

Hydrogen storage in metal-organic frameworks materials: improved HKUST-1 capacity (P-15H)

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1. Introduction

In gas storage on porous solids, gas is adsorbed on the material's surface. Research in this area arose as an alternative to other methods, such as compression and liquefaction require large amounts of energy and present some safety issues due to the high pressure involved to contain H₂.

Several solids, among metal-organic frameworks (MOFs) were studied for that purpose. MOFs are coordination polymers composed of organic ligands and metal or metal clusters. MOFs can be designed and synthesized according to specific needs.

The MOF known as HKUST-1¹ has demonstrated great adsorption capacities of H₂. This compound also has chemical and thermal stability and is relatively simple to obtain in both lab and large scale. These characteristics make this MOF a promising material for hydrogen storage.

HKUST-1 is composed of Cu (II) dimers equatorially coordinated by the carboxylates from benzene-1,3,5-tricarboxylic acid (BTC) and two open axial positions. The dimers form cubic 3D structures with two types of pores: 'channels' of 1 nm diameter and 'pockets' of 0.5 nm (Fig.1).

Adsorption energy depends on both non-specific (i.e. attraction-repulsion potential gas-solid) and specific interactions where molecule is adsorbed on the surface of an ionic or polar solid².

In this work, we modified the composition of HKUST-1 by replacing part of its ligand (BTC) with benzene-1,3-dicarboxylic acid (iBDC) in order to release a Cu coordination position and increase the specific interaction with the H₂.

2. Experimental

2.1 Synthesis

Five solids were prepared: HKUST-1 and a series named:

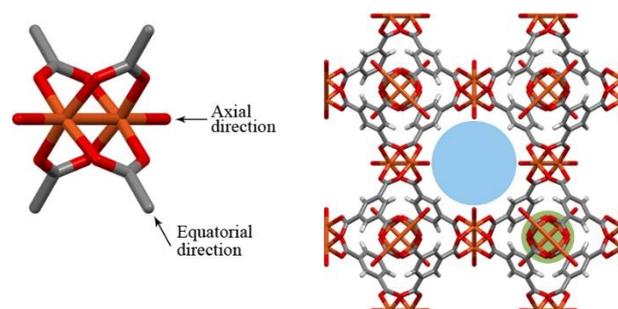


Fig. 1. Coordinate Cu dimer (left) and HKUST-1 structure (right). Light blue and green circles indicate channel and pocket pores. Cu orange, O red, C grey.

HKUST-1 and a series named SSC-1-XX, where XX is the molar fraction of BTC (X_{BTC}) in the MOF (see Table 1). In the synthesis procedure³, copper nitrate (II) trihydrate, 5.0 g, 20.7 mmol, was dissolved in 125 ml of a mixture of N, N-dimethylformamide (DMF): ethanol: water 1:1:1 in a 250 ml capped glass bottle. Different amounts of BTC and iBDC were added to the solution and heated in an oven at 80°C for 20 h. Crystals were rinsed with DMF and treated with methanol for solvent exchange; the latter procedure was performed overnight and repeated thrice with fresh solvent.

2.2 Characterization

Nuclear magnetic resonance (NMR) spectra were obtained in a Magneto Bruker UltraShield 14.1 Tesla, 1H 600.13 MHz. Samples were dissolved in TFA.

H₂ isotherms were obtained at 77 K and up to 8 bar in a Micromeritics ASAP 2050 equipment. Argon isotherm data were collected at 87 K in an Autosorb IQ with He cryocooler. The textural properties were evaluated from the argon adsorption data; micropore volume ($V_{\mu P}$) was calculated with Dubinin Radushkevich equation, and the total pore volume (V_{TP}) was obtained with Gurvich rule at $p/p^0 = 0.98$.

Before the adsorption experiments, the samples were outgassed at $5 \cdot 10^{-3}$ mmHg and 323 K for 12 h; then the temperature rose up to 453 K at 1 Kmin⁻¹ and held 3 h.

3. Results

Areas of peaks of BTC and iBDC in NMR spectra were used to calculate the X_{BTC} in samples (Table 1).

