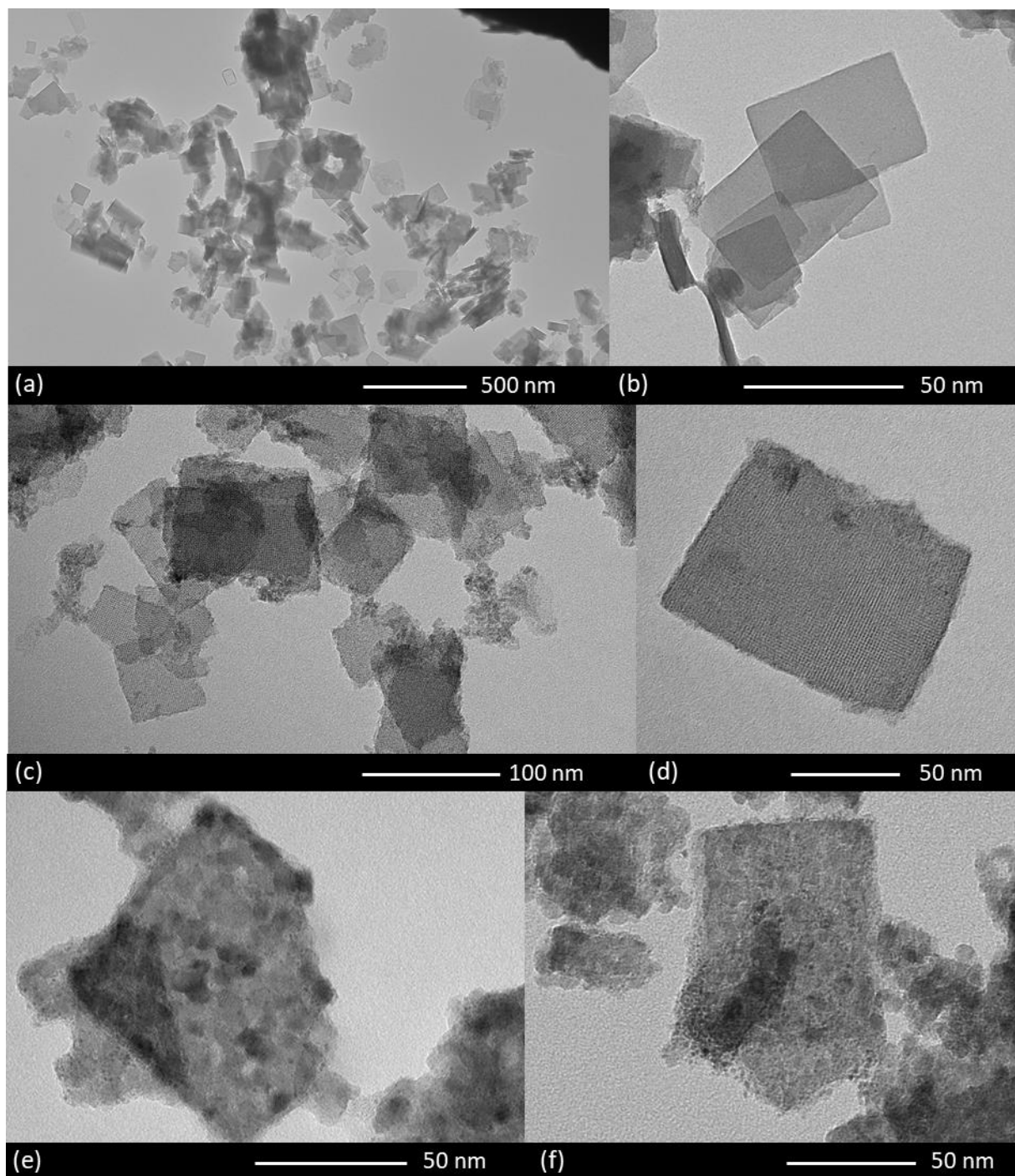


Figure 2.A.6: TEM images of **(a-b)** Ru/MIP-207, *in operando* pre-catalytic material, **(c-d)** Ru/TiO₂(*op.*)@250°C after 2 cycles retaining the lattice planes characteristic of crystalline MIP-207 with some evidence of degradation and **(e-f)** Ru/TiO₂(*op.*)@300°C after 3 cycles showing generation of small titania crystallites with potential Ru nanoparticles (small (1-2 nm) black particles).

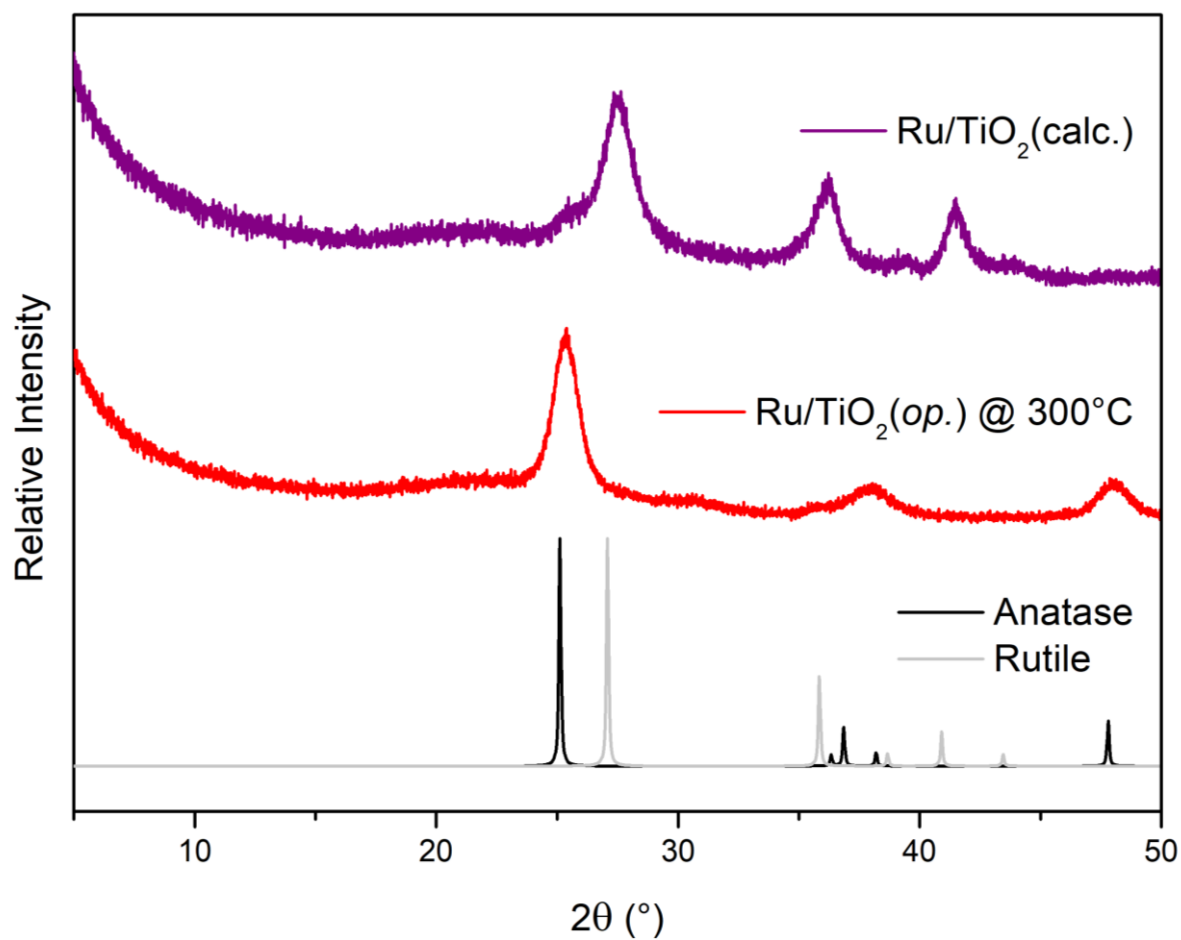


Figure 2.A.7: PXRD patterns of Ru/MIP-207 derived Ru/TiO₂; simulated anatase TiO₂ (black) and rutile TiO₂ (light grey), **Ru/TiO₂(op.)@300°C** after 3 cycles (red) exhibiting anatase character and **Ru/TiO₂(calc.)** (purple) exhibiting rutile character with trace amounts of rutile (shoulder at ~25°).

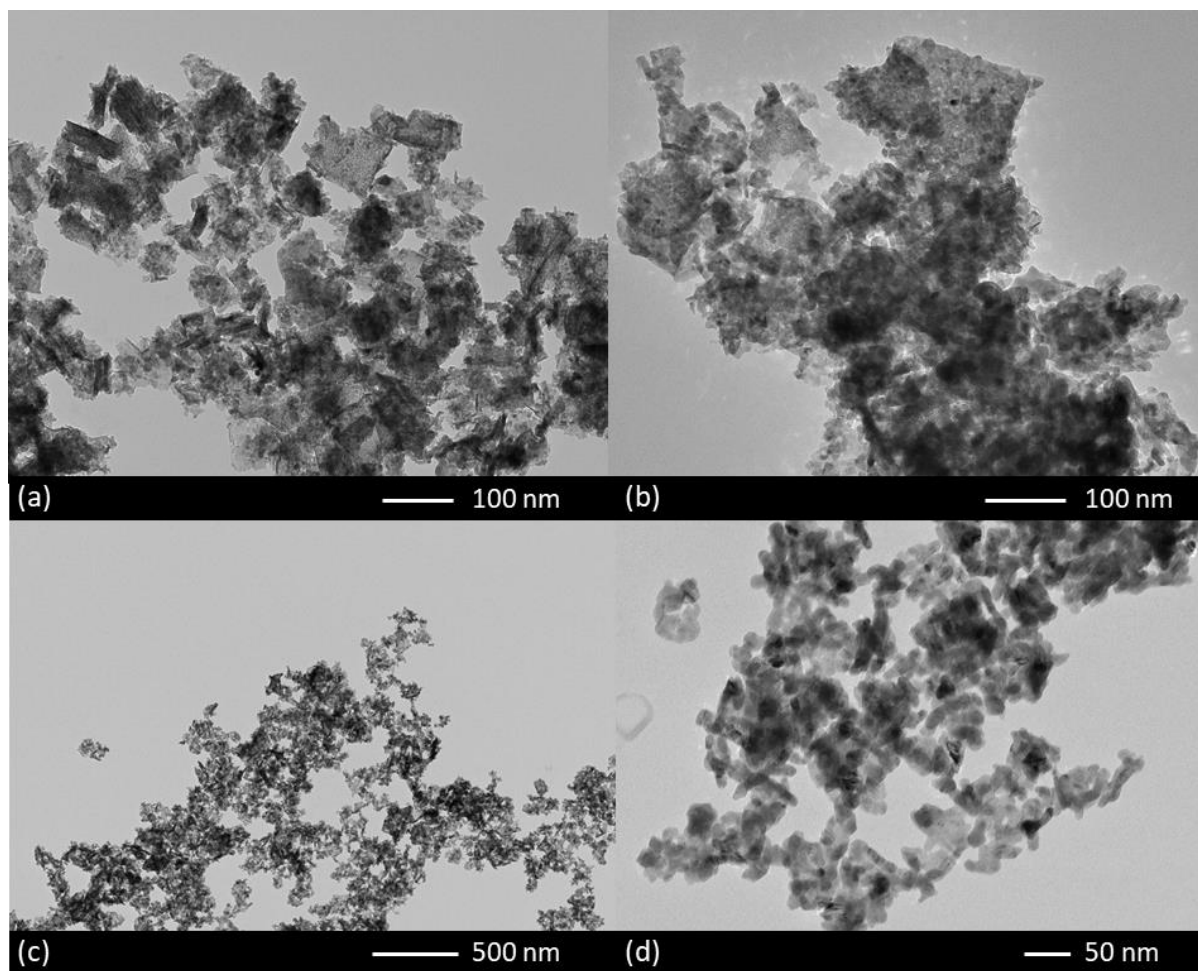


Figure 2.A.8: TEM images of **(a-b) Ru/TiO₂(calc.)**, calcined pre-catalytic material and **(c-d) Ru/TiO₂(calc.)@300°C** after 2 cycles exhibiting clear degradation of MIP-207 into small titania crystallites with potential Ru agglomerates (dark black regions).

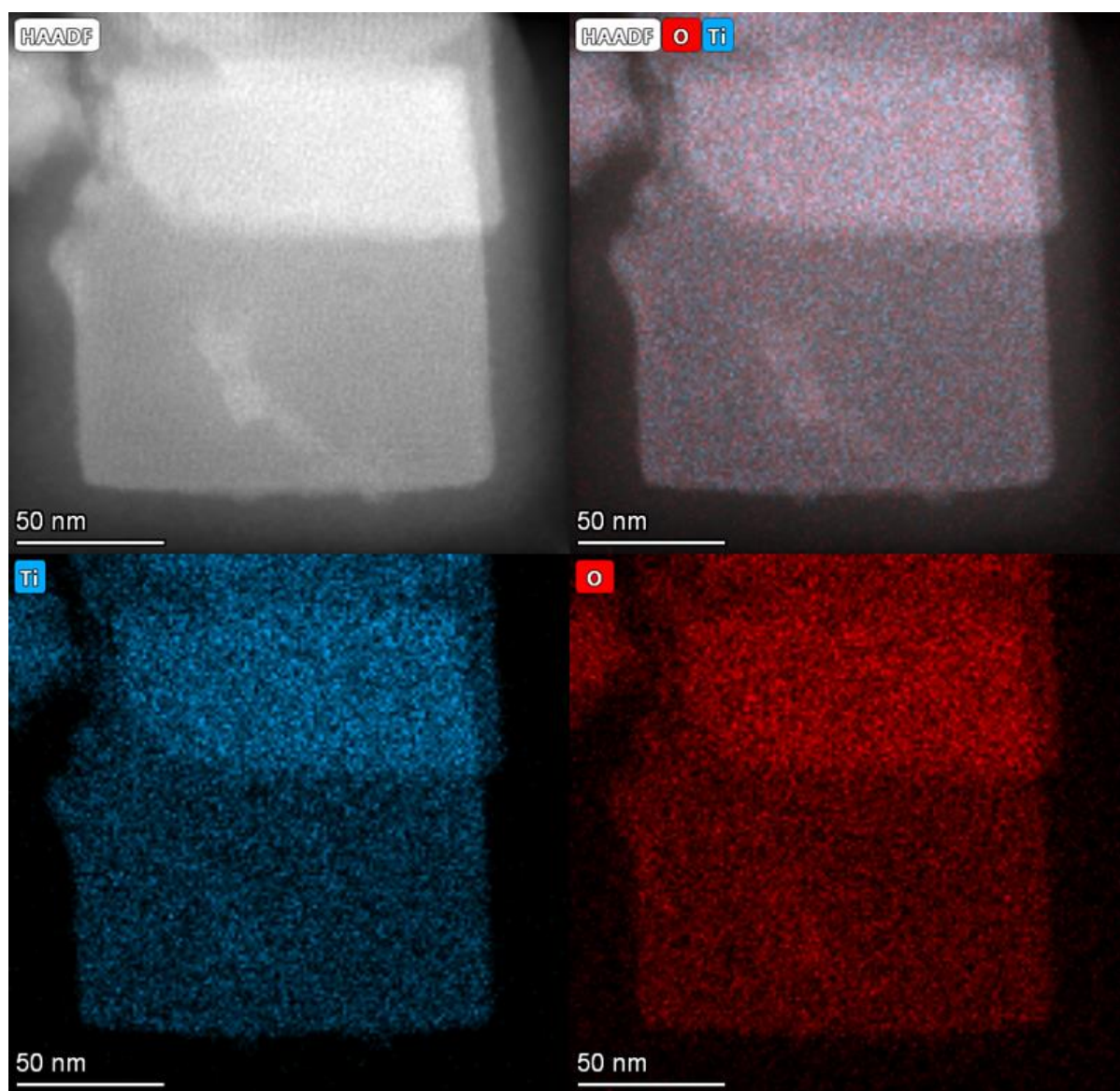


Figure 2.A.9: STEM-EDX images of MIP-207 as-synthesised revealing a homogenous distribution of Ti and O throughout the framework (Ti, blue; O, red).

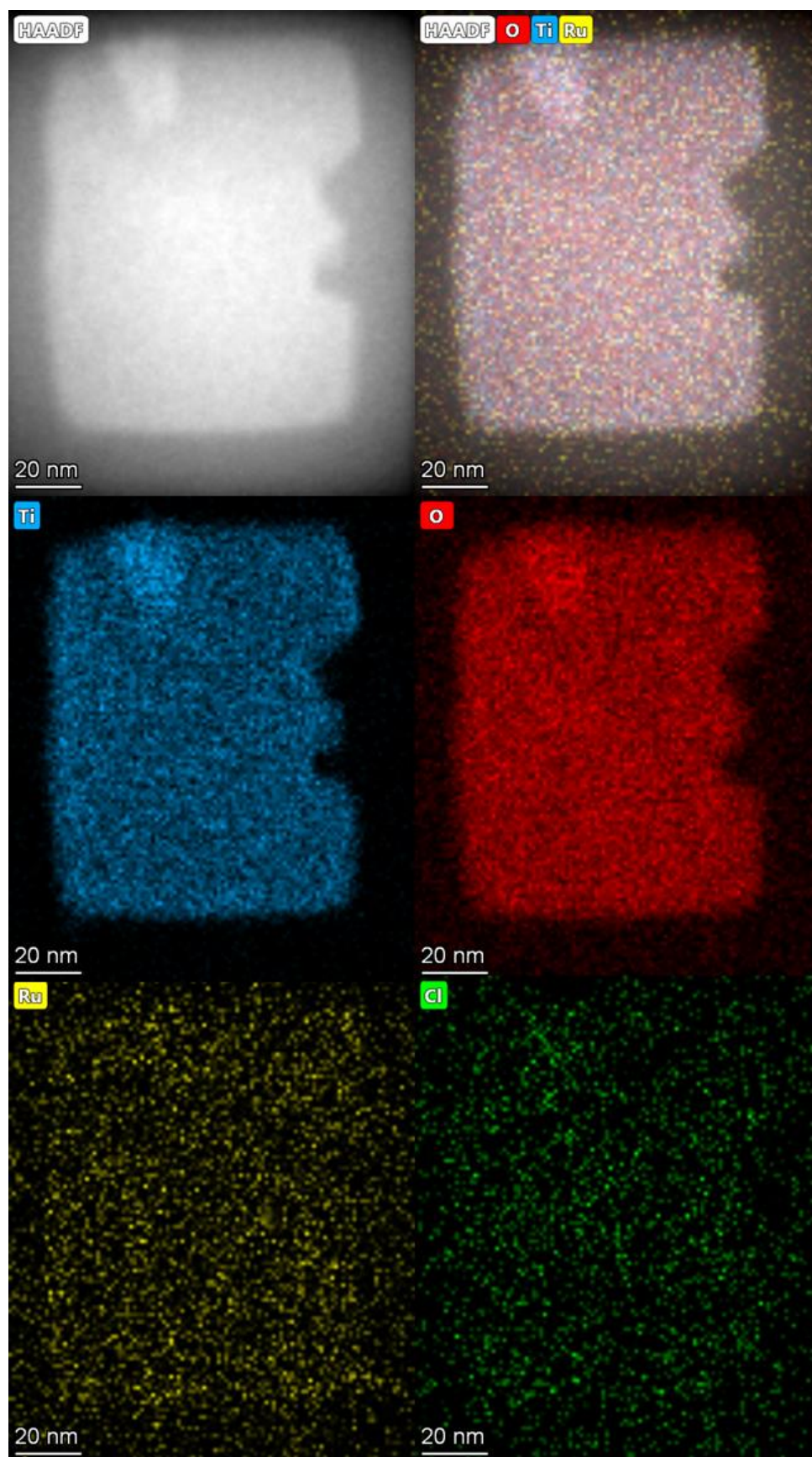


Figure 2.A.10: STEM-EDX images of Ru/MIP-207 revealing Ru is likely distributed throughout the framework (Ti, blue; O, red; Ru, yellow; Cl, green).

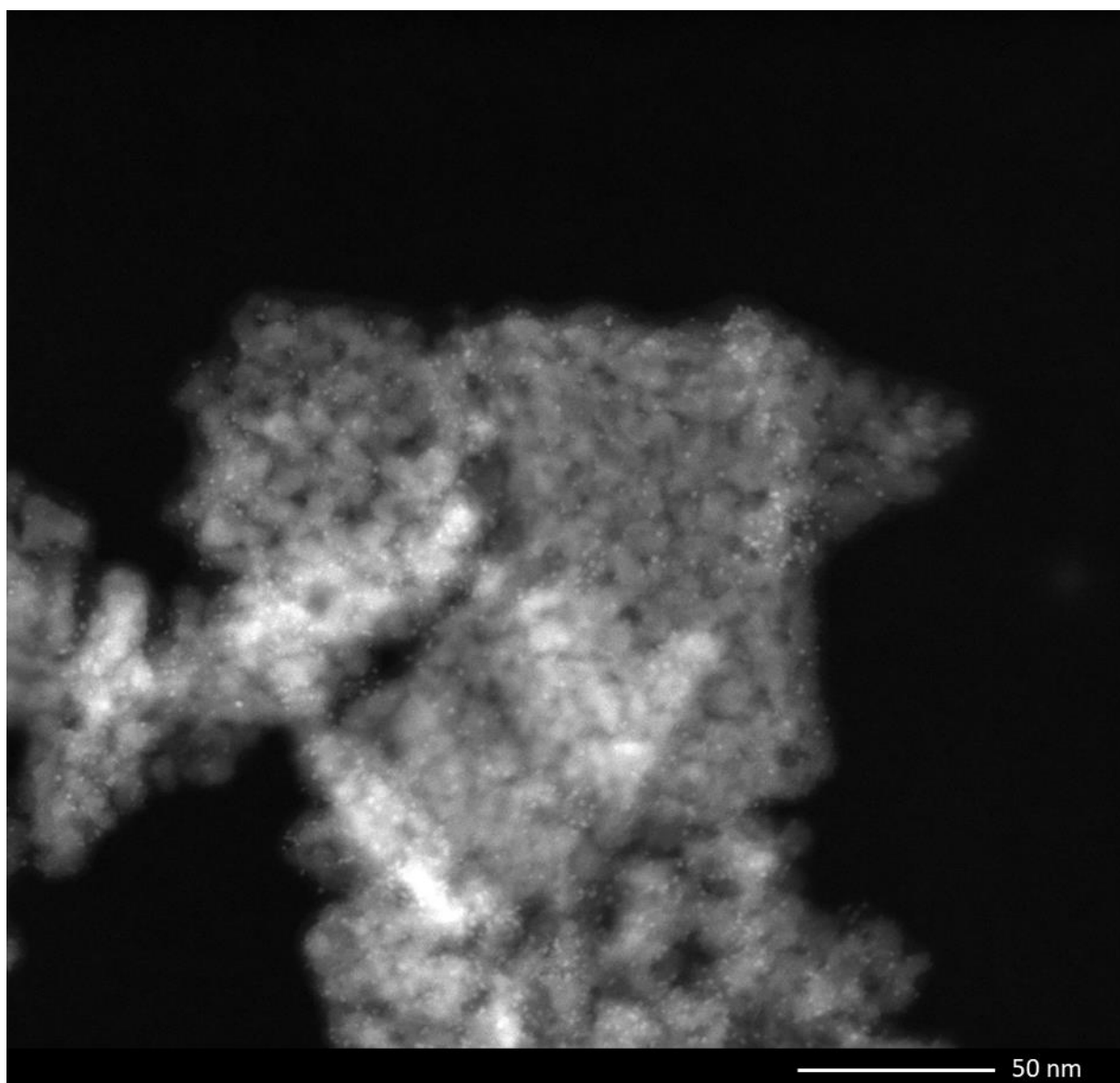


Figure 2.A.11: STEM-HAADF image of **Ru/TiO₂(*op.*)@300°C** revealing clear formation of small Ru nanoparticles.

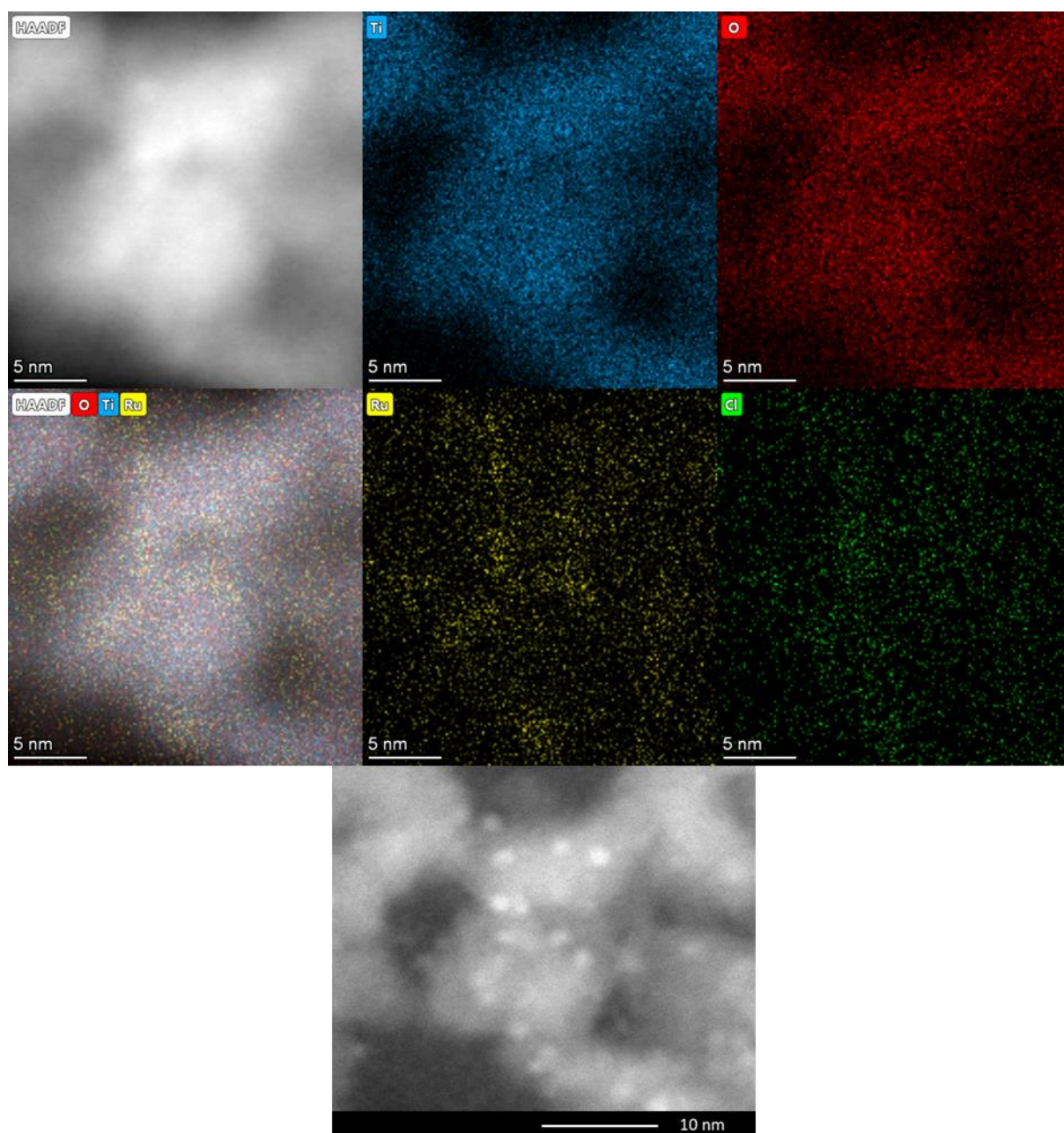


Figure 2.A.12: STEM-EDX images of **Ru/TiO₂(op.)@300°C** revealing an initial agglomeration of Ru nanoparticles throughout the framework (Ti, blue; O, red; Ru, yellow; Cl, green) including STEM-HAADF image of the scanned area (loss of features in original HAADF scan result due to multiple scans).

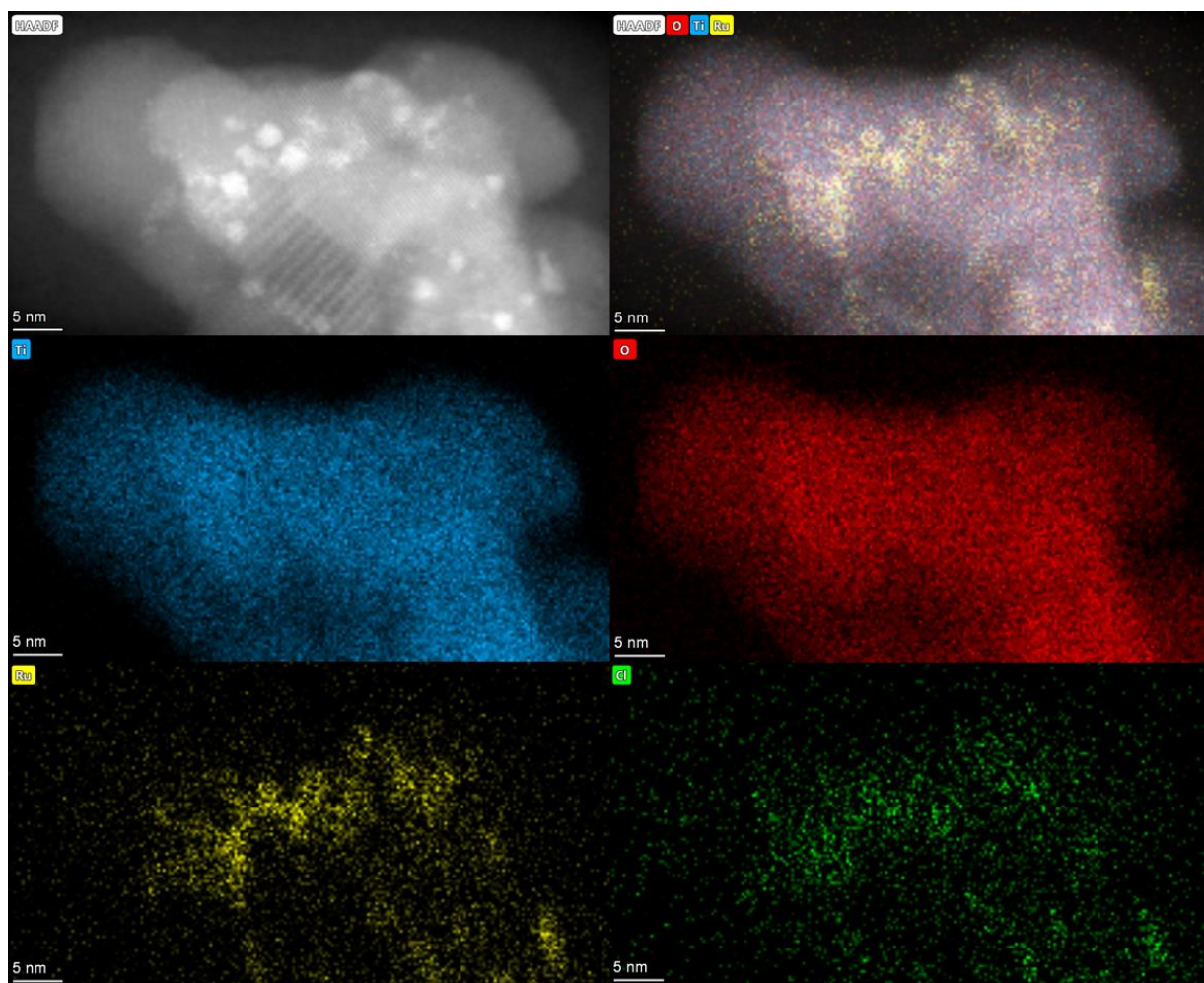


Figure 2.A.13: STEM-EDX images of **Ru/TiO₂(calc.)@300°C** revealing enhanced levels of Ru agglomeration (Ti, blue; O, red; Ru, yellow; Cl, green).

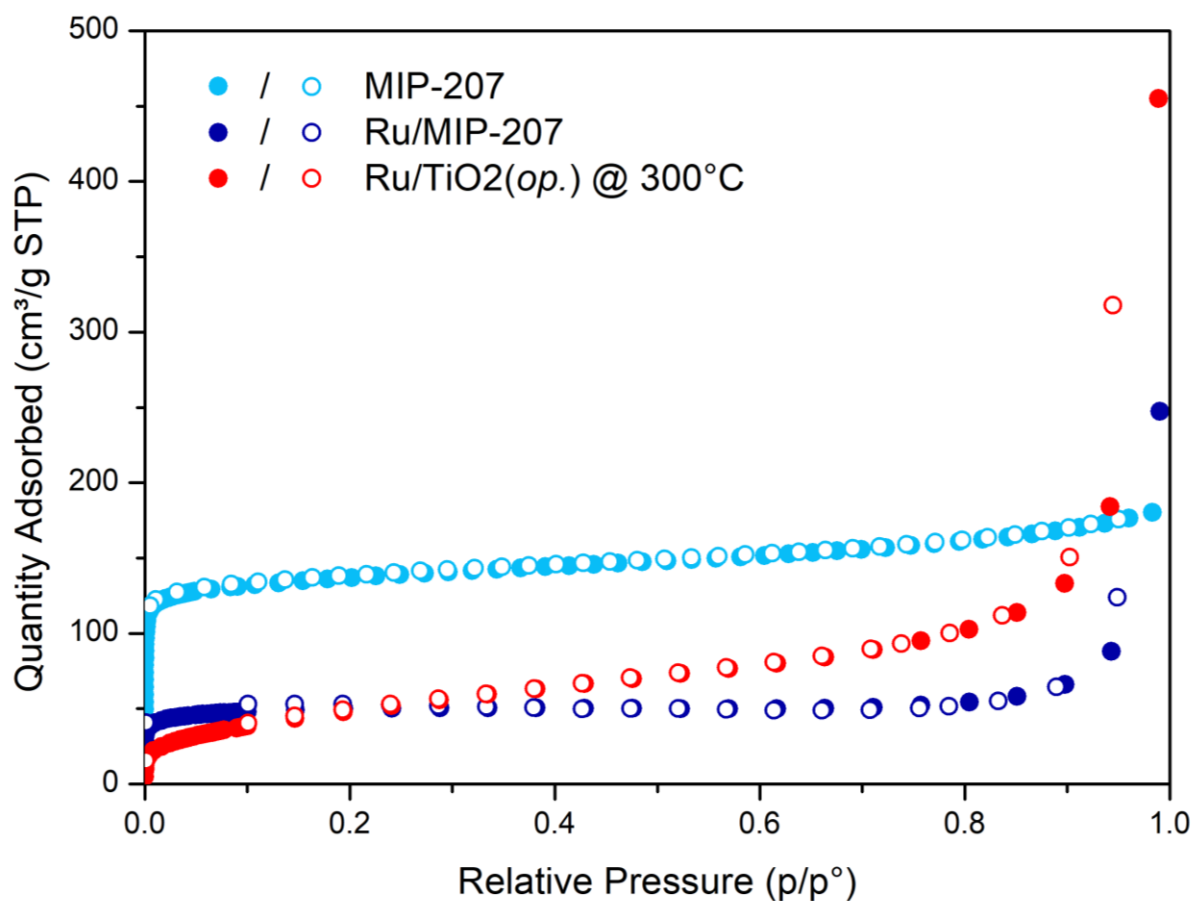


Figure 2.A.14: 77 K N₂ adsorption isotherm data collected for MIP-207 (blue); Ru/MIP-207 (dark blue), BET = 190 m² g⁻¹; and **Ru/TiO₂(op.)@300°C** (red), BET = 150 m² g⁻¹.

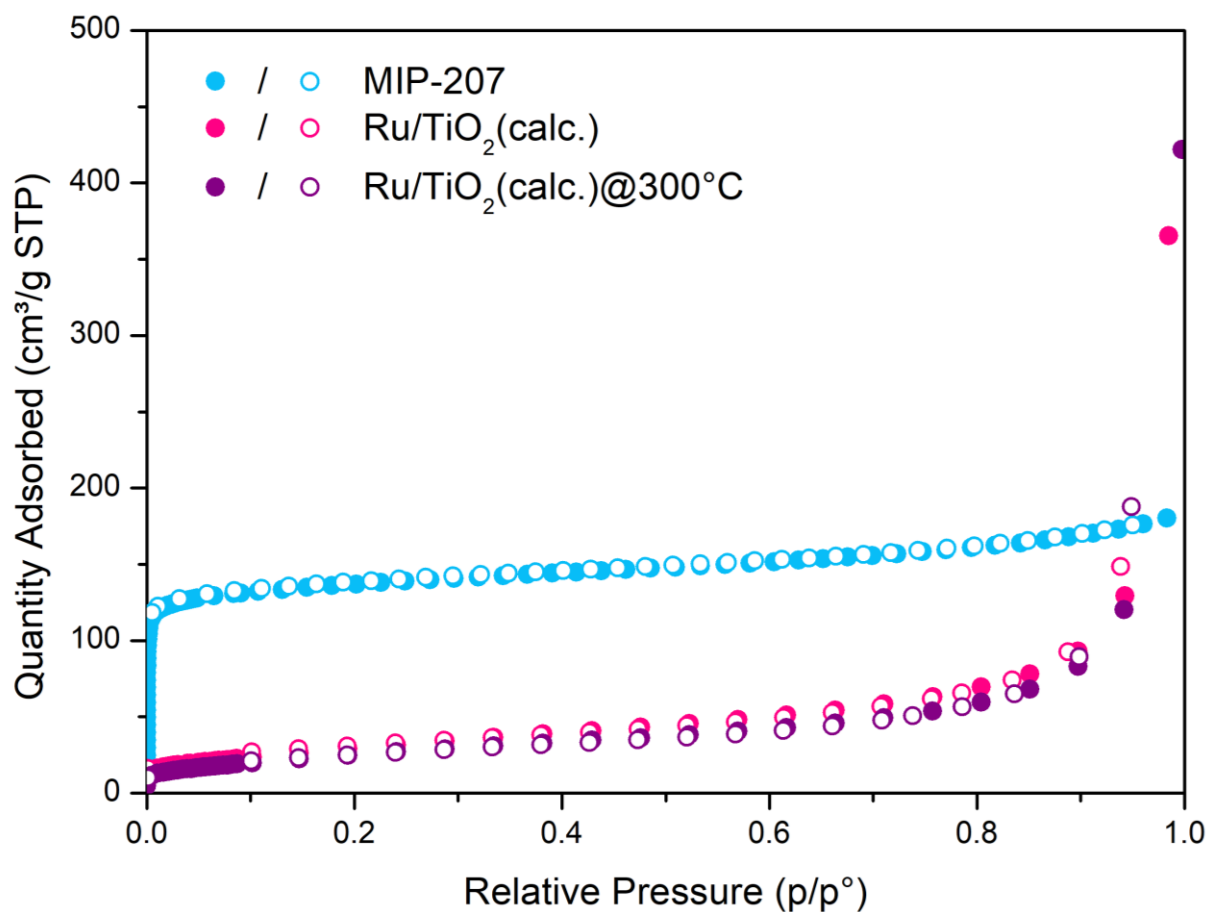


Figure 2.A.15: 77 K N₂ adsorption isotherm data collected for MIP-207 (blue); **Ru/TiO₂(calc.)** (pink), BET = 87 m² g⁻¹; and **Ru/TiO₂(calc.)@300°C** (purple), BET = 74 m² g⁻¹.

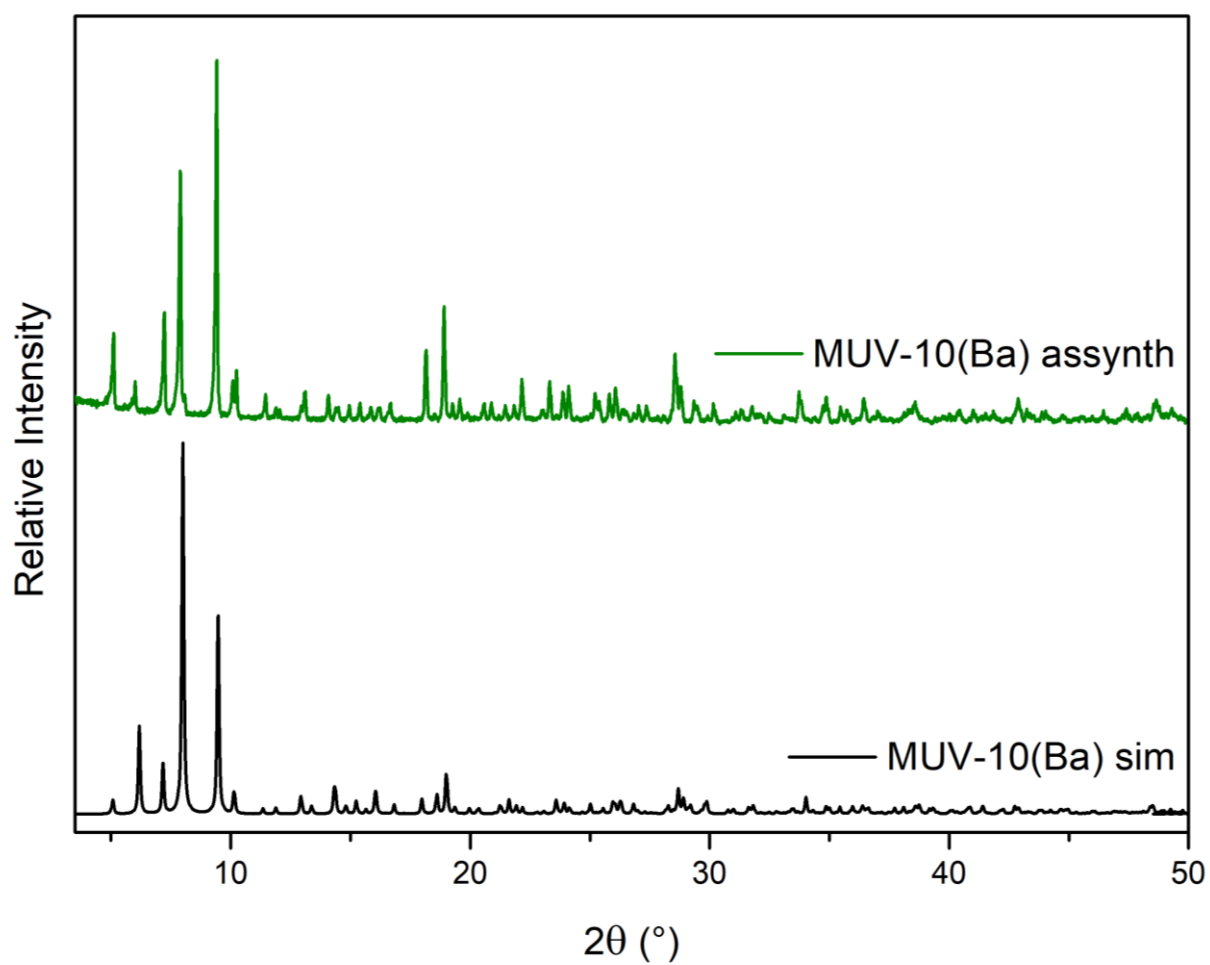


Figure 2.A.16: PXRD patterns of MUV-10(Ba); simulated MUV-10(Ba) (black) and MUV-10(Ba) as-synthesised (dark green).

Table 2.A.3: Crystallographic data collection and refinement parameters for MUV-10(Ba).

Sample	MUV-10(Ba)
Formula	C ₄₂ H ₂₆ Ba ₃ N ₂ O ₃₄ Ti ₃
Formula weight (g/mol)	1658.37
Temperature (K)	100(2)
Crystal system	Tetragonal
Space group	<i>P4/mbm</i>
a (Å)	24.635(4)
b (Å)	24.635(4)
c (Å)	14.292(3)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å³)	8673(3)
Z	4
ρ_{calc} (g/cm³)	1.270
Absorption coefficient (mm⁻¹)	1.668
F(000)	3192.0
Crystal size (mm³)	0.18 x 0.15 x 0.11
Wavelength	Synchrotron (λ = 0.71073)
2θ range for data collection (°)	2.338 to 57.190
Index ranges	-29 ≤ h ≤ 30, -31 ≤ k ≤ 32, -17 ≤ l ≤ 17
Reflections collected	106981
Independent reflections	5445 [R _{int} = 0.0287, R _{sigma} = 0.0097]
Data/restraints/parameters	5445/20/264
GOF on F²	1.082
R₁, [I ≥ 2σ (I)]	R ₁ = 0.0386, wR ₂ = 0.1315
wR₂ [all data]	R ₁ = 0.0387, wR ₂ = 0.1316
Largest diff. peak/hole (eÅ⁻³)	2.68/-1.22

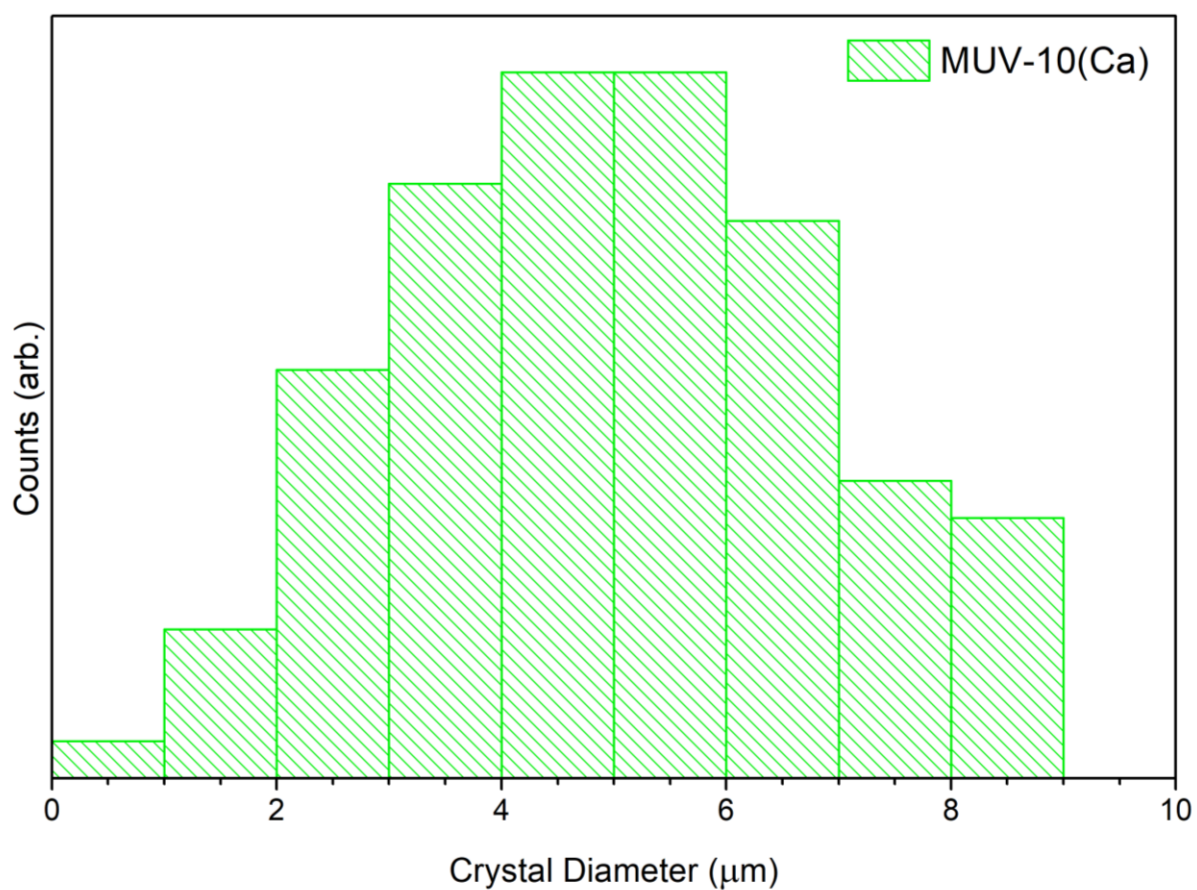


Figure 2.A.17: Size distribution of the crystal diameter for as-synthesised MUV-10(Ca). The average diameter is $5.0 \pm 1.9 \mu\text{m}$.

