

# Essay of Thesis Work

## GAS ADSORPTION APPLICATIONS OF POROUS METAL-ORGANIC FRAMEWORKS

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Porous metal-organic frameworks (MOFs) represent a new type of functional materials and have recently become a very hot research field due to their wide applications in catalysis, magnetism, gas storage/separation etc. This thesis mainly consists of three sections, and details the investigation of porous MOFs for gas adsorption applications, including hydrogen storage, methane storage, and selective gas adsorption.

Initiating with a comprehensive introduction to porous MOFs, the evaluation of them as on-board hydrogen storage media is addressed in the first section and several strategies to improve dihydrogen adsorption are offered in this study.

A major hurdle for hydrogen adsorbents lies in their low hydrogen adsorption enthalpies of 4~6 kJ/mol. Employing a novel biomimetic approach, some cobalt centers in entatic states have been created in the porous MOF material PCN-9 (PCN represent porous coordination network). Those entatic cobalt centers lead to PCN-9 with a high hydrogen affinity of 10.1 kJ/mol, and their accessibility for hydrogen molecules is confirmed using carbon monoxide as a probe.

Functionalizing the organic ligand with more aromatic rings is theoretically predicted to increase hydrogen bind energy, and it represents a useful method to achieve high hydrogen adsorption capacity in porous MOFs. This strategy is well illustrated in hydrogen adsorption studies of PCN-14, which was constructed from an anthracene derivative, 5,5'-(9,10-

anthracenediyl)di-isophthalate (adip). PCN-14 exhibits a high hydrogen uptake of 2.7 wt% at 77 K, 760 Torr, which can be attributed to the fused aromatic rings of the adip ligand

Catenation has long been considered a valuable way to increase hydrogen uptake in porous MOFs. Its impact on hydrogen uptake is quantitatively evaluated for the first time in the studies on catenated PCN-6 and non-catenated PCN-6', which can be controllably synthesized using a templating strategy. Catenation can lead to a 41% improvement of Langmuir surface area and 29% in gravimetric hydrogen uptake in the studied case. In addition, catenation also improves the excess gravimetric hydrogen uptakes with 7.2 wt% at 77 K, 50 bar and 0.93 wt% at 298 K, 50 bar in catenated PCN-6 vs. 4.2 wt% at 77 K, 50 bar and 0.40 wt% at 298 K, 50 bar in non-catenated PCN-6'. Moreover, PCN-6 exhibits a total gravimetric hydrogen uptake capacity of 9.5 wt% (corresponding to a total volumetric value of 53.0 g/L) at 77 K, 50 bar and 1.5 wt% at 298 K, 50 bar as well as a deliverable hydrogen amount of ~7.5 wt% (or 41.9 g/L) at 77 K, promising its great potential as a cryonic hydrogen storage medium. The mechanistic details of the interaction between hydrogen molecules and catenated or non-catenated MOFs are also elucidated unprecedentedly through inelastic neutron scattering studies, which reveal that catenation favors hydrogen-ligand interactions at high hydrogen loadings thus increasing hydrogen uptake in the catenated MOF compared to its non-catenated counterpart.

Compared to hydrogen, methane appears to be a more promising alternative for mobile applications in terms of near-term practical utilization and innovations necessary for commercialization. Methane storage application of porous MOFs is discussed in the second section. Stimulated by a theoretical simulation, the porous MOF, PCN-14, is constructed from a pre-designed anthracene derivative. It exhibits the highest methane uptake capacity among currently reported materials with the value of 230 v/v, which is 28% higher than the US DOE

target (180 v/v) for methane storage. This illustrates porous MOFs great potential for on-board methane storage application.

Gas separations represent important issues in industry, and currently they rely primarily on traditional inorganic zeolite materials. As a new type of zeolite analogues, porous MOFs have demonstrated great potential in separation applications due to their amendability of design and tunable pore sizes. The third section describes microporous MOFs as molecular sieves for selective gas adsorption application.

Increasing the bulkiness of the struts of the organic linker has been proved an effective way to restrict pore sizes for selective gas adsorption, as indicated in PCN-13 which can separate dihydrogen and dioxygen from dinitrogen and carbon monoxide.

A major concern in porous MOFs lies in their limited thermal stability, which prevents them from competing with inorganic zeolites in practical applications. The thermal stability can be greatly improved by introducing coordinatively linked interpenetration, as illustrated in PCN-17 which is stable up to 480 °C while maintaining permanent porosity. The coordinatively linked interpenetration also confines the pore size of PCN-17 for selective adsorption of dihydrogen and dioxygen over dinitrogen and carbon monoxide.

Compared to traditional inorganic zeolites whose pore sizes are normally fixed, the dynamic features of MOFs can produce materials with adjustable pore sizes. Based on an amphiphilic ligand BBDC, the first mesh-adjustable molecular sieve (MAMS) MAMS-1, whose pore sizes can be continuously tuned from 2.9 to 5.0 Å, is constructed for various gas separation applications. The extension of BBDC ligand to the BBPDC ligand, when reacted with different metal ions under solvothermal conditions generates a series of new MAMSs with similar molecular sieving effects to those observed in MAMS-1. For all of the MAMSs, there exists a

linear relationship between mesh size and temperature,  $D = D_0 + \alpha T$  ( $D$  - mesh size at temperature  $T$  K,  $D_0$ -mesh size at 0 K, and  $\alpha$ -constant),  $D_0$  and  $\alpha$  are only related to the *tert*-butyl group. Adjusting  $D_0$  and  $\alpha$  is expected to result in some new MAMSs which might be omnipotent for gas separation at near ambient temperatures.

As a relatively new class of materials, porous MOFs will continue to attract interest and inquiry by both academia and industry. They exhibit considerable potential for the adsorptive storage of both hydrogen and methane in energy applications as well as gas separation and purification in industrial applications as well illustrated in this dissertation. The emerging ability to tune pore size and pore wall functionality allow researchers to focus on those factors which hold to the most promise, increasing both the volume available for storage and the affinity of the network for the stored gas. In particular, as alternative fuels such as hydrogen and methane continue to be developed in automotive and other applications, the needs for effective storage technologies will continue to increase, and porous MOFs are well-positioned to remain at the forefront of this research. The expectation of this thesis is that it can serve not only as a reference brochure for the experienced researchers in the MOF field, but also as an introduction booklet for those who are interested in MOFs and those just enter this field.