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Davisson-Germer Prize Talk: Hydrogen storage in nanoporous materials[1]

YVES CHABAL, University of Texas at Dallas

To develop a hydrogen-based energy technology, several classes of materials are being considered to achieve the DOE targets for gravimetric and volumetric hydrogen densities for hydrogen storage, including liquids (e.g. ammonium borohydrides), clathrate structures, complex metal hydrides, nanostructured (e.g. carbon) an nanoporous materials. Fundamental studies are necessary to determine the ultimate hydrogen capacity of each system. Nanoporous Metal-organic Framework (MOF) materials are promising candidates for hydrogen storage because the chemical nature and size of their unit cell can be tailored to weakly attract and incorporate H_2 molecules, with good volumetric and mass density. In this talk, we consider the structure $M_2(BDC)_2(TED)$, where M is a metal atom (Zn, Ni, Cu), BDC is benzenedicarboxylate and TED triethylenediamine, to determine the location and interaction of H_2 molecules within the MOF. These compounds are isostructural and crystallize in the tetragonal phase (space group P4/ncc), they construct 3D porous structures with relatively large pore size ($\sim$7-8 A$^{\circ}$), pore volume ($\sim$0.63-0.84 cc/g) and BET surface area ($\sim$1500-1900 m^2/g). At high pressures (300-800 psi), the perturbation of the H-H stretching mode can be measured with IR absorption spectroscopy, showing a 35 cm^{-1} redshift from the unperturbed ortho (4155 cm^{-1}) and para (4161 cm^{-1}) frequencies. Using a newly developed non empirical van der Waals DFT method vdW-DFT),[2] it can be shown that the locus of the deepest H_2 binding positions lies within to types of narrow channels. The energies of the most stable binding sites, as well as the number of such binding sites, are consistent with the values obtained from experimental adsorption isotherms, and heat of adsorption) data.[3] Importantly, the calculated shift of the H-H stretch is $\sim$-30 cm^{-1} at the strongest binding points of the two channels, suggesting that the combination of IR and vdW-DFT gives a consistent and accurate picture of H_2 binding in MOF structures. These methods can therefore provide the fundamental information necessary to guide synthesis for improving H_2 uptake and release.

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