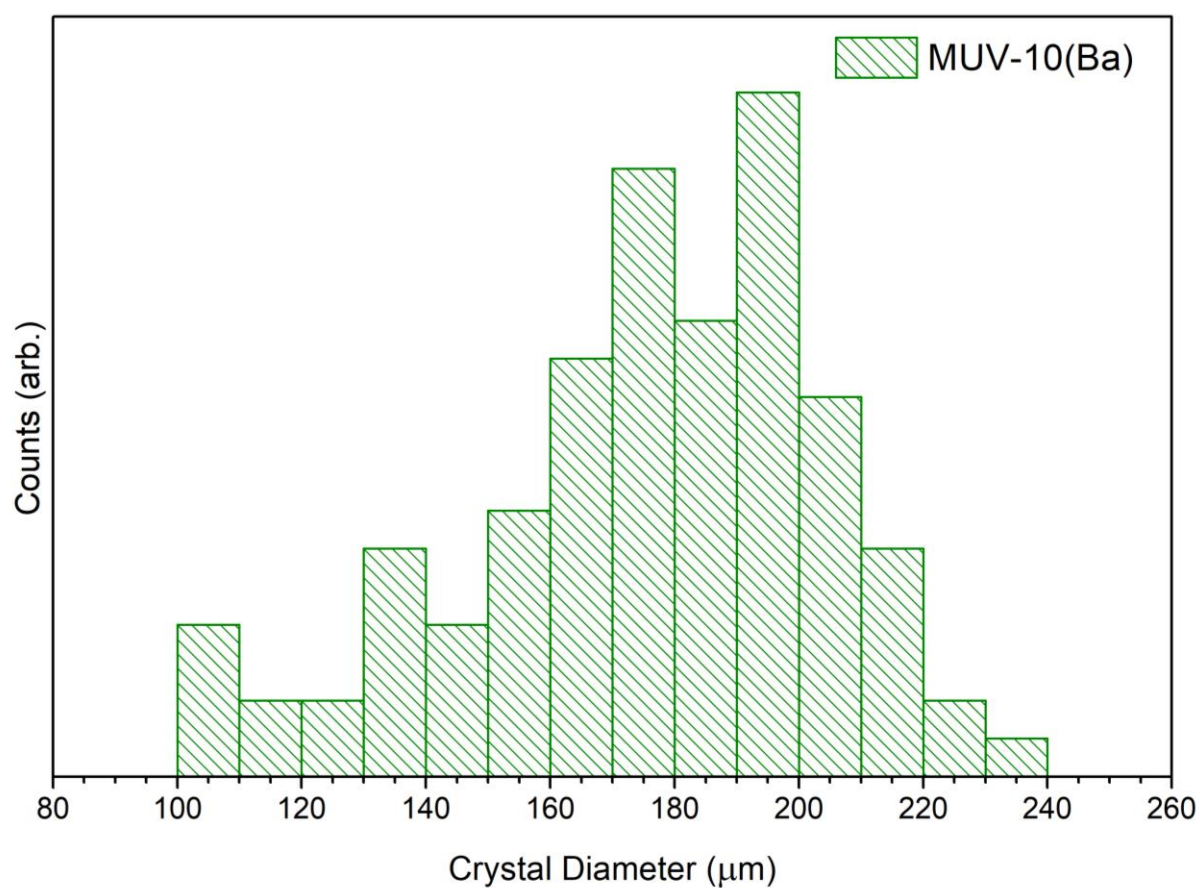


Figure 2.A.18: Size distribution of the crystal diameter for as-synthesised MUV-10(Ba). The average diameter is $176 \pm 28 \mu\text{m}$.

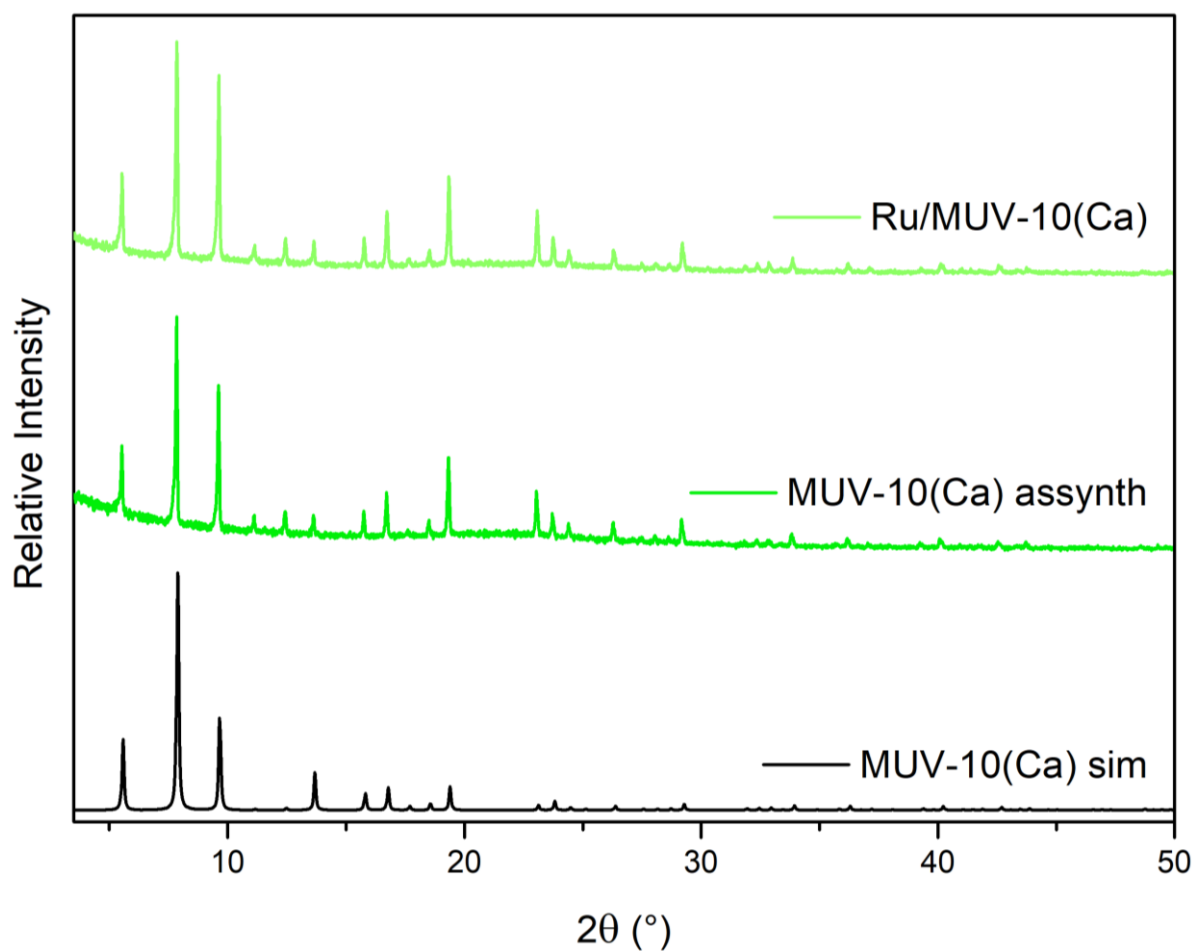


Figure 2.A.19: PXRD patterns of MUV-10(Ca); simulated MUV-10(Ca) (black), MUV-10(Ca) as-synthesised (green) and Ru/MUV-10(Ca) (light green).

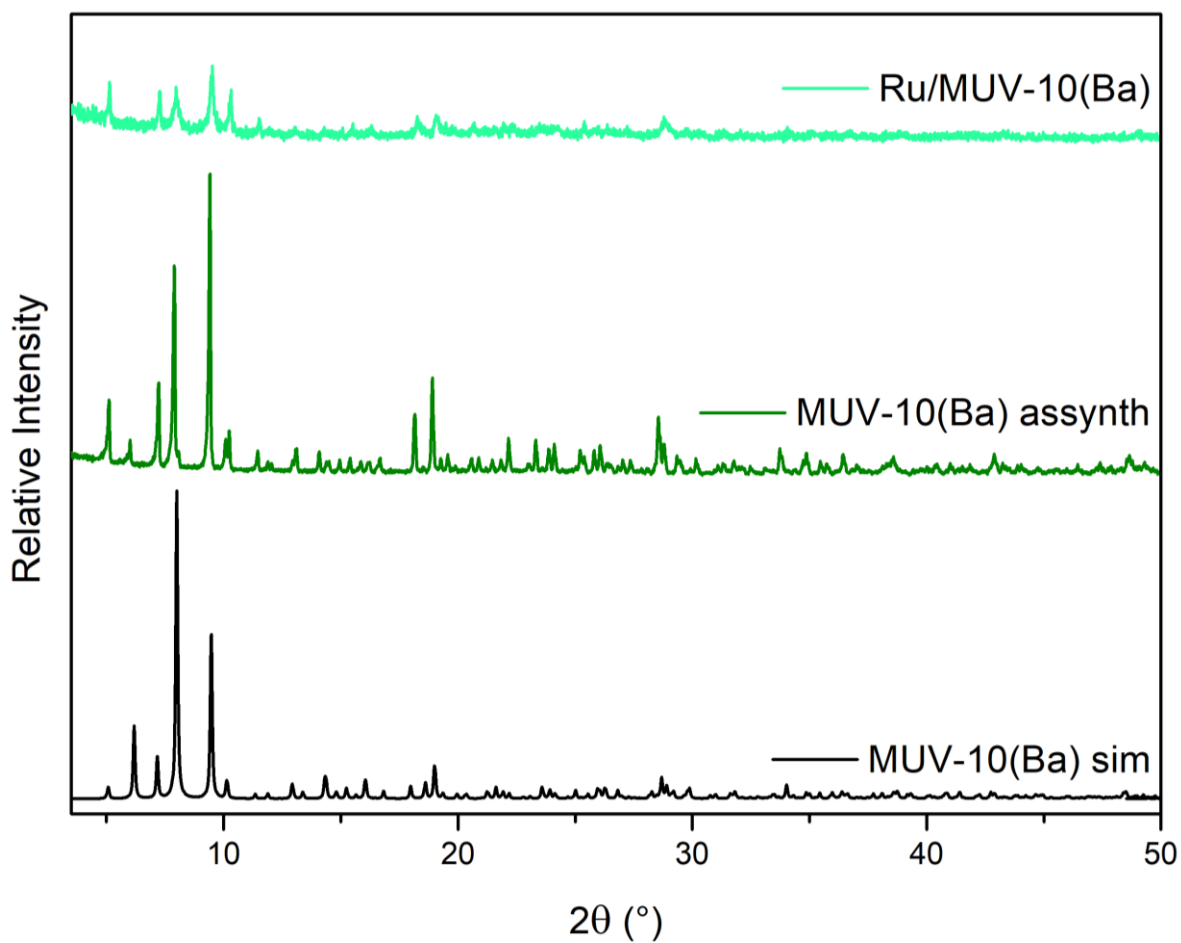


Figure 2.A.20: PXRD patterns of MUV-10(Ba); simulated MUV-10(Ba) (black), MUV-10(Ba) as-synthesised (dark green) and Ru/MUV-10(Ba) (aqua). The Ru/MUV-10(Ba) sample displays almost a complete loss in crystallinity.

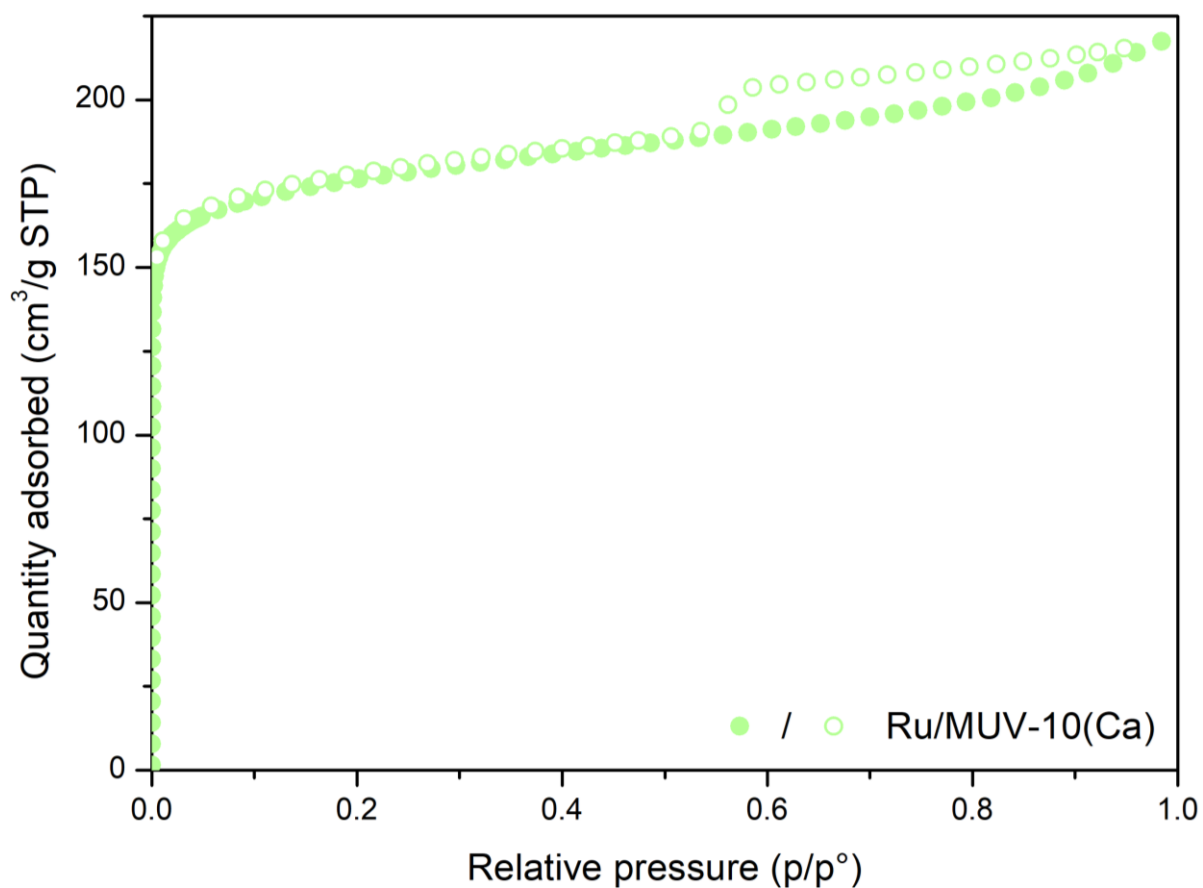


Figure 2.A.21: 77 K N₂ adsorption isotherm data collected for Ru/MUV-10(Ca) adopting a H4 type profile.

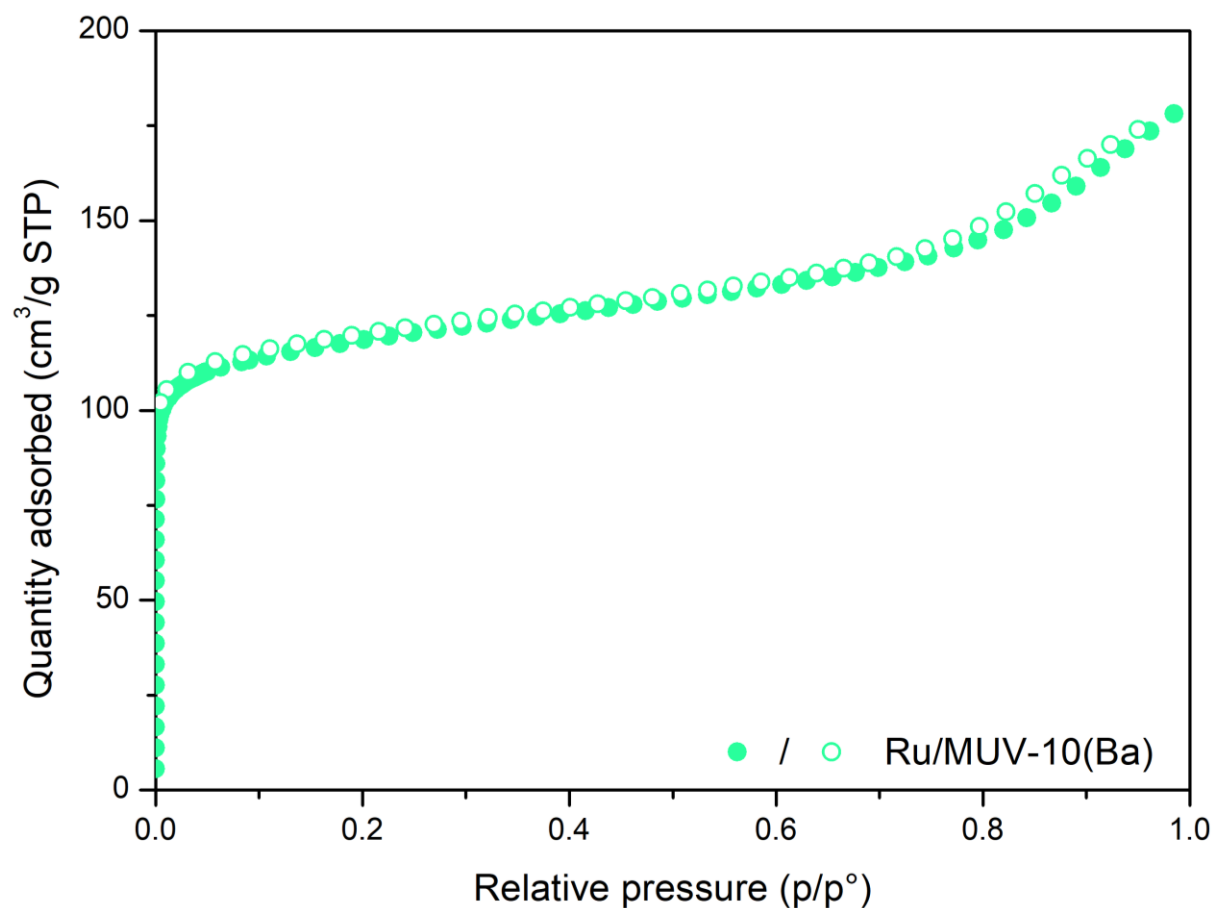


Figure 2.A.22: 77 K N₂ adsorption isotherm data collected for Ru/MUV-10(Ba) exhibiting reduced uptake compared to as-synthesised MUV-10(Ba), suggesting some degree of framework decomposition.

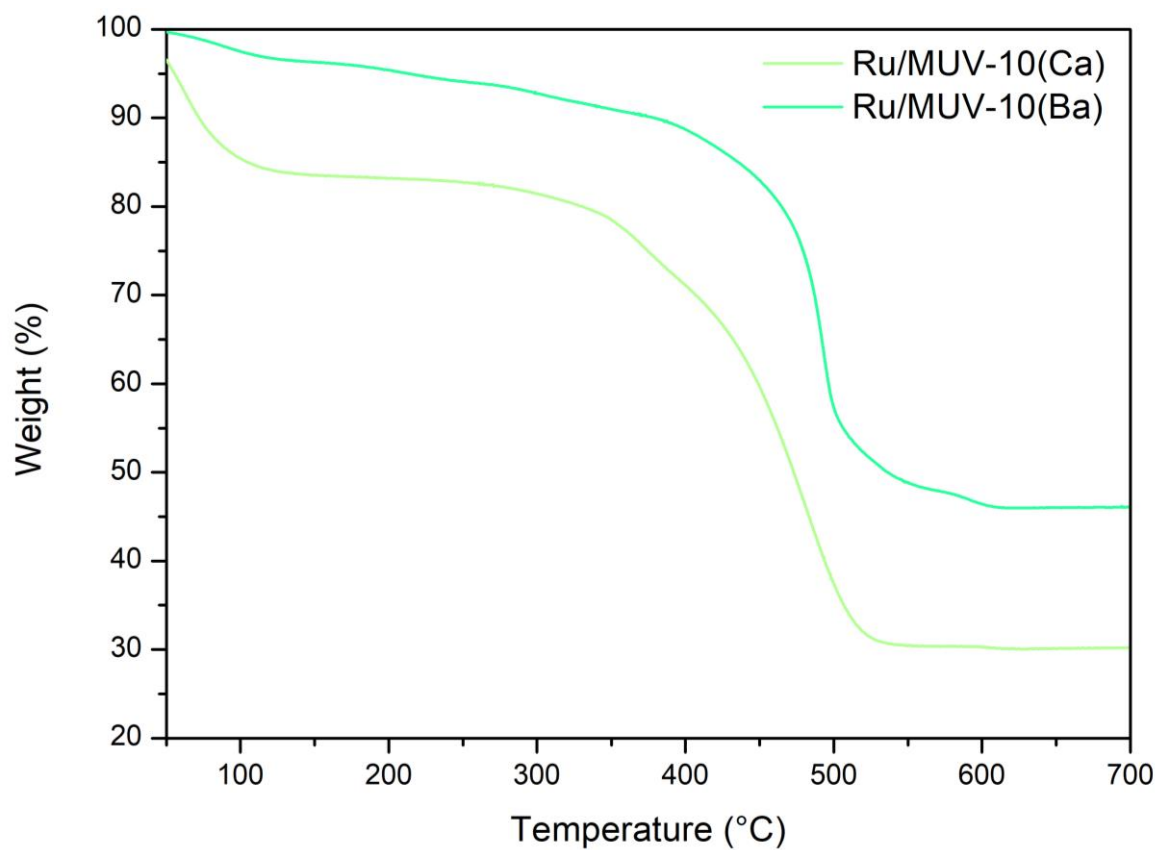


Figure 2.A.23: Thermogravimetric analysis of Ru loaded MUV-10(Ca) (light green) and MUV-10(Ba) (aqua).

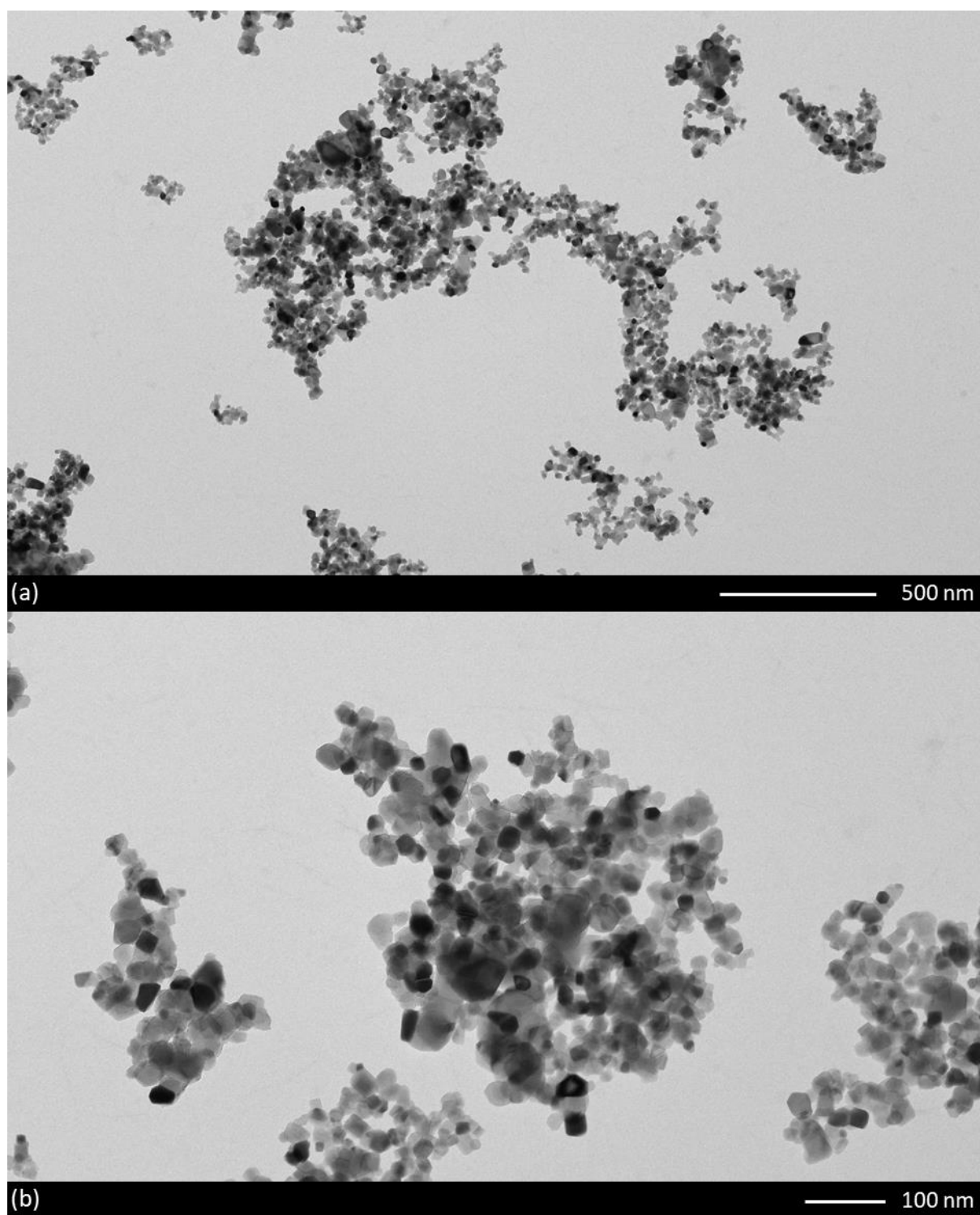


Figure 2.A.24: TEM images of **(a-b)** purchased TiO₂ composed of rutile and anatase (20:80).

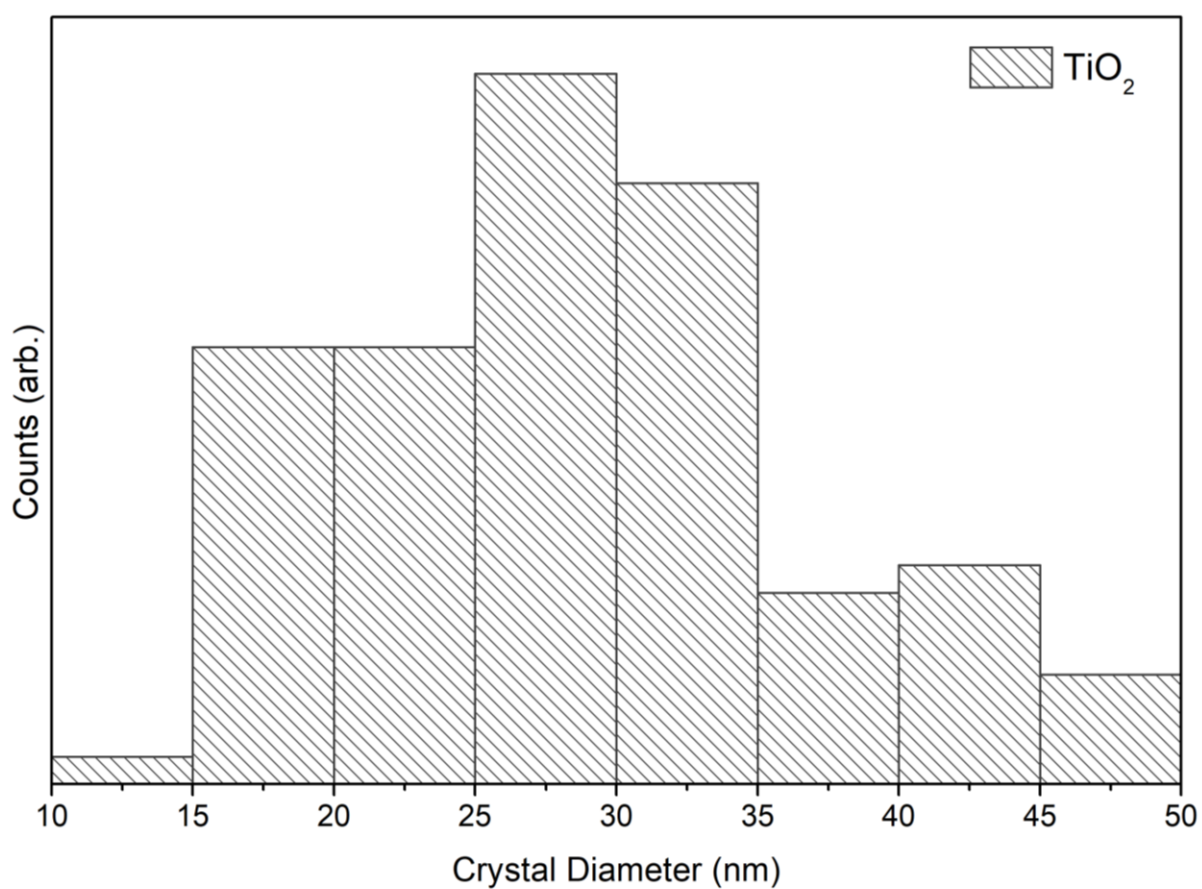


Figure 2.A.25: Size distribution of the crystal diameter for purchased TiO₂. The average diameter is 28 ± 8 nm.

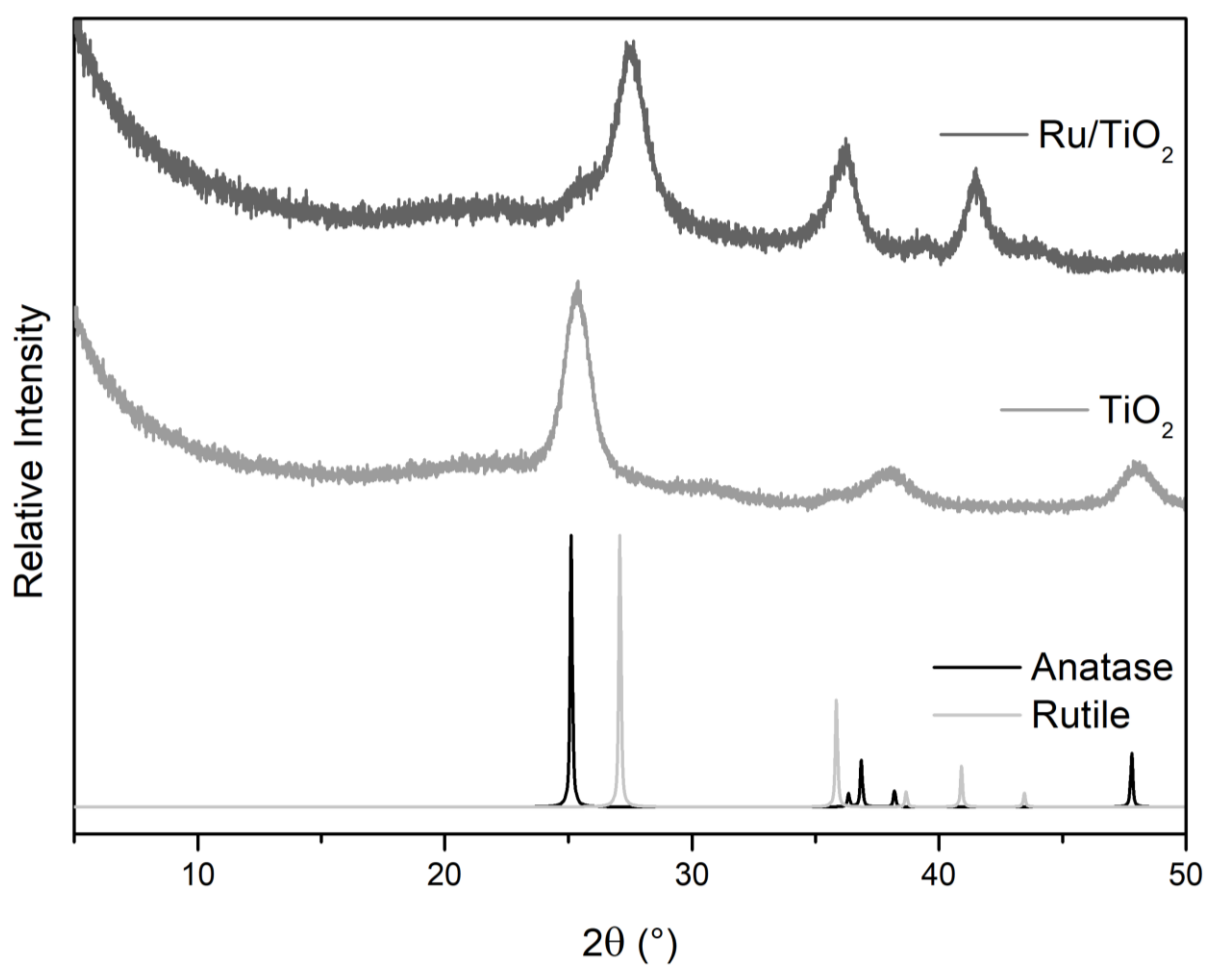


Figure 2.A.26: PXRD patterns of TiO₂; simulated anatase TiO₂ (black) and rutile TiO₂ (light grey), purchased TiO₂ (grey) and Ru/TiO₂ (dark grey).

Table 2.A.4: Summary of the catalytic reaction data including GC data for CO₂ methanation with **Ru/TiO₂(*op.*)_Ca**, **Ru/TiO₂(*op.*)_Ba**, **Ru/TiO₂(*calc.*)_Ca**, **Ru/TiO₂(*calc.*)_Ba** and **Ru/TiO₂(*std.*)**.

Catalyst	Cycle	Temperature (°C)	Reaction time (h)	Products (μmol)				% CO ₂ conversion	% CH ₄ selectivity
				CH ₄	CO	Long chain C	CO ₂		
Ru/TiO₂(<i>op.</i>)_Ca	1	300	0.5	60.94	0.00	1.34	50.02	55.46	97.85
	2	300	0.5	42.00	0.00	0.03	31.08	57.49	99.92
	3	300	0.5	39.64	0.00	0.06	26.21	60.24	99.84
	4	300	0.5	43.01	0.00	0.18	38.22	53.05	99.59
	5	300	0.5	40.41	0.00	0.46	56.96	41.78	98.88
Ru/TiO₂(<i>op.</i>)_Ba	1	300	0.5	41.90	7.32	8.52	159.21	26.62	72.57
	2	300	0.5	33.98	5.98	1.65	111.17	27.24	81.65
	3	300	0.5	36.13	5.78	2.66	98.96	31.05	81.08
	4	300	0.5	34.18	5.71	1.91	85.42	32.85	81.77
	5	300	0.5	39.71	5.42	2.05	71.26	39.84	84.16
Ru/TiO₂(<i>calc.</i>)_Ca	1	300	0.5	35.36	0.10	0.00	9.77	78.39	99.71
	2	300	0.5	35.90	0.10	0.00	8.09	81.65	99.73
	3	300	0.5	39.28	0.09	0.00	7.02	84.86	99.78
	4	300	0.5	37.19	0.06	0.00	6.34	85.46	99.84
	5	300	0.5	38.13	0.07	0.00	8.16	82.39	99.81

Table 2.A.4 cont.: Summary of the catalytic reaction data including GC data for CO₂ methanation with **Ru/TiO₂(*op.*)_Ca**, **Ru/TiO₂(*op.*)_Ba**, **Ru/TiO₂(*calc.*)_Ca**, **Ru/TiO₂(*calc.*)_Ba** and **Ru/TiO₂(*std.*)**.

Catalyst	Cycle	Temperature (°C)	Reaction time (h)	Products (μmol)				% CO ₂ conversion	% CH ₄ selectivity
				CH ₄	CO	Long chain C	CO ₂		
Ru/TiO₂(<i>calc.</i>)_Ba	1	300	0.5	40.11	0.12	0.00	12.15	76.80	99.71
	2	300	0.5	32.92	0.10	0.00	7.41	81.67	99.70
	3	300	0.5	28.63	0.09	0.00	8.80	76.54	99.69
	4	300	0.5	35.26	0.09	0.00	7.04	83.39	99.74
	5	300	0.5	37.75	0.09	0.00	7.40	83.64	99.75
Ru/TiO₂(<i>std.</i>)	1	300	0.5	37.18	0.24	0.00	10.15	78.67	99.35
	2	300	0.5	40.64	0.27	0.00	9.49	81.17	99.35
	3	300	0.5	34.93	0.15	0.00	8.01	81.40	99.57
	4	300	0.5	33.93	0.11	0.00	7.18	82.57	99.68
	5	300	0.5	35.90	0.14	0.00	6.23	85.27	99.62

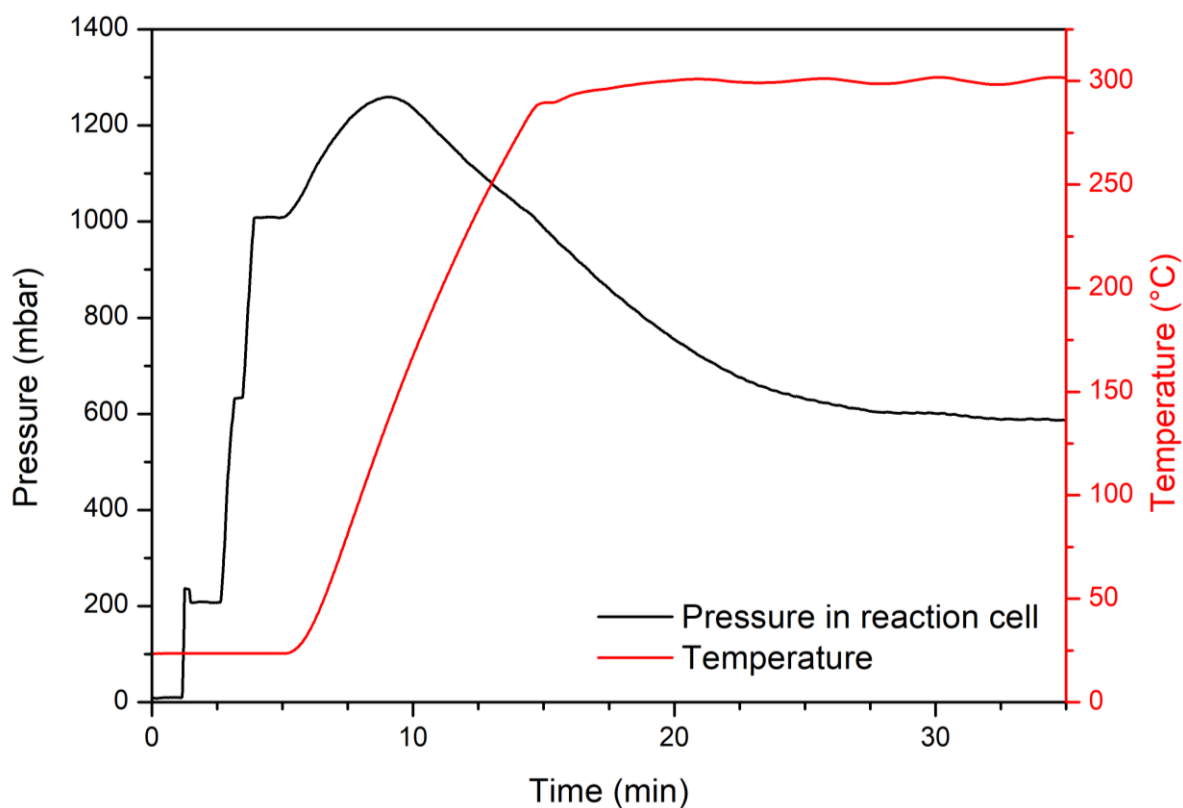


Figure 2.A.27: Typical catalytic reaction reactor cell pressure (black) and temperature (red) over reaction time. Between 0 – 5 minutes, CO₂ (200 mbar) and H₂ (1000 mbar) was introduced to the reaction cell and the reaction was started at the 5-minute mark. At the 35-minute mark, the reaction gas mixture was analysed via GC.

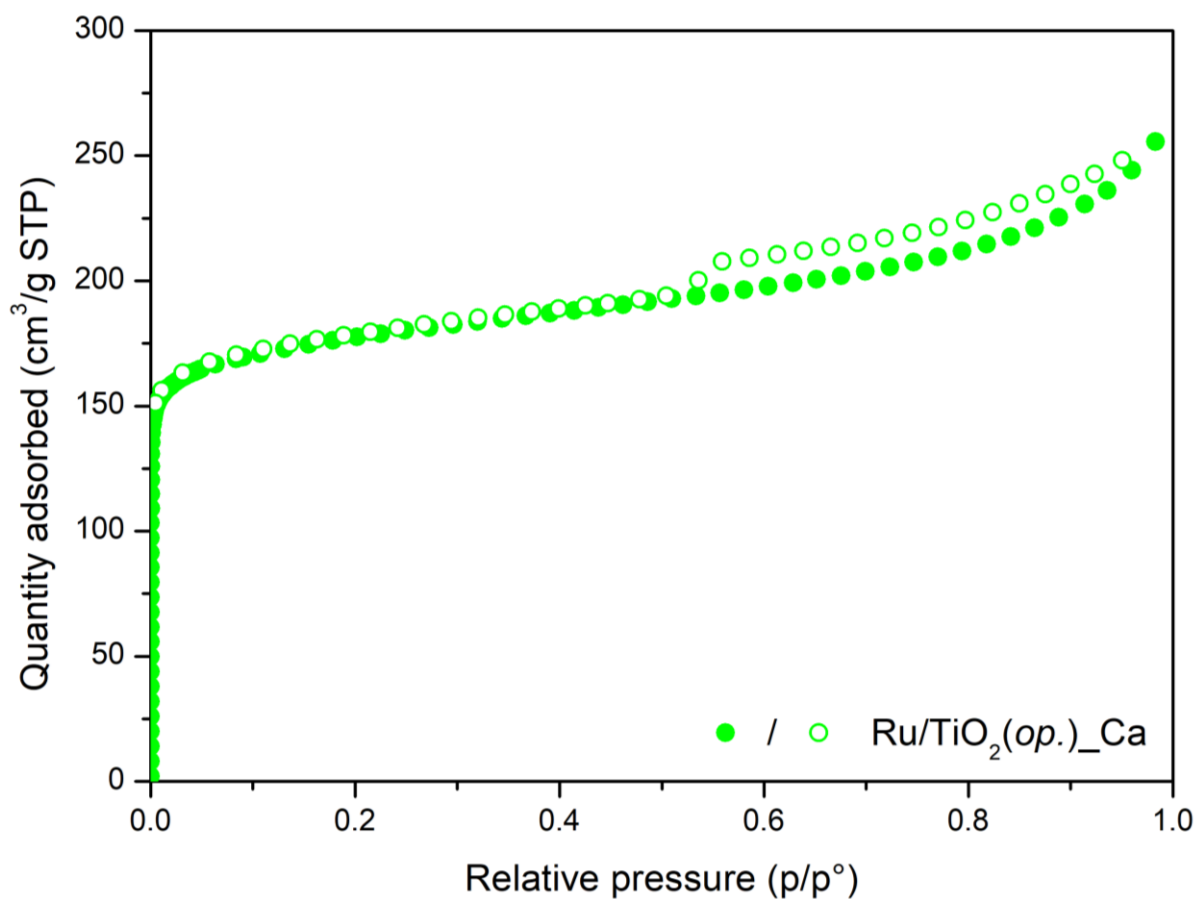


Figure 2.A.28: 77 K N₂ adsorption isotherm data collected for **Ru/TiO₂(op.)_Ca** after 5 cycles, adopting a H4 type profile, analogous to that of the material it was derived from, Ru/MUV-10(Ca).