From Ar isotherms (Fig.2) it can be seen that the highest gas uptake corresponds to HKUST-1, and the less is X_{BTC} , the less is the Ar adsorption. As for H₂ isotherms (Fig.3) it was observed that SSC-1-91 shows the highest uptake of the studied MOFs series.

Table 1. Molar composition of MOFs obtained from NMR spectra; micropore and total pore volume derived from Ar isotherms

Sample	X_{BTC}	$V_{\mu P}$	V_{TP}
HKUST-1	1.00	0.77	0.77
SSC-1-91	0.91	0.74	0.74
SSC-1-87	0.87	0.71	0.74
SSC-1-82	0.82	0.65	0.69
SSC-1-67	0.67	0.62	0.68

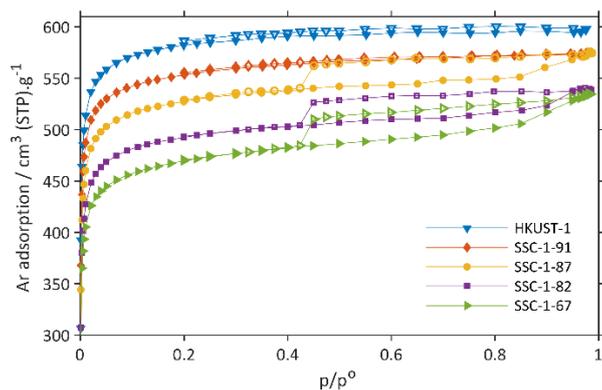


Fig. 2. Argon adsorption (solid marker) - desorption (empty marker) isotherms at 87 K for HKUST-1 and SSC-1 series.

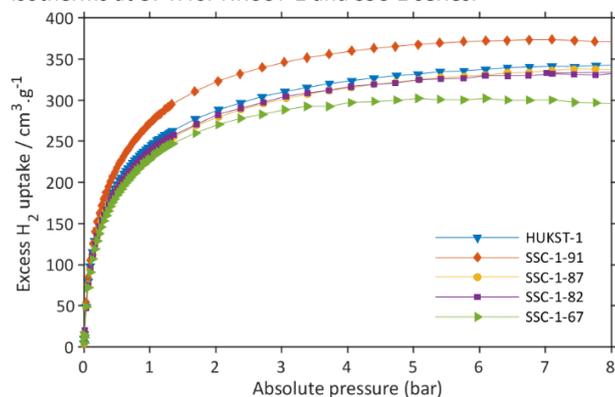


Fig. 3. H₂ adsorption isotherms at 77 K for HKUST-1 and SSC-1 series.

4. Discussion

Ar adsorption isotherms (solid marker in Fig.2) correspond to Type I isotherms according to IUPAC, which means that the solids are mainly microporous (i.e. pores < 2nm width). These pores are filled at low relative pressures due to their high interaction potential. The specific surface areas of these materials were between 1600 and 2005m²/g while micropore volume reaches the highest value in HKUST-1 (Table 1), and decreases as X_{BTC} becomes smaller in SSC-1-91/87/82/67 samples.

HKUST-1 and SSC-1-91 exhibit a reversible behavior (adsorption-desorption branches overlapped - Fig.2), while the rest of the samples show a hysteresis loop, which is an indicator of the presence of mesopores (i.e., pores between 2-50 nm width).

H₂ adsorption isotherms show a different trend: SSC-1-91 has the highest uptake. This can be explained as follows: the modification in the organic ligands releases a coordination position in Cu dimer since iBDC has a carboxylic group less than BTC; which increases the polarity of the surface. This improves the specific interactions with H₂ due to its quadrupole moment. This behavior is not observed in Ar isotherms because this gas is not a polar molecule.

The improvement in specific interactions in SSC-1-87/82/67 is compensated by mesopores in which the interaction potential is minor than in micropores. In addition, it was observed that the less X_{BTC} , the less total pore volume; these two reasons explain the reduction in H₂ adsorption in those materials.

5. Conclusions

A series of MOFs was successfully synthesized by replacing a part of the HKUST-1 original ligand. This led to an improvement in the adsorption due to a stronger specific interaction between H₂ and the surface of the SSC-1-91 solid.

References

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