LINKING THE HETERO-CHEMISTRY OF NANOPOROUS CARBONACEOUS MATERIALS TO THEIR PERFORMANCE

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Abstract

Nanoporous carbonaceous materials are used in many varied applications, including adsorption (e.g. CO_2 capture and hydrogen storage) and catalysis (e.g. oxidation and dehydration). The non-carbon atoms (or heteroatoms) of carbonaceous materials profoundly affects their character and performance in such applications. For example, the level of oxygen within the predominately carbon skeleton of these materials is known to dictate their mechanical and thermal stability. The performance of nanoporous carbons in CO_2 adsorption is, on the other hand, known to be a strong function of the nitrogen (and other basic) functionalities on their pore surfaces.

There are a wide variety of experimental methods available for determining the bulk and pore surface chemistry of carbonaceous materials. Due to the different underlying fundamentals of these methods, they can yield inconsistent results for what are nominally the same characteristics. This makes interpretation of experimentally observed behaviour of carbon materials challenging. The first aim of the research reported in this thesis is to distinguish the source of inconsistencies between the major methods for characterizing the oxygen chemistry of carbons. It is shown that differences in the results of the methods have a range of origins including spatial heterogeneity within carbon particles induced by diffusion-controlled activation, the differences in the probed volumes (e.g. bulk vs. surface), and in handling protocols prior to analysis.

The second major aspect of the thesis is focused on better understanding the effect that pore structure and surface nitrogen chemistry have on the CO_2 capture performance of nanoporous carbons. Hence, samples with different porous structures are modified with amination which is believed to have enhancing effect on the surface basicity without diminishing the structure. The simultaneous effects of nitrogen content and pore structure on the low, atmospheric and high pressure CO_2 capture performance of nanoporous carbons are analysed. It is shown that for low and atmospheric CO_2 capture, both N content and microporous structure have positive impact. However, at high pressures, nitrogen content seems to lose its enhancing effect and porous structure determines the capture performance.

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Nomenclatures

$R[4, 3]$	Particulate equivalent volume mean diameter (μm)
f_X	Relative fraction of element *X* in XPS analysis
A_X	Area under the peak of element *X* in XPS analysis
B_X	Sensitivity factor of element *X* in XPS analysis
$SGL(m)$	Sum of a Gaussian with a Lorentzian function
$G(100)$	$G(100)$ pure Gaussian function
$L(100)$	$L(100)$ pure Lorentzian function
ω_i^{TPD}	The fraction of functionality *i* obtained by TPD
ω_i^{XPS}	The fraction of functionality *i* obtained by XPS
$\widehat{\omega}_i^{TPD}$	The fraction of functionality *i* obtained from TPD scaled to yield the XPS net Wt% of oxygen
ω_O^{XPS}	Wt% of oxygen indicated by XPS
ω_O^{TPD}	Wt% of oxygen indicated by TPD
MHTT	Maximum heat treatment temperature
$\rho^*_{CO_2}(P)$	CO_2 adsorption capacity at pressure P normalised by the corresponding effective volume
$\rho_{CO_2}(P)$	CO_2 adsorption capacity at pressure P
$V_C(P)$	Pore volume known to have most influence on CO_2 adsorption at pressure P