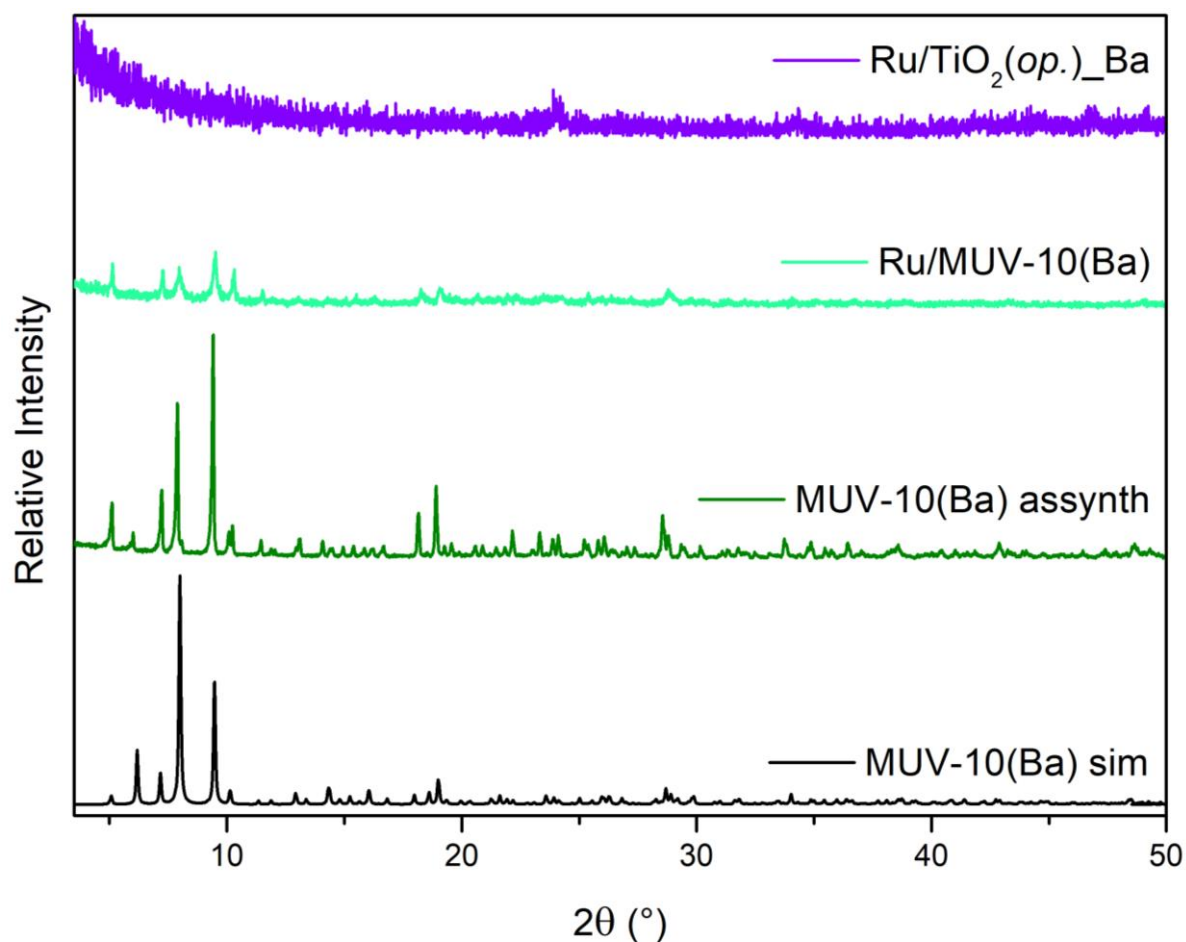


Figure 2.A.29: PXRD patterns of MUV-10(Ba); simulated MUV-10(Ba) (black), MUV-10(Ba) as-synthesised (dark green), Ru/MUV-10(Ba) (aqua) and **Ru/TiO₂(*op.*)_Ba** after 5 cycles (purple).

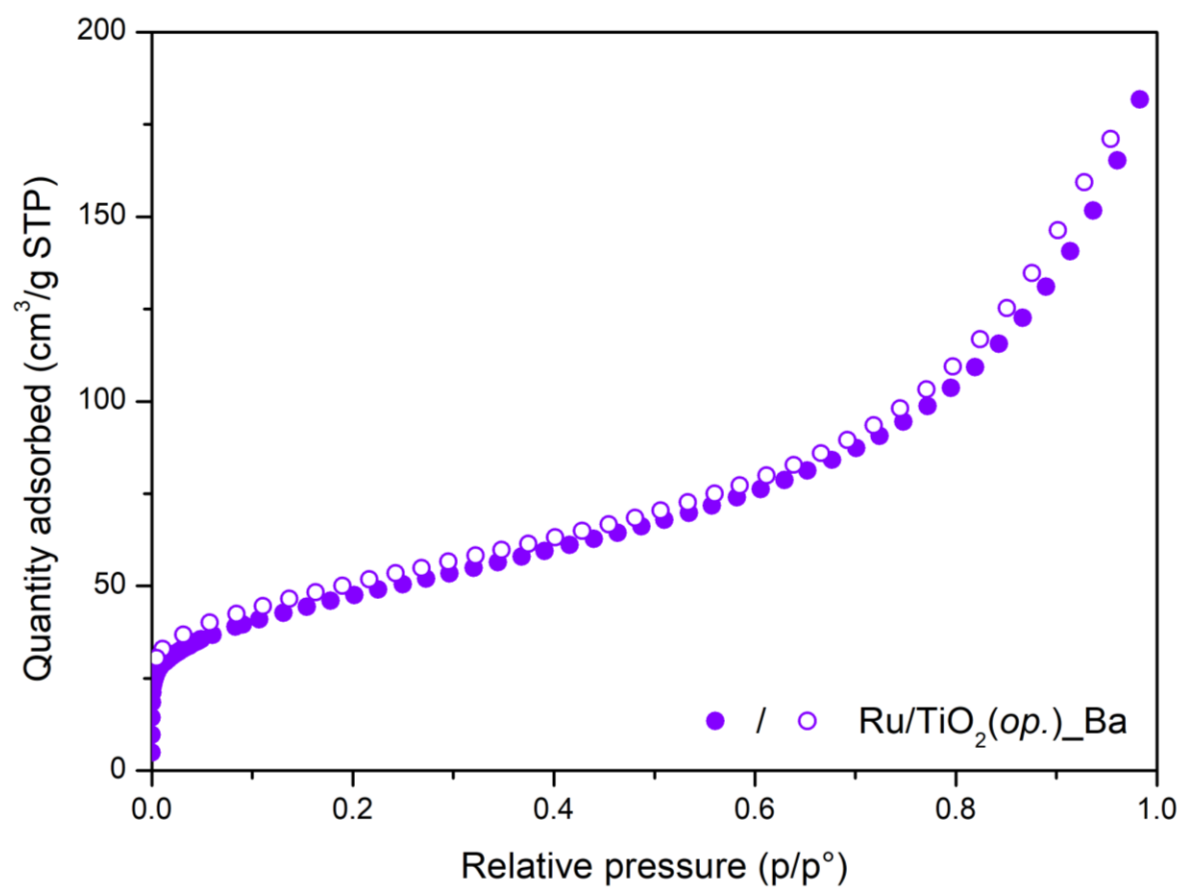


Figure 2.A.30: 77 K N₂ adsorption isotherm data collected for **Ru/TiO₂(op.)_Ba** after 5 cycles.

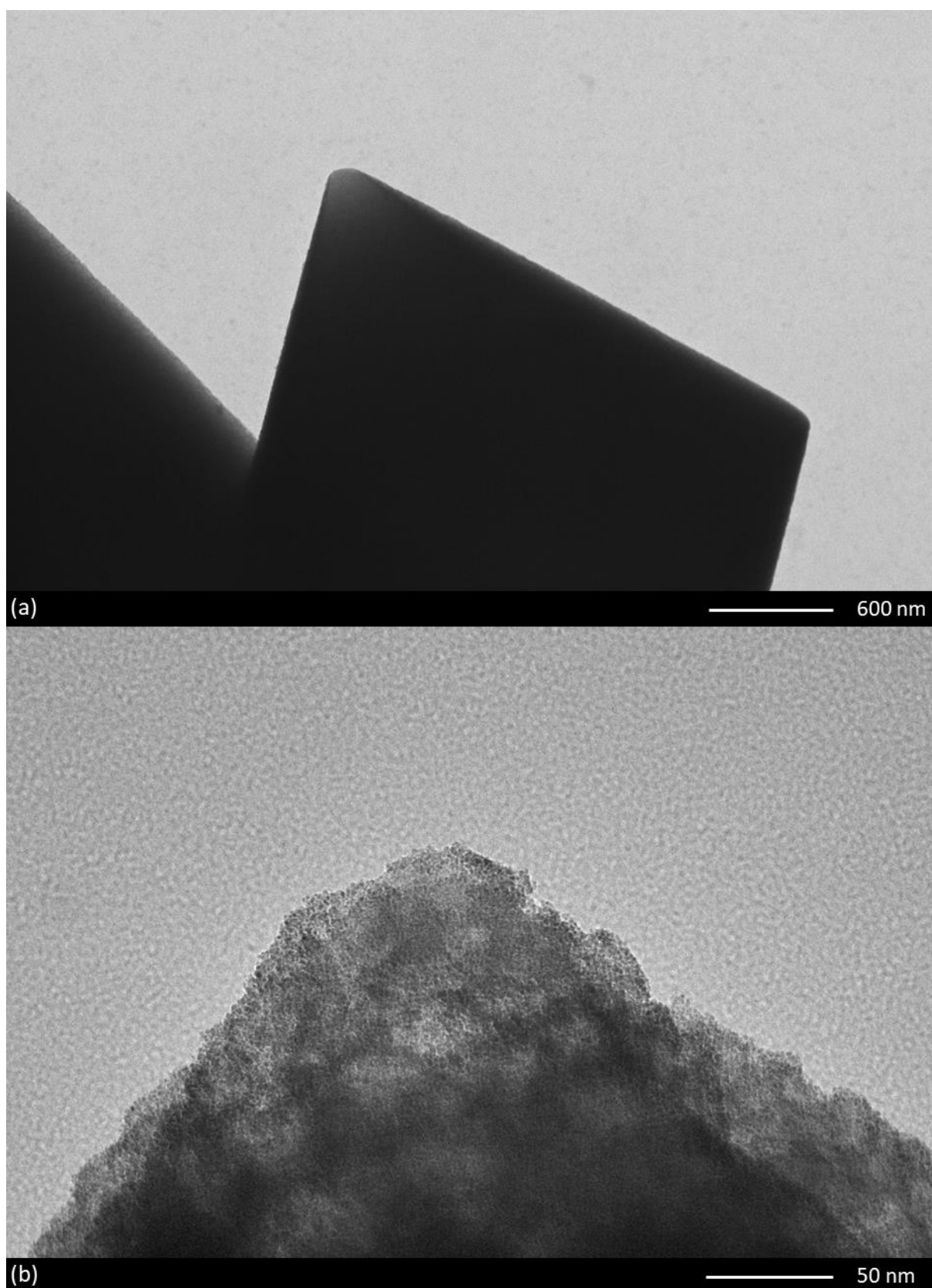


Figure 2.A.31: TEM images of **(a)** Ru/MUV-10(Ca) pre-catalysis and **(b)** Ru/TiO₂(*op.*)_Ca after 5 cycles. Formation of potential Ru nanoparticles (small (1-2 nm) black particles) are evident.

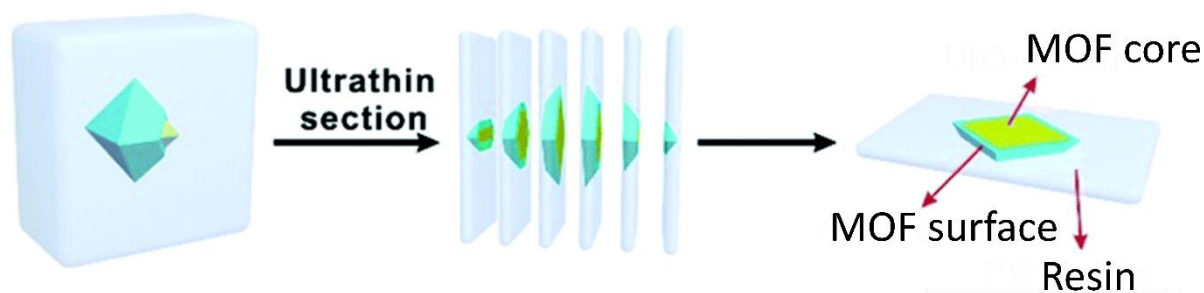


Figure 2.A.32: Schematic example of the process of microtomy of MUV-10(Ba). First, the MOF was embedded within a resin and sliced into ultrathin sections (100 nm). These sections were then mounted on copper TEM grids and used for subsequent analysis. This allowed access to the MUV-10(Ba) core previously inaccessible and suppressed the degradation of the framework under the electron beam (Figure adapted from ref. 123).

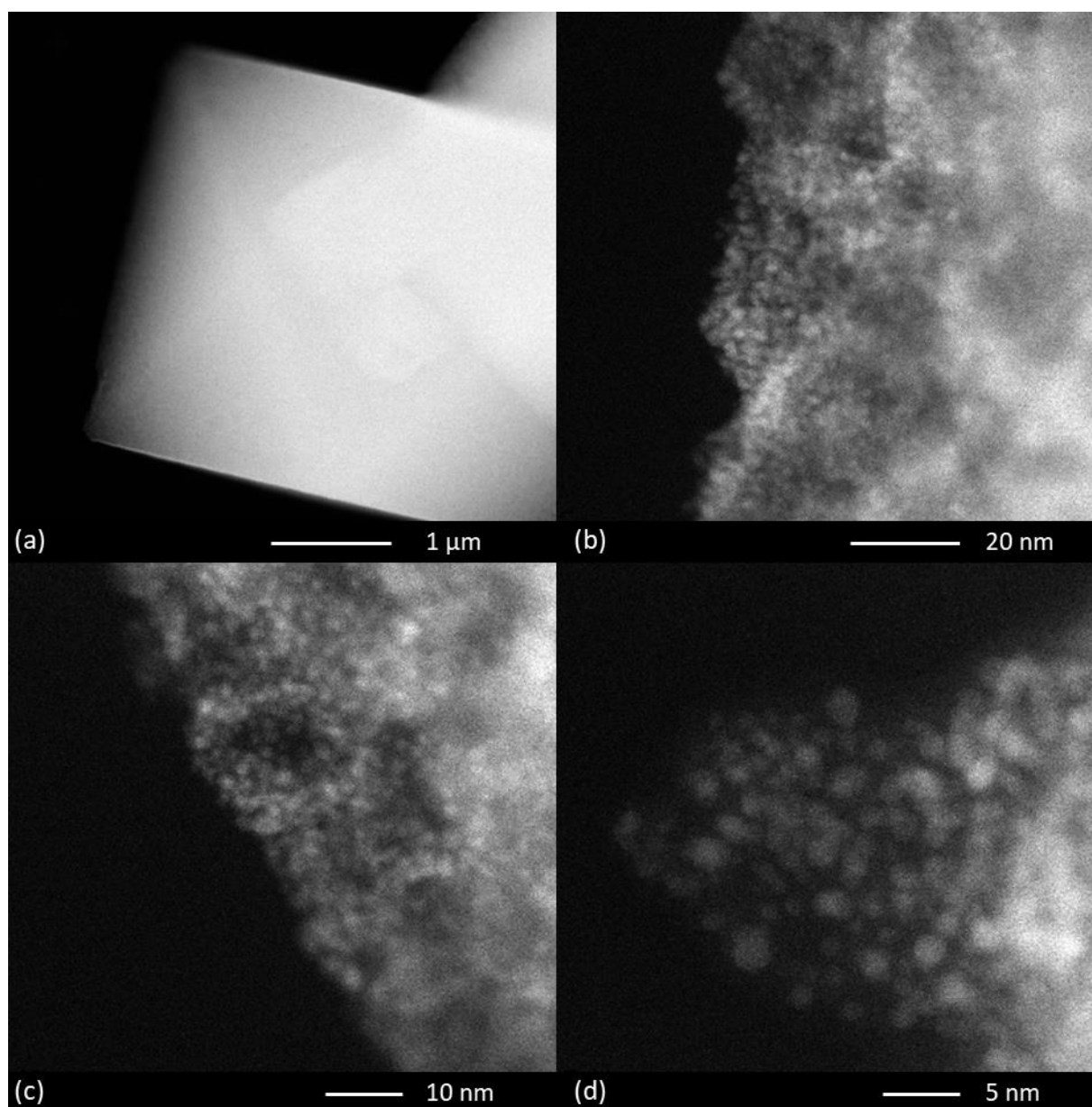


Figure 2.A.33: (a-d) STEM-HAADF images of **Ru/TiO₂(op.)_{Ca}** revealing clear formation of small, highly dispersed Ru nanoparticles.

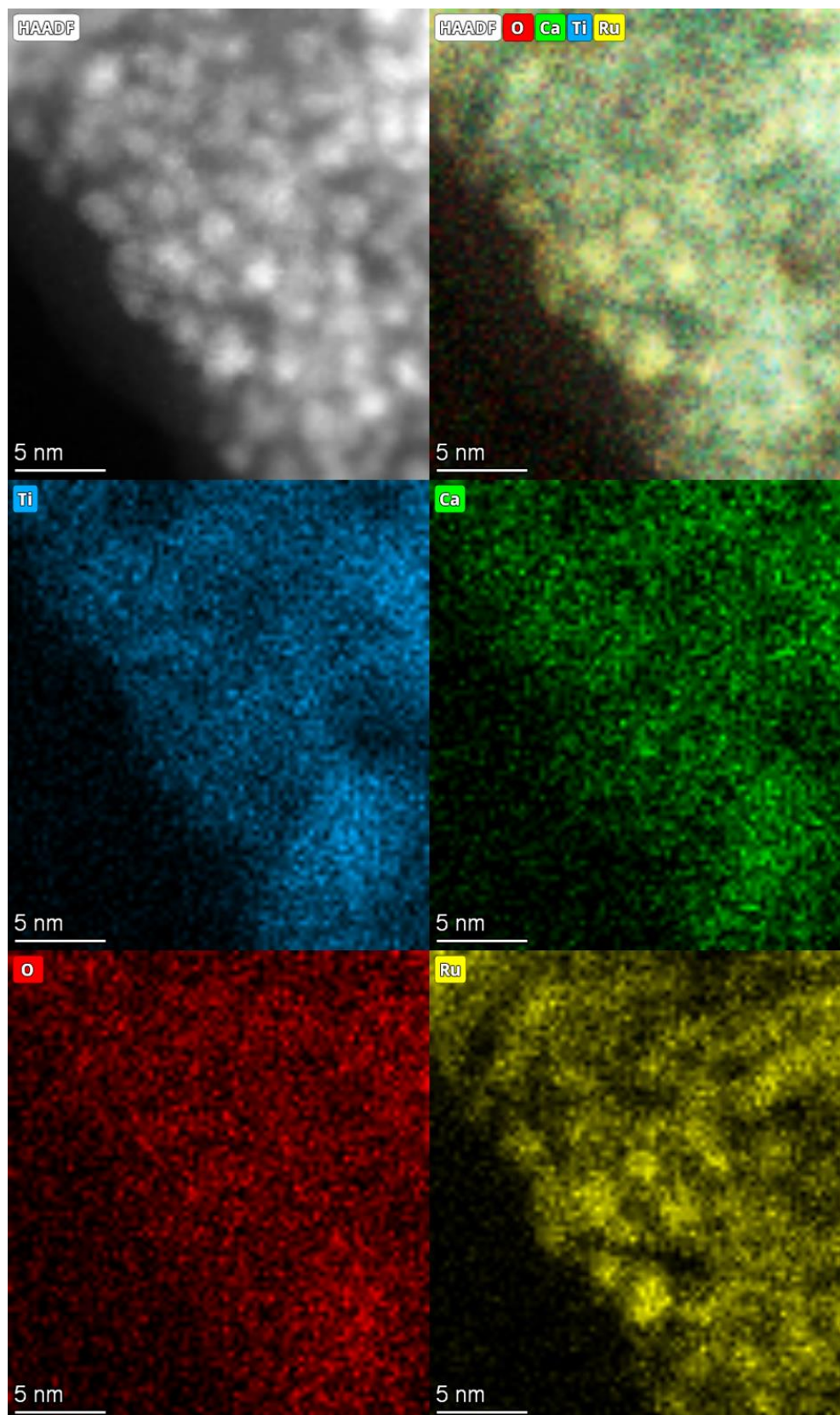


Figure 2.A.34: STEM-EDX images of **Ru/TiO₂(*op.*)_{Ca}** post-catalysis after 5 cycles revealing clear formation of small, highly dispersed Ru nanoparticles (Ti, blue; Ca, green; O, red; Ru, yellow).

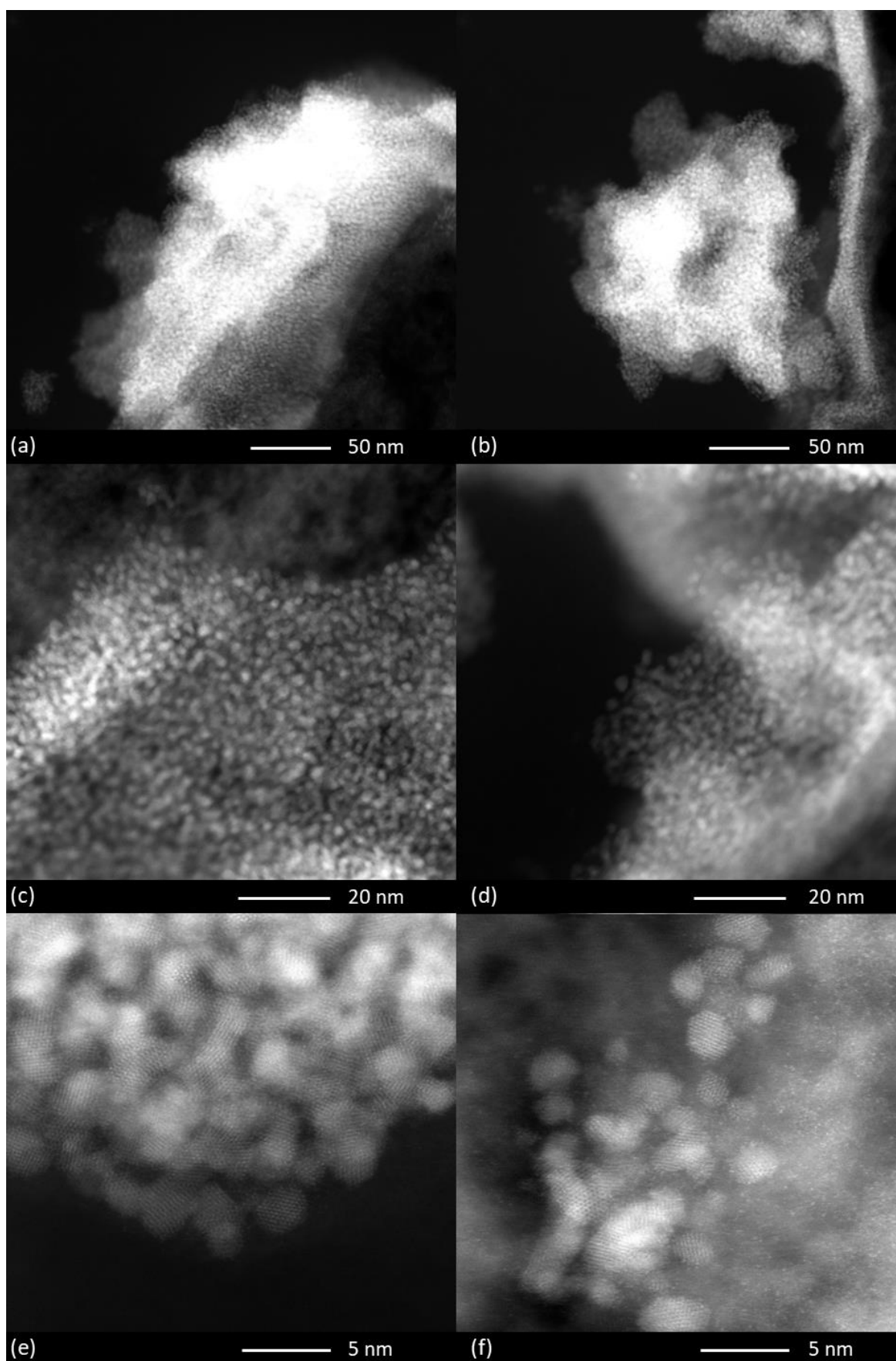


Figure 2.A.35: (a-f) STEM-HAADF images of **Ru/TiO₂(*op.*)_Ba** revealing clear formation of small, highly dispersed Ru nanoparticles.

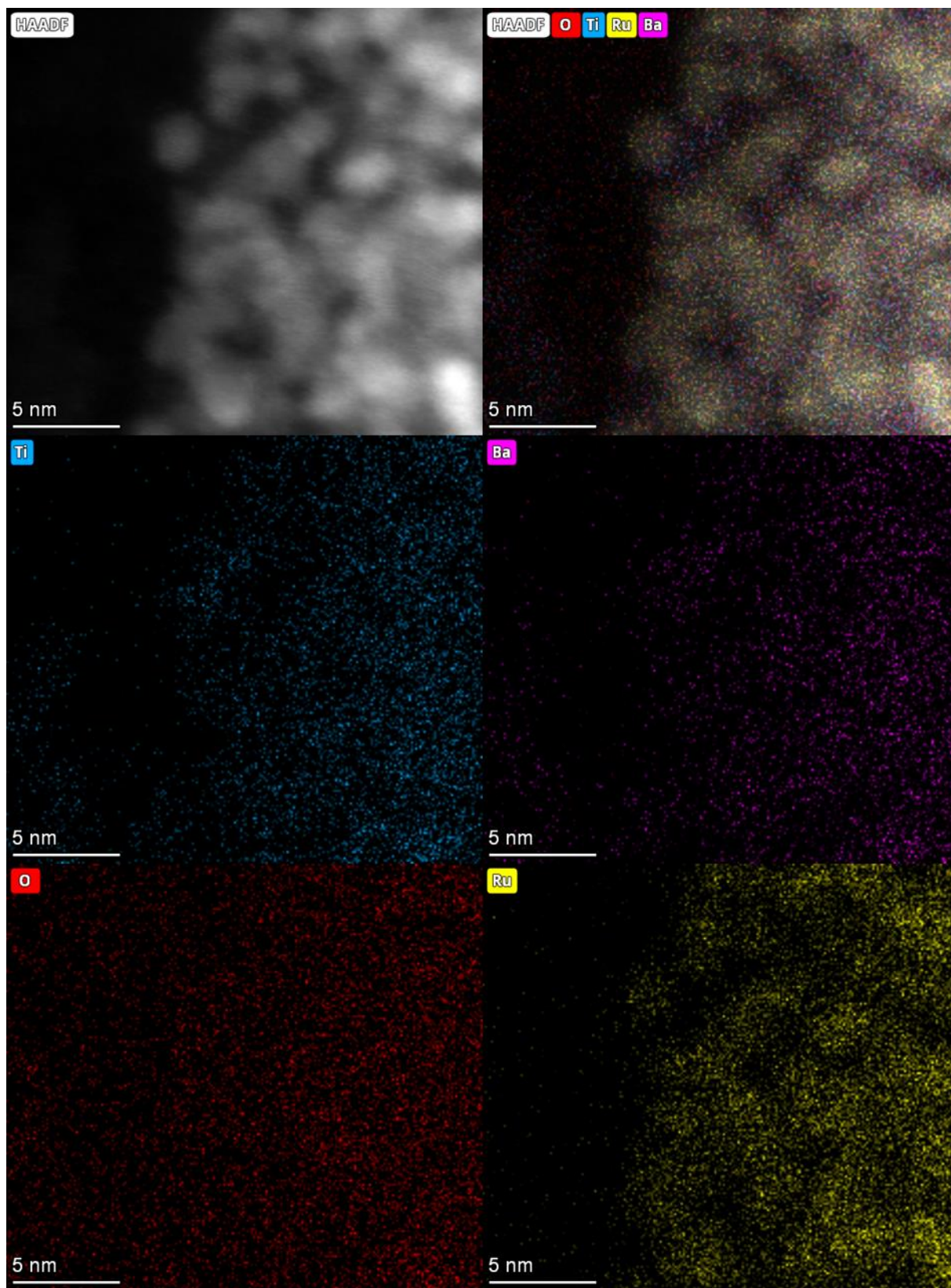


Figure 2.A.36: STEM-EDX images of **Ru/TiO₂(*op.*)_Ba** post-catalysis after 5 cycles revealing clear formation of small, highly dispersed Ru nanoparticles (Ti, blue; Ba, magenta; O, red; Ru, yellow).

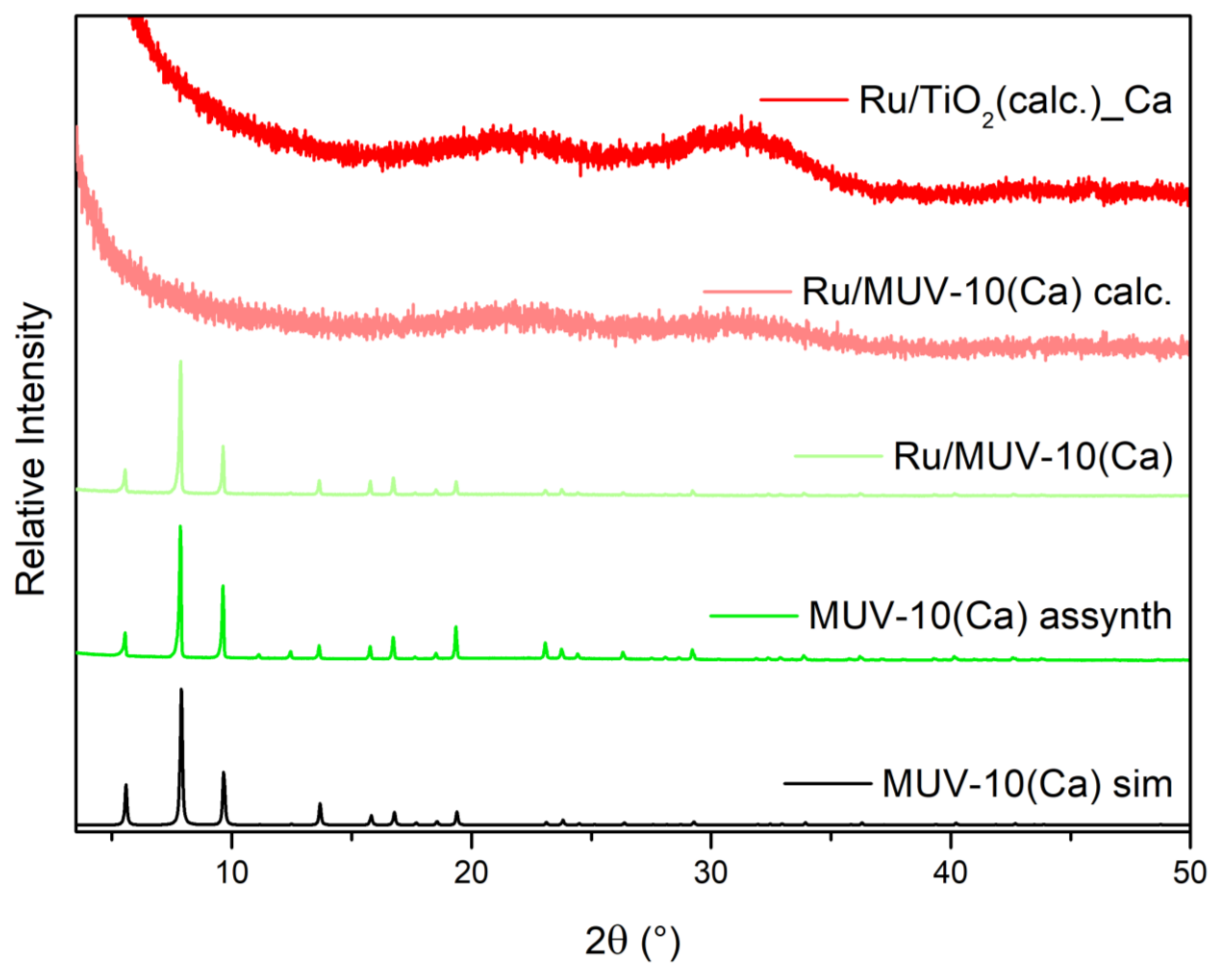


Figure 2.A.37: PXRD patterns of MUV-10(Ca); simulated MUV-10(Ca) (black), MUV-10(Ca) as-synthesised (green), Ru/MUV-10(Ca) (light green), Ru/MUV-10(Ca) calcined (salmon) and Ru/TiO₂(calc.)_Ca after 5 cycles (red).

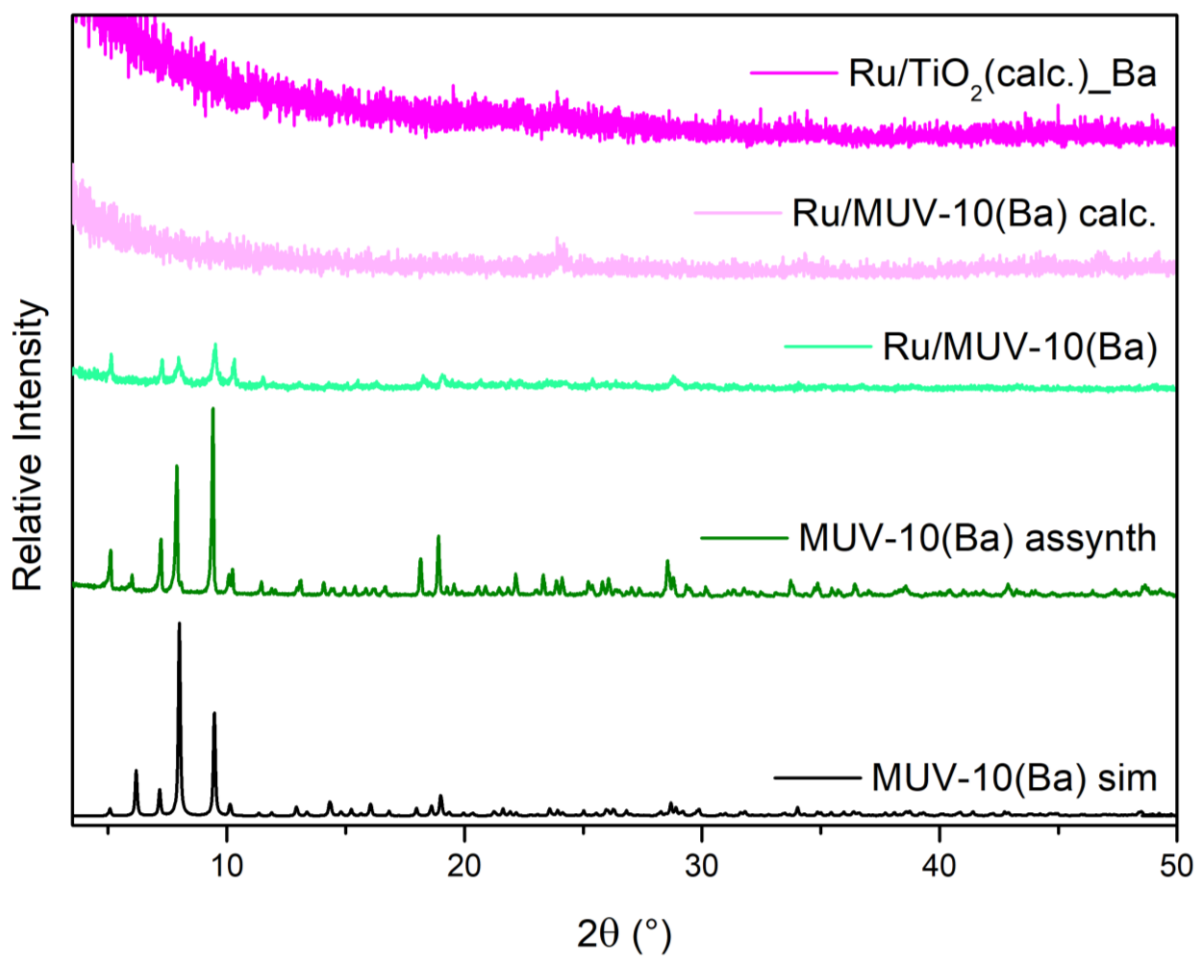


Figure 2.A.38: PXRD patterns of MUV-10(Ba); simulated MUV-10(Ba) (black), MUV-10(Ba) as-synthesised (dark green), Ru/MUV-10(Ba) (aqua), Ru/MUV-10(Ba) calcined (pink) and Ru/TiO₂(calc.)_Ba after 5 cycles (magenta).

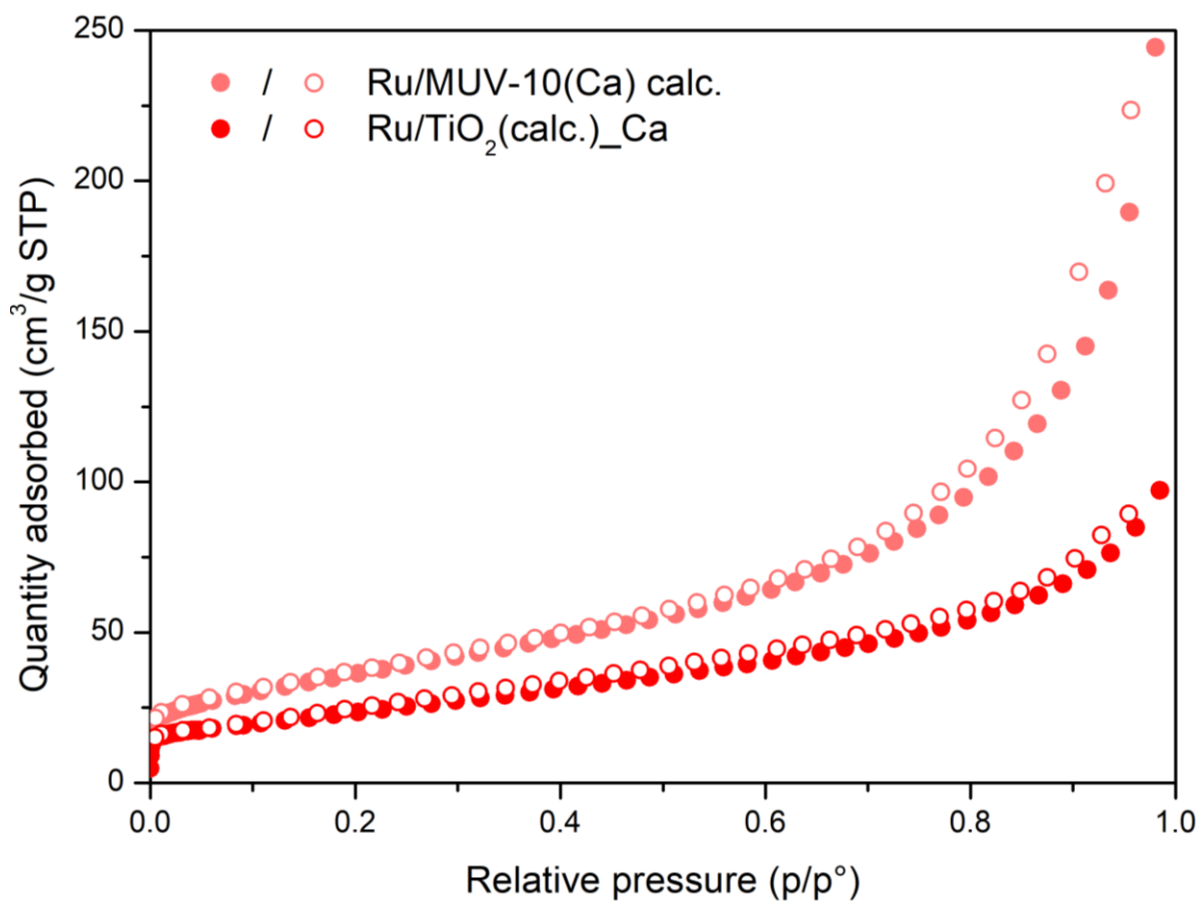


Figure 2.A.39: 77 K N₂ adsorption isotherm data collected for Ru/MUV-10(Ca) calcined (salmon) and Ru/TiO₂(calc.)_Ca after 5 cycles (red).

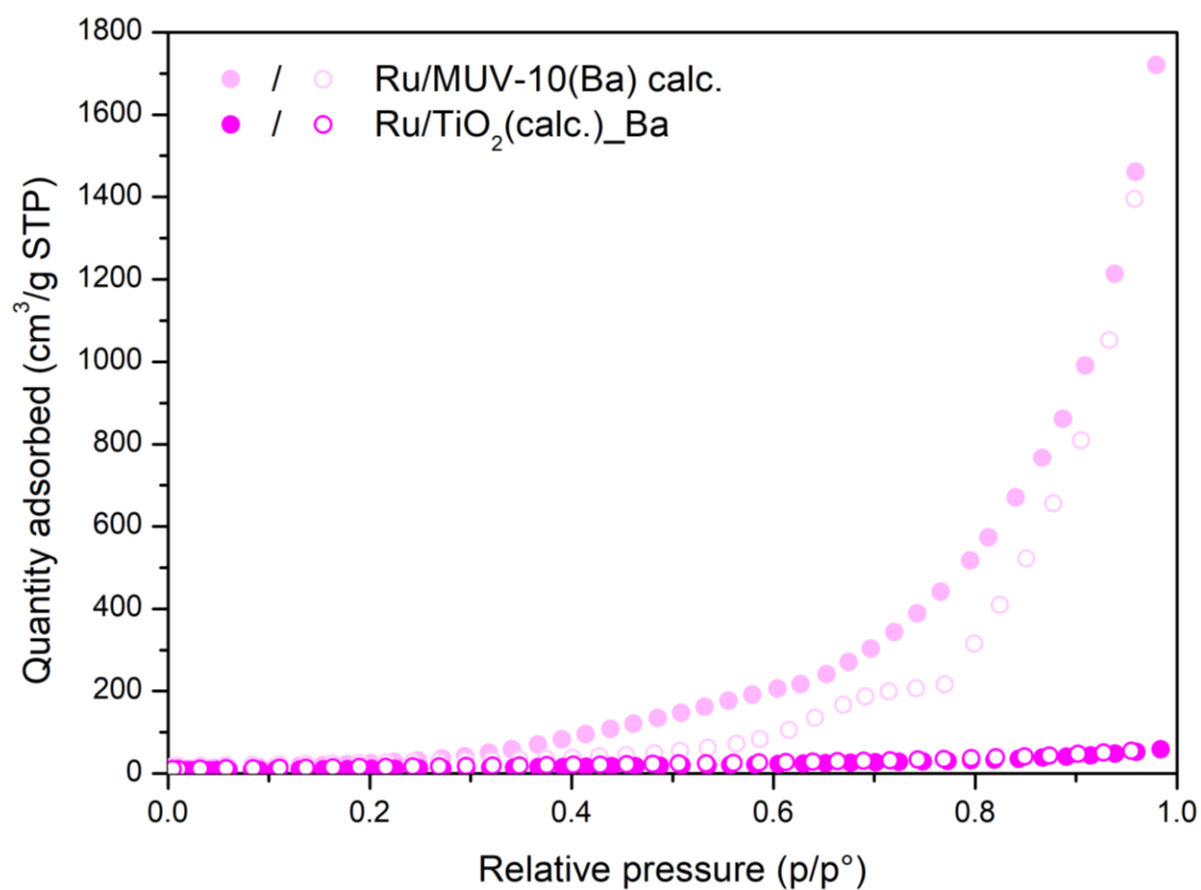


Figure 2.A.40: 77 K N₂ adsorption isotherm data collected for Ru/MUV-10(Ba) calcined (pink) and **Ru/TiO₂(calc.)_Ba** after 5 cycles (magenta).

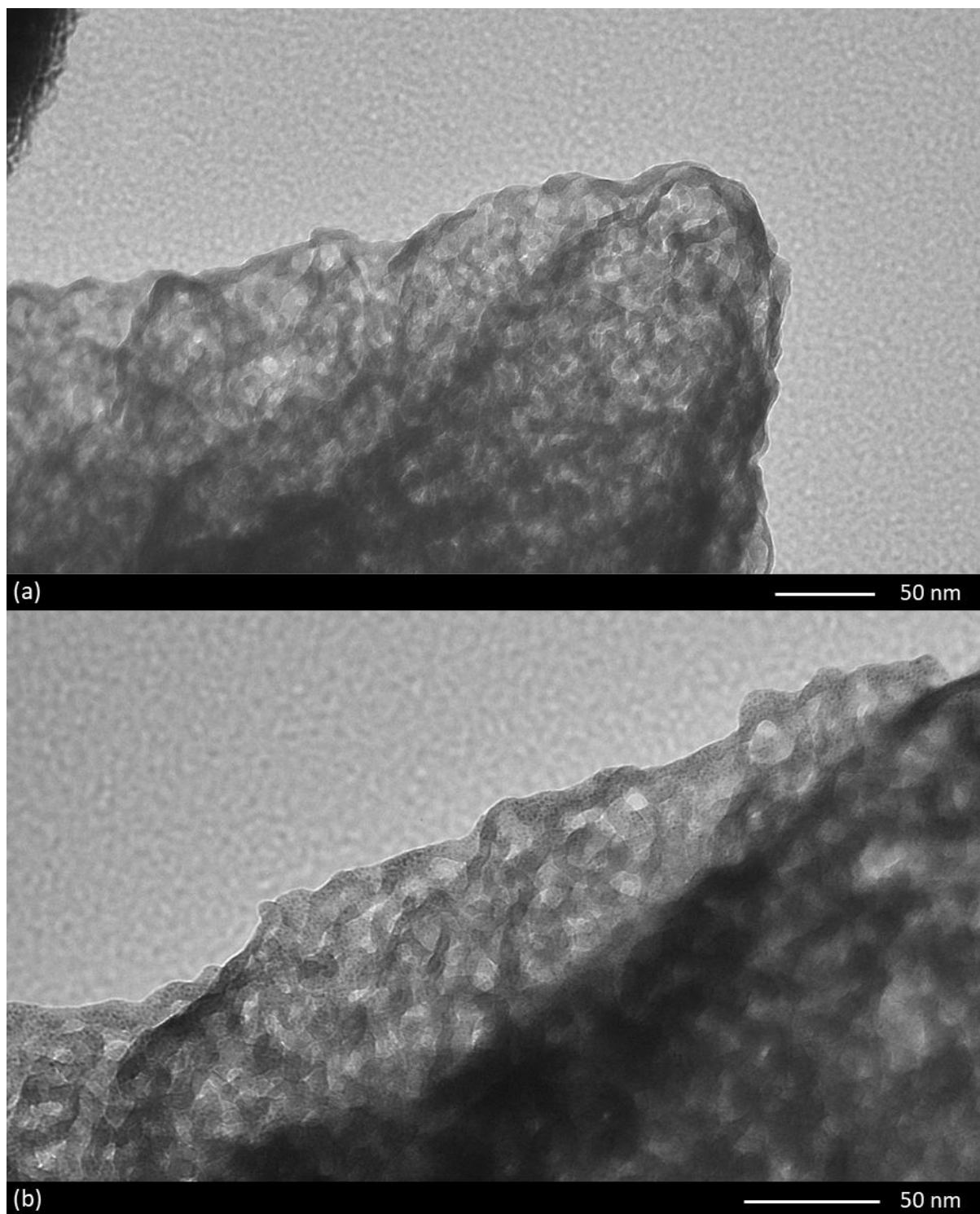


Figure 2.A.41: TEM images of **(a)** Ru/MUV-10(Ca) calcined and **(b)** Ru/TiO₂(calc.)_Ca after 5 cycles. Formation of potential Ru nanoparticles (small (1-2 nm) black particles) are evident in the Ru/TiO₂(calc.)_Ca sample whilst they are not observed for the Ru/MUV-10(Ca) pre-catalysis calcined sample.

