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Influence of Metal Doping of a MOF-74 Framework on Hydrogen Adsorption

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Abstract

Microporous Metal-Organic Framework (MOF) adsorbents are considered an interesting option for hydrogen storage. Due to their porous nature and unusually high surface areas, these materials show an exceptional H_2 uptake. Unfortunately, their interaction with H_2 molecules is weak, so cryogenic temperatures are required to reach competitive H_2 storage capacities. In this sense, the presence of coordinatively unsaturated and exposed metal centers in some MOF frameworks could increase the affinity for H_2 through stronger metal-H_2 interactions. In this preliminary work, the effect of doping a Zn^{2+}-MOF-74 framework with Co^{2+}, Cu^{2+} and Mg^{2+} on its adsorption properties for H_2 has been studied. Characterization studies suggest that the samples prepared have actually the MOF-74 structure, in which the different tested heteroatom ions have been successfully incorporated. The differences in H_2 adsorption at 77 K and 87 K between the MOF-74 samples doped with the mentioned divalent metal ions were discussed as a function of their free pore volume and amount of metal incorporation.

1 Introduction

Hydrogen is considered as the energy vector more promising because of its high efficiency and negligible environmental impact [1]. However, the difficulties associated to its producing, safely storing, and transporting in large quantities has limited its utility to date [2]. Hydrogen adsorption onto Metal-Organic Framework (MOF) materials is presented nowadays as a promising alternative among all technologies for hydrogen storage. It is now widely recognized that the interactions of hydrogen with porous host materials must be substantially increased in order to make MOFs efficient materials for H_2 storage.. In this sense, H_2-MOFs binding energies in the range 15-25 kJ/mol are clearly necessary [3], existing different approaches to face this challenge. Among them, the control of metal ion nature in open metal binding sites of certain metal-organic frameworks is probably one of the most promising. Crystallization of MOF materials with a given metal ion as well as metal doping of MOFs seem to be good alternatives to produce additional electrostatic forces contributing to increase the H_2 adsorption strength [4].

Kubas [5] described that the interaction metal-H_2 takes place through the *d* orbitals of a transition metal (M) with antibonding orbitals of the hydrogen molecule. The complexes M–H_2 can reversibly bind H_2, with a binding energy in the range 20–160 kJ/mol, which partially overlaps with the appropriate heat of adsorption range for high H_2 uptake at room temperature [3, 6]. Kubas binding strategy has been recently followed to enhance H_2 binding with metal (transition metal) sites in MOFs [7a].

Theoretical [6] and experimental [7] studies with MOFs containing open metal sites of different elements (Zn, Mn, Co, Ni, Fe, Mg, V, Sc, etc.) have shown that it is possible to get high binding energies with H_2 up to 46.5 (theoretical studies) and 13.7 kJ/mol (experimental studies). Among these MOF materials, MOF-74 is an interesting material due to its relatively high affinity to hydrogen molecules, its thermal stability and its potential composition range [7c,d]. This material has been fully substituted with divalent metals ions such as Mg^{2+}, Ni^{2+}, Fe^{2+} and Co^{2+},but to the best of our knowledge, no partial substitution has been reported so far [8]. Apart from its application in gas adsorption uses, the doping of this material can have important implication in other fields like catalysis and semiconductor materials

In this work, partial isomorphic substitution of Zn-based MOF-74 clusters by Co^{2+}, Cu^{2+} and Mg^{2+} cations during the solvothermal synthesis, as well as its effect over their H_2 affinities and adsorption capacities, are studied and discussed.

2 Experimental Section

2.1 Synthesis

MOF-74 ($Zn_2(C_8H_2O_6)(DMF)_2(H_2O)_2$) was prepared basically following the procedure published elsewhere [10], in which 2,5-dihydroxybenzene-1,4-dicarboxylic acid and zinc nitrate tetrahydrated are dissolved in N,N-dimethylformamide. Once the reactants are dissolved, deionized water is added to form a mixture of molar composition 1 H_2DHBDC : 2,9 Zn : 523 DMF : 107 H_2O. This mixture is heated up to 100 ºC for 20 h to yield yellow needle crystals. After decanting and rinsing with DMF, the solid product was immersed in methanol for 6 days, during which the activation solvent was decanted and freshly refilled three times. The solvent was removed under vacuum at 150 °C, yielding the porous material. Metal-doped MOF-74 materials, denoted as Co10-MOF-74, Cu10-MOF-74 and Mg10-MOF-74, were synthesized following the same procedure but substituting 10 molar % of Zn by Co, Cu or Mg, respectively, using nitrate salts as metal sources.

