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RESEARCH HIGHLIGHT

Metal-Organic Framework Assisted Synthesis of Single Atom Catalysts for Energy Applications

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Metal single-atom catalysts (M-SACs) are emerging as a new research frontier because of their low-coordination metal atoms and uniform structures. As a representation of maximum atom utilization efficiency, M-SACs demonstrate unique properties in a wide variety of heterogeneous catalysis and electrocatalytic processes.^[1,2] Metal-organic frameworks (MOFs) are composed of metal-containing nodes and organic linkers, and are typically characterized as atomically dispersed metal sites. With the versatility of metal ions and ligands, the direct pyrolysis of MOFs serves as an ideal route for preparing various M-SACs. However, this seemingly simple strategy is still highly challenging due to the drastic reactive processes that occur at high temperature which rapidly convert metal ions to aggregated nanoparticles. Very recently, Yadong Li *et al.* developed a general synthetic strategy for M-SACs preparation by utilizing particular zeolitic imidazolate frameworks (ZIFs), a kind of MOF that are topologically isomorphic with zeolites.^[3-5] The resultant M-SACs (M = Fe, Co, Ni) demonstrated excellent activities for energy-related electrocatalytic reactions.

The most important principle of this methodology is the utilization of low boiling point atoms, such as Zn (mp 420 °C, bp 907 °C), in ZIF-8 and Zn/Co bimetallic ZIF-67, which evaporated at high temperature, leaving abundant N-rich defects. As a result, the isolated metal ions were closely anchored through N-coordination, avoiding their aggregation during pyrolysis. For the synthesis of Fe and Ni single-atoms in an N-carbon matrix (Fe-SAs/CN and Ni-SAs/CN), Fe(acac)₃ and Ni(NO₃)₂ were selected as metal sources, respectively, and were confined in the molecular-cages of ZIF-8 (Figure 1).^[3,4] Co-SAs/CN was synthesized from a partially Zn replaced ZIF-67 with a Zn/Co = 1:1 (Zn/Co-ZIF-67) precursor (Figure 1).^[5] After pyrolysis at 900-1000 °C in an Ar atmosphere, the metal ions were thermally reduced and atomically dispersed in the N-carbon matrix. This was directly observed by high-angle annular dark-field scanning transmission electron microscopy. The precise molecular structures of these isolated metal atoms were well-identified by extended X-ray absorption fine structure and X-ray absorption near-edge structure. As shown in Figure 1, the ZIF-8 derived Fe-

SAs/CN and Ni-SAs/CN, and Zn/Co-ZIF-67 derived Co-SAs/CN, show a 4, 3, and 2 metal coordination number with surrounding N atoms, respectively.

With precise N-coordination and high metal loadings of 1.5–4 wt. %, all M-SACs showed superior electrocatalytic activities. For example, Fe-SAs/CN demonstrated a half-wave potential of 0.9 V for the oxygen reduction reaction in alkaline electrolyte, a key cathodic step for proton exchange membrane fuel cells, even outperforming commercial Pt/C and most non-precious-metal catalysts.^[3] Ni-SAs/CN exhibited an excellent turnover frequency for the electroreduction of CO₂ (5273 h⁻¹), with a Faradaic efficiency for CO generation of 71.9%.^[4]

In summary, Yadong Li *et al.* developed a general and well-designed method for the simple preparation of a variety of M-SACs with the assistance of ZIFs. The accurately controlled methodology involved in these studies may present some guidelines for the rational design and accurate modulation of M-SACs for broader applications.

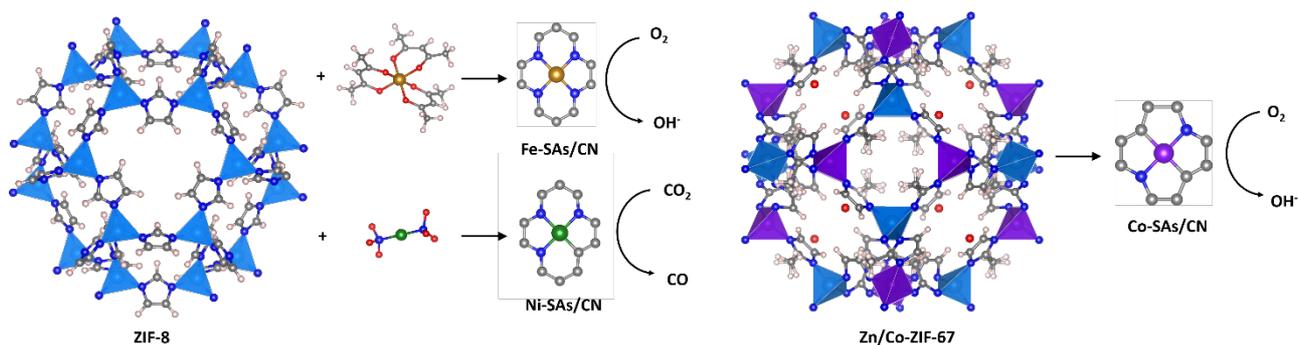


Figure 1. Schematic illustration of the precursor and structures of Fe, Ni, and Co single atoms supported in N-carbon matrices. Color code: grey: carbon; royal blue: nitrogen; white: hydrogen; red: oxygen; light blue: zinc; brown: iron; green: nickel; purple: cobalt.

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