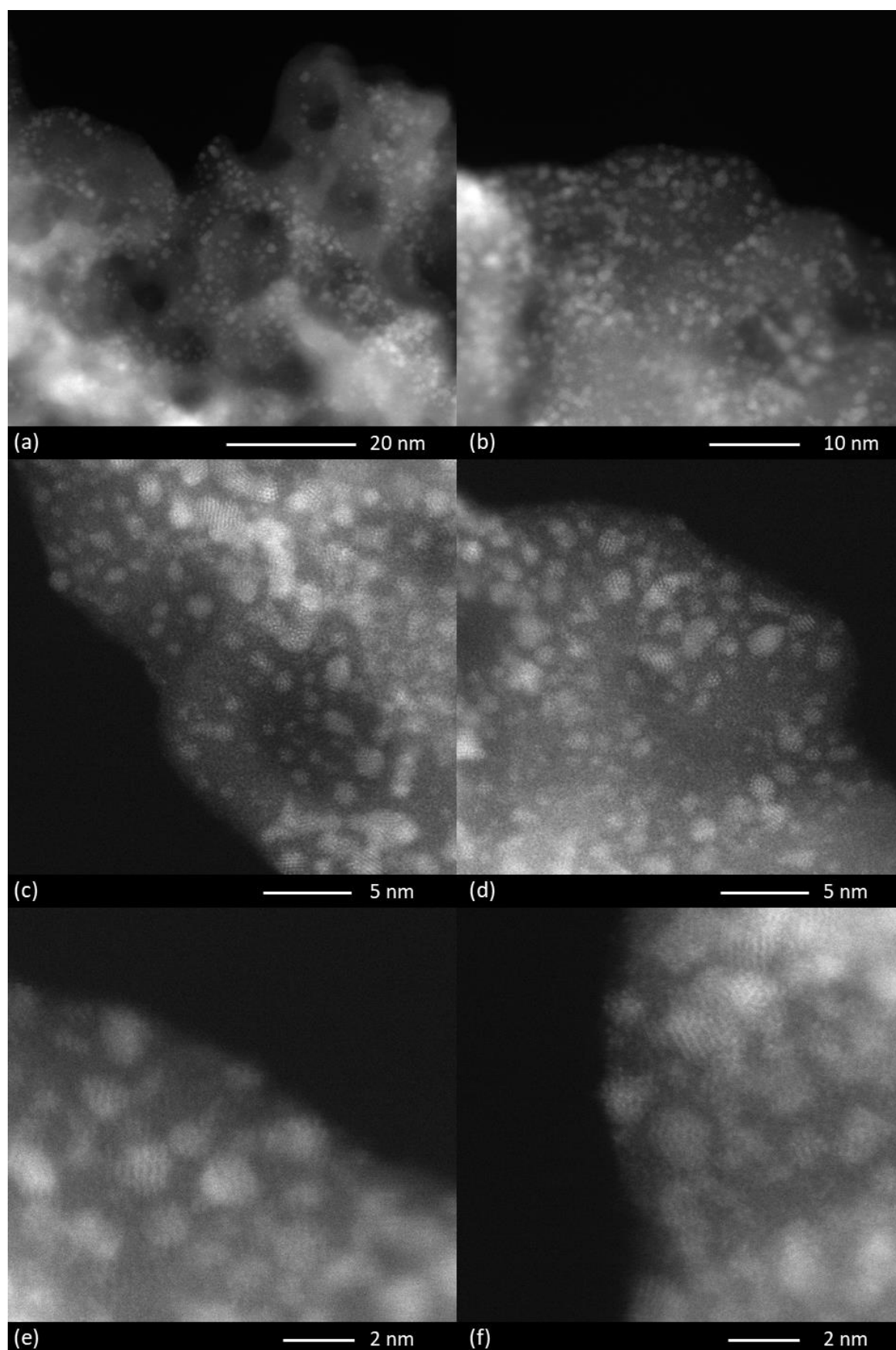


Figure 2.A.42: (a-f) STEM-HAADF images of **Ru/TiO₂(calc.)_Ca** revealing clear formation of small, highly dispersed Ru nanoparticles.

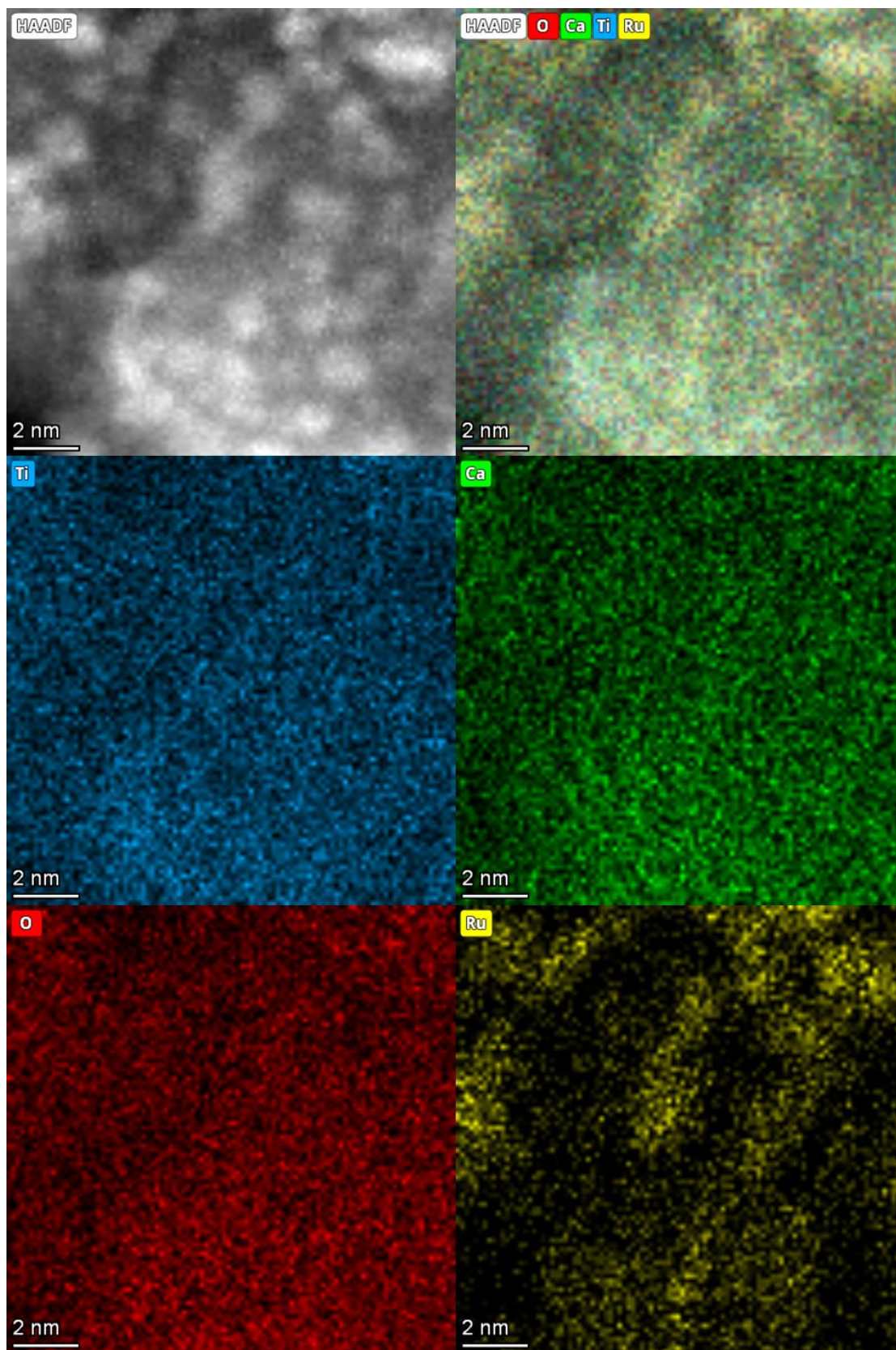


Figure 2.A.43: STEM-EDX images of **Ru/TiO₂(calc.)_Ca** post-catalysis after 5 cycles revealing clear formation of small, highly dispersed Ru nanoparticles (Ti, blue; Ca, green; O, red; Ru, yellow).

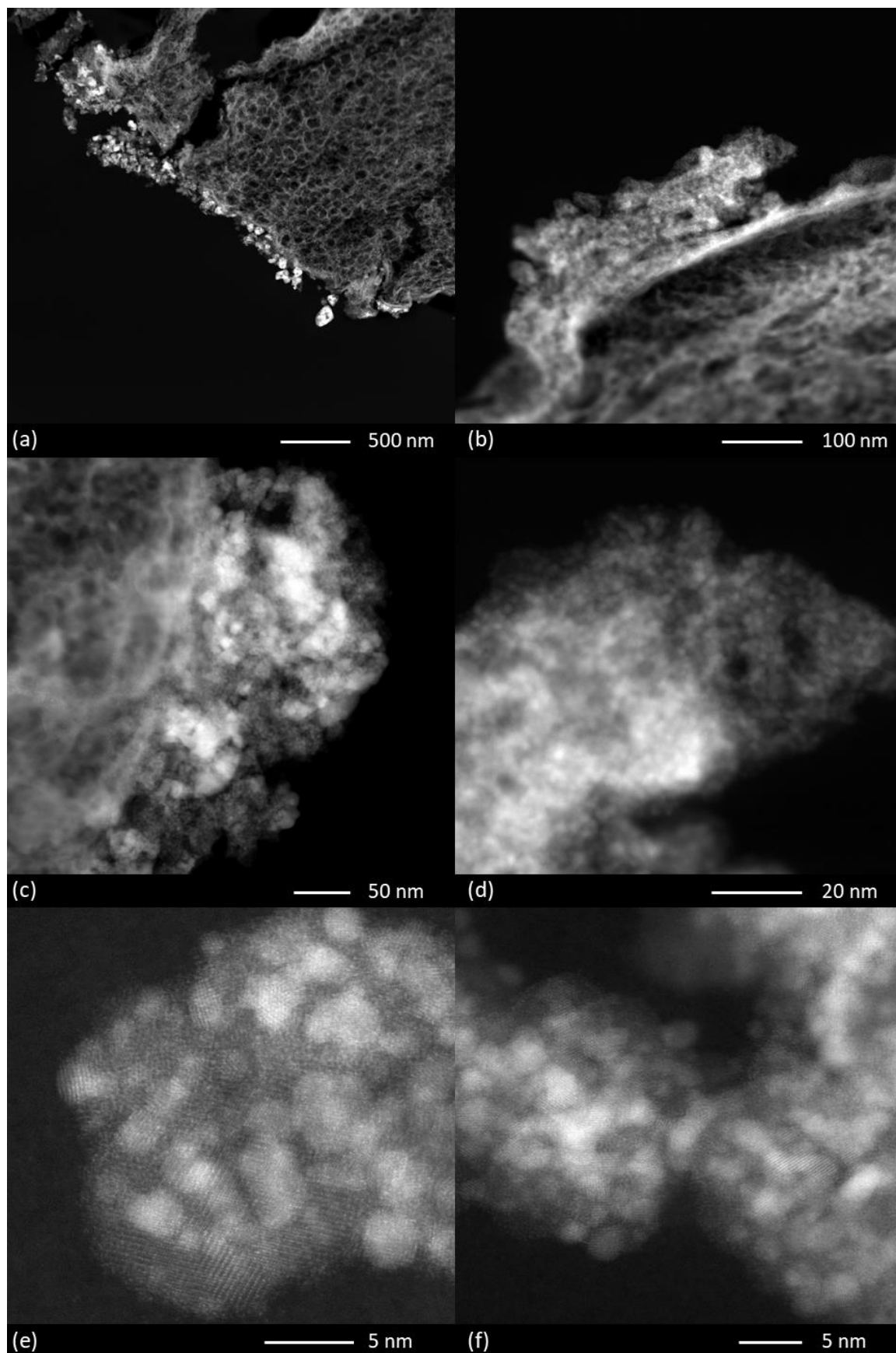


Figure 2.A.44: (a-f) STEM-HAADF images of **Ru/TiO₂(calc.)_Ba** revealing clear formation of highly dispersed Ru nanoparticles, both small and large.

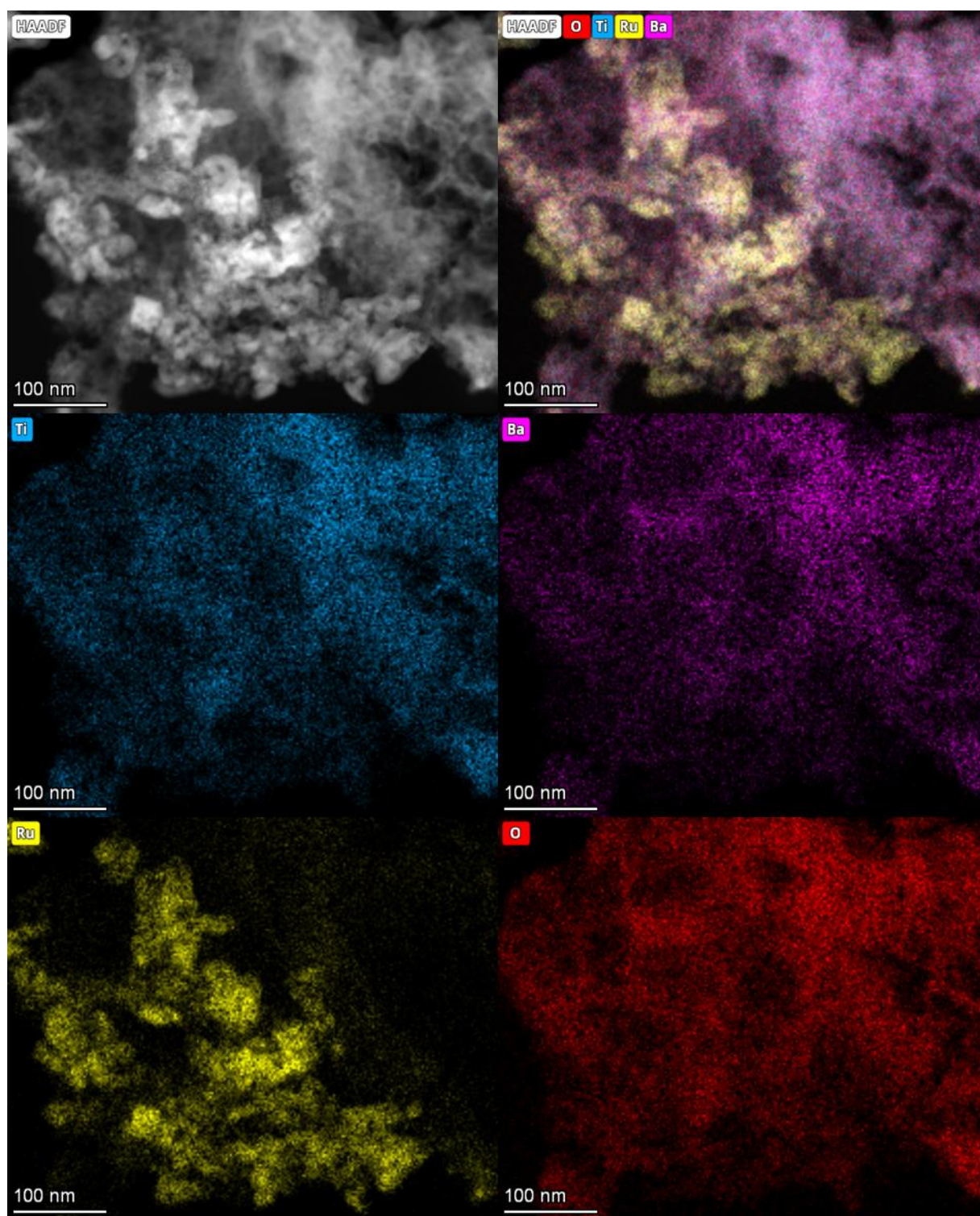


Figure 2.A.45: STEM-EDX images of **Ru/TiO₂(calc.)_Ba** post-catalysis after 5 cycles revealing clear formation of large, dispersed Ru nanoparticles (Ti, blue; Ba, magenta; O, red; Ru, yellow).

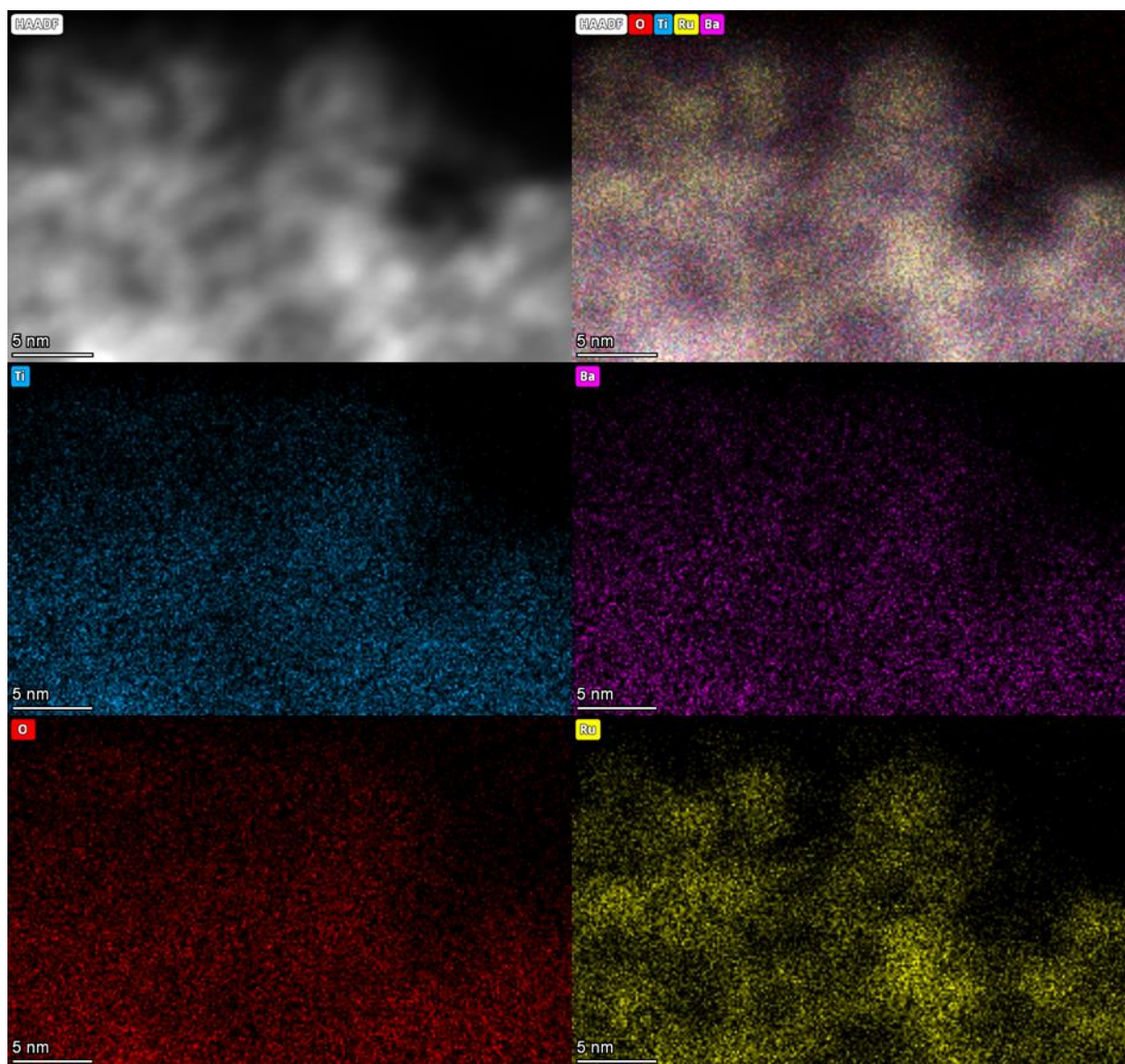


Figure 2.A.46: STEM-EDX images of **Ru/TiO₂(calc.)_Ba** post-catalysis after 5 cycles revealing clear formation of small, highly dispersed Ru nanoparticles (Ti, blue; Ba, magenta; O, red; Ru, yellow).

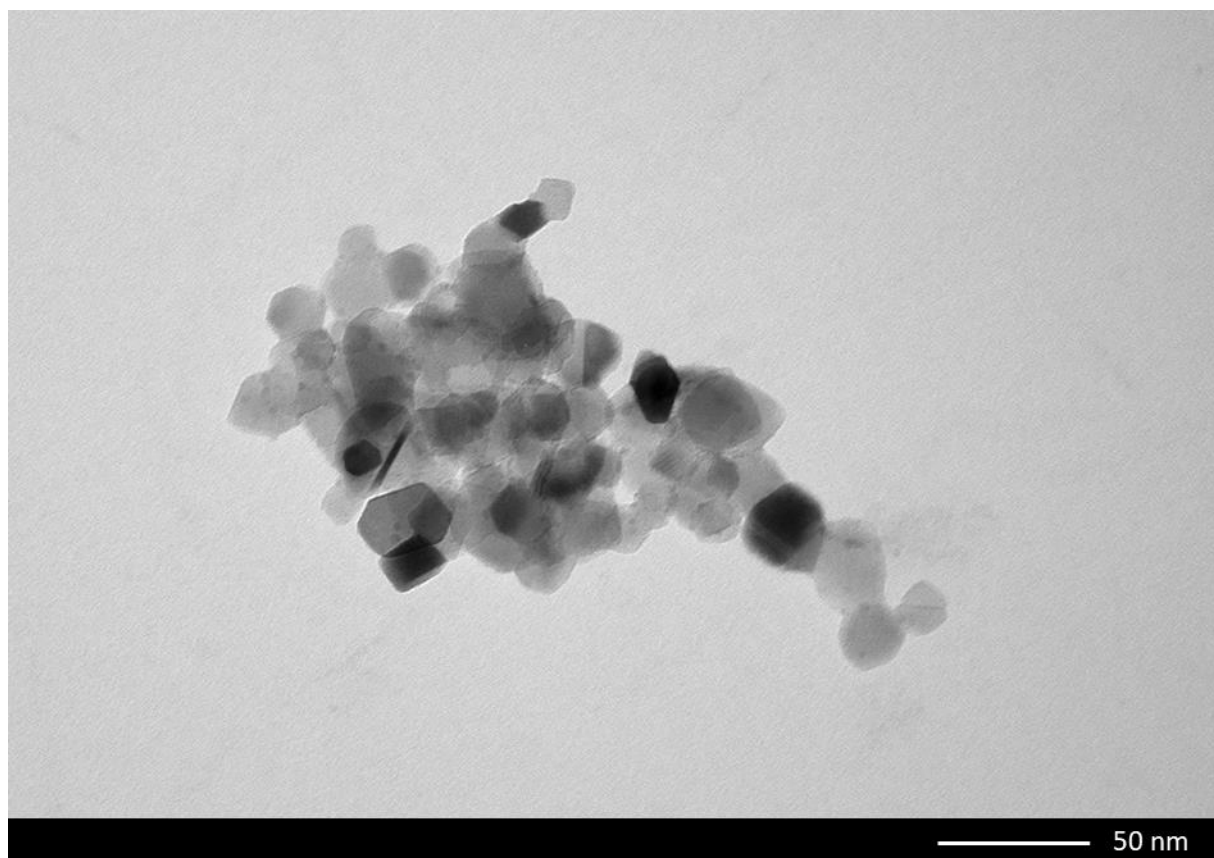


Figure 2.A.47: TEM image of **Ru/TiO₂(std.)**. Formation of potential Ru nanoparticles (small (1-2 nm) dark particles) are evident.

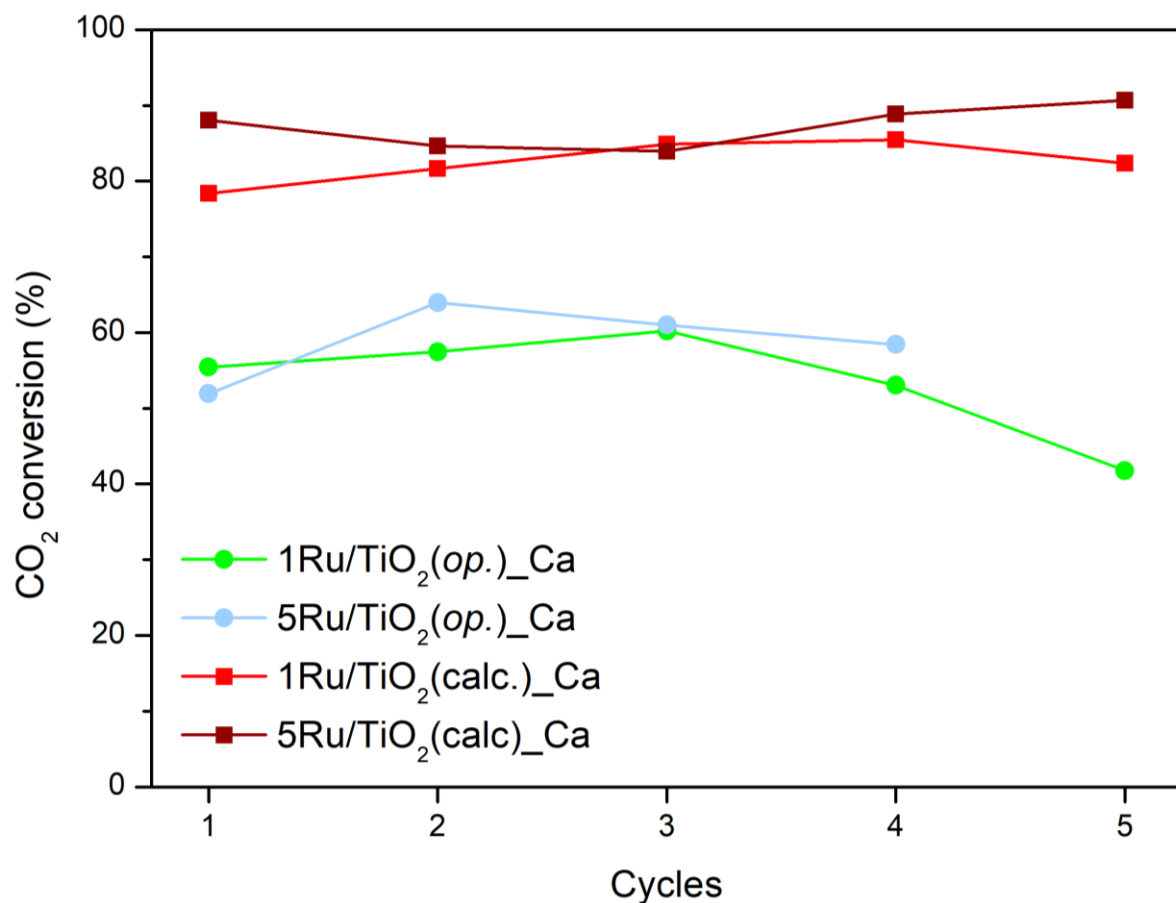


Figure 2.A.48: CO₂ conversion (%) for CO₂ methanation catalysed via MOF derived **Ru/TiO₂(op.)** (●) and **Ru/TiO₂(calc.)** (■) on the batch reactor comparing different Ru wt. % loadings.

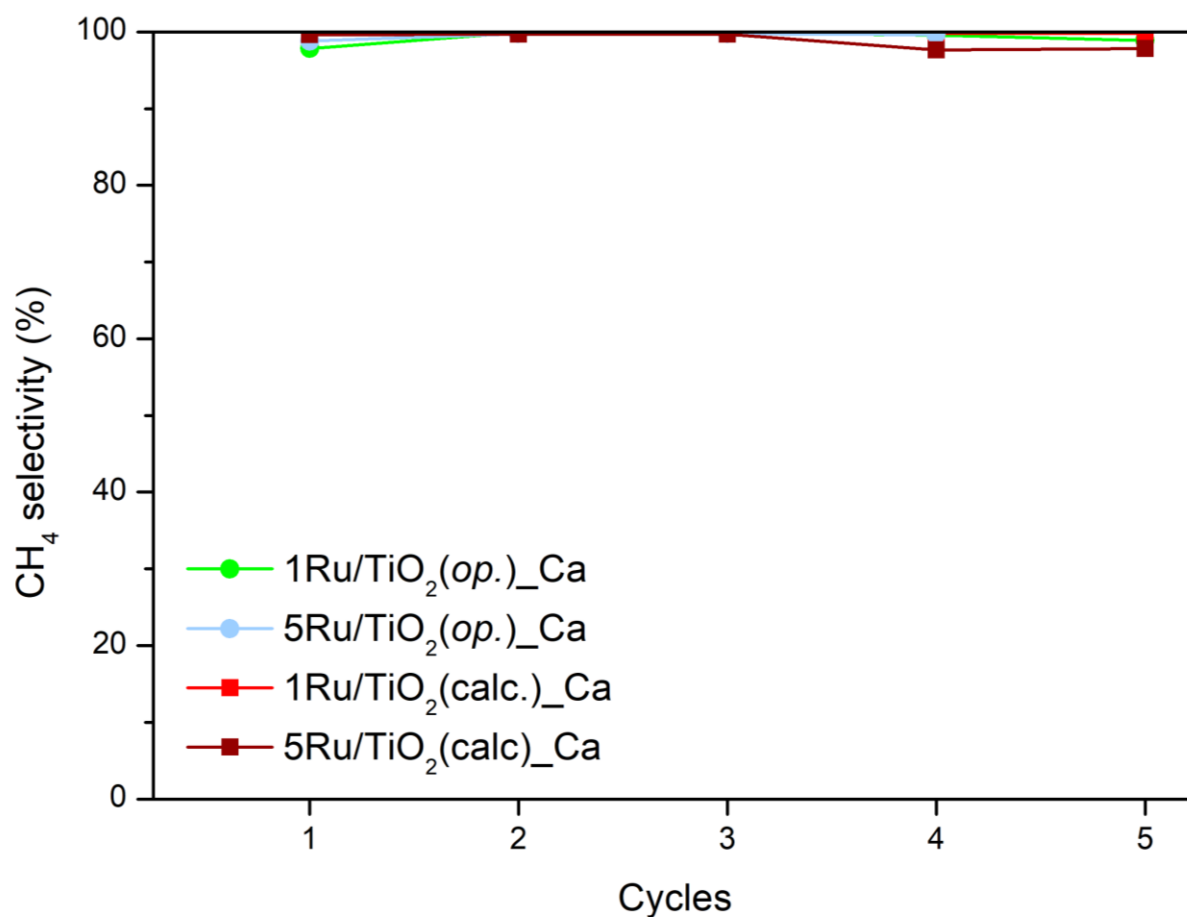


Figure 2.A.49: CH₄ selectivity (%) for CO₂ methanation catalysed via MOF derived Ru/TiO₂(op.) (●) and Ru/TiO₂(calc.) (■) on the batch reactor comparing different Ru wt. % loadings.

Table 2.A.5: Summary of the catalytic reaction data including GC data for CO₂ methanation with **5Ru/TiO₂(*op.*)_Ca** and **5Ru/TiO₂(*calc.*)_Ca**.

Catalyst	Cycle	Temperature (°C)	Reaction time (h)	Products (μmol)				% CO ₂ conversion	% CH ₄ selectivity
				CH ₄	CO	Long chain C	CO ₂		
5Ru/TiO₂(<i>op.</i>)_Ca	1	300	0.5	50.10	0.00	0.61	46.94	51.93	98.79
	2	300	0.5	37.94	0.09	0.00	21.42	63.97	99.76
	3	300	0.5	34.40	0.08	0.00	22.04	61.01	99.77
	4	300	0.5	36.40	0.13	0.00	25.97	58.45	99.65
5Ru/TiO₂(<i>calc.</i>)_Ca	1	300	0.5	36.88	0.13	0.00	5.03	88.02	99.65
	2	300	0.5	35.73	0.11	0.00	6.49	84.67	99.69
	3	300	0.5	34.08	0.10	0.00	6.53	83.96	99.71
	4	300	0.5	33.56	0.80	0.00	4.31	88.85	97.67
	5	300	0.5	36.19	0.80	0.00	3.79	90.70	97.84

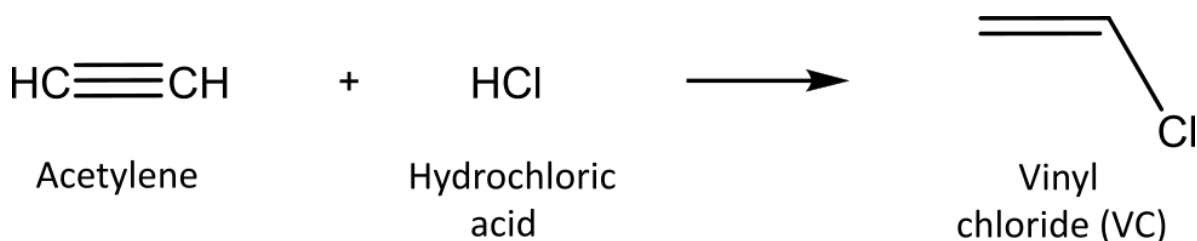
CHAPTER 3

TOWARDS ISOLATION OF GOLD COMPLEXES WITHIN MnMOF-1

Chapter 3. Towards Isolation of Gold Complexes within MnMOF-1

3.1 Introduction

Gold, an element highly prized throughout history due to its lustre, workability, and resistance to corrosion, was typically overlooked in chemical circles due to its perceived inherent inertness. But in the past 40 years, this broadly accepted truth has been exposed as a misconception, and gold-based research has increased markedly.¹ Accordingly, unlike its metallic neighbours, its chemistry is much less developed due to its late start and is typically interpreted through transition metals with analogous properties.² One area profiting from the growing investigation into gold and its activity, is within homogeneous and heterogeneous catalysis. The first examples of catalytic activity of Au nanoparticles were investigated in the 1970's by Parravano's group, demonstrated in oxygen/hydrogen transfer reactions and NO reduction by dihydrogen.³⁻⁵ This research, however, was not further expanded upon until 1989 when Haruta *et al.* reported Au nanoparticles displayed remarkable activity towards CO and H₂ oxidation, CO₂ hydrogenation, the water-gas shift reaction, NO reduction, and catalytic combustion of methanol, when supported on metal oxides such as titania (TiO₂), iron(III) oxide (Fe₂O₃) and cobalt tetraoxide (Co₃O₄).⁶⁻¹³ These results helped catapult the curiosity into the catalytic activity of Au nanoparticles we see today.¹⁴⁻¹⁶ Of growing interest is the potential commercial application of gold-based catalysts for the hydrochlorination of acetylene (see Scheme 3.1).



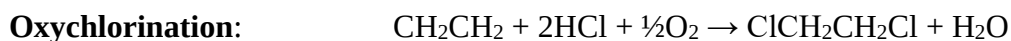
Scheme 3.1: The hydrochlorination of acetylene, producing VC, the precursor to PVC.

3.1.1 Vinyl Chloride and Polyvinylchloride production

Chloroethene (VC) is the desired product of this hydrochlorination. Typically, VC is used as a feedstock material in its polymerisation to form PVC, a plastic valued for its applications in areas such as construction, healthcare products, electronics and sports.¹⁸ Annually, 90% of the VC produced is used as a feedstock for VC monomer polymerisation to form PVC.¹⁹ Ceresana reported 42 million tonnes of PVC was produced in 2016, comprising 16% of total plastic production alone.^{19,20} This is forecast to grow, anticipated to reach 56.2

million tonnes by 2026.²⁰ Considering this, in accordance with the amount of PVC produced annually, underlines the importance of producing its monomer, VC.

Production of VC is traditionally achieved via the mercuric chloride (HgCl_2) catalysed hydrochlorination of acetylene. Conventional catalysts are composed of HgCl_2 supported on activated carbon (AC). As fossil fuel dependency increased in society, feedstock material derived from oil acquisition increased in abundance and a second route for VC production emerged to contest the more traditional HgCl_2 catalysed pathway. As opposed to the more direct route traditionally offered, production via fossil fuel-based feedstock is more involved. To summarise, the new route proceeds through initial production of ethylene dichloride (EDC) from ethylene, before subsequently thermally cracking EDC, to produce VC.²⁰ Formation of EDC from ethylene is accessible through two main reactions, direct chlorination or oxychlorination. Direct chlorination is desirable owing to lower reaction temperatures and production of fewer by-products, but the need for chlorine gas (Cl_2) proves problematic due to HCl formation following thermal cracking of EDC, highly undesirable in large scale operations.²¹ Comparatively, oxychlorination produces EDC and water from the reaction between ethylene, hydrochloric acid and oxygen.²¹ Evidently, HCl produced during thermal cracking can be reused during the oxychlorination of ethylene in the initial steps, making it the preferred and employed route. This process is depicted in Scheme 3.2.



Scheme 3.2: General reaction of the production of VC via oxychlorination before subsequent thermal cracking of EDC.

The selected production method for VC via either direct hydrochlorination of acetylene using HgCl_2 or oil derived products depends upon the location of manufacture. In Western countries, ethylene is readily available and cheap, owing to availability of oil-based material and its collected by-products during petroleum refinement. This paves the way for oxychlorination of ethylene followed by thermal cracking as the preferred method of VC production in Western countries.²² Conversely, in the East, specifically China, the hydrochlorination of acetylene is favoured.²³ Primarily as coal is both readily available and inexpensive in China, a critical component in the formation of the HgCl_2 carbon-supported

catalyst, rendering the method more economically favourable.²³ In 2016, approximately 13 million tonnes of VC was produced by the hydrochlorination of acetylene.²³ Looking to the future, due to the forecast increasing demand for PVC-based products, VC production will need to increase to meet this demand. It is safe to assume this will result in increased production globally, including within China where the less desirable production of VC via hydrochlorination of acetylene using a mercury-based catalyst, will continue to grow.

3.1.2 Mercuric Chloride Catalysed Hydrochlorination of Acetylene

As touched upon previously, the active catalyst employed for the hydrochlorination of acetylene is HgCl_2 supported on AC. The properties of AC make it ideal in this application, as not only does it have high surface areas (approximately $1000\text{-}2000\text{ m}^2\text{ g}^{-1}$) retained during exposure to HCl at elevated temperatures (commonly between $180\text{-}220^\circ\text{C}$ for hydrochlorination of acetylene), but it exhibits high absorptivity of HgCl_2 , critical to readily reach loadings sufficient for catalysis (5-12 wt% HgCl_2).^{19,24,25} However, numerous issues surround the application of the mercury-based catalyst. Mercury, long infamous for its toxicity to living organisms, and the potential for environmental devastation, exists as the primary concern for this reaction. In the event of significant losses from the system, threats such as poisoning onsite workers and polluting the surrounding environment may eventuate. This does not take into account minor losses which, over time, can accumulate and become problematic. As a result, these factors make production of VC via HgCl_2 catalysed hydrochlorination of acetylene less desirable.

Compounding these concerns is research providing evidence of expected release of mercury into the environment due to VC production through the mercury-based catalyst. The temperature the reaction is run at ($180\text{-}220^\circ\text{C}$), in conjunction with hot spots formed within the reactor due to excess heat release owing to the exothermic nature of the reaction, is sufficient to volatilise loaded HgCl_2 .^{19,24-26} Once volatilised, the HgCl_2 can condense on cooler catalysts within the system. Not all of the volatilised HgCl_2 , however, condenses. The effect is two-fold, not only does the catalytic material in use deactivate, but release to the surrounding area is significant. Accordingly, these losses are so profound that the production solely of the catalyst commands 60% of current mercury production annually, exceeding 10000 tonnes per year.^{19,24} The concern becomes substantially more evident when an anticipated best-case scenario of mercury losses from this process to the environment is calculated at 3.7%, equivalent to 600 g of mercury lost per tonne of VC produced.²⁷ The need to address and rectify the potential

dangers relating to the use of mercuric chloride supported on AC for the hydrochlorination of acetylene, both to workers and the environment, is clear.

Recently, owing to the issues surrounding the mercury catalysed hydrochlorination of acetylene, development of a suitable, environmentally friendly replacement catalyst has begun growing in importance. The Minamata convention on mercury, held in 2013, can be attributed for the push. The convention is aimed at protecting human life and the environment from detrimental effects relating to mercury, primarily by phasing out many mercury-based processes.²⁸ Notably, mercury-based catalysts used in the production of VC are directly mentioned and cautioned against. On the 18th of May, 2017, the convention was ratified and for the now 133 parties, consisting of 128 signatories, the convention became legally binding.^{28,29} Of note, mercury-based materials are not permitted for use in VC production facilities constructed after 2017, and all mercury-based materials currently in use in existing facilities must be phased out by 2022.²⁸ This ensures that VC manufacture, which generates the largest global demand for production of mercury based materials, will shift to a mercury free process, eliminating over half the current global mercury operations.

3.1.3 Gold for the Hydrochlorination of Acetylene

Evidently, the need to identify and develop alternative catalysts for the hydrochlorination of acetylene is of growing importance. Recently, resulting from the directions specified by the Minamata convention, and research conducted in the 70's and 80's, this push has increased considerably, identifying gold as an ideal candidate for replacement. In 1975, initial research into the hydrochlorination of acetylene using 30 different metal chlorides supported on activated carbon was conducted by Shinoda.³⁰ At the time of publication, the activity of the analysed catalysts was compared against their respective metal cation electron affinity to determine if any correlation existed, depicted in Figure 3.1(a). Unfortunately, no detectable correlation was identified, yet the raw data provided a suitable platform for future research into identifying a correlation to the observed activity. Any advances made into solving this problem would enable the identification and prediction of active catalysts for the hydrochlorination of acetylene. Indeed, this problem remained unsolved for a decade until in 1985, Hutchings identified the standard electrode potential as the elusive variable correlating to the activity of the metal chlorides, depicted in Figure 3.1(b).³¹ The standard electrode potential was targeted as opposed to the electron affinity on the basis that hydrochlorination of acetylene involves a two-electron addition step, whereas electron affinity is instead a one-

electron addition step.²⁴ Considered under this context, it is no surprise that electron affinity does not correlate with the metal chlorides activities for the hydrochlorination of acetylene. From the newly correlated data, based on its high standard electrode potential, gold was identified as suitable candidate for the hydrochlorination of acetylene.

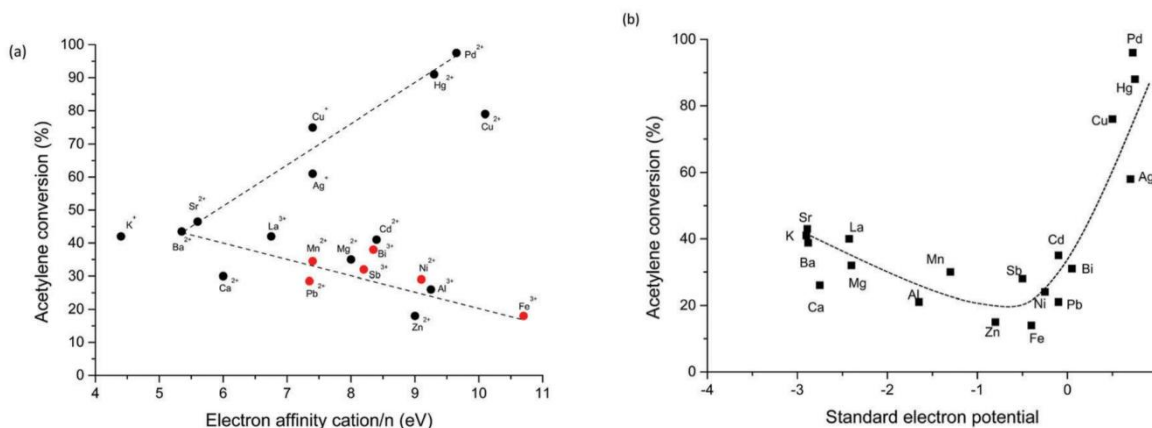


Figure 3.1 (a) Metal cation electron affinity correlated against the activities of metal chlorides supported on activated carbon for the hydrochlorination of acetylene. **(b)** The standard electrode potential correlated against the previously measured activities of metal chlorides supported on activated carbon for the hydrochlorination of acetylene (Figure adapted from ref. 19).

Buoyed by identifying gold as a potential replacement for mercuric chloride, research has begun into forming the gold-based materials. Not only is gold a target for the hydrochlorination of acetylene, but the diagonal relationship it holds with palladium, renowned for its application in a multitude of catalysed reactions, has long made it a target for such catalytic reactions. However, the activity palladium exhibits is yet to be realised by the majority of its gold-based analogues. Such a characteristic can be attributed to the so termed ‘redox gold problem’, resulting from the unwillingness of gold to engage in $M^{x/x+2}$ redox processes.^{32,33} Comparatively, the standard electrode potential (E°) for palladium between Pd(0) and Pd(II) is 0.92V, whereas for gold, between Au(I) and Au(III), it is higher at 1.41V, thus making oxidative addition using gold more challenging.³⁴ Commonly, to circumvent this issue, external oxidants are employed to assist in the Au(I) $\rightarrow$ Au(III) transition. Using strong external oxidants, however, is typically undesirable.^{35,36} Nevertheless, being able to replace palladium-based catalysts with gold-based variants remains desirable due to its biocompatibility relative to palladium, which possesses a higher toxicity. Evidently, the main holdback limiting the application of gold as a catalyst relates to the redox gold problem, which is typically tackled via three main approaches. These include (1) using directing groups, (2) using highly

electrophilic initiation motifs and (3) by tuning the ancillary ligand on the catalytic Au centre.³⁷⁻⁴⁰

Recent work conducted by Harper *et al.* has elegantly demonstrated a means to enforce the Au(I) $\rightarrow$ Au(III) transition.³⁷ They have performed oxidative addition, transmetalation, and reductive elimination at a Au centre, in the formation of biaryl products.³⁷ This is the first example of a Au-based catalytic cycle mirroring that of Pd-catalysed biaryl formations, a key step in the quest to realise the catalytic potential Au-based materials hold, specifically through the enforcement of the oxidative addition step. The work was achieved through targeting Au(I) complexes with coordination numbers greater than the typically observed 2. The preference for linear geometries exhibited by Au(I) compounds stems from the reduction in the energy gap between the 5d and 6s orbitals owing to the relativistic effects on Au derived from the stabilisation of the latter. As a result, the 5d orbital undergoes expansion and thus allows for efficient formation of s/d or s/p hybridizations due to the little energy differences arising between the s, p, or d states.^{41,42} Examples of higher coordination numbers for Au(I) exist and it's on the basis of these materials existing outside this favourable linear geometry that the oxidative addition can be facilitated. By employing chelating bidentate ligands with small bite angles (ligand–metal–ligand bond angle of the chelating bidentate ligand), the reactivity to facilitate oxidative additions for late transition metal complexes is enhanced.⁴³ Through straining the ML₂ fragment, the resulting square planar geometry that ensues following oxidative addition is made more accessible due to the imparted preorganisation and the fragments increase in energy.⁴⁰ It is on this premise that the previous work operates. The key takeaway from the research is that remarkably, through the use of a relatively simple bipy derivative, a trigonal planar Au(I) complex, active for oxidative addition, can be accessed. The issue, however, that still persists when developing new gold-based catalysts for the hydrochlorination of acetylene is the catalytic cycle, and that it still remains fully unelucidated. If further inroads are made into identifying the cycle, primarily in determining its fundamental steps, the subsequent result will enable the development and formation of more efficient gold catalysts.

Current advances into the elucidation of the hydrochlorination of acetylene catalysed via gold-based materials has enabled the identification of some key steps. Initial investigation via *in situ* X-ray absorption spectroscopy by Malta *et al.* has revealed the presence of both Au(I) and Au(III) oxidation states in the active material (gold catalyst supported on carbon).⁴⁴ Building on these results by using DFT calculations and experiments, Zhao *et al.* investigated

the mechanism of the hydrochlorination of acetylene by Au(I) and Au(III) supported on activated carbon.⁴⁵ A proposed catalytic cycle, based on the calculations, is depicted in Figure 3.2. By using this cycle, in conjunction with new insights from experimentally supporting data into the mechanism of the catalyst, the development of a suitable replacement catalyst for the hydrochlorination of acetylene is envisioned.

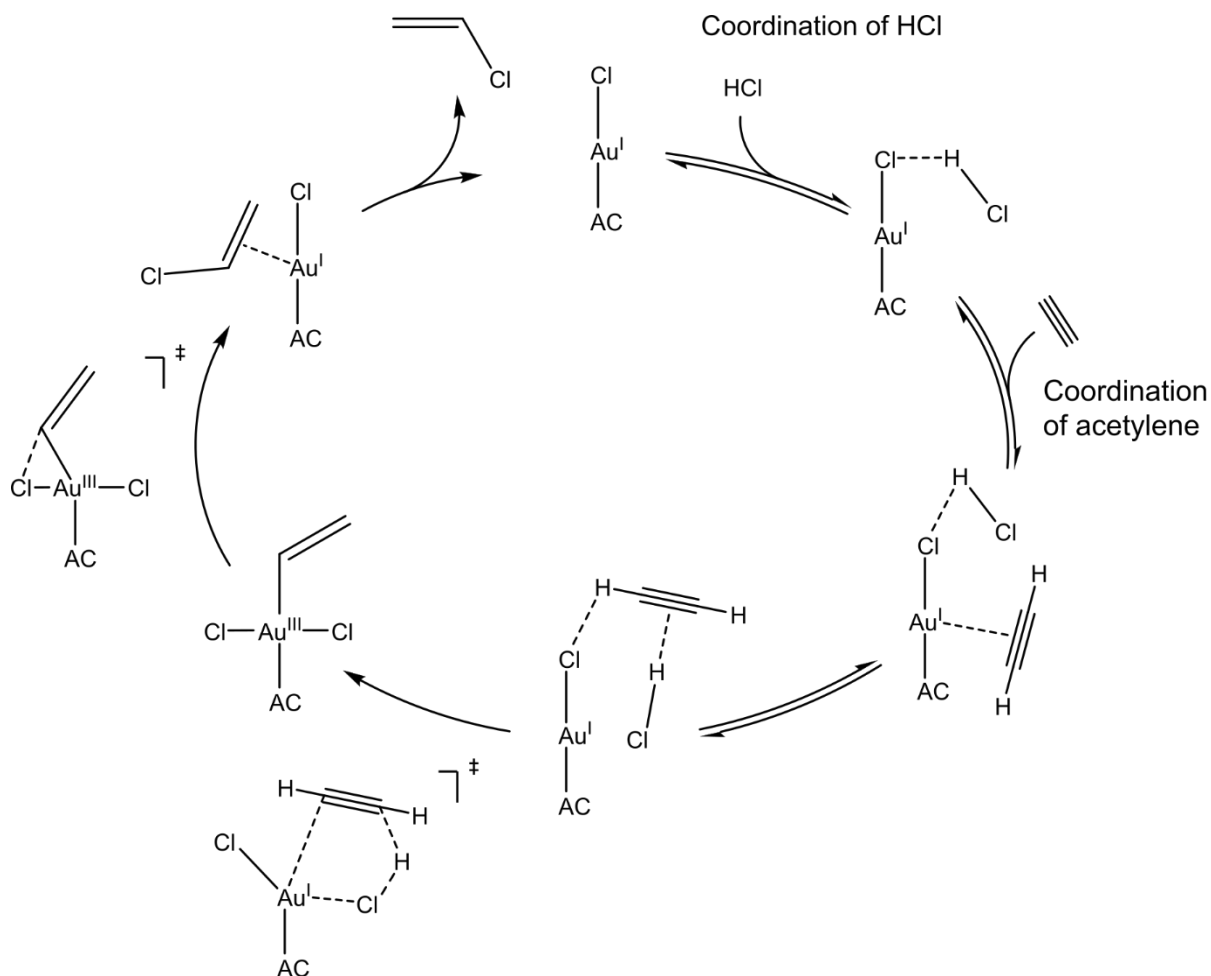


Figure 3.2: Au(I)/Au(III) supported on activated carbon (AC) catalysed hydrochlorination of acetylene reaction mechanism based off DFT calculations, including transition states ($\ddagger$) (redrawn from ref. 45).

3.2 Post-synthetic Metalation of MnMOF-1

3.2.1 Isolating Reactive Metal Complexes in Crystalline Supports for SCXRD Analysis

SCXRD is one of the most powerful tools in the arsenal for material characterisation, enabling atom identification and connectivity in three-dimensional space.⁴⁶ Indeed, so powerful is the technique that enantiomers and enantiomorphs of chiral molecules and crystal structures respectively can be distinguished in certain cases.⁴⁷ Strict requirements to access such data, however, are required. Single crystals of high quality with minimal to no defects are critical, making SCXRD inaccessible for many materials.

Crystalline materials acting as supports offer a pathway to produce direct structural evidence of highly reactive species. This is evidenced in the isolation and structural characterisation of heme-NO complexes supported on sterically bulky ligands (depicted in Figure 3.3).⁴⁸ However, due to the limited capacity of gas movement within the cavities formed by the packing of the coordinating ligands, crystal degradation and loss of long-range order can occur. The intrinsic porosity and crystallinity of MOFs, and their propensity for tunability, make them unique and well suited as platforms for SCXRD-based studies. By using MOFs as crystalline supports to anchor metal complexes post-synthetically, reactions can be undertaken with the pores of the framework. Ensuring the transitions occurring are single crystal to single crystal, they can be probed via SCXRD. Indeed, applying MOFs for the isolation of reactive catalytic intermediates for SCXRD analysis has been exhibited elegantly by previous work conducted within the group, explored in 3.2.2.



Figure 3.3: Crystal structures of the formed $[(\text{TPP})\text{Fe}(\text{NO})(\text{OC}(=\text{O})\text{CF}_3)]$ (**2**) via NO binding to $[(\text{TPP})\text{Fe}(\text{OC}(=\text{O})\text{CF}_3)]$ (**1**), before which remained unelucidated in the solution phase (C, grey; N, blue; O, red; F, green; Fe, orange) (Figure adapted from ref. 48).

3.2.2 MnMOF-1s Application Towards Isolating and Characterising Reactive Intermediates

MnMOF-1, develop within the group, is constructed from manganese chloride and bis(4-(4-carboxyphenyl)-1H-3,5-dimethylpyrazolyl)methane (LH₂).⁴⁹ The material is formed from the solvothermal synthesis of the two aforementioned compounds in DMF and water, resulting in rhombic crystals. The crystals are constructed of Mn₃(II)(L)₂ metal nodes bridged by the same ligand, L, occupying a unique conformation relative to those within the node, L'. In the L form, the bis-pyrazole moieties of bis(4-(4-carboxyphenyl)-1H-3,5-dimethylpyrazolyl)methane are coordinated, along with the terminal carboxylates to the Mn within the MOF cluster. However, when occupying the L' form, visualised as pillaring ligands between 'sheets' of the Mn₃(II)(L)₂ region of the MOF in Figure 3.4, the bis-pyrazole moiety is free and, in theory, capable of post-synthetic metalation. The inherent flexibility imparted around the methylene hinge of the bis-pyrazole moiety is reflected in the material. Both the *anti* and *syn* conformations of the ligand (see Appendix 3.8, Figure 3.A.1) can be accessed whilst in its L' form, resulting in structural flexibility of the MOF. The extremes of this are evident when comparing the desolvated MOF, which adopts the *anti* conformation, relative to the metalated material, which adopts the *syn* conformation, depicted in Figure 3.5. Numerous quantitative metalations at this site with metals such as Mn, Ir, Rh and Cu, have proven the bis-pyrazole moiety is indeed capable of quantitative post synthetic metalation.⁵⁰⁻⁵³ This is supported by SCXRD structures for each of the respective metalations, in addition to many more, indicating MnMOF-1 acts as an ideal crystalline support to tether metal complexes to.

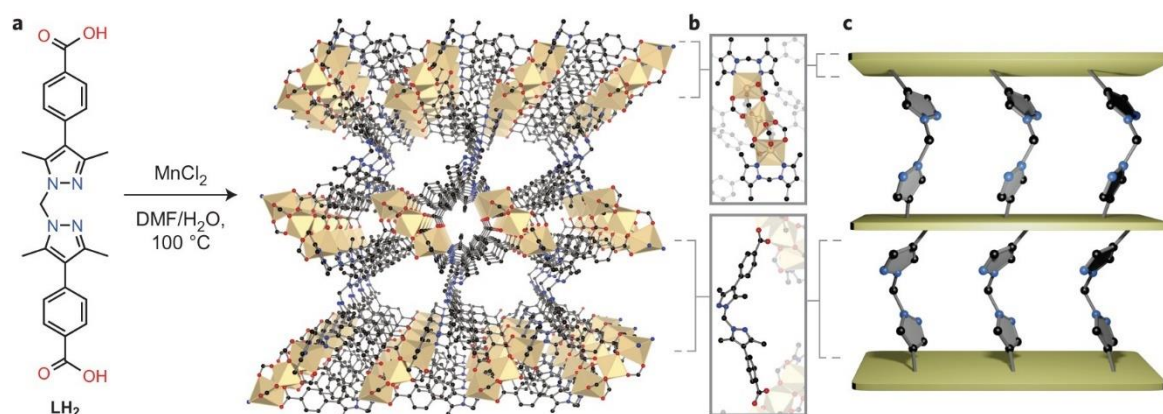


Figure 3.4: (a) The solvothermal synthesis conditions for the formation of MnMOF-1, the SCXRD structure obtained for which, is depicted from the *c*-axis. (b) Enlarged representations of the Mn-based node (upper) and the pillaring L' form of the ligand (lower). (c) Schematic representation of MnMOF-1 as the 'sheets' of Mn₃(II)(L)₂ pillared by the L' form of the ligand (C, black; N, blue; O, red; Mn, beige) (Figure reprinted from ref. 49).

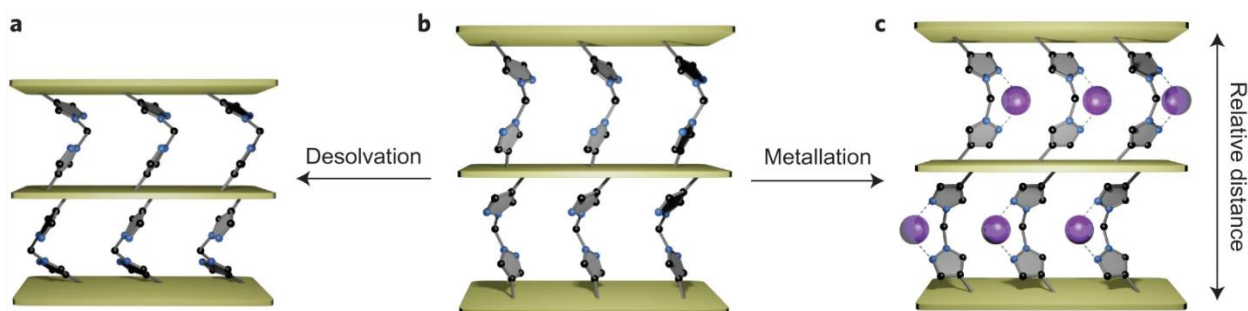


Figure 3.5: Schematic representation of the flexibility of MnMOF-1 resulting from the inherent flexibility about the methylene hinge in the bis-pyrazole moiety in the (a) desolvated phase, (b) solvated phase and (c) metalated phase (Figure adapted from ref. 49).

Further to this, MnMOF-1 presents as an ideal crystalline material to potentially probe Au-based catalysts for the hydrochlorination of acetylene through SCXRD. As mentioned, previous work within the group has exhibited the use of MOFs to investigate catalytic intermediates via SCXRD. Critically, this work utilised MnMOF-1. In 2017, Burgun *et al.* used MnMOF-1 to elucidate the intermediates and products of all steps in the reaction cycle of the carbonylation of methyl bromide (MeBr).⁵⁴ By forming MnMOF-1. $[\text{Rh}(\text{CO})_2][\text{Rh}(\text{CO})_2\text{Cl}_2]$ and subsequently exposing the metalated material to MeBr vapour under an inert atmosphere in dry acetonitrile, MnMOF-1. $[\text{Rh}(\text{CH}_3\text{CN})_2(\text{COMe})\text{Br}]\text{Br}$ was isolated within the MOF and characterised via SCXRD. To complete the reaction cycle and regenerate the active catalyst, dried crystals of MnMOF-1. $[\text{Rh}(\text{CH}_3\text{CN})_2(\text{COMe})\text{Br}]\text{Br}$ were exposed to CO at 80°C. This facilitated the reductive elimination of BrCOMe and the generation of MnMOF-1. $[\text{Rh}(\text{CO})_2]\text{Br}$, subsequently shown to be active for BrCOMe production. The cycle, in the form of acquired crystal structures, is depicted in Figure 3.6.

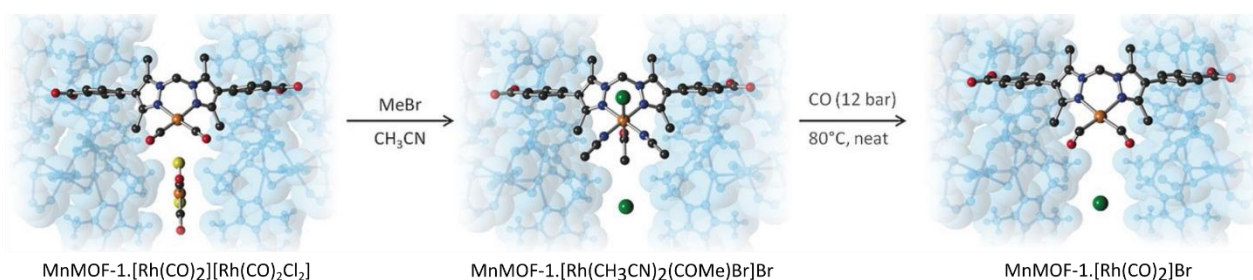


Figure 3.6: SCXRD structures following the carbonylation of MeBr, starting at the initial catalytic starting material, the formation of the catalytic intermediate and the generation of the reaction product, including conditions for the transformations. All structures are viewed along the *a*-axis of MnMOF-1, the backbone of which is represented in blue (C, black; N, blue; O, red; Rh, orange; Br, green; Cl, yellow) (Figure adapted from ref. 54).

The results indicate that MnMOF-1 is an ideal material for the isolation of Au complexes within to attempt to elucidate key steps of the Au-catalysed hydrochlorination of acetylene. In addition, the bidentate nature of the bis-pyrazole moiety with MnMOF-1 is anticipated to assist in the proposed work. As discussed previously, the main limitation preventing the widespread application of gold as a catalyst hinges on the ‘redox gold problem’. Of the three approaches to facilitate the oxidative addition step, using directing groups, highly electrophilic initiation motifs or tuning of the ancillary ligand on the Au centre, the latter is the most desirable.

Armed with the aforementioned findings, presented by Harper *et al.*, that oxidative additions can be enforced for Au based materials when using Au(I) complexes with coordination numbers exceeding 2, MnMOF-1 further presents as an ideal material.³⁷ This is due to the free metalation site, the bis-pyrazole moiety. Not only is the bipy derivative used in the previous example similar in composition to the bis-pyrazole moiety, but it typically coordinates metals at this site in a bidentate fashion. This is supported by all previous reported metalations within MnMOF-1 exhibiting the *syn* conformation of the pyrazoles, thus indicating it typically acts as a ‘bidentate’ ligand. As such, it is anticipated that the coordination of Au(I) complexes within will follow this behaviour, ideally forming a strained complex active to oxidative additions.

The proposed work undertaken and presented in chapter 3 is primarily focused on the isolation of a Au complex within MnMOF-1, a crystalline MOF support, for SCXRD characterisation. This is hoped to enable further studies to elucidate fundamental steps in the gold-catalysed hydrochlorination of acetylene. The synthesis pathways investigated, and subsequent characterisation of such materials will be focused on in the first part of the chapter, whereas the second part will investigate the unique structural flexibility exhibited by the target material and its resulting implications on concurrent work proceeding within the group.

3.3 Metalation of MnMOF-1 with Gold

3.3.1 Metalations with Au(III)

During initial trials, Au(III), recognised as commonly exhibiting trigonal planar geometries, was selected for attempts at metalating MnMOF-1. The typical trigonal planar geometry, in conjunction with the bis-pyrazole moiety of MnMOF-1 and its bidentate chelating nature of metal centres, was considered opportune for the coordination of Au within the framework. Au(III) chloride [AuCl₃], was selected for subsequent metalation tests.

As previously discussed, MnMOF-1 has inherent flexibility about the methylene hinge within the bis-pyrazole moiety of the pillaring ligands. This enables both the *syn* and *anti* conformations to be accessed within the MOF. Recent work on solvated MnMOF-1 has displayed that the specific solvent strongly influences the orientation adopted by the bis-pyrazole moiety.⁵⁵ Due to the trigonal planar geometry of [AuCl₃], the *syn* orientation of the bis-pyrazole moiety is necessary and solvents promoting this form were employed. Acetonitrile (MeCN) solvated MnMOF-1 is known to exhibit the *syn* orientation and, as such, metalation attempts were conducted with MeCN (experimental 3.6.2.3). As an added precaution, based on the likely precedent that upon successful metalation, the resulting complex would exhibit high reactivity, all metalations were conducted under inert atmospheres of argon and dry solvents were utilised. In addition, Au complexes are infamous for their instability to light and thermal stimuli. As such, as an added layer of protection, all metalations were wrapped in aluminium foil to prevent exposure of the crystals to light.^{56,57} All subsequent metalations with Au compounds followed these conditions. Metalation attempts in MeCN for [AuCl₃] are summarised in Table 3.1.

Table 3.1: Metalation attempts using dry MeCN at specified temperatures, for a specified time period. All metalations were conducted in an inert Ar atmosphere and protected from light exposure. Crystal colour and crystal form represents the colour and form of MnMOF-1 crystals post-metalation. The Au:Mn ratio as determined by EDX is specified.

Au(X)	Au(III)		
Complex	[AuCl ₃]		
Temperature (°C)	25	40	60
Time (h)	48	48	48
Crystal colour	Pale Yellow	Yellow	Yellow
Crystal form	Crystalline, severely cracked	Crystalline, severely cracked	Crystalline, severely cracked
EDX ratio Au:Mn	0.12:3	0.37:3	1.83:3

Initial metalation attempts at room temperature afforded pale yellow crystals with low loadings of Au within (~12% metalation), as characterised via scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). As MOFs are crystalline materials, the abundance of the metals constructing the material will remain constant relative to open sites capable of metalation throughout the crystal. The molecular formula of MnMOF-1 is

[Mn₃(L)₂(L')], indicating there is a 1:3 ratio of open metalation sites to manganese present in the structural nodes. As such, the anticipated occupation of Au at the bis-pyrazole site can be calculated based on the relative Au:Mn ratios determined via SEM/EDX. A 100% occupation of the metalation sites by a Au complex is given by a Au:Mn ratio of 1:3. The Au(III) loadings within MnMOF-1 were substantially increased at higher temperatures (40°C, ~37 % metalation), indeed at 60°C, the predicted metalation exceeded the anticipated 1:3 ratio (~183 % metalation). This may have been a result of excess Au material on, or within the material. To confirm whether metalation had indeed been successful, SCXRD analysis was targeted. Unfortunately, SCXRD data was unable to be collected as metalation engendered cracking of the crystals and loss of long-range order at all temperatures trialled. As a result of the poor crystal quality, along with the potential for isolation of Au(III), these test were deemed unsatisfactory and attempts shifted solely to Au(I) complexes, for reasons explored in 3.3.2. Nevertheless, these results indicated metalation with Au is indeed likely possible, provided the right conditions can be uncovered.

3.3.2 Metalations with Syn Conformational Promoting Solvents

Following initial attempts with Au(III), a number of Au(I) complexes were identified as potential candidates for the metalation of MnMOF-1. Following implementation of Au(I) within for SCXRD studies, if permitted, further analysis of the resulting intermediates produced during the hydrochlorination of acetylene would proceed. Au(I) was favoured over Au(III) as the transition from the former to the latter can be facilitated due to the chelating nature of the bis-pyrazole moiety and the potential formation of a strained Au(I) complex. To this end, Au(I)XZ (X representing a halide, Z representing a neutral ligand) complexes were explored. Gold(I) chloride [Au(I)Cl], chloro(dimethylsulfide)gold(I) [Au(I)Cl(SMe₂)] and chloro(tetrahydrothiophene)gold(I) [Au(I)Cl(THT)] were all identified as potential candidates.

Critical to the success of the proposed work is to enforce conditions that will facilitate the coordination of Au(I) in a bidentate fashion at the bis-pyrazole moiety. This would enable the formation of a strained Au(I) complex, ensuing from the bis-pyrazoles small (<180°) bite angle. Both MeCN and *para*-xylene (p-xylene) exhibit the *syn* orientation and, as such, initial metalation attempts with Au(I) (experimental 3.6.2.3) were conducted within these solvents. Metalations attempts in MeCN and p-xylene for the aforementioned Au complexes are summarised in Tables 3.2 and 3.3 respectively.

Table 3.2: Metalation attempts using dry MeCN at specified temperatures, for a specified time period. All metalations were conducted in an inert Ar atmosphere and protected from light exposure. Crystal colour and crystal form represents the colour and form of MnMOF-1 crystals post-metalation. The Au:Mn ratio as determined by EDX is specified.

Au(X)	Au(I)		
Complex	[AuCl]	[AuCl(SMe ₂)]	[AuCl(THT)]
Temperature (°C)	25	25	25
Time (h)	24	48	48
Crystal colour	Brown	Clear	Clear
Crystal form	Powder	Crystalline	Crystalline
EDX ratio Au:Mn	-	0.08:3	0.03:3

Table 3.3: Metalation attempts using dry p-xylene at specified temperatures, for a specified time period. All metalations were conducted in an inert Ar atmosphere and protected from light exposure. Crystal colour and crystal form represents the colour and form of MnMOF-1 crystals post-metalation. The Au:Mn ratio as determined by EDX is specified.

Au(X)	Au(I)		
Complex	[AuCl]	[AuCl(SMe ₂)]	[AuCl(THT)]
Temperature (°C)	25	25	25
Time (h)	24	48	48
Crystal colour	Brown	Purple	Purple
Crystal form	Powder	Crystalline	Crystalline
EDX ratio Au:Mn	-	-	-

From the attempted metalations, conclusions and insights were drawn from the resulting materials and used in the identification and development of improved pathways to target.

When considering [AuCl], both attempted metalations in MeCN and p-Xylene led to a brown, powder-like material forming. This is in stark contrast to the initially crystalline MOF material. Regardless, the powders were collected and washed with the respective dry solvent (×5) to remove any excess AuCl remaining. The washed powder was dried under vacuum and analysed via PXRD (see Appendix 3.8, Figure 3.A.2). Relative to the pristine MOF, it is evident the isolated material has lost its crystallinity and has thus degraded. It is theorised this is a direct consequence of the high solubility of the complex in the two solvents. AuCl readily dissolves

into both MeCN and p-xylene leading to rapid uptake of the complex into the pores of MnMOF-1. This likely results in rapid metalation inducing conformational changes of the bis-pyrazole moiety and thus changes in the dimensions of the MOF itself. This rapid changing of orientation is considered to cause the degradation of the crystals as the over flexibility of its components facilitates its automatus disintegration into a powder.

In attempts to alleviate the stress placed on the system due to excessive amounts of AuCl, repeat attempts were trailed at 0°C to limit the solubility of the complex and the speed at which it was able to interact with the MOF. Identical degraded, powder-like products were obtained. As a result, alternative syntheses utilising different Au complexes with lower solubility in the metalation solvents were instead pursued, limiting the issues attributed to excessive diffusion through the framework.

Next, metalations with [AuCl(SMe₂)] and [AuCl(THT)] were targeted. In MeCN after 48 hours, the crystals of MnMOF-1 remained clear and identical to those of the pristine MOF. To determine if any Au had ben coordinated at the bis-pyrazole site, the crystals were collected and washed with the relative dry solvent (×5). The crystals were dried under vacuum and subject to SEM/EDX analysis. The collected spectra (see Appendix 3.8, Figure 3.A.3 relative to an expected successful spectra), display loadings of Au relative to Mn at essentially 0:1 (~0 % metalation), indicating the material remains unmetalated. Trace readings of Au in the spectra may indicate small amounts within the MOF, either in the pores of the material or occupying metalation sites. Conversely, it may also originate from remaining Au precursor unwashed from the samples due to their relative insolubilities in MeCN. In order to elucidate if the former was the case, metalations for longer periods were conducted. In both cases, however, this led to the deposition of metallic Au onto the surface of the vials, evident in Figure 3.A.4, see Appendix 3.8, and the resulting crystals were coloured purple and extensively cracked. Purple colouration when working with gold-based compounds is characteristic of the formation of nanoparticles, an ominous sign tell-tale of the inability to isolate the Au complex at single sites throughout the MOF.⁵⁸ As such, metalations with Au(I) materials in MeCN were discontinued and different solvents were pursued.

Tests then shifted to the second identified solvent promoting the *syn* conformation of the bis-pyrazole moiety within the MOF, p-xylene. Metalations with [AuCl(SMe₂)] and [AuCl(THT)], identical to those conducted in MeCN, yielded purple crystals, the colour characteristic of Au nanoparticles. Unfortunately, all subsequent tests conducted in p-xylene

formed such crystals. Consequently, p-xylene was excluded from future metalation tests owing to this attribute.

3.3.3 Metalations with both Syn and Anti Conformational Promoting Solvents

In the previous section it was determined that solvents promoting the *syn* conformation of the bis-pyrazole moiety were unsuccessful. Therefore we investigated solvents that exhibit disorder at the bis-pyrazole moiety. This means both the *syn* and *anti* conformation are promoted. Methanol and acetone were identified as two solvents within this group.⁵⁵ Metalations attempts in MeOH and acetone are summarised in Tables 3.4 and 3.5 respectively.

Table 3.4: Metalation attempts using dry MeOH at specified temperatures, for a specified time period. All metalations were conducted in an inert Ar atmosphere and protected from light exposure. Crystal colour and crystal form represents the colour and form of MnMOF-1 crystals post-metalation. The Au:Mn ratio as determined by EDX is specified.

Au(X)	Au(I)	
Complex	[AuCl(SMe ₂)]	[AuCl(THT)]
Temperature (°C)	25	25
Time (h)	1	1
Crystal colour	Purple	Purple
Crystal form	Crystalline	Crystalline
EDX ratio Au:Mn	-	-

Table 3.5: Metalation attempts using dry acetone at specified temperatures, for a specified time period. All metalations were conducted in an inert Ar atmosphere and protected from light exposure. Crystal colour and crystal form represents the colour and form of MnMOF-1 crystals post-metalation. The Au:Mn ratio as determined by EDX is specified.

Au(X)	Au(I)	
Complex	[AuCl(SMe ₂)]	[AuCl(THT)]
Temperature (°C)	25	25
Time (h)	48	48
Crystal colour	Clear	Clear
Crystal form	Crystalline	Crystalline
EDX ratio Au:Mn	0:3	0:3

Metalations in MeOH and acetone were unsuccessful. Notably, metalations conducted in MeOH yielded purple crystals within half an hour. This was a result of nanoparticle formation. This was reflected in repeat attempts, further limiting light exposure and degassing with Ar for longer periods to ensure all air had been displaced. Subsequently, MeOH was excluded from further attempts. In addition, metalations in acetone were also unsuccessful, fuelled by the limited solubility of the Au complexes. Accordingly, when acetone-based metalations were left for extended periods, metallic Au was deposited onto the surface of the vials and the resulting crystals turned purple. This mirrored metalations attempts in MeCN for both [AuCl(SMe₂)] and [AuCl(THT)]. Much like MeOH, these tests indicate acetone was unlikely to promote favourable metalation conditions and it was thus omitted from future tests.

3.3.4 Metalations with Anti Conformational Promoting Solvents and Reactive Complexes

Taking inspiration from organometallic literature examples enabling isolation of three coordinate Au(I) complexes, an analogous pathway to those typically conducted was considered. Metalation of MnMOF-1 with Au(I) in solvents promoting the *syn* conformation of the bis-pyrazole moiety, and solvents promoting disorder (both the *syn* and *anti* conformation) at this site, within MnMOF-1, exhibited little success. Accordingly, solvents promoting the *anti* conformation remained untested and were subsequently explored. Due to the preferred *anti* orientation of the bis-pyrazole moiety promoted by such solvents and the strong affinity to linear geometries of Au(I), metalation at the site was envisioned as the formation of a digonal complex. On the assumption a digonal complex would form, attempts to access the trigonal planar geometry could proceed. We propose a method to access the trigonal planar geometry by inducing a conformation preference change of the bis-pyrazole moiety from *anti* to *syn* by solvating post metalation in *syn* promoting solvents. In addition, the isolation of digonal complexes inside MnMOF-1, currently unreported in the metalated structures collected, in itself, would make for an interesting material with presumably unexpected properties.

Trigonal Au(I) compounds containing two nitrogen donors, similar to those provided by the bis-pyrazole moiety of MnMOF-1, were targeted in literature. Au(I) itself in a trigonal form is uncommon, but with the added constraints, two compounds could be identified. [PhB(3-(C₂F₅)Pz)₃]Au(C₂H₄) and [(κ²-bipy)Au-(η²-C₂H₄)] [NTf₂], depicted in Figure 3.7, were isolated and characterised via SCXRD by Dias *et al.* and Harper *et al.*^{37,59}

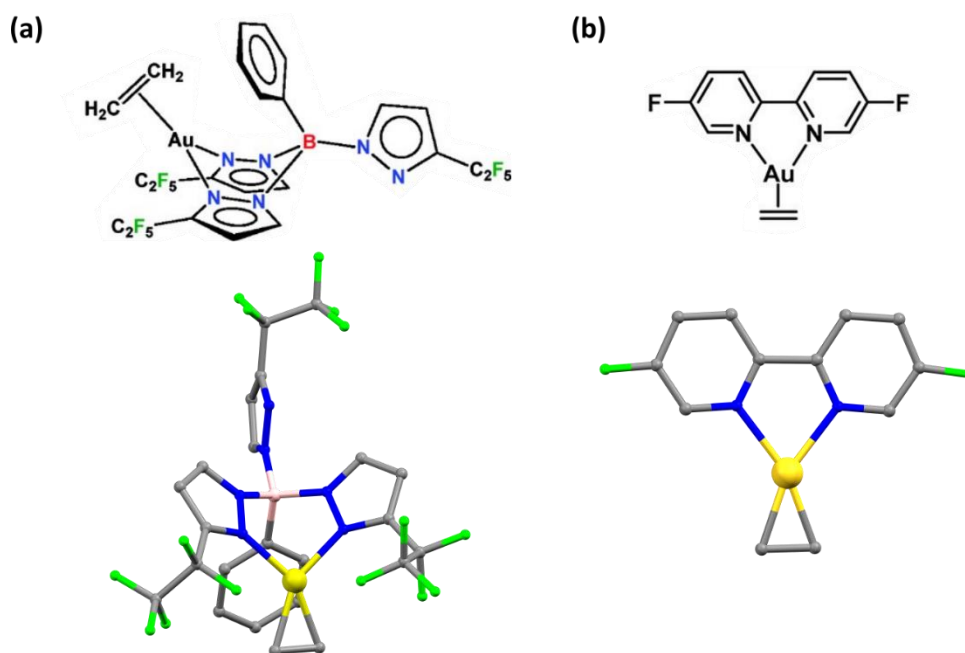
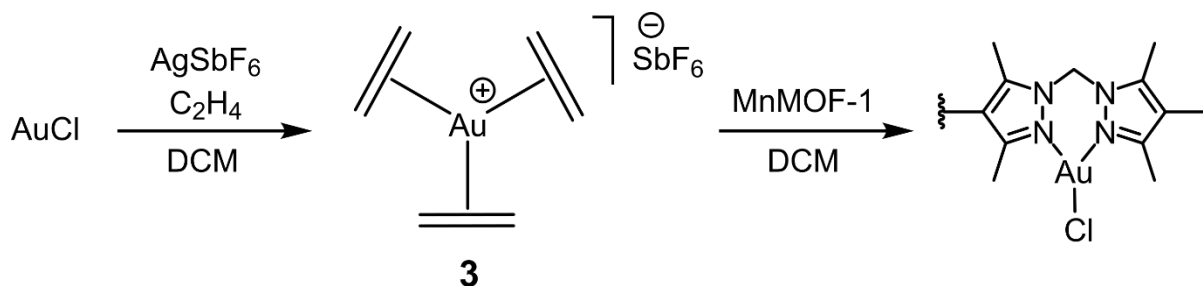


Figure 3.7: SCXRD structures of **(a)** $[\text{PhB}(3\text{-(C}_2\text{F}_5)\text{Pz})_3]\text{Au}(\text{C}_2\text{H}_4)$ and **(b)** $[(\kappa^2\text{-bipy})\text{Au-(}\eta^2\text{-C}_2\text{H}_4)][\text{NTf}_2]$ ($[\text{NTf}_2]$ omitted) and their skeletal representations. Both are examples of trigonal planar Au(I) complexes with N-donors representative of those located within the metalation site of MnMOF-1 (C, grey; N, blue; Au, yellow; F, green; B, pink) (Figure adapted from ref. 36 and 58).

In both presented examples, the resulting organometallic compound consists of ethylene as the auxiliary ligand. Analysis of the C=C and Au-C bond reveal relative elongation and contraction in each bond respectively, respective to two-coordinate $[\text{LAu}(\eta^2\text{-alkene})]^+$ cations.⁵⁹ Such observations indicate enhanced π -back-donation, strengthening the Au-C bonds and thus stabilising the complex. From the syntheses of the compounds, a potential pathway to metalate MnMOF-1 was conceived. Mirroring that of $[(\kappa^2\text{-bipy})\text{Au-(}\eta^2\text{-C}_2\text{H}_4)][\text{NTf}_2]$, the initial synthesis of $[\text{Au}(\text{C}_2\text{H}_4)_3]^+$, subsequently followed by the metalation of the desired material was attempted. This process is summarised in Scheme 3.3.



Scheme 3.3: Formation of $[\text{Au}(\text{C}_2\text{H}_4)_3](\text{SbF}_6)$ (**3**), from AuCl, for the proposed subsequent metalation of MnMOF-1 and the resulting desired product.

Initially, $[\text{Au}(\text{C}_2\text{H}_4)_3](\text{SbF}_6)$ (**3**) was formed to attempt the metalation of MnMOF-1 (see experimental section 3.6.2.4). Direct characterisation of the isolated clear filtrate containing **3** was not undertaken due to its extremely high reactivity to air and reactivity to light.⁶⁰ The clear colouration of the solution, recovered via canula, in conjunction with the formation of a white precipitate (silver chloride (AgCl)), which was removed, supported its formation. The prepared solution of **3** in DCM was added to MnMOF-1 in dry DCM and left for 24 hours. DCM exhibits disorder at the bis-pyrazole moiety, meaning both conformations are promoted, importantly including the *syn* conformation, indicating metalation in the anticipated trigonal geometry could potentially be accessed. After 24 hours, however, a black precipitate had formed at the base of the vial. The black precipitate is characteristic of the decomposition of **3**.⁶⁰ Whilst this result is a further indication $[\text{Au}(\text{C}_2\text{H}_4)_3](\text{SbF}_6)$ had been successfully synthesised, attempts at collecting the crystals were unfortunately unsuccessful as the black precipitate derived from the degradation of $[\text{Au}(\text{C}_2\text{H}_4)_3](\text{SbF}_6)$ had encompassed the MOF crystals. Consequently, the proposed metalation with **3** was not pursued further.

Simultaneously, metalations using solvents promoting the *anti* conformation of the bis-pyrazole moiety were ongoing. Et_2O is one such solvent that promotes this conformation and was employed for subsequent testing. Metalations attempts in Et_2O are summarised in Table 3.6.

Table 3.6: Metalation attempts using dry Et_2O at specified temperatures, for a specified time period. All metalations were conducted in an inert Ar atmosphere and protected from light exposure. Crystal colour and crystal form represents the colour and form of MnMOF-1 crystals post-metalation. The Au:Mn ratio as determined by EDX is specified.

Au(X)	Au(I)	
Complex	$[\text{AuCl}(\text{SMe}_2)]$	$[\text{AuCl}(\text{THT})]$
Temperature ($^{\circ}\text{C}$)	25	25
Time (h)	96	96
Crystal colour	Pale Yellow	Pale yellow
Crystal form	Crystalline	Crystalline
EDX ratio Au:Mn	1.01:3	1.96:3

The attempted metalations with both $[\text{AuCl}(\text{SMe}_2)]$ and $[\text{AuCl}(\text{THT})]$ showed positive results. Due to the relative insolubility of the complexes in Et_2O , metalations were permitted to continue for extended periods of time. The resulting crystals were collected, washed, and analysed via SEM/EDX. The former returned Au:Mn ratios of 1.01:3, indicating 100 % metalation of the material, provided detected Au was indeed coordinated at the bis-pyrazole moiety. The latter returned Au:Mn ratios of 1.96:3, almost double that of what was expected, but nonetheless indicating its potential for success. Due to the success of metalations with $[\text{AuCl}(\text{SMe}_2)]$, refinement of metalation conditions using $[\text{AuCl}(\text{THT})]$ were suspended during characterisation of the $[\text{AuCl}(\text{SMe}_2)]$ derived materials.

Initial metalation conditions contained undissolved $[\text{AuCl}(\text{SMe}_2)]$ in the bottom of the vial with MnMOF-1 crystals. Upon collection of the crystals, excess $[\text{AuCl}(\text{SMe}_2)]$ was unable to be dissolved and washed away through solvent exchange with Et_2O . The undissolved $[\text{AuCl}(\text{SMe}_2)]$ led to the formation of nanoparticles and the degradation of the MOF evidenced by complete reduction in PXRD peak intensity (Figure 3.8). To prevent nanoparticle formation, an improved synthesis enabling removal of excess complex was designed (experimental 3.6.2.5). This was achieved through inserting a small vial containing the complex, within the vial containing MnMOF-1, as depicted in Figure 3.A.5, see Appendix 3.8. Following the metalation, the complex could be readily removed, and the crystals were subsequently easily washed. This process, however, required further refinement as vials had to be rotated 90° daily to ensure any solubilised complex could access the crystals, but, more importantly, results were inconsistent, commonly exhibiting metalations below 100% (see Appendix 3.8, Figure 3.A.6).

Once identifying the MOF and complex required separation to avoid degradation of the metalated MOF, the persisting issue relating to the solubility of $[\text{AuCl}(\text{SMe}_2)]$ required alleviation. As opposed to the conditions in experimental 3.6.2.5, the crystals were instead targeted as the component to be isolated. To ensure complex access to the crystals, they were held within a cellulose filter, whilst the complex was continuously stirred to promote dissolution into Et_2O . The setup is depicted in Figure 3.A.7, see Appendix 3.8. Accordingly, the increased solubilisation of $[\text{AuCl}(\text{SMe}_2)]$ yields shorter metalation times of 48 hours. The synthesis conditions are accessible in experimental 3.6.2.6. Pale yellow crystals, quantitatively metalated, as characterised via SEM/EDX (see Appendix 3.8, Figure 3.A.8), are reproducible via this method. Consideration to the instability of the resulting material, however, must be given. Not only is it sensitive to air, but the sample also displays light sensitivities. Exposure to either stimuli for mere minutes results in the degradation of the material, characterised by the

transition to purple crystals, suggesting nanoparticle formation. TEM analysis of the purple crystals supports this theory (Figure 3.9). The dark, spherical particles, contrasting against the relatively light and uniform MOF material are indicative of Au nanoparticle formation.

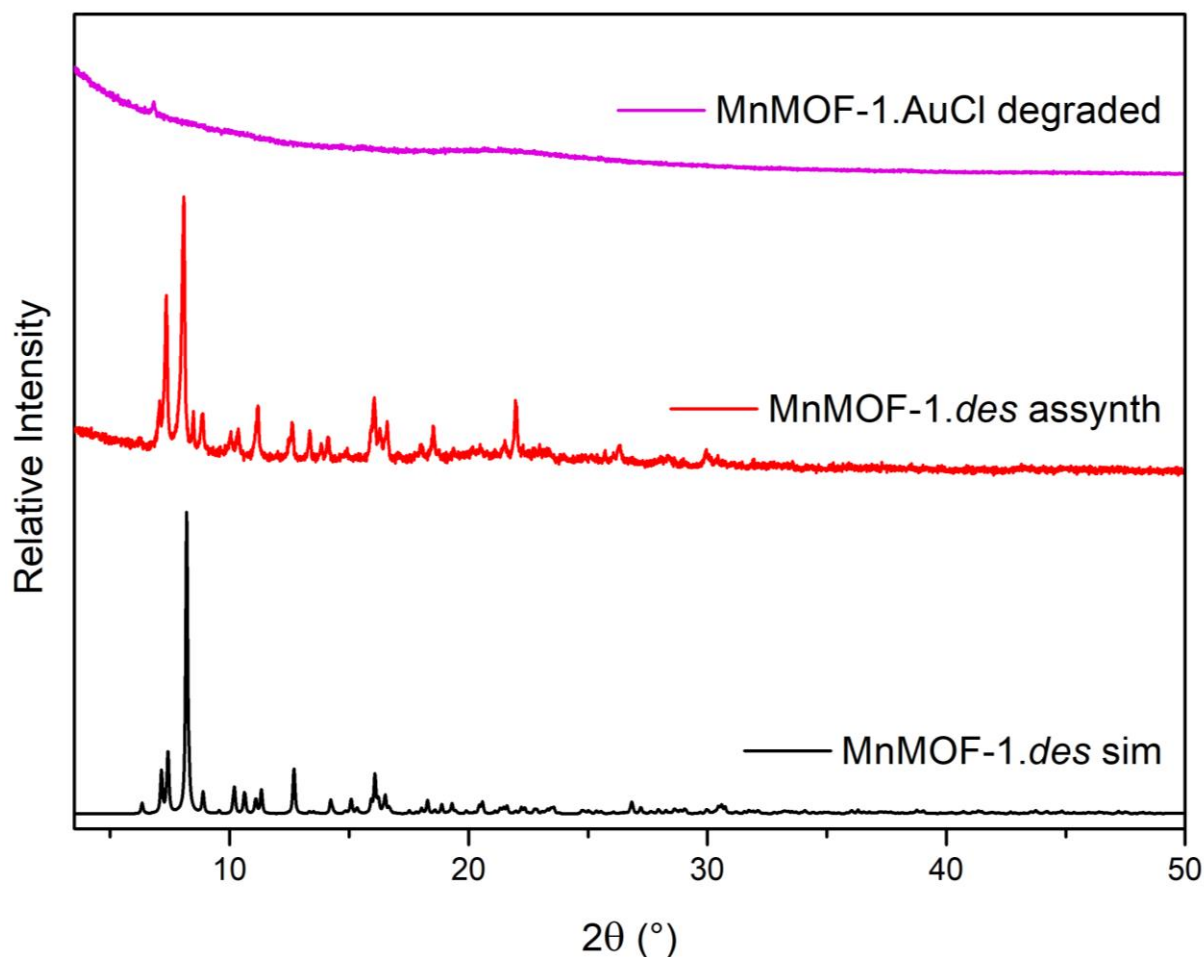


Figure 3.8: Powder X-ray diffraction patterns of MnMOF-1 samples; simulated desolvated MnMOF-1 (black), MnMOF-1 as-synthesised (red) and nanoparticle containing, degraded MnMOF-1.AuCl (pink).

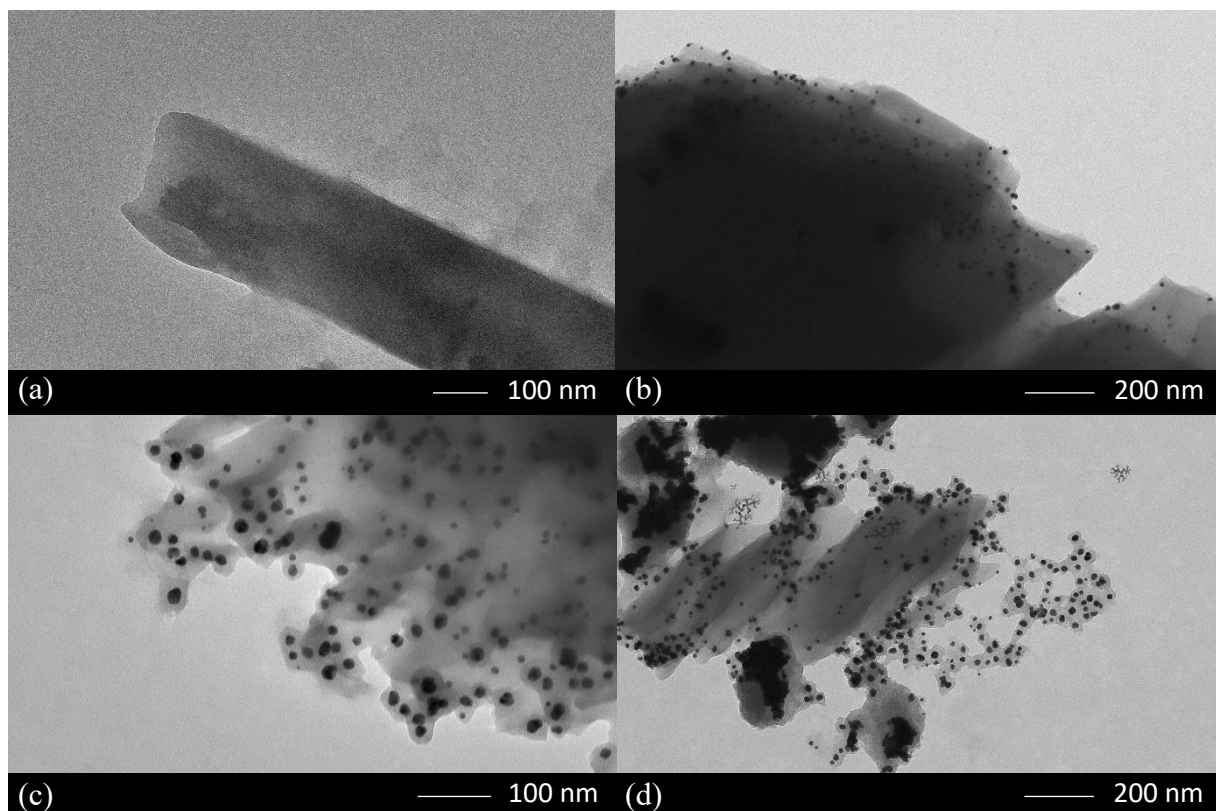


Figure 3.9: (a) MnMOF-1.AuCl imaged after meticulous preparation preventing nanoparticle formation (b-d) compared relative to the same material after its subsequent degradation to purple crystals exhibiting the clear formation of nanoparticles.

Further analysis of data obtained via SEM/EDX reveals insights into the coordination environment around the Au centre. Initially as the $[\text{AuCl}(\text{SMe}_2)]$ complex, both Cl and S (in the form of SMe_2) are coordinated in a 1:1:1 Au:Cl:S ratio. In the prepared material, the 1:1 Au:Cl ratio is retained, but only contains trace amounts of S relative to both Au and Cl are detected. This data suggests, upon coordination to the nitrogen(s) of the bis-pyrazole moiety, SMe_2 is displaced, resulting in the MnMOF-1.AuCl complex. Crystals of MnMOF-1.AuCl were collected and dried under vacuum to examine their crystallinity via PXRD. Figure 3.10 shows the PXRD powder patterns of MnMOF-1 and the simulated desolvated and DMF solvated derivatives, simulated MnMOF-1.AuCl and the collected MnMOF-1.AuCl. Due to the intrinsic flexibility of the bis-pyrazole moiety, and the different orientations it can exhibit when in the pillaring L' form, the crystal structure can change drastically. This is evident when comparing the simulated PXRD patterns from the generated crystal structures of the desolvated and DMF solvated MnMOF-1 forms. This flexibility is expected to be retained in MnMOF-1.AuCl in which the simulated pattern is somewhat consistent with the DMF solvated MnMOF-1 crystals. The crystal structure, its collection, and solution are outlined in 3.3.5. Due to the

collection of the crystals in toluene, a different solvent to DMF, and with the consideration AuCl is coordinated within, small differences to the materials structure are expected and account for those observed in the patterns. Nevertheless, the overall character of the two patterns are consistent. Similarities between the collected MnMOF-1.AuCl pattern and the simulated MnMOF-1.AuCl pattern suggest the successful metalation of MnMOF-1 with Au. The collected pattern, however, is considerably lower in intensity. This is a result of sample degradation following both light and air exposure during sample loading into the capillaries. The peak at 5.1° , representative of the (020) plane which lies along the $\text{Mn}_3(\text{II})(\text{L})_2$ sheets of MnMOF-1, exhibits the greatest reduction in intensity, relating to the loss in long range order along the plane. The degradation of the material is evidenced by this reduction, and the reduction of the other peaks composing the pattern of MnMOF-1.AuCl. The retention of crystallinity following metalation with $[\text{AuCl}(\text{SMe}_2)]$, however, was confirmed, albeit forming a material with strong sensitivities to air and light.

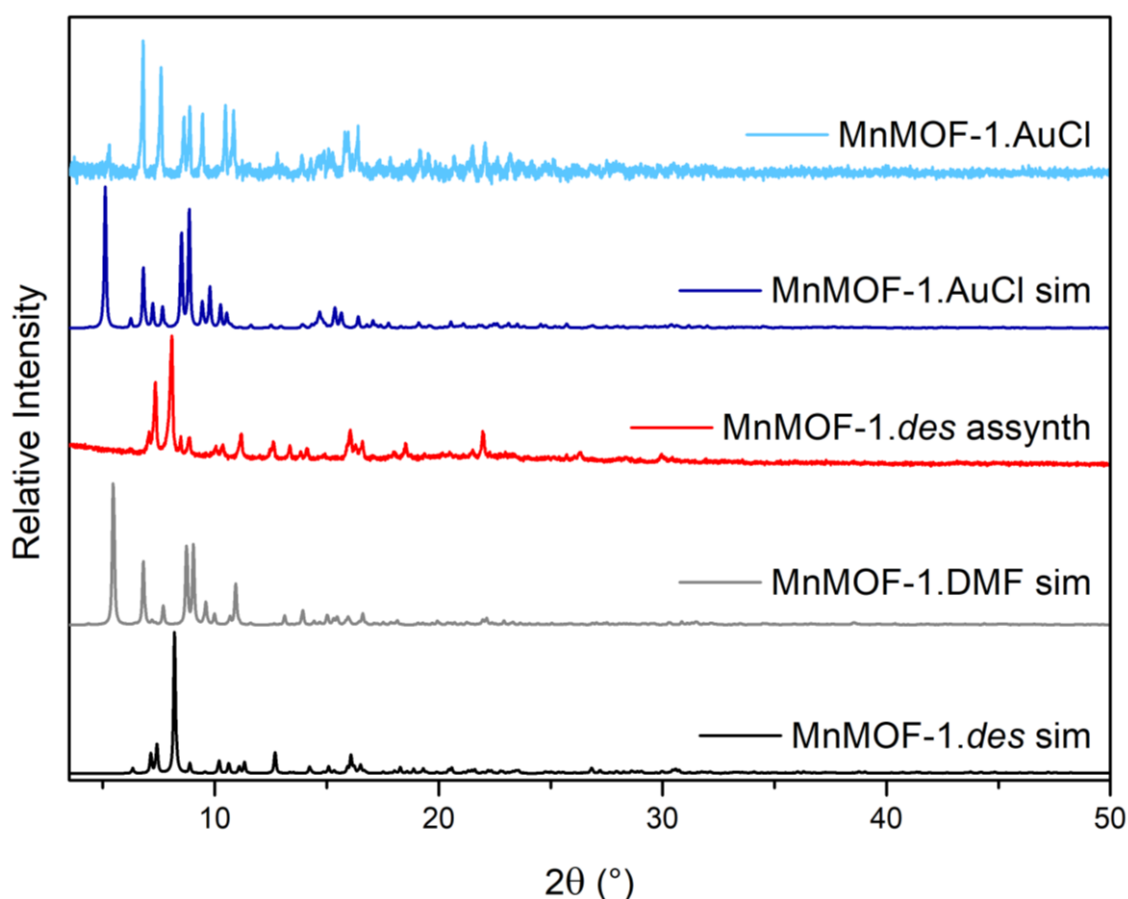


Figure 3.10: Powder X-ray diffraction patterns of MnMOF-1 samples; simulated desolvated MnMOF-1 (black), simulated DMF solvated MnMOF-1 (grey), MnMOF-1 as-synthesised (red), simulated MnMOF-1.AuCl (dark blue) and MnMOF-1.AuCl, metalated with $[\text{AuCl}(\text{SMe}_2)]$ (blue).

3.3.5 SCXRD Characterisation of MnMOF-1.AuCl

To elucidate the coordination environment adopted by Au at the bis-pyrazole site, SCXRD structural characterisation of MnMOF-1.AuCl was undertaken. To collect SCXRD data (experimental 3.6.3), the crystals were mounted on Mitigen mounts in paratone-N oil, limiting exposure to air and moisture. This itself posed a challenge as not only are the crystals both air and light sensitive, but issues arose due to the use of Et₂O as a solvent. This led to substantial cracking of the crystals during picking, stemming from rapid Et₂O evaporation from both the microscope slide used for crystal picking (even using cryoprotectants), and from within the crystals, promoting rapid structural changes that led to loss of long-range order. In order to overcome such challenges, crystals of MnMOF-1.AuCl were washed with toluene, a less volatile, non-coordinating solvent. This ensured both the retention of crystallinity during crystal picking as rapid evaporation of solvent out of framework was avoided, and retention of the coordination environment at the metalation site as coordination of the introduced solvent (toluene) will not occur. It is imperative this washing step was conducted immediately preceding selection and freezing of the crystals as the degradation of the crystals, signified by the resulting purple colouration, occurred within 30 minutes of the initial wash with toluene.

Remarkably, despite the highly sensitive nature of MnMOF-1.AuCl, a single crystal structure was able to be obtained. MnMOF-1.AuCl has a monoclinic crystal system, with the *P*2₁/*c* space group commonly encountered for forms of MnMOF-1.⁵⁵ The asymmetric unit consists of one manganese node of the form [Mn₃L₂L'₁], in which the open bis-pyrazole moiety adopts the *anti* conformation. AuCl is coordinated to one of the nitrogen atoms of the bis-pyrazole moiety, forming a digonal coordination complex (Figure 3.11). The Au-N and Au-Cl bond lengths of 1.923(5) Å and 2.244(4) Å respectively, are consistent with literature examples of SCXRD structurally characterised N-Au-Cl fragments.⁶¹⁻⁶⁸ The similarity is well demonstrated in [Re(NAuCl)Cl₂(PMe₂Ph)₃] complex, reported by Beuter *et al.*, in which the Au-N and Au-Cl bond lengths in the N-Au-Cl fragment are almost identical at 1.976 Å and 2.243 Å respectively.⁶¹ The N-Au-Cl fragment angle is 174.6(2)°, near linear. The reduction from 180°, the expected angle for Au(I) based materials, may result from packing effects experienced within the MOF.⁶² The crystallographic information of MnMOF-1.AuCl is reported in Table 3.A.1, see Appendix 3.8.

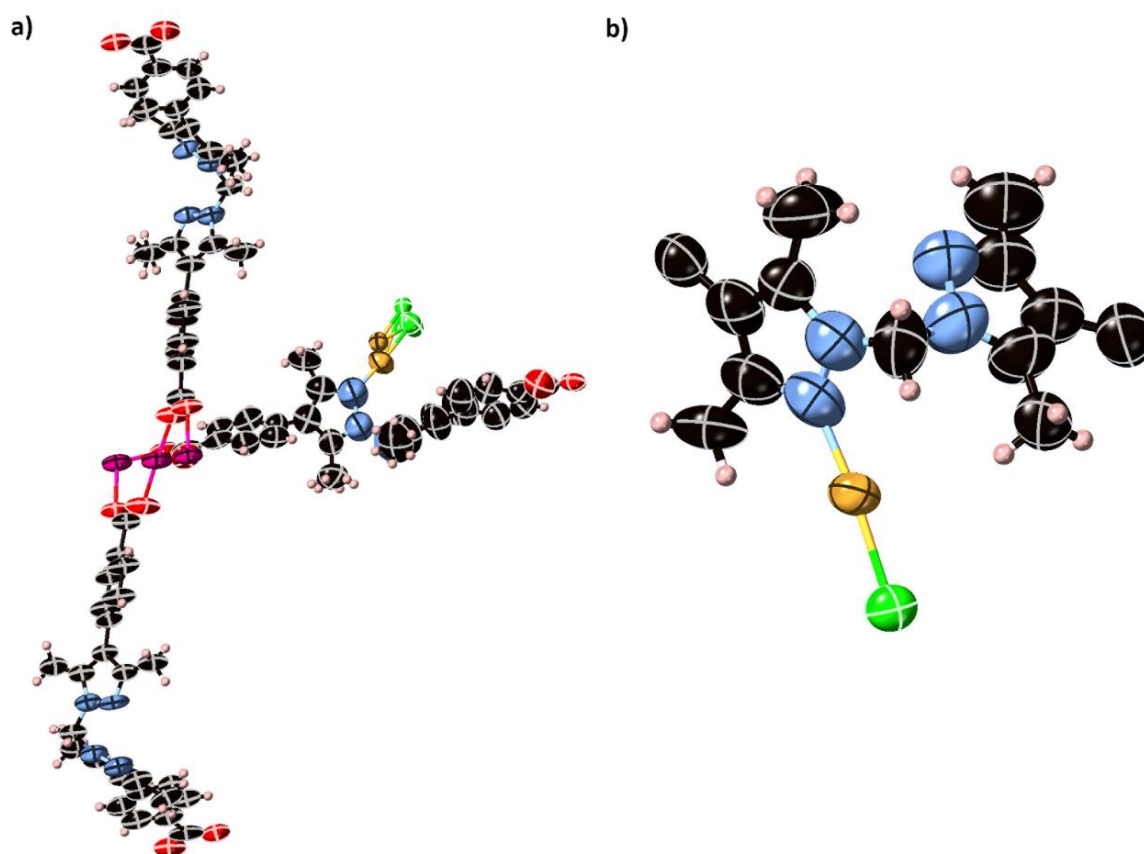


Figure 3.11: (a) The asymmetric unit of MnMOF-1.AuCl, with toluene solvent molecules omitted for clarity and (b) the bis-pyrazole moiety exhibiting the *anti* conformation and its metalation with AuCl adopting a two-coordinate digonal geometry. All non-hydrogen atoms are represented by ellipsoids at the 50% probability level. The second Au centre is depicted in (a) but removed from (b) for clarity, the electron density map (Figure 3.12) of the structure exhibits this second site (C, black; H; white; N, blue; O, red; Mn, pink; Au, yellow; Cl, green).

Refinement of the structural model was complicated by significant disorder within the structure, primarily originating at the AuCl moiety. As such, extensive SIMU, which constrains atomic displacement parameters (ADPs) of relatively close atoms similar to one another, RIGU, which ensures bonded atoms displacement parameters are similar along the bond, and DFIX, which restrains atom pair distances between one another as a fixed value within an estimated standard deviation (esd) range, were required. The combination of these constraints enabled elucidation of the metalation site's structure. The AuCl moiety is disordered, with the disorder model used being supported by the electron density map (Figure 3.12). The associated disorder of the bis-pyrazole ligand, was unable to be modelled. In addition, electron density of 3.25 toluene molecules within the pores of the material were accounted for by the solvent masking routine of Olex2.

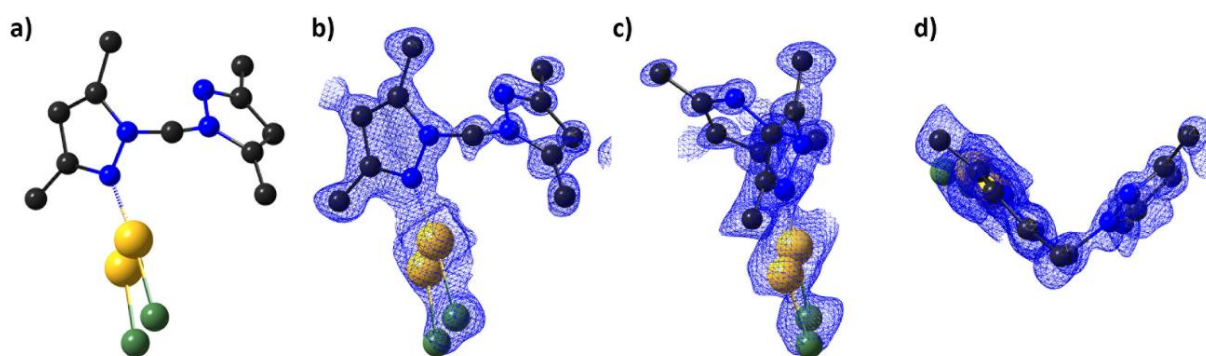


Figure 3.12: (a) The bis-pyrazole moiety of MnMOF-1.AuCl including the coordinated, disordered Au centre with the overlaid electron density map viewed from the (b) front, (c) side and (d) top (C, black; N, blue; Au, yellow; Cl, green).

3.3.6 Gas Adsorption Characterisation of MnMOF-1.AuCl

Notably, not only is this the first example of quantitative metalation of MnMOF-1 with Au, but it is the first example of metalation of the bis-pyrazole moiety in the *anti* conformation of MnMOF-1. All previous metalations have occurred in the *syn* conformation, exploiting its bidentate nature. As a result, it is anticipated that due to this coordination environment, some flexibility of the original MOF relating to the flexibility about the methylene hinge would be retained. This is opposed to the metalated material in the *syn* conformation essentially ‘locking’ the bis-pyrazole moiety and preventing the flexibility exhibited by the unmetalated MOF. Gas adsorption properties of the formed materials provides a suitable platform to probe this flexibility.

Dynamic adsorption behaviour is characteristic for flexible MOF materials, identified as enhancements in accessible surface area as a direct result of pressure-induced transitions in the structure of the material.⁶⁹ This is evident in the N₂ isotherms for unmetalated MnMOF-1 compared against a metalated counterpart, MnMOF-1.CoCl₂ (Figure 3.13).⁴⁹ Flexibility of the material, recognised as an inflexion point in the isotherm upon adsorption ($P/P_0 = 0.025$), followed by a hysteretic desorption, occurs for the unmetalated material, but is absent for the metalated material. This is due to rotation about the methylene hinge, which is permitted for the former, but disallowed for the latter. During activation of crystals, the unmetalated site is free to rotate between the *syn* and *anti* conformations, enabling the collapse of the material into a more favoured condensed state. Comparatively, in the metalated material, the bis-pyrazole site is essentially ‘locked’ in the *syn* orientation due to incorporation of both N-donors within the incorporated complex, resulting in the previously exhibited flexibility not being permitted.

The N₂ isotherm for MnMOF-1.AuCl was collected, following activation from Et₂O, and is depicted in Figure 3.13. Based off its structure, the observed S-type adsorption profile indicates the flexibility of the material. The profile, however, is considerably different to that of the unmetalated MOF. As opposed to rapid uptake at low relative pressure, inclusive of the gate-opening event, MnMOF-1.AuCl exhibits minimal uptake at low relative pressure before rapidly increasing following the gate-opening event ($P/P_0 = 0.025$), followed by hysteretic desorption. A possible mechanism is the blocking of pores by the Au centre, absent in the unmetalated material, preventing the low relative pressure uptake. Subsequently, following the gate-open event, these channels are opened allowing the influx of gas. The gate-opening phenomenon, including the characteristic S-Type isotherm, has been displayed in MOFs previously with rotatable macrocycles initially blocking the pore window, capable of being ‘unlocked’.⁷⁰

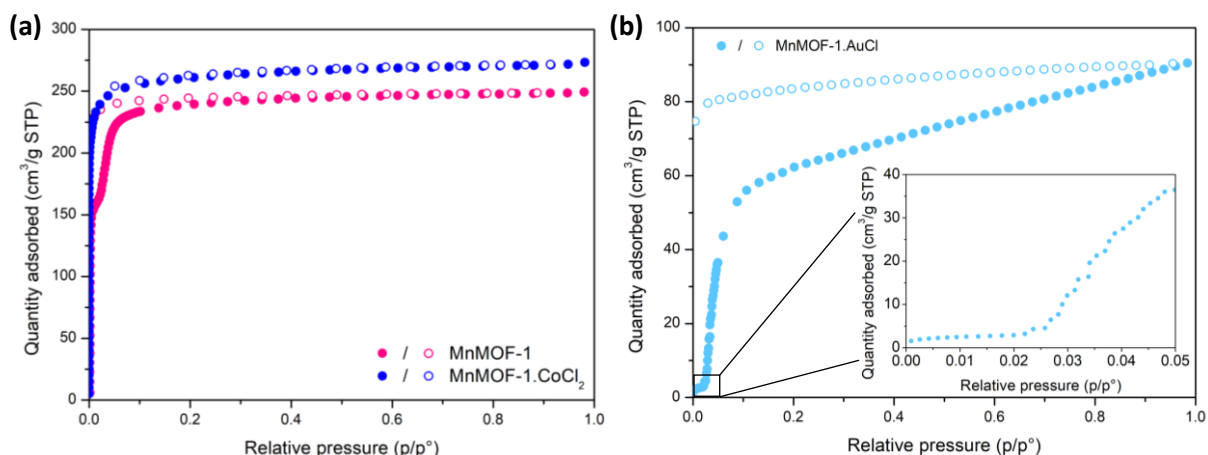


Figure 3.13: 77 K N₂ adsorption isotherm data collected for **(a)** MnMOF-1 (pink) and MnMOF-1.CoCl₂ (dark blue) and **(b)** MnMOF-1.AuCl (blue), highlighting the gate opening event at $P/P_0 = 0.025$.

The metalation of MnMOF-1 with [AuCl(SMe₂)] affords crystals of MnMOF-1.AuCl, the single crystal structure of which was collected, exhibiting quantitative metalation of the bis-pyrazole sites in the *anti* conformation. This is the first example of MnMOF-1 being metalated in such a way. In addition, due to the coordination environment adopted, the material retains the inherent flexibility of the unmetalated material, unlike previous metalations of the material. The result provides a unique example of accessing interesting coordination geometries within MnMOF-1.

3.3.7 *Syn-promoting Solvent Washing of MnMOF-1.AuCl to Induce Structural Transformation*

Isolation of Au with MnMOF-1 and its subsequent characterisation, in itself, is a substantial achievement owing to the relative instability of the resulting material. Once fully characterised, attention turned to attempting to induce structural transformation of the material by promoting the *syn* conformation of the bis-pyrazole moiety in order to isolate a three coordinate Au(I) centre to be used in fundamental studies of the reaction mechanism of the hydrochlorination of acetylene. Both MeCN and p-xylene, known to be *syn* conformational promoting solvents, were trialled.

Metalated crystals of MnMOF-1.AuCl were washed with the aforementioned solvents and subsequently analysed. Unfortunately, both washings resulted in the formation of purple crystals, indicating nanoparticle formation. Fortunately, the decomposition in p-xylene took 30 mins, a relatively long time in comparison to the mere minutes required when washing with MeCN. The p-xylene washed crystals were subsequently analysed via SCXRD. From all collected data sets, the Au centre was unable to be substantially identified. The orientation of the pillaring ligand, however, was elucidated. Unfortunately, the bis-pyrazole moiety remained in the *anti* conformation, analogous to that of the original material suggesting the desired structural transformation was unable to be promoted.

Further washings with both *syn* and *anti* conformational promoting solvents were trialled, but much like the previous solvents, nanoparticle formation within the MnMOF-1.AuCl crystals was observed after short periods of time. As a result, single crystal structures were unable to be obtained. New efforts to access the trigonal planar geometry by looking at exchanging the anionic chloride ligand coordinated to the Au centre to introduce new substituents and promote this change were attempted. Much like the washing method, nanoparticle formation was inevitable. Unfortunately, the instability of MnMOF-1.AuCl to numerous stimuli restricted its ability to be used as a platform for probing the hydrochlorination of acetylene mechanism via SCXRD.

3.4 Coordination Modulated On-Off Switching in MnMOF-1

Flexible materials have received great interest in recent times owing to the promise they hold over a diverse range of applications.⁷¹ Within the field, dynamic MOFs (MOFs exhibiting flexibility) have quickly attracted significant investigation into the properties they possess, emerging as excellent materials for gas storage and separation, sensing, and guest capture and release.⁷²⁻⁷⁸ Flexibility is imparted into MOFs via four main structural modes of flexibility. These include breathing, swelling, linker rotation and subnetwork displacement and are typically induced through exposure to external stimuli including gas adsorption and desorption phenomena, temperature, mechanical pressure, and light.⁷⁹⁻⁸⁵ Whilst these more classical modes of flexibility present as ways to impart structural flexibility within MOFs, discovering novel pathways to realise this flexibility is of continuous interest, granting new blueprints in which chemists may go about designing bespoke frameworks for targeted applications.

Ongoing work in our research laboratory has focussed on the properties of Cu(I) metalated MnMOF-1. The diverse coordination geometries exhibited by Cu(I), including 2, 3 and 4, led to postulating interconversion between different coordination geometries may serve as an avenue to control flexibility within a given flexible MOF (MnMOF-1).⁸⁶ Within MnMOF-1, whilst the bis-pyrazole site acts as chelating moiety for Cu(I) centres (3 or 4 coordinate), it would essentially be ‘locked’, but conversion of the Cu(I) centre into a digonal complex (2 coordinate), envisioned as a transformation from two to one N donors from the pyrazoles, would serve as a mean to ‘unlock’ the flexible MOF material.

Consequently, MnMOF-1 was metalated with [CuCl] in MeCN. The resulting crystals were collected, washed with fresh MeCN, and analysed via SCXRD. Analysis of the collected data set displayed disorder at the metalation site. Refinement revealed both an ionic bis-acetonitrile $[\text{Cu}(\text{MeCN})_2]\text{Cl}$ species, and a neutral $[\text{Cu}(\text{MeCN})\text{Cl}]$ species. Quantitative formation of MnMOF-1.CuCl, through desolvation of the Cu centres, was facilitated by washing metalated crystals with non-polar, non-coordinating solvents such as toluene, diethyl ether, or alkanes. Characterisation of the material by SCXRD exhibits a well-defined trigonal planar complex (see Appendix 3.8, Figure 3.A.9).

77 K N_2 gas adsorption isotherms for MnMOF-1.CuCl, activated from pentane at 100°C, were collected (Figure 3.14a). The observed S-type adsorption profile, composed of minimal uptake at low relative pressure before rapidly increasing following the gate-opening event ($P/P_0 = 0.3$), followed by hysteretic desorption, is typical for flexible MOF materials.⁶⁹

Comparatively, the same material activated from different solvents, such as Et₂O, exhibits the same S-type profile, but the gate-opening event is shifted ($P/P_0 = 0.1$) (see Appendix 3.8, Figure 3.A.10). TGA-MS measurements performed on activated samples show characteristic m/z fragments relating to the relevant solvents activated from (see Appendix 3.8, Figure 3.A.11). As such, the shifting relative pressure for the gate-opening event is attributed to solvent which becomes trapped within the pores upon the collapse of the activated material.⁸⁷ Conversely, activation of MnMOF-1.CuCl from Et₂O at room temperature, followed by collection of a 77 K N₂ gas adsorption isotherm (Figure 3.14b), yielded a Type-1 isotherm profile.

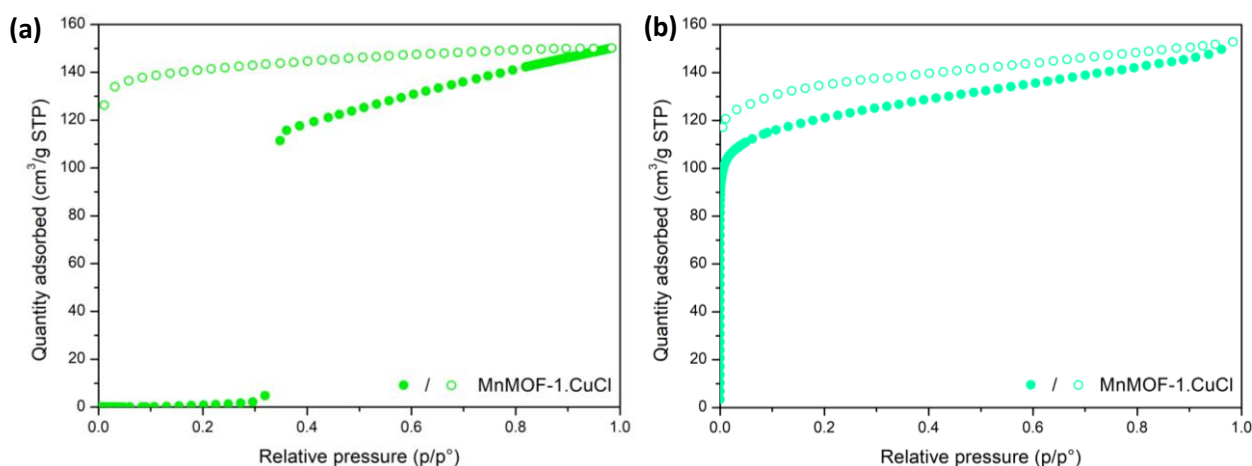


Figure 3.14: 77 K N₂ gas adsorption isotherms of **(a)** MnMOF-1.CuCl (green), activated from pentane at 100°C and **(b)** MnMOF-1.CuCl (aqua), activated from Et₂O at room temperature.

To further investigate the results, DFT calculations were performed on the MnMOF-1.CuCl subunit (see Appendix 3.8, Figure 3.A.12). This revealed the digonal MnMOF-1.CuCl species was slightly energetically preferred over the trigonal planar MnMOF-1.CuCl species. Compared against DFT calculations for the analogous halide species replacing Cl with Br and I, this preference is reversed, and the trigonal planar species is instead energetically favoured (see Appendix 3.8, Figure 3.A.13). To test this, the MnMOF-1.CuBr and MnMOF-1.CuI species were prepared through anion metathesis of MnMOF-1.CuCl in dry methanol using [NaBr] or [NaI] respectively. SXCRD structures were collected for both revealing retention of the coordination environment (see Appendix 3.8, Figure 3.A.14 and 3.A.15). Subsequent 77 K N₂ adsorption isotherms of the two halide analogues, activated from pentane at 100°C, yielded Type-I-like profiles analogous to those of the ‘locked’ metalated MnMOF-1 (see Appendix 3.8, Figure 3.A.16). The identified inflexion shoulders at low relative pressure originates from conformational freedom at the trigonal planar sites.⁶⁵

Further evidence, in the form of single crystal structures, were sought for the activated MnMOF-1.CuCl to investigate the phenomena observed. The collected data set was unable to be fully modelled, owing to positional disorder at the Cu(I) centre. Nevertheless, refinement of the MOF structure exhibited clear adoption of the *anti* conformation at the bis-pyrazolyl site. This result, in consult with the previous findings, strongly suggests a temperature dependent structural transition from the open solvated phase to a closed phase is occurring. This indicates a trigonal planar to digonal coordination geometry switch of the Cu(I) centre, enabling the ‘unlocking’ of the bis-pyrazole unit.

In order to confirm the proposed geometric transition, control materials were sought to identify if they exhibit identical experimental features. The MnMOF-1.CuBr and MnMOF-1.CuI trigonal planar complexes were suitable controls for the ‘locked’ trigonal planar phase, owing to their affinity for the trigonal planar geometry indicated by DFT studies. Critically, however, data corresponding to a complex exhibiting a digonal geometry coordinated to one N donor of the bis-pyrazole moiety was required to truly corroborate the coordination modulated transition. We hypothesized that the MnMOF-1.AuCl could provide invaluable insight into the adsorption profile of a linear complex within MnMOF-1. Not only are Au and Cu both coinage metals, sharing similar properties, the desired geometry, complete with identical ligands coordinated, was a perfect fit. The unique coordination environment of Au(I) within MnMOF-1, driving its investigation into its properties, proved to be pivotal in providing the crucial evidence of the proposed geometric transition of Cu(I). The 77 K N₂ gas adsorption isotherm of MnMOF-1.AuCl, consisting of an identical S-type isotherm profile to that of the ‘unlocked’ MnMOF-1.CuCl, strongly supports the formation of a digonal species. Additionally, activation of MnMOF-1.AuCl from pentane shifts the gate-opening event to a higher relative pressure ($P/P_0 = 0.06$) (see Appendix 3.8, Figure 3.A.17), consistent with activation of MnMOF-1.CuCl from different solvents. In conjunction with the previously discussed results, the evidence provided by the adsorption profile of MnMOF-1.AuCl, and the mutable coordination chemistry offered by Cu(I), strongly supports, through careful activation, the isolation of MnMOF-1.CuCl in both a trigonal planar geometry, exhibiting structural rigidity, and a digonal geometry, exhibiting structural flexibility.

3.5 Summary

In summary, MnMOF-1 was successfully metalated with Au(I) using [AuCl(SMe₂)]. The resulting material was characterised via SCXRD, showing a linear, two coordinate complex, the first example of this coordination geometry in MnMOF-1. The unique properties of the material were studied, discovering retention of the MOFs intrinsic flexibility, afforded by the rotation about the methylene hinge of the bis-pyrazole moiety in the ligand adopting the pillaring position, L'. Unfortunately, the instability of the material, led to inability to promote the trigonal planar geometry of Au(I). Nevertheless, the unique material emerged as a suitable control for expectations to be based off for future linear complexes within MnMOF-1. This has been impeccably exemplified in its critical role in both determining and confirming the coordinational switching from trigonal planar to digonal geometries of MnMOF-1.CuCl through temperature induced switching.

Further investigation into accessing trigonal planar geometries of Au(I) for SCXRD studies, concerned with elucidating the mechanism of Au-catalysed hydrochlorination of acetylene, should proceed. Many avenues present, however, on the basis of the work conducted herein, it is suggested analysis of MOF structures with coordination sites, without the flexibility offered by MnMOF-1, be targeted as an ideal starting point. In addition, research into crystalline supports outside of MOFs should be expanded. This will enable identification of a suitable support to isolate Au(I) in a trigonal planar orientation to promote the difficult oxidative addition step. SCXRD studies of the resulting material, in conditions replicating different steps of the hydrochlorination of acetylene, will enable elucidation of its mechanism, generating unrivalled insight into Au-based catalysts, opening the door for the development of improved catalysts.

3.6 Experimental

3.6.1 Materials and Measurements

Unless otherwise stated, all chemicals were obtained from commercial sources and used as received. Solvents were dried using literature procedures and degassed with Ar prior to use. Specifically, MeCN and DCM were distilled over CaH₂ under N₂; p-xylene and Et₂O were distilled from Na/benzophenone under N₂; MeOH was dried by refluxing over Mg under N₂; acetone was distilled over CaSO₄ under N₂. Powder X-ray diffraction data were collected on a Bruker Advanced D8 diffractometer (capillary stage) using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$, 40 kW/ 40 mA, $2\theta = 2 - 52.94^\circ$, Φ rotation = 20 rotation/min at 1 sec exposure per step, with 5001 steps using 0.3, 0.5 and 0.8 mm glass capillaries). Simulated powder X-ray diffraction patterns were generated from single crystal data using Mercury 4.2.0. Electron dispersive X-ray analysis was collected with an Oxford Instruments Ultim Max 170 EDX attachment on a FEI Quanta 450 FEG environmental scanning electron microscope with a tungsten filament electron source (spot size 3, 20 KeV). Samples for SEM analysis were dry loaded onto adhesive carbon tabs on aluminium stubs and carbon coated (5 nm) prior to analysis. Transmission electron microscopy images were collected using a FEI Tecnai G² Spirit TEM with a LaB₆ filament operating at 120 kV. Images were captured via an in-column Olympus-SIS Veleta CCD camera. Samples for TEM analysis were wet loaded from 70% aqueous EtOH onto copper TEM grids.

3.6.2 Synthetic Methods

3.6.2.1 Bis(4-(4-carboxyphenyl)-1H-3,5-dimethylpyrazolyl)methane (LH₂).

LH₂ was prepared according to a literature procedure.⁸⁹

3.6.2.2 MnMOF-1

MnMOF-1 was prepared according to a literature procedure.⁴⁹

3.6.2.3 General Metalation Conditions of MnMOF-1

Unless otherwise stated, all metalations were conducted following general metalation conditions of MnMOF-1. In a 4 mL vial, a sample of MnMOF-1 in DMF (4 mL) was washed with the respective dry solvent for metalation tests (5x4 mL) under Ar flow. Following each solvent exchange, the solution was degassed with Ar and allowed to soak 1h between washings. If the solvent promoted the *anti* conformation of the bis-pyrazole moiety of MnMOF-1, initial

washing with acetone (5x4 mL) under Ar flow was required. Under Ar flow, the respective Au complex (0.2 mmol) was added, the vial was sealed under Ar, wrapped in aluminium to restrict light exposure, and left for 48 hours at 25°C. The resulting crystals were washed with the respective dry solvent (5x4 mL) under Ar flow to give MnMOF-1.(respective Au complex).

3.6.2.4 $[Au(C_2H_4)](SbF_6)$

$[Au(C_2H_4)](SbF_6)$ was prepared according to a literature procedure with minor alterations.⁶⁰ Dichloromethane (5 mL) saturated with ethylene by bubbling through for 15 minutes was added to AuCl (50 mg, 0.25 mmol) and AgSbF₆ (73 mg, 0.21 mmol). The mixture was stirred for 5 hours under an ethylene atmosphere at room temperature. Ethylene was gently bubbled into the mixture hourly (5x5 min) to maintain an ethylene rich solution. The white precipitate (AgCl) was removed from the clear solution via filtration via a canula with a cotton wool plug and filter-paper into a separate vial with positive Ar pressure, then degassed with Ar and used immediately.

3.6.2.5 MnMOF-1.AuCl

In a 8 mL vial, a sample of MnMOF-1 in DMF (4 mL) was washed with the acetone (5x4 mL) and freshly distilled Et₂O (5x4 mL) under Ar flow. Following each solvent exchange, the solution was degassed with Ar and allowed to soak 1h between washings. Under Ar flow, $[AuCl(SMe_2)]$ (58.9 mg, 0.2 mmol) was added to the 8 mL vial within an open 1 mL glass vial, taking care to ensure all $[AuCl(SMe_2)]$ remained within the 1 mL vial and the solvent level covered the opening of the 1 mL vial (see Appendix 3.8, Figure 3.A.5). The 8 mL vial was sealed under Ar and wrapped in aluminium to restrict light exposure. The 8 mL vial was left for 4 days at 25°C and rotated 90° after every 24 h. The resulting crystals were washed with the freshly distilled Et₂O (5x4 mL) under Ar flow to give MnMOF-1.AuCl.

3.6.2.6 MnMOF-1.AuCl Revised

In a 4 mL vial, a sample of MnMOF-1 in DMF (4 mL) was washed with the acetone (5x4 mL) and freshly distilled Et₂O (5x4 mL) under Ar flow. Following each solvent exchange, the solution was degassed with Ar and allowed to soak 1h between washings. Freshly distilled Et₂O (5 mL) was added to a 20 mL vial with a cellulose filter, stirrer bar and support holding the cellulose filter above the base of the vial, enabling efficient stirring (see Appendix 3.8, Figure 3.A.7) under Ar flow. A sample of MnMOF-1 in dry Et₂O (4 mL) was added to the cellulose filter under Ar flow. $[AuCl(SMe_2)]$ (58.9 mg, 0.2 mmol) was added to the vial, taking

care to ensure all $[\text{AuCl}(\text{SMe}_2)]$ remained outside the cellulose filter under Ar flow. The vial was sealed under Ar, wrapped in aluminium to restrict light exposure, and stirred for 48 hours at 25°C. The resulting crystals were collected and washed with freshly distilled Et_2O (5x4 mL) under Ar flow to give MnMOF-1.AuCl.

3.6.3 Single Crystal X-ray Diffraction Data

Single crystals were mounted in Paratone-N oil on a nylon loop. Single crystal X-ray data were collected at 100(2) K on the MX2 beamline of the Australian Synchrotron using the BluIce software interface, $\lambda = 0.7108 \text{ \AA}$.⁹⁰ Absorption corrections were applied using multiscan methods using XDS, the structures solved using SHELXS, and refined by full-matrix least squares on F^2 by SHELXL, interfaced through the program Olex2.⁹¹⁻⁹⁵ In general, all atoms were refined anisotropically and hydrogen atoms were included as invariants at geometrically estimated positions, unless specified otherwise in additional details in supporting information. The data was treated with the solvent masking feature of Olex2. CIF data have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number CCDC 2100596.

3.6.4 Gas Adsorption Analysis

3.6.4.1 Activation Protocol

In a typical activation procedure, crystals of MnMOF-1.AuCl were loaded wet into sorption analysis tubes from the respective dry solvent under Ar flow, limiting light exposure. The samples were then dried under a vacuum at room temperature for 3 h to yield activated samples.

3.6.4.2 Gas Adsorption Measurements

Gas adsorption isotherms were measured using volumetric methods on a micromeritics 3-Flex analyser (Micromeritics Instrument Corporation, Norcross, GA, USA) at 77 K (using a cryo-cooler circulator). UHP grade (99.999 %) N_2 was used for all measurements.

3.7 References

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3.8 Appendix

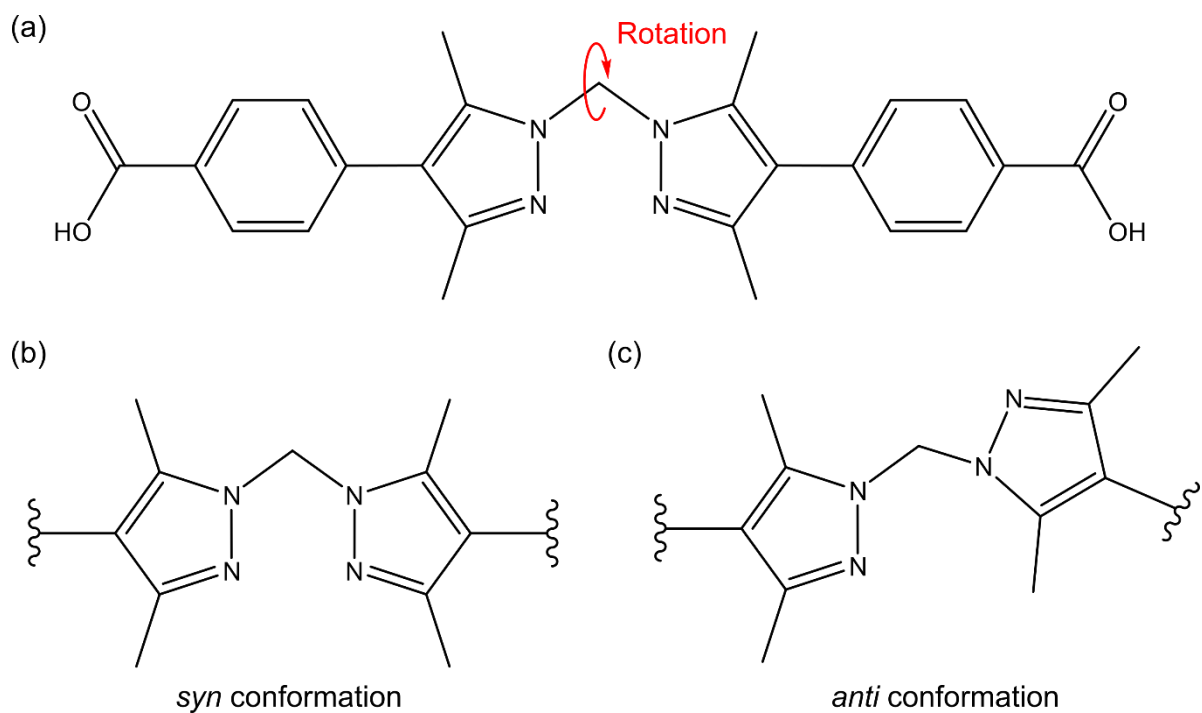


Figure 3.A.1: (a) bis(4-(4-carboxyphenyl)-1H-3,5-dimethylpyrazolyl)methane (LH₂) indicating the inherent flexibility about the methylene hinge allowing access to both the (b) *syn* conformation of the bis-pyrazole moiety and the (c) *anti* conformation of the bis-pyrazole moiety.

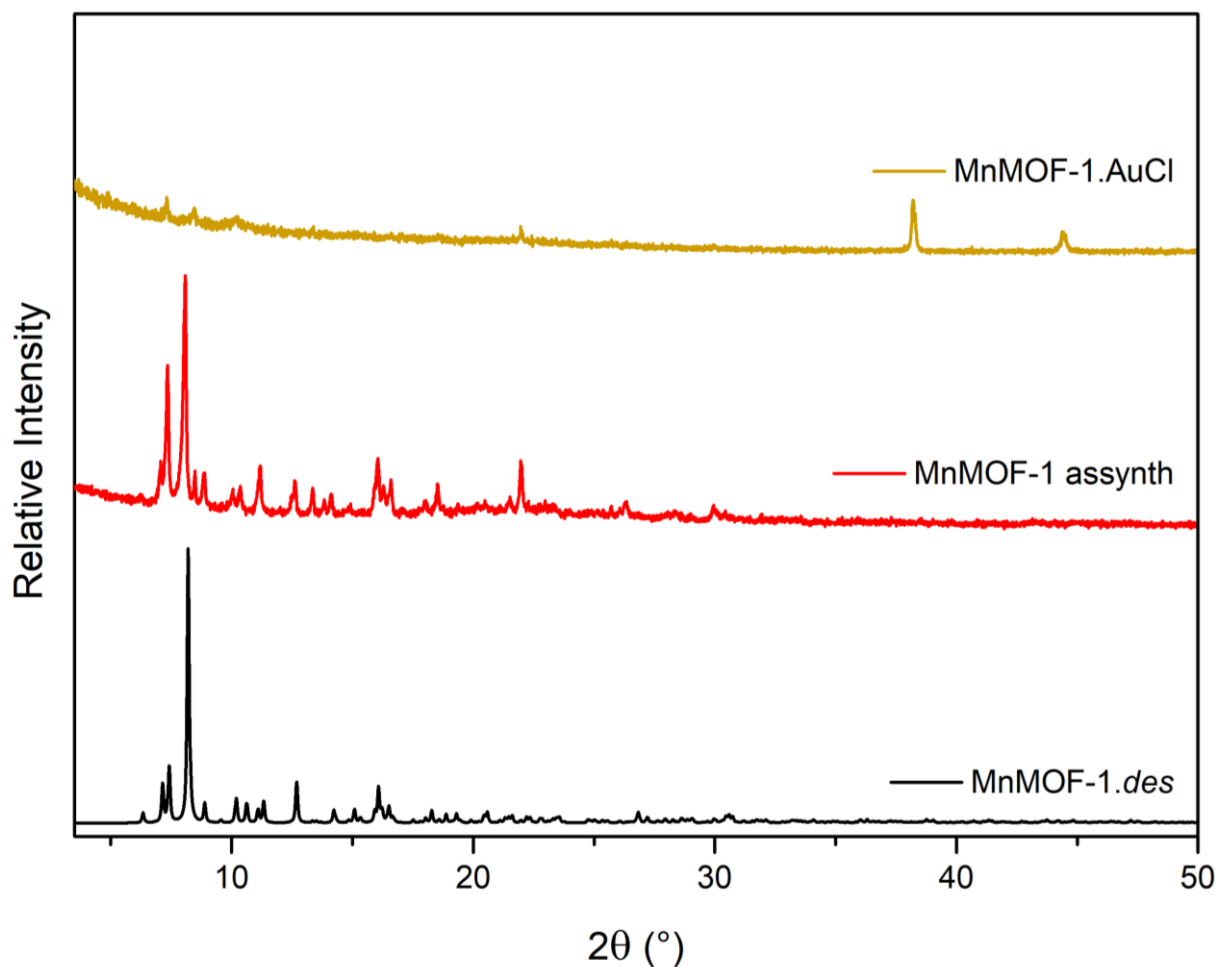


Figure 3.A.2: PXRD patterns of desolvated MnMOF-1 simulated (black), desolvated MnMOF-1 as-synthesised (red) and MnMOF-1.AuCl (dark yellow).

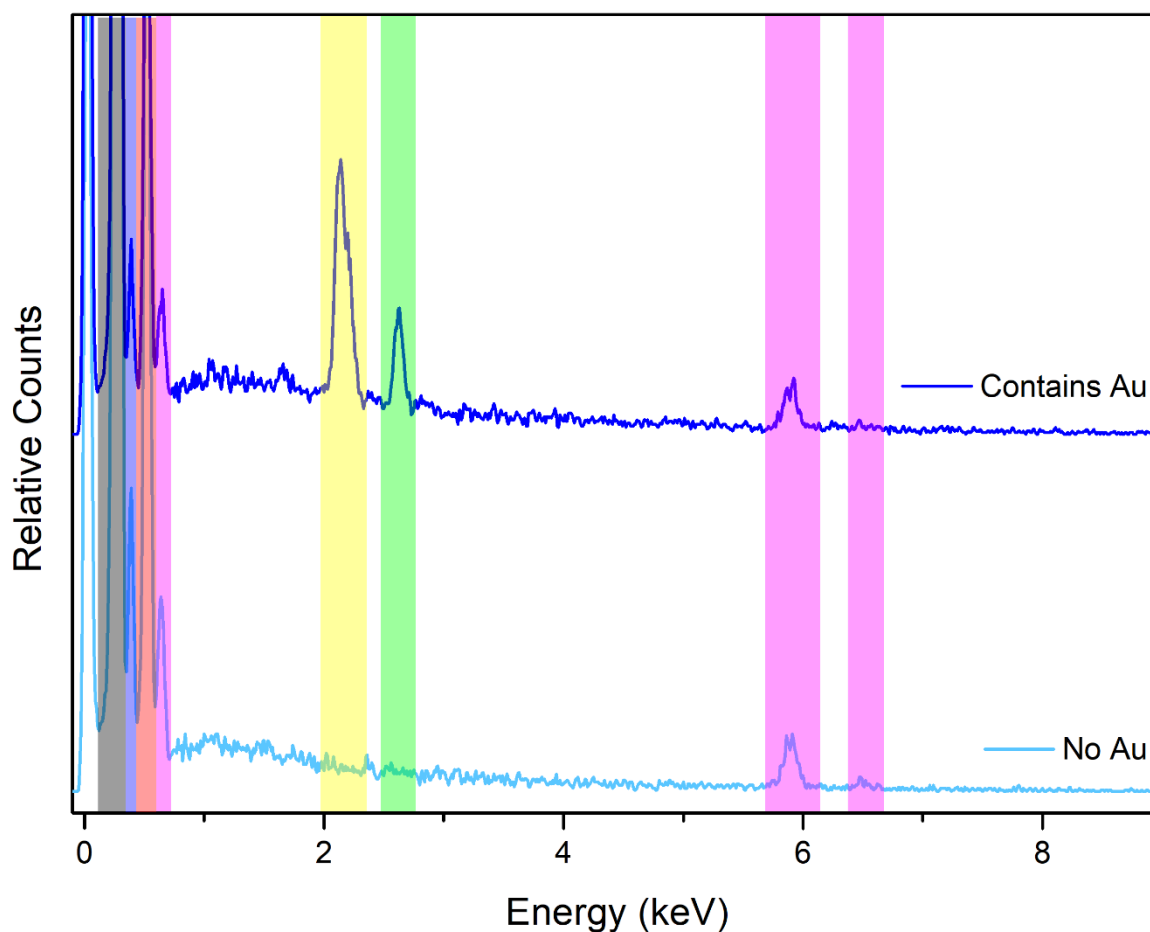
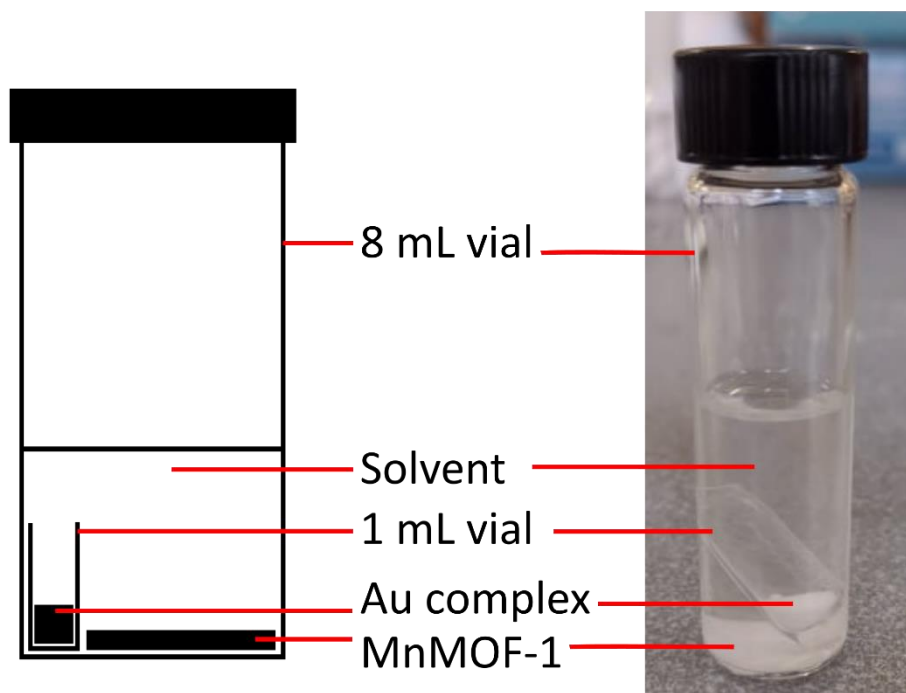


Figure 3.A.3: Representation of EDX spectra for MnMOF-1 metalated with Au from which atomic %, obtained from scanned areas of crystals, can be used to determine metalation %. Both spectra were acquired from crystals of MnMOF-1.AuCl metalated under both unsuccessful (blue) and successful conditions (dark blue). The upper spectra exhibits the expected Au loading, the lower, as observed for the trialled *syn* promoting solvents, exhibits no Au loading. Elemental peaks related to the relevant element (C, grey; N, blue; O, red; Mn, pink; Au, yellow; Cl, green).



Figure 3.A.4: Deposition of metallic Au onto the surface of the vial following metalation of MnMOF-1 with $[\text{AuCl}(\text{SMe}_2)]$ and $[\text{AuCl}(\text{THT})]$ in MeCN.

(a)



(b)



Figure 3.A.5: Metalation of MnMOF-1 with $[\text{AuCl}(\text{SMe}_2)]$, the conditions for which are outlined in experimental 3.6.2.5. **(a)** Schematic representation of the components for the synthesis and **(b)** the position adopted during metalation.

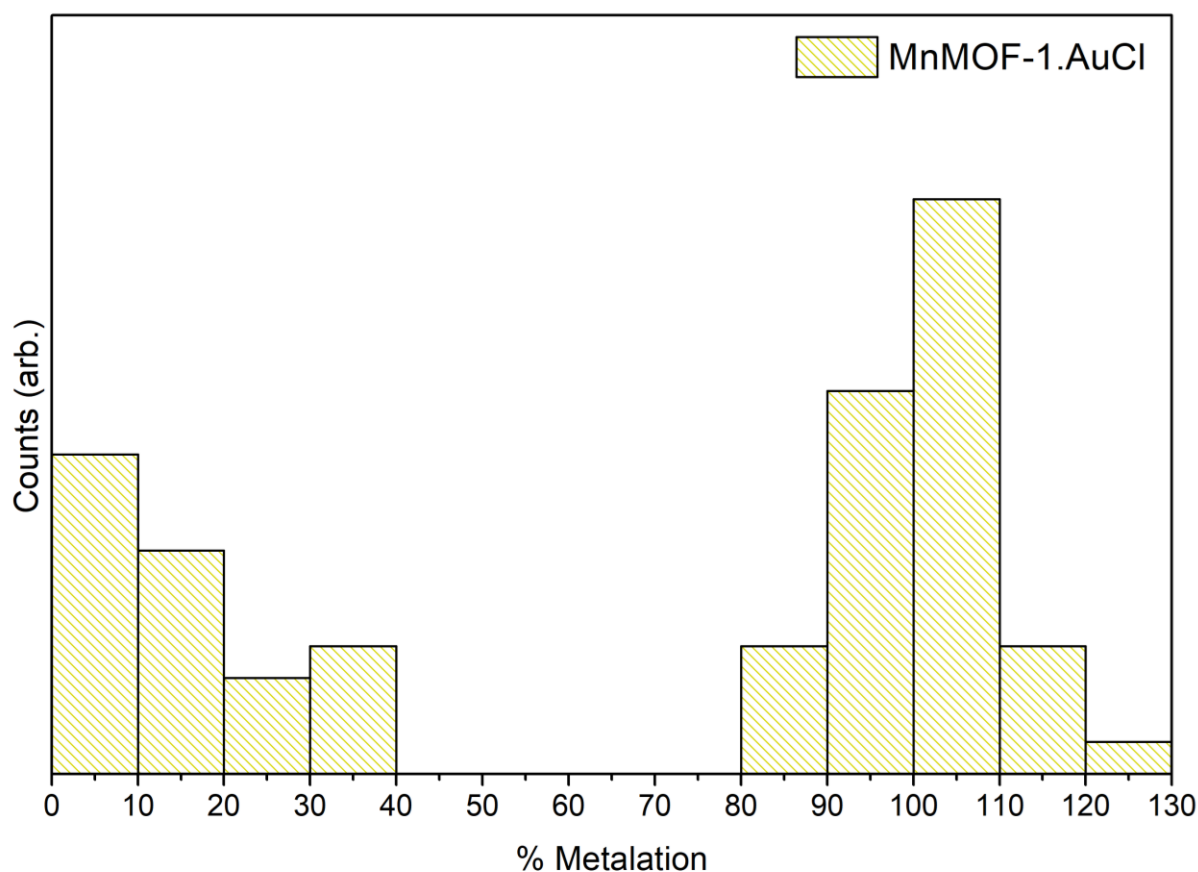


Figure 3.A.6: Au metalation percentages of MnMOF-1 with $[\text{AuCl}(\text{SMe}_2)]$, the conditions for the synthesis are outlined in experimental 3.6.2.5. Metalation percentages were inconsistent, commonly exhibiting metalations below 100%.

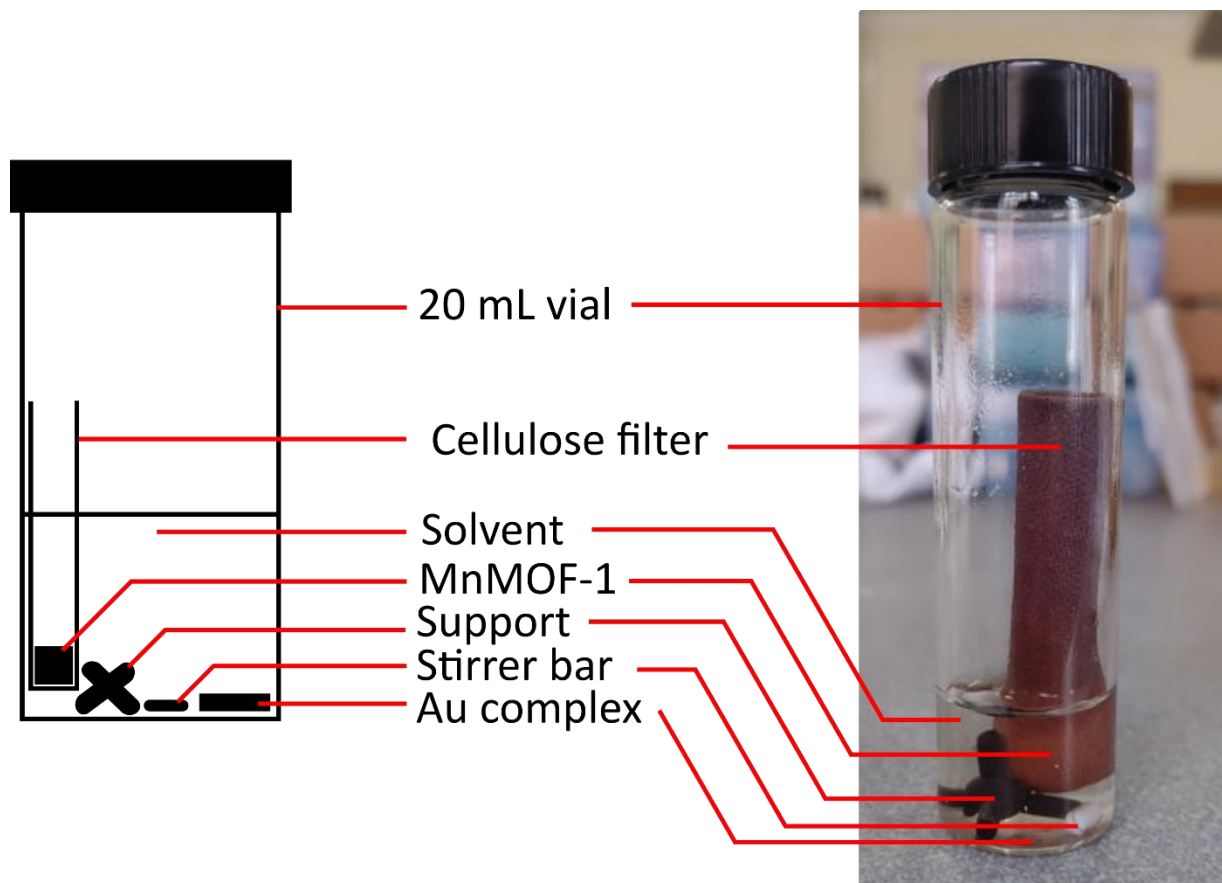


Figure 3.A.7: Revised metalation of MnMOF-1 with $[\text{AuCl}(\text{SMe}_2)]$, the conditions for which are outlined in experimental 3.6.2.6. Schematic representation of the components for the synthesis.

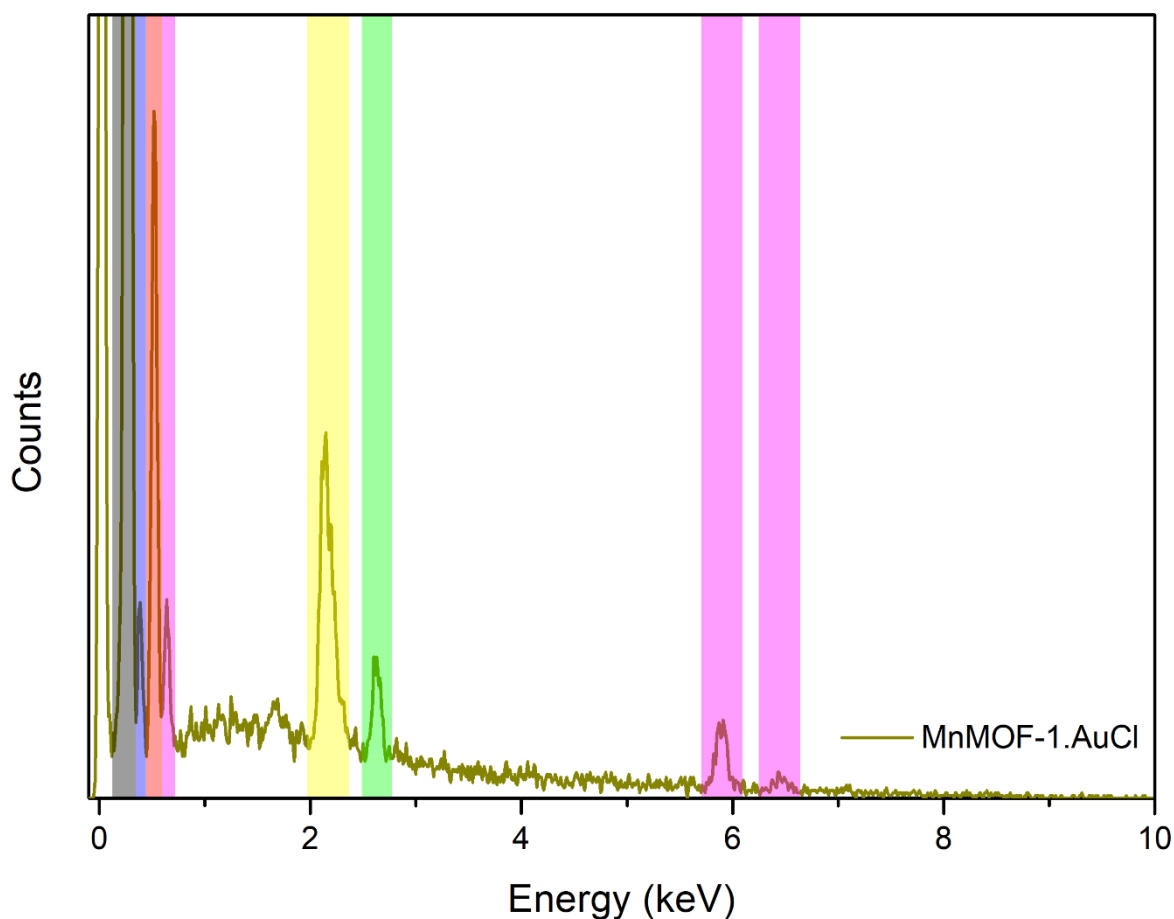


Figure 3.A.8: EDX spectra for MnMOF-1.AuCl, obtained from scanned areas of crystals, used to determine metalation percentages of, on average, 100%. Elemental peaks related to the relevant element (C, grey; N, blue; O, red; Mn, pink; Au, yellow; Cl, green).

Table 3.A.1: Crystallographic data collection and refinement parameters for MnMOF-1.AuCl.

Sample	MnMOF-1.AuCl
Formula	$C_{75}H_{66}Au_{0.65}Cl_{0.65}Mn_3N_{12}O_{12}$
Formula weight (g/mol)	1643.28
Temperature (K)	100(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	13.026(3)
b (Å)	34.629(7)
c (Å)	24.547(5)
α (°)	90
β (°)	95.71(3)
γ (°)	90
Volume (Å³)	11018(4)
Z	4
ρ_{calc} (g/cm³)	0.991
Absorption coefficient (mm⁻¹)	1.262
F(000)	3334.0
Crystal size (mm³)	0.16 x 0.06 x 0.02
Wavelength	Synchrotron ($\lambda = 0.71073$)
2θ range for data collection (°)	2.04 to 64.212
Index ranges	$-18 \leq h \leq 18, -46 \leq k \leq 46, -32 \leq l \leq 32$
Reflections collected	190059
Independent reflections	28690 [$R_{int} = 0.1383, R_{sigma} = 0.0911$]
Data/restraints/parameters	28690/262/946
GOF on F²	1.043
R₁, [$I \geq 2\sigma(I)$]	$R_1 = 0.1194, wR_2 = 0.3392$
wR₂ [all data]	$R_1 = 0.1584, wR_2 = 0.3639$
Largest diff. peak/hole (eÅ⁻³)	1.19/-1.30
CCDC number	2100596

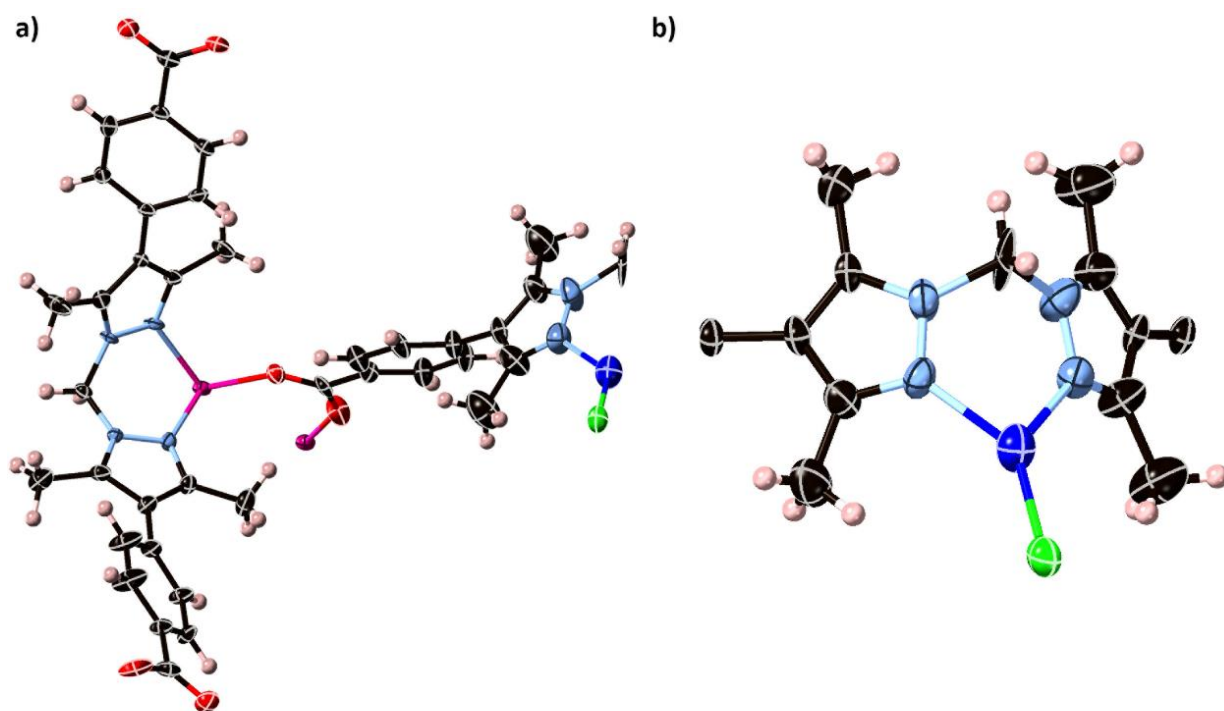


Figure 3.A.9: (a) the asymmetric unit of MnMOF-1.CuCl, toluene solvent molecules have been omitted for clarity and (b) the bis-pyrazole moiety exhibiting the *syn* conformation and its metalation with CuCl adopting a three-coordinate trigonal planar geometry. All non-hydrogen atoms are represented by ellipsoids at the 50% probability level (C, black; H; white; N, light blue; O, red; Mn, pink; Cu, dark blue; Cl, green).

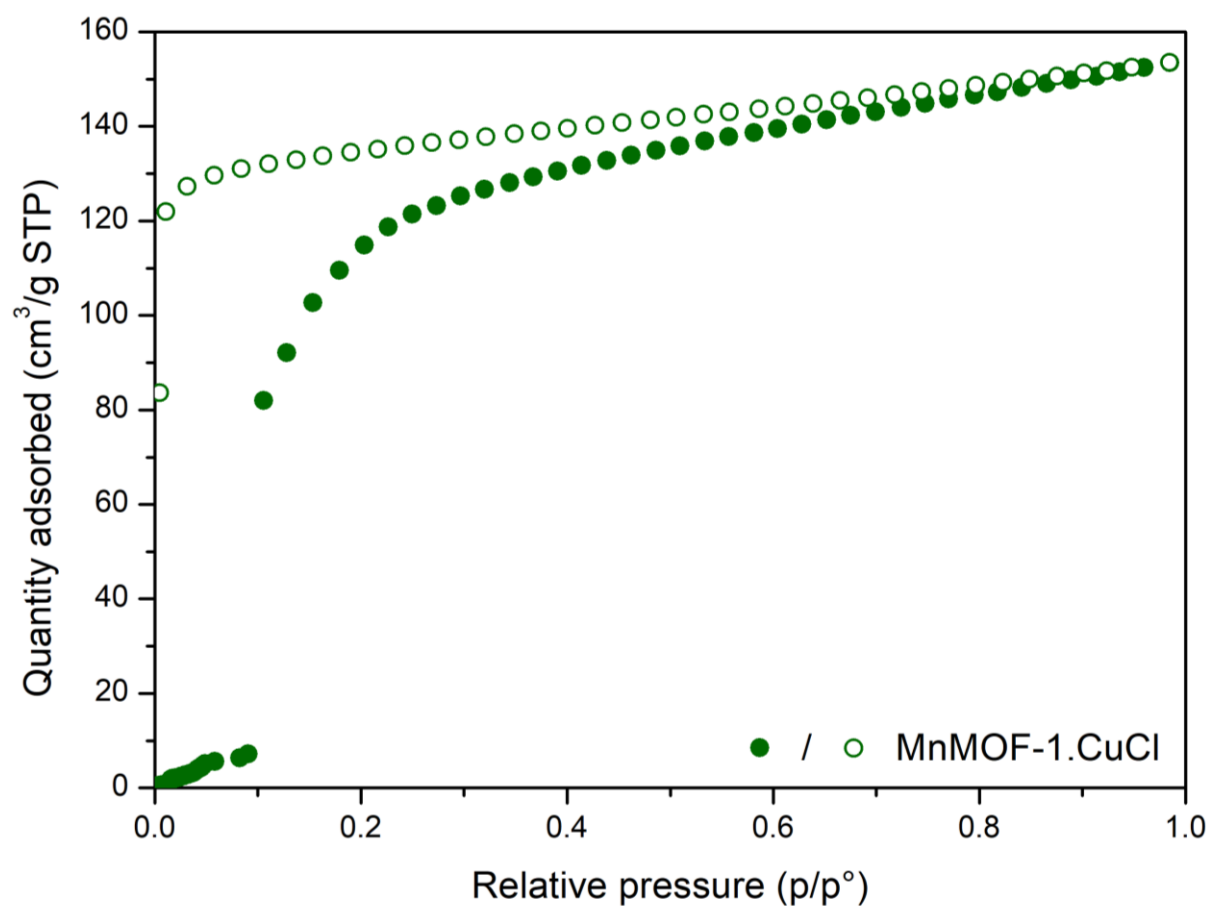


Figure 3.A.10: 77 K N₂ gas adsorption isotherms of MnMOF-1.CuCl, activated from Et₂O at 100°C.

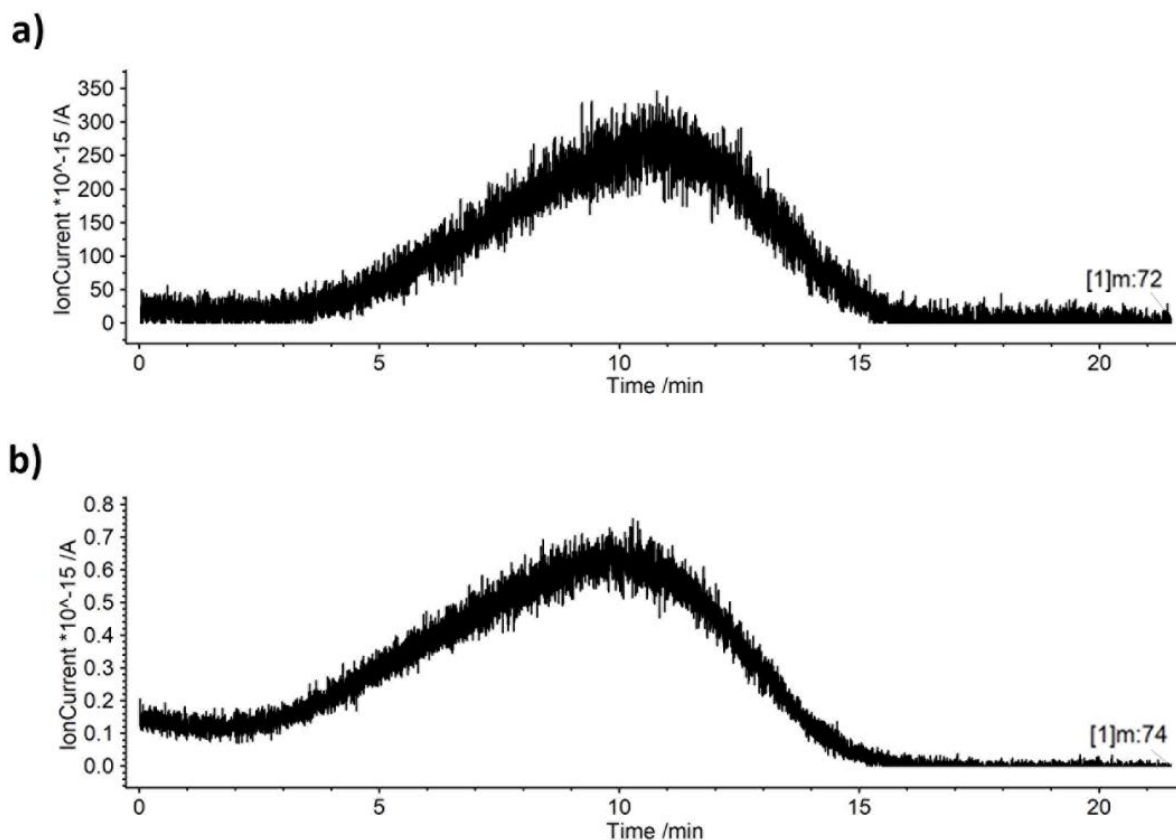


Figure 3.A.11: Mass spectra detection counts of residual trapped solvent molecules during the TGA analysis of activated MnMOF-1.CuCl from **(a)** n-pentane ($m/z_{\text{pentane}} = 72$) and **(b)** diethyl ether ($m/z_{\text{ether}} = 74$). TGA conditions: 45°C – 300°C at 10°C/min under N₂ flow.

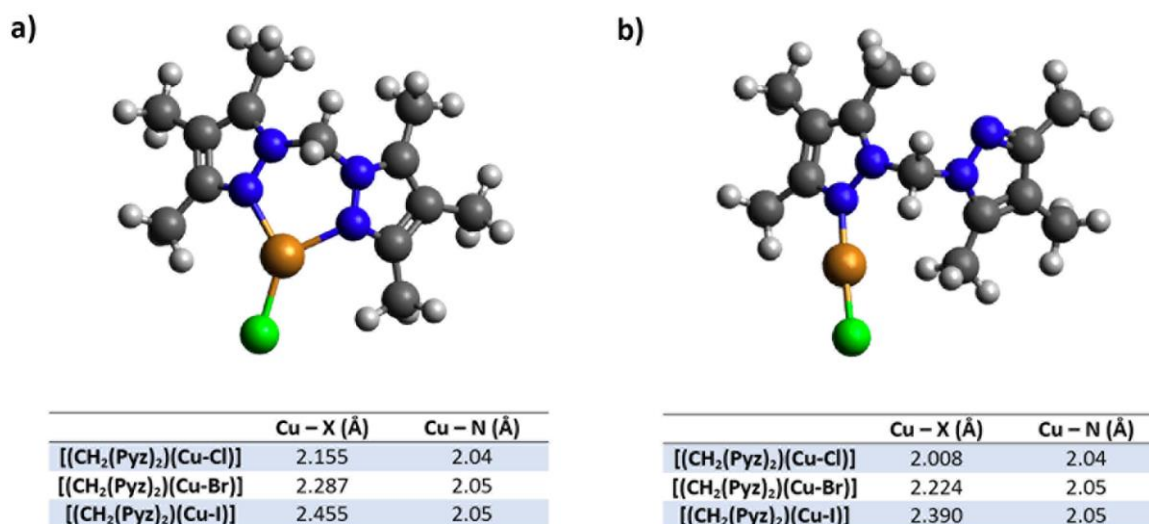


Figure 3.A.12: Theoretical model obtained for the bis-pyrazole – Cu – halide system, with the corresponding Cu-X and Cu-N bond distances for **(a)** trigonal planar *syn* conformation and **(b)** digonal *anti* conformation. Initial conformations were provided from dihedral scans (N-N-N-N) that used the BP86 density functional and efficient coulomb with the chain of spheres exchange algorithms (RIJCOSX).⁹⁶⁻⁹⁸ A combination of the def2-SVP for C, N, H atoms and def2-TZVP for Cu and halogens were applied with the def2/J auxiliary basis set for all atoms.^{99,100} These dihedral scans highlight the relative potential energy of the two and three-coordinate forms of the complexes (C, black; H; white; N, blue; Cu, copper; Cl, green).

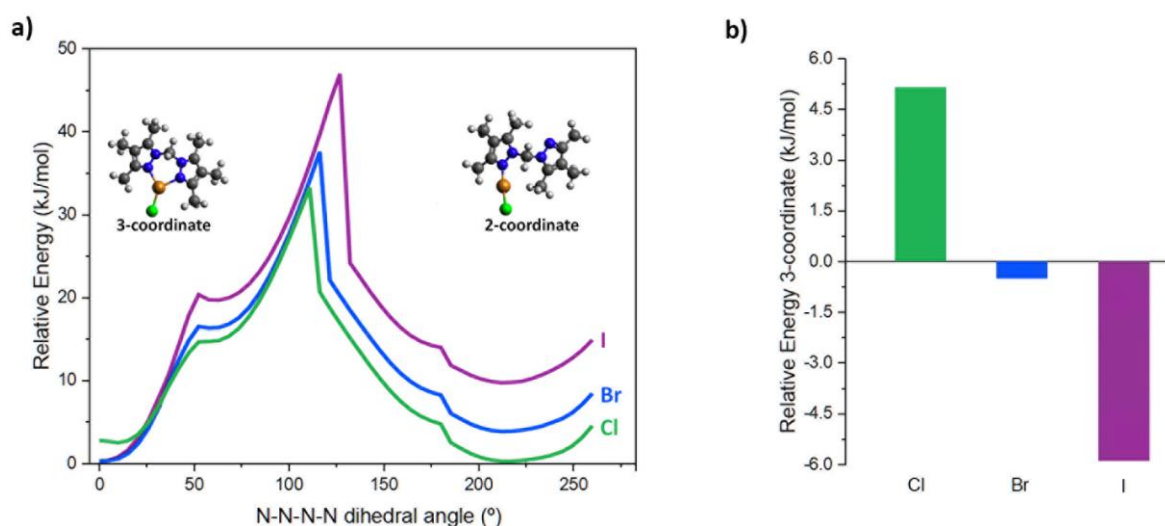


Figure 3.A.13: **(a)** Calculated relative energy levels for the bis-pyrazole – Cu – halide system at different N-N-N-N dihedral angles. **(b)** Relative energy of the 3-coordinate (trigonal planar) conformation versus the 2-coordinate (linear) conformation for each bis-pyrazole – Cu – halide system. The Cu-Cl complex is clearly favouring a linear conformation, unlike the other Cu-X systems.

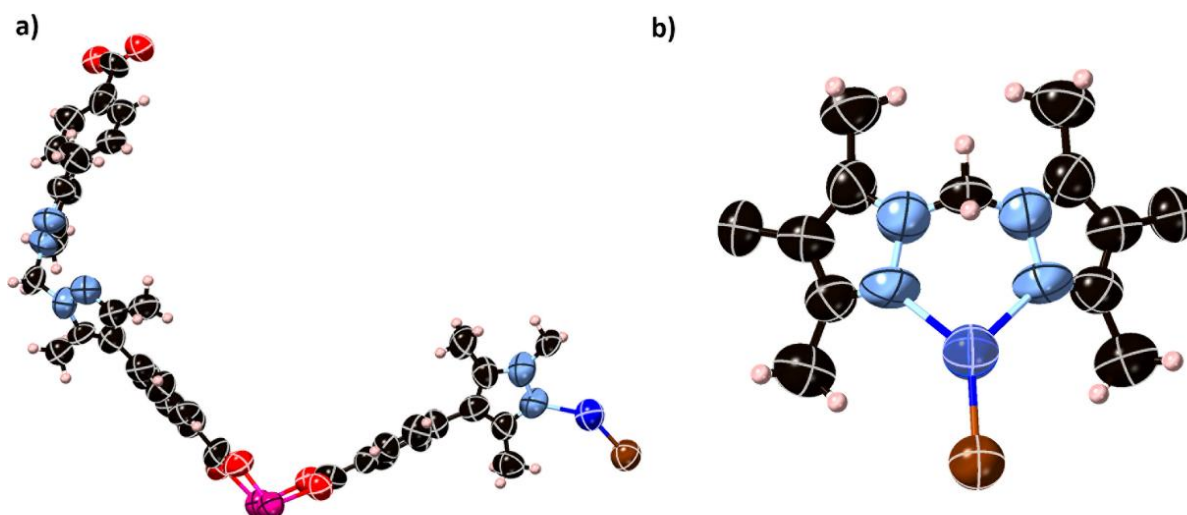


Figure 3.A.14: (a) the asymmetric unit of MnMOF-1.CuBr, cyclohexane solvent molecules have been omitted for clarity and (b) the bis-pyrazole moiety exhibiting the *syn* conformation and its metalation with CuBr adopting a three-coordinate trigonal planar geometry. All non-hydrogen atoms are represented by ellipsoids at the 50% probability level (C, black; H; white; N, light blue; O, red; Mn, pink; Cu, dark blue; Br, brown).

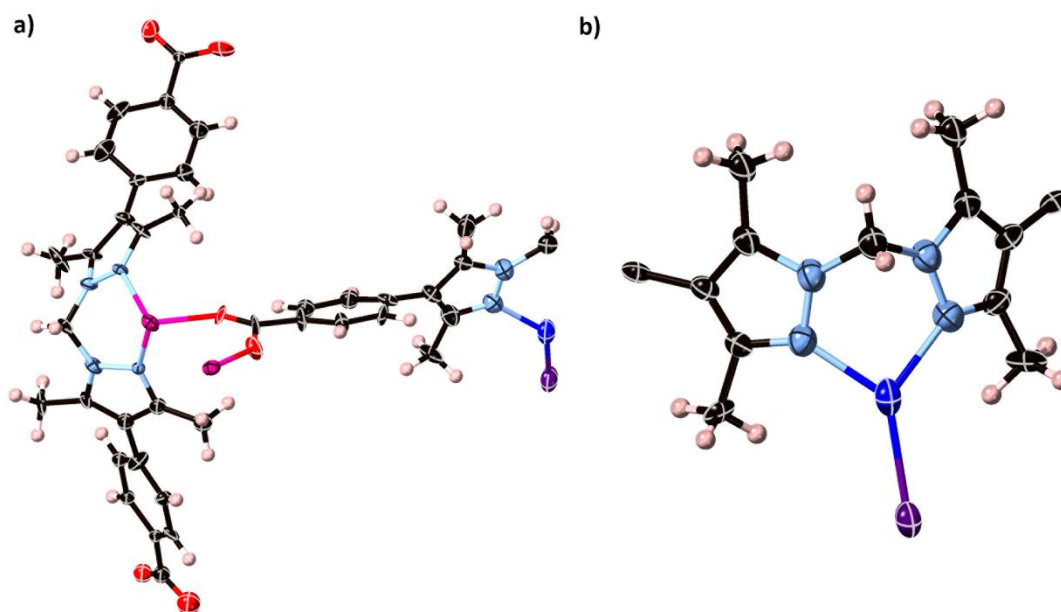


Figure 3.A.15: (a) the asymmetric unit of MnMOF-1.CuI, cyclohexane solvent molecules have been omitted for clarity and (b) the bis-pyrazole moiety exhibiting the *syn* conformation and its metalation with CuI adopting a three-coordinate trigonal planar geometry. All non-hydrogen atoms are represented by ellipsoids at the 50% probability level (C, black; H; white; N, light blue; O, red; Mn, pink; Cu, dark blue; I, purple).

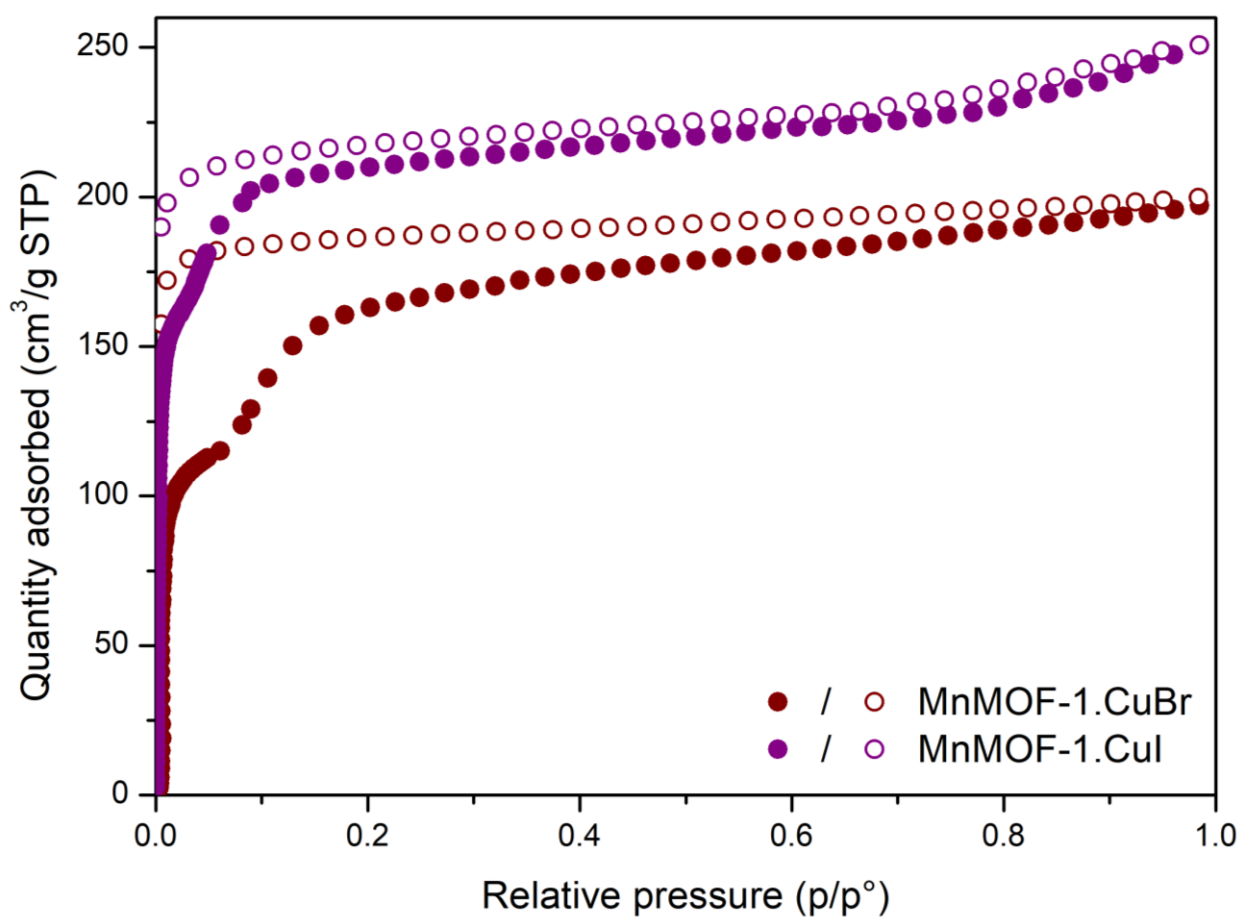


Figure 3.A.16: 77 K N₂ gas adsorption isotherms of MnMOF-1.CuBr, activated from pentane at 100°C (brown) and MnMOF-1.CuI, activated from pentane at 100°C (purple).

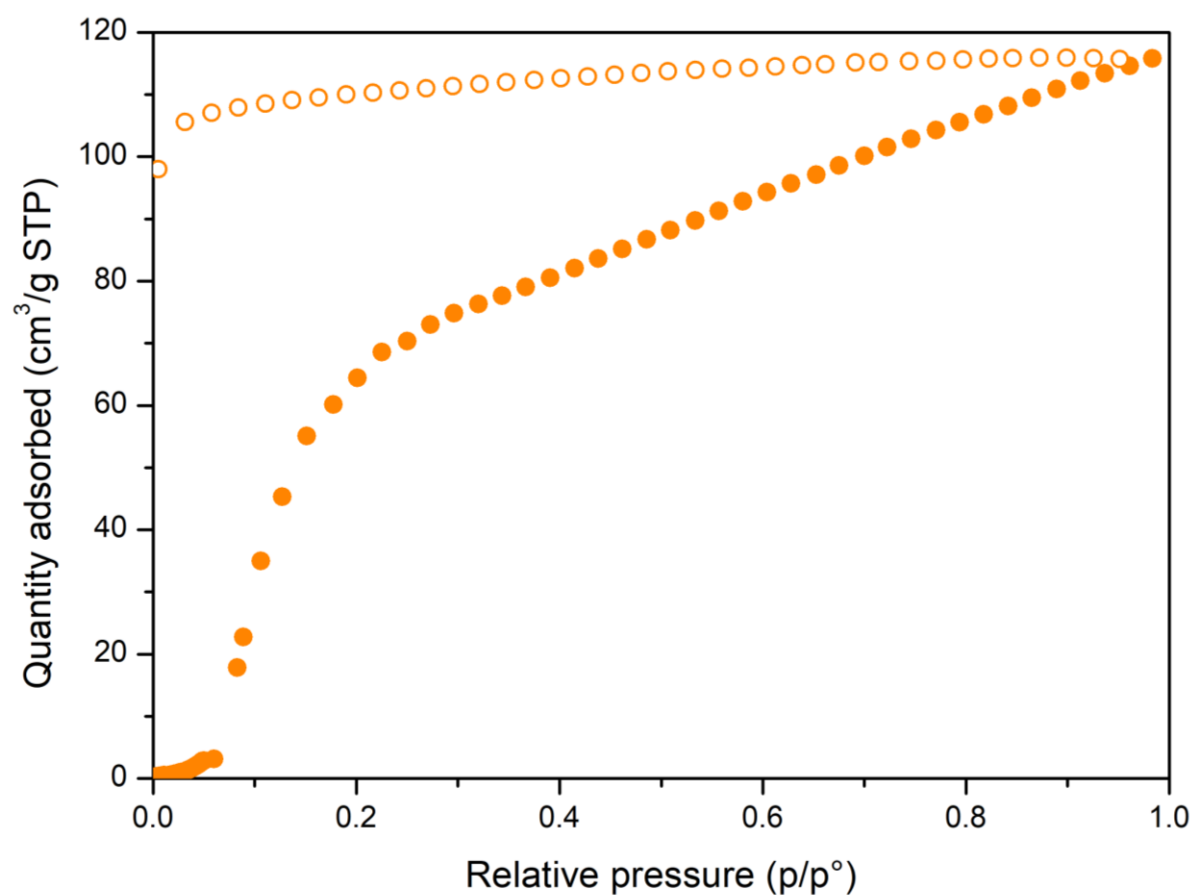


Figure 3.A.17: 77 K N₂ gas adsorption isotherm of MnMOF-1.AuCl, activated from pentane at room temperature.

CHAPTER 4

CONCLUSION

Chapter 4. Conclusion

4.1 Conclusion

Herein, the application of metal-organic frameworks as porous supports for encapsulation of metallic compounds for both fundamental and application-based research has been reported. The intrinsic properties of MOFs have been exploited to showcase the unique materials afforded through these processes, which are otherwise inaccessible via typical means. Two distinct avenues of the post-synthetic modification of MOFs have been studied in detail in this thesis; the post-synthetic metalation of MnMOF-1 with Au(I) and MOF-derived Ru/TiO₂, formed by incipient wetness impregnation for CO₂ methanation. Both areas have the potential to influence within research and hold significance in solving global issues, as discussed in Chapter 1 and the relevant introductions to Chapters 2 and 3.

In Chapter 2, analysis of accessible Ti MOFs was undertaken resulting in the identification and synthesis of two previously reported frameworks, MIP-207 and MUV-10(X), where X is Ca or Ba. MIP-207 is a pure Ti MOF composed of two-dimensional MOF sheets held together through intermolecular H-bonding. Conversely, the MUV-10(X) MOF family are heterometallic Ti-based MOFs with a three-dimensional structure. The differences in properties between the two MOFs provide ideal platforms to investigate and compare the formation of MOF-derived titania-based supports for catalytic studies.

CO₂ methanation is gaining momentum as a future technology holding great promise for CCU; however development of energy efficient processes are required to allow it to become economically viable. Current technologies centre around the use of Ni-based catalysts, but these are prone to degradation due to reaction conditions required for suitable conversions. Relative to Ni, Ru exhibits improved activities with exceptional stability at low catalyst loadings (~1 wt. %) which exhibits excellent low temperature (< 300°C) activity on titania. Recently, MOF derived catalysts have been demonstrated to exhibit enhanced reactivity relative to catalyst of identical composition prepared via conventional means.¹ The intrinsic porosity of MOFs lend themselves to easy Ru loading via IWI. Ru loaded MIP-207 and MUV-10(X) are excellent materials to investigate the formation of MOF-derived catalysts via calcination and under reaction conditions (*in operando*).

Calcined and *in operando* Ru/MIP-207, Ru/MUV-10(Ca) and Ru/MUV-10(Ba) MOF-derived catalysts were prepared and their activities for CO₂ methanation in terms of CO₂ conversion and CH₄ selectivity under batch reaction conditions were investigated. Both

calcined and *in operando* Ru/MIP-207 MOF-derived catalysts deactivated after consecutive cycles due to sintering of Ru on the pure rutile and anatase phases produced under the respective activation conditions. Conversely, calcined and *in operando* Ru/MUV-10(Ca) and Ru/MUV-10(Ba) MOF-derived catalysts exhibited high CO₂ conversions and near 100% CH₄ selectivity for all samples excluding the *in operando* Ru/MUV-10(Ba) derived catalyst. The differences for the Ru/MUV-10(Ba) derived catalysts were attributed to unreacted carbon content remaining within the centre of the partially activated catalyst facilitating the carbon-based by-product formation. Future research into MOF-derived Ru/MUV-10 samples under flow reaction conditions is recommended to build a complete image of the activities. The Ru/MUV-10 MDCs should be compared relative to highly active samples, and characterised post-catalysis to elucidate the behaviours observed, under these more industrially relevant conditions.

Chapter 3 focused on the isolation of a complex of Au(I) within MnMOF-1 formed via post-synthetic metalation at the free bis-pyrazole sites. In recent times, Au has received a resurgence in investigation due to its catalytic properties. Indeed, the digonal relationship it holds with Pd, renowned for its catalytic prowess, is the source of inspiration for investigating Au-based materials in catalysis. Additionally, at the time of writing, the Minamata Convention requires the complete phasing out of all mercury-based materials currently in use in vinyl chloride production facilities by this year, 2022, which is fuelling research into Au-based catalysis. It was discovered in 1985 that Au is one of the most promising candidates for the hydrochlorination of acetylene.² This has fuelled the investigation into Au-based catalysis for the replacement of Hg-based catalyst for the hydrochlorination of acetylene.

Au unfortunately suffers from the so termed ‘redox gold problem’ resulting from the unwillingness of gold to engage in $M^{x/x+2}$ redox processes. This typically hinders the application of Au-based catalysts as the standard electrode potential between Au(I) and Au(III) is relatively high at 1.41 V. One strategy to facilitate the Au(I) → Au(III) transition is through targeting Au(I) complexes with coordination numbers exceeding the typically observed 2. By straining the Au(I)L₂ fragment, the resulting square planar geometry that ensues following oxidative addition is made more accessible due to the imparted preorganisation, and the fragment’s increase in energy. Initially, we envisioned the free bis-pyrazole moiety of MnMOF-1, a chelating bidentate site with small bite angles, as an ideal location to form a trigonal planar Au(I) complex. The inherent crystallinity of the framework would provide an unrivalled platform to investigate the reaction mechanism of the hydrochlorination of acetylene via Au, allowing for the development of improved materials.

Successful metalation of MnMOF-1 was achieved with Au(I) using $[\text{AuCl}(\text{SMe}_2)]$. Despite targeting a trigonal planar Au(I) complex, the inherent flexibility about the methylene hinge of the bis-pyrazole moiety facilitated the post-synthetic metalation in the *anti*-configuration to form a digonal complex. SCXRD revealed the formation of a linear, two coordinate AuCl complex, the first example of this coordination geometry in MnMOF-1. This unique material displayed an adsorption profile consistent with a dynamic MOFs, indicating the retention of the inherent flexibility of MnMOF-1. The material acts as an example for future linear complexes within the framework. Further investigations into accessing trigonal planar geometries of Au(I) for Au-catalysed hydrochlorination of acetylene is recommended. This will fill the current gap in knowledge related to the reaction mechanism, providing invaluable information during catalyst design, leading to enhanced materials moving forward.

Concurrent work occurring in the group has focussed on the integration and analysis of the properties of Cu(I) halide complexes within MnMOF-1.³ The intrinsic porosity offered by MnMOF-1 and the diverse coordination geometries exhibited by Cu(I) led us to postulate interconversion between different coordination geometries may serve as an avenue to control the flexibility of MnMOF-1 through locked (bis-pyrazole moiety metalated at both uncoordinated N centres) and unlocked (bis-pyrazole moiety metalated at one uncoordinated N centres). Interestingly, the CuCl metalated MnMOF-1 displayed a remarkably similar S-type adsorption profile analogous to that of the AuCl metalated MnMOF-1. In this case, the as-synthesised Au metalated MnMOF-1 played a critical role in confirming and determining that the coordination environment switched from trigonal planar to digonal geometries of MnMOF-1.CuCl in response to temperature.

The work in this thesis has explored the application of MOFs as crystalline supports for integration of metallic components via two contrasting strategies. In both instances, unique materials were formed, respectively revealing crucial insights into discovering a novel method of controlling structural flexibility within a MOF and developing highly active Ru/TiO₂ MOF derived catalysts for CO₂ methanation. Opportunity for further exploration and expansion into the different areas exist and are strongly encouraged. Identifying applications for metal coordination controlled flexibility of a MOF may reveal new and novel areas for such materials. Further catalytic testing and refinement of MOF-derived Ru/TiO₂ catalysts could lead to the development of highly active catalysts for CO₂ methanation. On this note, using MOFs as crystalline supports for the integration of metallic components can lead to the development of

unique materials with broad potential and scope for applications, justifying future work into the field

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Coordination modulated on-off switching of flexibility in a metal–organic framework†

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Stimuli-responsive metal–organic frameworks (MOFs) exhibit dynamic, and typically reversible, structural changes upon exposure to external stimuli. This process often induces drastic changes in their adsorption properties. Herein, we present a stimuli-responsive MOF, 1-[CuCl], that shows temperature dependent switching from a rigid to flexible phase. This conversion is associated with a dramatic reversible change in the gas adsorption properties, from Type-I to S-shaped isotherms. The structural transition is facilitated by a novel mechanism that involves both a change in coordination number (3 to 2) and geometry (trigonal planar to linear) of the post-synthetically added Cu(I) ion. This process serves to 'unlock' the framework rigidity imposed by metal chelation of the bis-pyrazolyl groups and realises the intrinsic flexibility of the organic link.

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Introduction

Metal–organic frameworks (MOFs) are a class of network solids that have been widely explored for their potential applications in gas storage^{1–4} and separations.^{5–7} These research efforts have demonstrated that MOFs can exhibit unique, and typically reversible, structural flexibility that can result in dynamic adsorption properties.^{8–12} For example, Fe(bdp) and Co(bdp) (bdp = 1,4-benzenedipyrazolate) show pressure dependent adsorption of methane that is associated with a reversible transition between collapsed and expanded phases.¹³ Another remarkable case is DUT-49, which undergoes a structural transformation that yields a 50% reduction in the unit cell volume resulting in negative gas adsorption.^{10,14}

Structural modes of flexibility observed in MOFs include breathing, swelling, linker rotation and subnetwork displacement.¹⁵ Typically, these processes are triggered by gas adsorption and desorption phenomena^{16–18} but can also be induced by temperature,¹⁹ mechanical pressure,²⁰ and light.^{21,22} Indeed,

such external stimuli have been employed to control the gas adsorption properties of flexible frameworks; examples include molecular sieving of CO₂/N₂ and CO₂/CH₄, which could be realised *via* mechanical pressure in MIL-53,²³ and incorporation of photoswitchable azo-benzene units into the MOF backbone of PCN-123, which is isostructural with MOF-5, to modify its CO₂ adsorption properties.²⁴ Temperature can also drastically affect the structure of flexible MOFs, for example, inducing significant structural expansion and reversible ion capture.^{25,26} These studies highlight that the novel adsorption characteristics of flexible MOFs are determined by the structural origin of flexibility and the type of stimulus. Thus, uncovering new mechanisms that engender reversible phase transitions will expand this area of MOF chemistry and broaden the scope of potential applications.²⁷

Work in our laboratory has shown that a manganese(II)-based MOF, **1** ([Mn₃(L)₂L']), where L = L' = bis(4-carboxyphenyl)-3,5-dimethyl-pyrazol-1-yl)methane, and L' possesses a free N,N' chelating site) can retain crystallinity following post-synthetic metalation and consecutive chemical reactions at the extra-neous metal site.^{28–32} We have shown that this is primarily due to the intrinsic flexibility of the organic linker which alleviates strain on the framework caused by changes in geometry of the chelated metal ion during reactions.³³ A salient example is cobalt(II) metalated **1** which undergoes a reversible, temperature-dependent, conversion between octahedral 1·[Co(H₂O)₄]Cl₂ and tetrahedral 1·[CoCl₂] geometries at the post-synthetic metalation site (Fig. 1).²⁸ These previous observations prompted us to investigate whether coordination chemistry could be exploited as a novel strategy to achieve stimuli-responsive flexibility in **1**. With this in mind, we chose to

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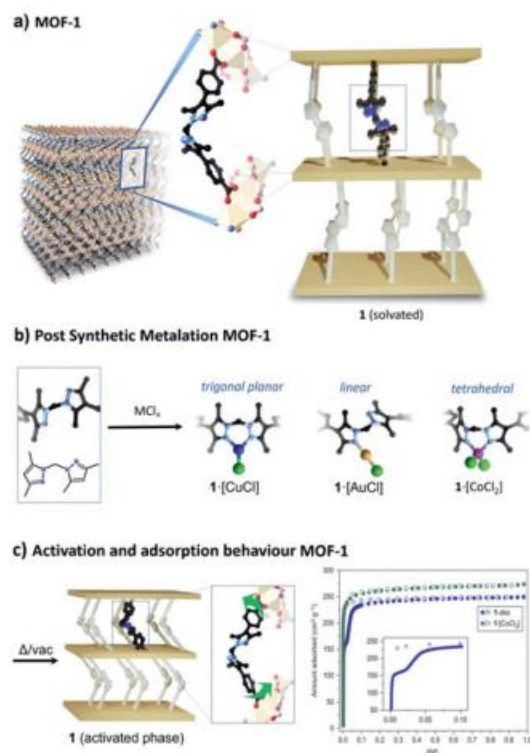


Fig. 1 (a) A key feature of MOF 1 is the flexible organic linker which bridges sheets of Mn(II) trimers; this structural element has been simplified into a schematic representation to aid the reader. (b) Free *N,N'*-chelation sites in 1 readily undergo post-synthetic metalation with transition metal salts and complexes including CuCl, AuCl(dms) (dms = dimethylsulfide) and CoCl₂. (c) To provide some context to the studies reported, we note that activation of MOF 1 leads to contraction of the framework due to the flexibility of the non-metalated bridging linker; this manifests in the 77 K N₂ isotherm in the form of a pronounced inflexion (filled circles represent adsorption and open circles represent desorption data points).²⁶ Notably, the inflexion is absent when the material is metalated with CoCl₂, which imparts rigidity into the bridging linker (C, black; N, pale blue; Cu, orange; Cl, green; Au, yellow; Co, pink).

metalate 1 with Cu(I) as it exhibits diverse low coordinate geometries (e.g. 2 (linear), 3 (trigonal planar) and 4 (tetrahedral) are known)³⁴ that can be interconverted under carefully controlled conditions.^{30,35} In addition, we recently demonstrated that 1 can support both tetrahedral and trigonal planar geometries for Cu(I).³⁰ Thus, we speculated whether a flexible MOF material could be realised by modulating the Cu(I) coordination geometry, *i.e.* switching from a rigid framework (Cu(I) is chelated) to a flexible framework (Cu(I) is monodentate).

Here we report the temperature dependent switching of 1-[CuCl] from a rigid to flexible system. This conversion is associated with a dramatic change in the gas adsorption properties that show Type-I and S-shaped isotherms for the rigid and flexible forms, respectively. The novel mechanism underpinning this structural transformation involves a change in coordination number (3 to 2) and geometry (trigonal planar to

linear) of the post-synthetically added Cu(I) ion which serves to 'unlock' the rigidity imposed by chelation of the bis-pyrazolyl group. Given the tailorable synthesis of MOFs and vast number of coordination complexes that are known, we believe that this work provides general design principles for the synthesis of stimuli-responsive flexible MOF materials.

Results and discussion

1-[CuCl] was synthesised by immersing single crystals of 1 in a solution of CuCl in acetonitrile. Single crystal X-ray diffraction (SCXRD) revealed that the metalated product, 1-[Cu(MeCN)Cl], is a mixture of disordered tetrahedral Cu(I) centres; an ionic bis-acetonitrile [Cu(MeCN)₂]Cl and a neutral [Cu(MeCN)Cl] species.³⁰ Washing the crystals with non-polar solvents (e.g. toluene, diethyl ether, or alkanes) drives the quantitative formation of the non-solvated, trigonal planar species, 1-[CuCl] (Fig. 1). Conversion of the disordered tetrahedral species to a well-defined trigonal planar complex was confirmed by SCXRD data, which revealed a porous framework of $V_{\text{cell}}/Z = 2677.6 \text{ \AA}^3$, with a Cu–Cl bond distance of 2.203(4) Å, commensurate with other literature examples (Fig. S1 and S2†).^{36–38}

We assessed the adsorption properties of 1-[CuCl] by performing 77 K N₂ adsorption isotherms. Sample activation from *n*-pentane at 100 °C gave rise to an adsorption profile that showed negligible N₂ uptake until $P/P_0 = 0.3$ followed by steep uptake of N₂ to a maximum value of 150 cm³ g^{−1} and a hysteric desorption (Fig. 2 and S3a†). The features of this isotherm

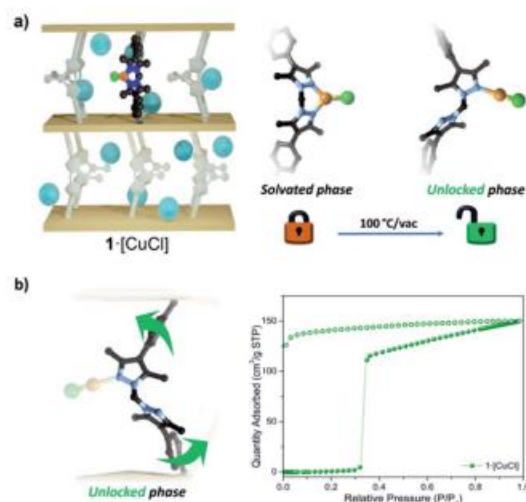


Fig. 2 (a) Schematic representation of the principal processes associated with the activation of 1-[CuCl] under 100 °C per vacuum conditions, that lead to framework contraction due to the formation of a linear, 'unlocked' N–CuCl site which allows the MOF to access the intrinsic flexibility of the organic linker. (b) 77 K N₂ adsorption isotherm of 1-[CuCl]-unlocked after activation under vacuum from *n*-pentane at 100 °C for 90 minutes. A clear gate-opening effect is observed due to the inherent flexibility of the digonal complex, giving the isotherm an S-shaped profile characteristic of flexible frameworks.

are typical for flexible MOF materials where a pressure-induced transition yields an enhancement in accessible surface area.³⁹ In addition, we activated $1 \cdot [\text{CuCl}]$ from different dry solvents, including methanol, acetone, and diethyl ether. Interestingly, although the isotherms obtained from these solvents show an analogous profile, the gate opening pressure is shifted to $P/P_0 = 0.1$ (Fig. S4†). We attribute this phenomena to the presence of residual solvent molecules trapped within the collapsed framework upon activation that can lower the activation energy for phase transitions.⁴⁰ This hypothesis is supported by TGA-MS measurements performed on activated samples of $1 \cdot [\text{CuCl}]$ showing residual solvent (Fig. S5 and S6†). It is noteworthy that dynamic adsorption behaviour is also observed for non-metalated **1**, where a gate-opening event takes place at very low pressure ($P/P_0 = 0.025$) producing an inflexion in the isotherm (Fig. 1c). This step originates from the intrinsic flexibility of the bridging linker which, when not metalated, is free to rotate during activation and, allows for the framework pores to collapse. This process has been previously elucidated from SCXRD data obtained from activated crystals of **1** (Fig. 1).²⁸ The pronounced step observed in the 77 K N_2 isotherm of $1 \cdot [\text{CuCl}]$ suggests that during activation the framework undergoes a structural transition from the open solvated phase to a closed phase. We hypothesised that this transformation is facilitated by a change in coordination geometry around the Cu(i) centre from trigonal planar to digonal, which unlocks the ligand flexibility and triggers the formation of the collapsed, $1 \cdot [\text{CuCl}]$ -unlocked, phase (Fig. 2). We note that Cu(i) complexes are known to readily access a digonal geometry.^{35,41–48} Indeed, density functional theory (DFT) calculations performed on representative molecular subunits reveal that there is a slight energetic preference for the digonal $1 \cdot [\text{CuCl}]$ -unlocked over the trigonal planar $1 \cdot [\text{CuCl}]$ species ($\sim 5 \text{ kJ mol}^{-1}$). However, for the analogous Br and I species, the trigonal planar coordination is thermodynamically favoured (Fig. S7 and S8†). We examined $1 \cdot [\text{CuCl}]$ via Raman spectroscopy to ascertain if there are structural differences between as-synthesised and $1 \cdot [\text{CuCl}]$ -unlocked. The spectra show clear and non-reversible changes, suggesting that a different, thermodynamically-favoured Cu(i) geometry is formed during thermal activation, and is retained throughout the subsequent isotherm (Fig. S9 and S10†). To gain further insight into the $1 \cdot [\text{CuCl}]$ -unlocked phase we performed SCXRD experiments using a synchrotron X-ray source. The resulting diffraction data was solved in the space group $P\bar{1}$ with a unit cell volume per formula unit (V_{cell}/Z) of $2148.5 \text{ \AA}^3$ (20% volume decrease from $1 \cdot [\text{CuCl}]$). This volume is notably similar to those obtained from the structure of, non-metalated, **1** ($V_{\text{cell}}/Z = 2174.7 \text{ \AA}^3$).²⁸ Refinement of the structure showed that the bis-pyrazolyl sites of the bridging linker clearly adopt an 'anti' configuration which is consistent with the hypotheses that the closed phase is digonal. However, due to positional disorder, we were unable to resolve the coordination environment of the Cu(i) centre (Fig. S11 and S12†). Nonetheless, based on the collapsed structure observed, the coordinated $[\text{Cu}-\text{Cl}]$ would be in close proximity to neighbouring framework atoms and such interactions would stabilise the closed structure, consistent with the higher gate-opening pressure observed compared to

non-metalated **1**. To confirm that Cu(i) is retained in the conversion from $1 \cdot [\text{CuCl}]$ to $1 \cdot [\text{CuCl}]$ -unlocked we carried out energy-dispersive X-ray spectroscopy (EDX). The resulting data afforded the expected ratio Mn : Cu : Cl ratio of 3 : 1 : 1 (Table S1†). Furthermore, we examined samples of the $1 \cdot [\text{CuCl}]$ -unlocked via transmission electron microscopy (TEM) and found no evidence that the Cu(i) ions had migrated from the coordinating linker to form nanoparticles (Fig. S14†).

Next, we compared the 77 K N_2 adsorption profile of $1 \cdot [\text{CuCl}]$ -unlocked to two sets of control samples: (i) a bonafide digonal complex $1 \cdot [\text{AuCl}]$; and (ii) $1 \cdot [\text{CuBr}]$ and $1 \cdot [\text{CuI}]$ that, according to previously discussed DFT simulations, show a thermodynamic preference for the trigonal planar geometry (Fig. S7 and S8†). $1 \cdot [\text{AuCl}]$ was synthesised by metalating **1** with $[\text{AuCl}(\text{dms})]$ (dms = dimethylsulfide) in diethyl ether, a solvent known to favour the 'anti' conformation at the N,N' -coordination site.³³ SCXRD analysis revealed a linear AuCl complex coordinated to a single N -donor site in **1** (Fig. 1, Fig. S15 and S16†), and EDX analysis of the crystals (Table S2 and Fig. S17†)

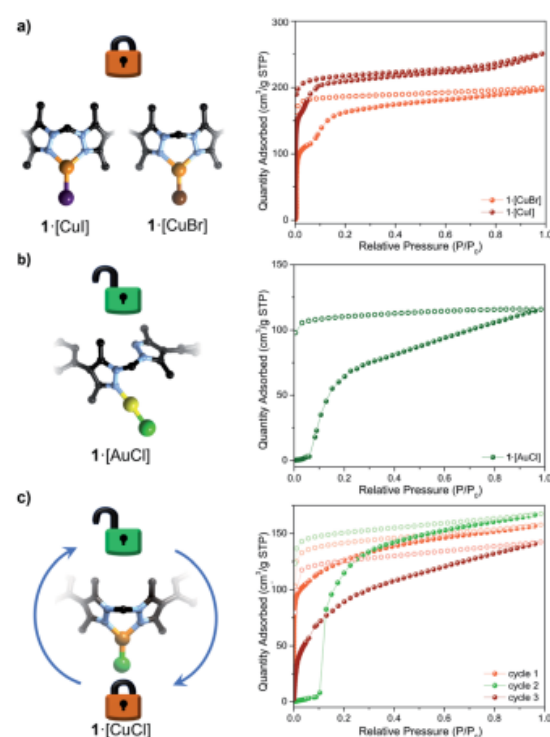


Fig. 3 (a) 77 K N_2 adsorption isotherm of $1 \cdot [\text{CuBr}]$ (orange) and $1 \cdot [\text{CuI}]$ (dark red) under 100°C /vacuum activation conditions, that maintain their trigonal planar conformation and act as 'permanently-locked' control samples. (b) 77 K N_2 adsorption isotherm of the 'permanently-unlocked' $1 \cdot [\text{AuCl}]$ sample activated at room temperature, which allows the MOF to access the intrinsic flexibility of the organic linker. (c) 77 K N_2 3-cycle adsorption isotherm of $1 \cdot [\text{CuCl}]$ after activation under mild conditions, then heated at 100°C for 90 minutes, and finally resoluted and reactivated under mild conditions. A clear gate-opening effect is observed after heating, giving the isotherm an S-shaped profile characteristic of flexible frameworks.

confirmed the expected Mn : Au : Cl ratio of 3 : 1 : 1. Samples of $1\cdot[\text{AuCl}]$ were activated at room temperature from diethyl ether and *n*-pentane prior to performing a N_2 77 K adsorption isotherm. The S-type adsorption profile of $1\cdot[\text{AuCl}]$ (Fig. 3b and S18†) was analogous to that of $1\cdot[\text{CuCl}]$ -unlocked, showing a gate-opening step at $P/P_0 = 0.1$. This data suggests that the adsorption behaviour of $1\cdot[\text{CuCl}]$ -unlocked is consistent with a digonal $1\cdot[\text{CuCl}]$ species.

Metalation of **1** with CuBr and CuI directly yielded structurally ill-defined multinuclear species within the MOF. To overcome this issue, we employed anion metathesis of $1\cdot[\text{CuCl}]$ with NaBr or NaI in dry methanol for 24 and 48 hours, respectively.^{29,30} In both cases, EDX analysis of the crystals indicated that quantitative halide exchange had occurred (see Mn : Cu : X 3 : 1 : 1 ratios; X = Br, I; Table S3 and Fig. S20†). Single crystal quality for the bromide and iodide exchanged MOFs was excellent, permitting their examination by SCXRD. In both instances, a trigonal planar Cu(I)-halide complex was observed (Fig. 3), with Cu–X bond lengths of 2.268(3) and 2.455(6) Å for the bromide and iodide derivatives, respectively (Fig. S21–S24†). We note that trigonal planar halide complexes of Cu(I) are rare,⁴⁹ and these results present an unusual example in which three halide species are accessible *via* simple solvent and anion exchange chemistry within a MOF matrix. 77 K N_2 isotherms were collected on samples of $1\cdot[\text{CuBr}]$ and $1\cdot[\text{CuI}]$ under the same activation conditions employed for $1\cdot[\text{CuCl}]$ -unlocked. $1\cdot[\text{CuBr}]$ and $1\cdot[\text{CuI}]$ exhibit Type-I-like profiles that are consistent with a 'locked' trigonal planar conformer ($S_{\text{BET}} = 492 \text{ m}^2 \text{ g}^{-1}$ for $1\cdot[\text{CuBr}]$, $727 \text{ m}^2 \text{ g}^{-1}$ for $1\cdot[\text{CuI}]$, Fig. 3a, S25 and S26†). Both isotherms display an inflexion shoulder after the microporous region attributed to conformational freedom at the trigonal planar sites.⁵⁰ The combined structural and gas adsorption data (*vide supra*) of the control samples suggests that in the activated phase Cu(I) adopts a linear conformation subsequent to thermal activation and that the gate-opening phenomena is due to the underlying flexibility of organic link coordinating in a monodentate fashion.

Two sought after properties of flexible MOF materials are reversible gas adsorption and on/off porosity switching.^{18,51,52} Thus, we investigated if the activated phases $1\cdot[\text{CuCl}]$ -locked

(trigonal planar) and $1\cdot[\text{CuCl}]$ -unlocked (digonal) could be accessed independently, and if the transition from a rigid to flexible phase could be triggered *in situ* by an external stimulus (Fig. 4). Given that DFT studies indicate a low energy barrier for the conversion of trigonal planar $1\cdot[\text{CuCl}]$ to a digonal $1\cdot[\text{CuCl}]$, we thought that mild activation conditions may allow for $1\cdot[\text{CuCl}]$ -locked to be isolated, and its gas adsorption properties examined. Samples of $1\cdot[\text{CuCl}]$ activated at room temperature from either diethyl ether or *via* supercritical CO_2 were assessed by 77 K N_2 gas adsorption isotherms (Fig. S28†). In both instances, the isotherm profiles were Type-I S_{BET} surface area values of $565 \text{ m}^2 \text{ g}^{-1}$ (ether activation) and $441 \text{ m}^2 \text{ g}^{-1}$ (scCO_2 activation), and show an analogous shoulder to the trigonal planar $1\cdot[\text{CuI}]$ and $1\cdot[\text{CuBr}]$ species, albeit less pronounced. Remarkably, following activation, the crystals remained in excellent condition allowing for their structures to be determined using SCXRD. Analysis of the diffraction data afforded the expected trigonal planar geometry for the Cu(I) ion, with no crystallographically defined solvent molecules within the MOF pores (Fig. S30 and S31†). Next, we explored the potential switching from the open to the closed phase of the MOF *in situ*. After collecting an isotherm on the open phase, the sample was heated at 100°C for 90 min. A second 77 K N_2 isotherm was then carried out on the heated sample, showing a drastic change in the isotherm profile; from Type-I to the S-type profile characteristic of $1\cdot[\text{CuCl}]$ -unlocked (Fig. 3c). Lastly, this same sample of $1\cdot[\text{CuCl}]$ -unlocked was re-solvated *via* immersion of the material in dry MeCN. This process led to the recovery of the initial tetrahedral complex, $1\cdot[\text{Cu}(\text{MeCN})\text{Cl}]$ (referred hereafter as $1\cdot[\text{CuCl}]$ -resolv for clarity, Fig. S32 and S33†). This sample was activated, either after washing with diethyl ether at room temperature or supercritical CO_2 , and a third N_2 isotherm was performed at 77 K after recovering the trigonal planar conformation. As expected, a non-gated adsorption profile was observed again for both samples, although slightly reduced S_{BET} values were recorded ($S_{\text{BET}} = 292 \text{ m}^2 \text{ g}^{-1}$ (ether), $264 \text{ m}^2 \text{ g}^{-1}$ (scCO_2); Fig. 3c and S32†). We attribute this reduction of surface area and total uptake values to slight structural degradation upon the three solvent-exchange-activation-isotherm measurement cycles.

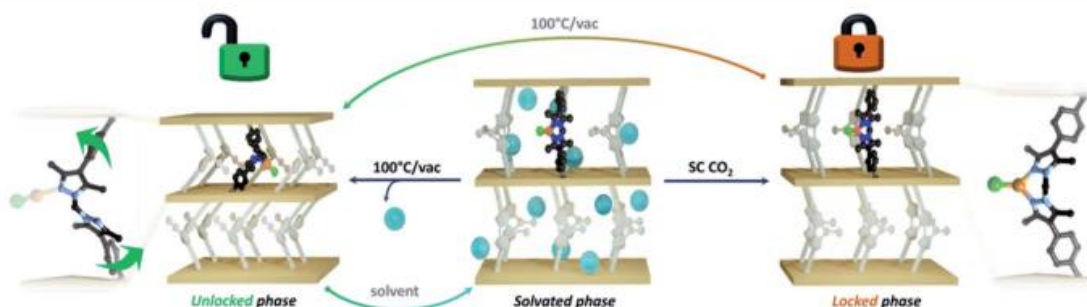


Fig. 4 Schematic representation of the principal processes associated with the activation of $1\cdot[\text{CuCl}]$ under mild (SC CO_2) and harsh (100°C per vacuum) conditions. Mild conditions lead to an open 'locked' framework with trigonal planar geometry retained at the N,N' -CuCl sites while harsher conditions lead to framework contraction due to the formation of a linear, 'unlocked' N -CuCl site which allows the MOF to access the intrinsic flexibility of the organic linker in a reversible fashion.

Conclusions

In summary, we have uncovered a new mechanism for realising structural flexibility in MOFs that allows for control of the bulk material adsorption properties. Due to the mutable coordination chemistry of Cu(I), $1\cdot[\text{CuCl}]$ can be isolated as a rigid, trigonal planar $1\cdot[\text{CuCl}]$ -locked, or flexible, digonal $1\cdot[\text{CuCl}]$ -unlocked species by careful choice of activation conditions. These materials engender distinct gas adsorption characteristics; $1\cdot[\text{CuCl}]$ -locked affords a Type-I isotherm typical of a rigid microporous material while $1\cdot[\text{CuCl}]$ -unlocked yields an S-shaped isotherm profile that is characteristic of flexible MOFs. Furthermore, heating samples of $1\cdot[\text{CuCl}]$ -locked triggers a structural transition to $1\cdot[\text{CuCl}]$ -unlocked, providing a simple approach to stimuli-induced on-off porosity switching. Likewise, re-solvating $1\cdot[\text{CuCl}]$ -unlocked recovers the initial complex, and consequently, the rigidity of the material. Throughout these phase transitions crystallinity was retained, permitting structural elucidation of each step via SCXRD, and thus providing deep insight into the mechanism underlying these transformations. We believe that coordination-modulated flexibility could be employed to design new MOF materials that are composed of intrinsically flexible linkers that can coordinate transition metals. In addition, such materials could show desirable performance characteristics for application to areas such as molecular sensing.

Experimental section

Materials and methods

All reagents were obtained from commercial sources and used without further purification. Unless otherwise stated, all reactions and sample handling were performed under an argon atmosphere using standard Schlenk techniques. Solvents were dried and distilled using literature procedures and degassed with Ar prior to use. Specifically, acetonitrile (MeCN) was dried from CaH_2 under N_2 ; methanol was dried by refluxing over Mg beads under N_2 followed by distillation and storage over 4 Å molecular sieves; acetone was dried and distilled from CaSO_4 under N_2 ; and pentane, cyclohexane, toluene and diethyl ether were dried over Na/benzophenone. NaBr and NaI used for anion exchange were stored in a 120 °C drying oven. $1\cdot[\text{AuCl}]$ is light-sensitive and must be handled and stored accordingly.

Characterisation

SEM imaging and Energy-Dispersive X-ray (EDX) spectroscopy data were collected using a Philips XL30 field-emission scanning electron microscope (FESEM) operating at 20.00 kV. TEM images were collected on a FEI Tecnai G2 Spirit microscope. The samples were sonicated in dry methanol for 20 minutes to ensure a good delamination of the crystals and improve the overall dispersibility. Thermogravimetric analysis (TGA) of activated $1\cdot[\text{CuCl}]$ -unlocked from diethyl ether and *n*-pentane were collected on a Netzsch STA449 F3 Jupiter + QMS403 Aeolos® Quadro thermogravimetric analyser, coupled to

a Mass-Spectrometry detector fixed at MW = 72 (pentane) and 74 (diethyl ether).

Raman spectroscopy

Raman spectrum was collected using an alpha300 RS from WITec with activated sample sealed in a glove box under N_2 atmosphere. The excitation wavelength was 532 nm, integration time was 120 s with 4 times of accumulations, the grating is G3 1200 g mm^{-1} (BLZ = 500 nm). Two equivalent batches of as-synthesised $1\cdot[\text{CuCl}]$ were transferred to two different Raman sample cells (see Fig. S9†) within a glove box. The former (Cell#1) was left undisturbed, while the latter (Cell#2) was activated under temperature and vacuum for 8 hours to ensure a complete conformational change. The Raman spectra of both cells were then collected before running an *in situ* N_2 adsorption isotherm at 77 K on the activated sample. A final Raman spectrum, post-isotherm, was then collected to spot any potential conformational change during the desorption step.

Gas sorption measurements

Gas adsorption isotherms (77 K N_2 , 195 K CO_2) were measured on a Micromeritics 3-flex Surface Area Analyser, and on an ASAP 2020 Surface Area and Pore Size Analyser. Unless otherwise specified, wet crystals of **1** were loaded under argon to the adsorption cell, and the final mass was corrected after the isotherm data collection. Specific activation conditions are described in the main text and in the caption text of the corresponding ESI figures.†

Single crystal and powder X-ray diffraction

Single crystals were mounted in paratone-N oil on a nylon loop. SCXRD data for $1\cdot[\text{Cu}(\text{MeCN})\text{Cl}]$,³⁰ $1\cdot[\text{CuCl}]$, $1\cdot[\text{CuCl}]$ -locked, $1\cdot[\text{CuCl}]$ -unlocked, $1\cdot[\text{CuCl}]$ -resolv, $1\cdot[\text{CuBr}]$, $1\cdot[\text{CuI}]$, and $1\cdot[\text{AuCl}]$ were collected at 100 K on the MX1 or MX2 beamlines of the Australian Synchrotron using the BluCE software interface,³³ operating at $\lambda = 0.7108$ Å. Single crystal X-ray data for $1\cdot[\text{CuCl}]$ was collected at 150(2) K on an Oxford X-Calibur single crystal diffractometer ($\lambda = 0.71073$ Å). N_{tot} reflections were merged to N unique (R_{int} quoted) after a multi-scan absorption correction (proprietary software) and used in the full matrix least squares refinements on F^2 . Unless otherwise stated in the additional refinement details, anisotropic displacement parameter forms were refined for the non-hydrogen atoms; hydrogen atoms were treated with a riding model [weights: $(\sigma^2(F_o)^2 + (aP)^2 + (bP)^2)^{-1}$; $P = (F_o^2 + 2Fc^2)/3$]. Neutral atom complex scattering factors were used; computation used the SHELXL program.³⁴ Pertinent results are given in the manuscript, while views of the asymmetric units, additional refinement details, and X-ray experimental and refinement data (Table S3 and Fig. S9–S22†) are given in the ESI.† Full details of the structure determinations have been deposited with the Cambridge Crystallographic Data Centre as CCDC #s 2100590–2100596.†

Powder X-ray diffraction data was collected on a Bruker Advance D8 diffractometer equipped with a capillary stage using Cu K α radiation ($\lambda = 1.5418$ Å). Simulated powder X-ray diffraction (PXRD) patterns were produced from the single

crystal data using Mercury Software. $1 \cdot [\text{CuCl}]$ -unlocked PXRD was collected after activating the sample under vacuum at 100°C for 90 min inside a Pyrex capillary, flame sealed under vacuum prior to the measurement.

DFT simulations

A representative molecular model of the framework, as used in a previous study,²⁹ where the framework was cleaved at the pyrazole C4 position and capped with methyl functionality was employed to investigate the coordination of bis-pyrazole system. Geometry optimizations of this molecule coordinated to a Cu centre with a series of halogens (Cl, Br, I) in either a two or three-coordinate conformation used the PBE0 density functional⁵⁵ employed by the ORCA software package.^{56,57} The polarized triple-zeta basis set def2-TZVP⁵⁸ was used and tight SCF convergence criteria were implemented to obtain reliable accuracy. Dispersion corrections (D3-BJ) were also applied.⁵⁹ Further information is detailed in ESI (see Fig. S7 and S8†) and representative data files are available online in the data repository <https://github.com/jackevansadl/supp-data>.

Synthetic procedures

H₂L. The ligand bis(4-(4-carboxyphenyl)-1H-3,5-dimethylpyrazolyl)methane (H₂L) was synthesized following a previously reported procedure.²⁸

1. Single crystals of **1** were prepared as previously reported.²⁸ Briefly, 31.6 mg of H₂L and 24.2 mg of MnCl₂·4H₂O were dissolved in 6 mL of a DMF : H₂O mixture (2 : 1 v/v). The solution was transferred to a scintillation vial and heated at 100°C for 48 h. The as-obtained colourless plate-shaped crystals were washed with DMF ($3 \times 10\text{ mL}$) and kept under solvent prior to their use.

1·[Cu(MeCN)Cl]. Single crystals of **1** (~24 mg) were placed in a 4 mL glass vial and washed with freshly distilled acetonitrile ($5 \times 5\text{ mL}$) under Ar flow (the solution was degassed with Ar after each exchange, and the sample was allowed to soak for 1 h between washings). CuCl (30 mg) was added and the vial was sealed under Ar and left undisturbed at 4°C for 72 h. The resulting yellow crystals were washed with freshly distilled acetonitrile ($5 \times 5\text{ mL}$) and stored under Ar.

1·[CuCl]. Crystals of $1 \cdot [\text{CuCl}(\text{MeCN})]$ were washed under Ar flow with freshly distilled MeOH ($5 \times 5\text{ mL}$), acetone ($5 \times 5\text{ mL}$) and a non-polar solvent (toluene, *n*-pentane, cyclohexane) ($5 \times 5\text{ mL}$) allowing the sample to soak for 1 h in between washings.

1·[CuCl]-locked. Crystals of $1 \cdot [\text{CuCl}]$ were washed in Et₂O ($5 \times 5\text{ mL}$) allowing the sample to soak for 1 h between washings. The sample was then activated under dynamic vacuum for 90 min at room temperature and backfilled with Argon.

1·[CuCl]-unlocked. Crystals of $1 \cdot [\text{CuCl}]$ were slowly activated under dynamic vacuum (pressure slope: -10 mbar min^{-1}) in an adsorption cell and then heated at 100°C for 2 hours after reaching full vacuum.

1·[CuCl]-resolv. Crystals of $1 \cdot [\text{CuCl}]$ -unlocked were backfilled with Argon and soaked in dry acetonitrile for 2 hours.

1·[AuCl]. Single crystals of **1** (~24 mg) were placed in a cellulose filter within a 4 mL glass vial and washed with freshly

distilled Et₂O ($5 \times 5\text{ mL}$) under Ar flow (the solution was degassed with Ar after each exchange, and the sample was allowed to soak for 1 h between washings). AuCl(dms) (dms = dimethylsulfide) (10 mg) was added to the ether phase and the vial was sealed under Ar and left under stirring in the dark at room temperature for 48 h. The resulting pale-yellow crystals were taken out of the filter, washed with freshly distilled Et₂O ($5 \times 5\text{ mL}$) and stored under Ar in the dark.

Anion exchange protocol for 1·[CuBr] and 1·[CuI]. Crystals of $1 \cdot [\text{CuCl}]$ were soaked in dry methanol. Dry NaBr or NaI (~100 mg) was then loaded to a small glass ampule and subsequently submerged in the 4 mL vial containing the MOF sample. The solution was degassed with Ar, and the vial was sealed and allowed to stand at room temperature for 24 h or 48 h, respectively. Under Ar flow, the ampule containing undissolved salt was removed and the resulting brown crystals were washed with freshly distilled methanol ($5 \times 5\text{ mL}$), acetone ($5 \times 5\text{ mL}$) and *n*-pentane ($5 \times 5\text{ mL}$).

Data availability

Representative data files for computational calculations are available online in the data repository <https://github.com/jackevansadl/supp-data>.

Author contributions

J. A. and C. J. D. conceived the project. J. A., R. A. P. and M. T. H. performed all the synthesis, characterisation, and SCXRD data collection for all the $1 \cdot [\text{CuX}]$ (X = Cl, Br, I) samples. S. T. synthesised and characterised $1 \cdot [\text{AuCl}]$. Z. S. and Y.-B. Z. carried out the *in situ* Raman spectroscopy, and provided all the equipment for the measurements. J. D. E. performed the computational calculations. C. J. S. refined all the SCXRD data. J. A., M. T. H. and C. J. D. prepared the final manuscript and ESI. C. J. S. and C. J. D. supervised this work and acquired the financial support for the project. All authors collectively discussed the results, provided insightful inputs, and peer-reviewed the manuscript prior to submission.

Conflicts of interest

There are no conflicts to declare.

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