2.2 Characterization techniques

Powder X-Ray Diffraction (PXRD) patterns were obtained in a Philips XPERT PRO using CuKα (λ = 1,542 Å) radiation. In order to avoid the effects of preferred crystal orientation, crystals were grounded. Mica sample was used as an internal standard to calculate the displacement error of the instrument. Thermogravimetric analyses (TGA) were carried out in a 100 ml/min flowing air atmosphere at a heating rate of 5 ºC/min up to 1000 ºC, using a TA Instruments SDT 2860 apparatus. Metal contents of the materials were measured by ICP (Inductively Coupled Plasma) atomic emission spectroscopy on a Varian Vista AX CD system. N_2 adsorption isotherms were measured on an AutoSorb equipment (Quantachrome Instruments). Previously, 0.02-0.04 g of the sample was in-situ evacuated under high vacuum for 18 h at 150 ºC. The micropore surface area values were calculated by the Brunauer-Emmett-Teller (BET) and Langmuir methods. Hydrogen adsorption isotherms were obtained in a Hiden Analytical Intelligent Gravimetric Analyser equipped with an ultra high vacuum system. The buoyancy effects were corrected as a function of temperature taking into account the void volume of the cell determined with He at 77 K, and assuming that the amount of He adsorbed is negligible.

3 Results and Discussions

Powder X-ray diffraction (XRD) patterns of as-prepared non-doped and Metal-doped samples show that MOF-74 is the unique crystalline phase present in all samples [10], except for Cu10-MOF-74, where some reflections of an unidentified phase were detected (Figure 1).

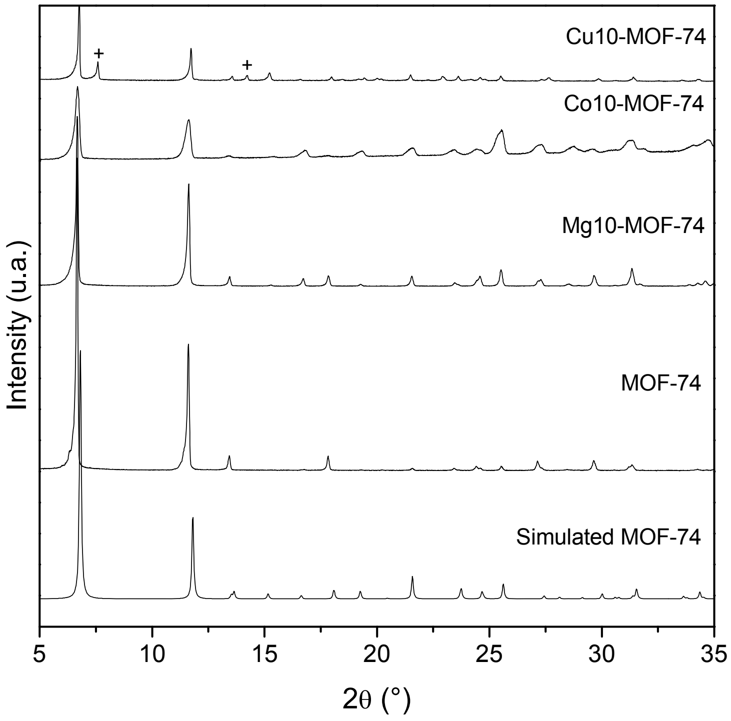

Figure 1: Experimental powder XRD patterns of MOF-74 materials. (+: Unidentified phase).

All powder XRD patterns were indexed on the basis of a face-centered hexagonal unit cell with resulting values summarized in Table 1, which are in good agreement with their ionic radii (Zn^{2+} > Cu^{2+} > Mg^{2+} > Co^{2+}). The differences in the unit cell parameters obtained qualitatively support the metal incorporation into the MOF-74 framework.

Table 1: Unit Cell Parameters of MOF-74 materials.

Sample	Co content (wt. %)	Parameter *a* = *b*	Parameter *c*
MOF-74	0	26.188	6.771
Co10-MOF-74	14	26.098	6.841
Cu10-MOF-74	17	26.144	6.781
Mg10-MOF-74	5	26.106	6.790

Thermogravimetric analysis (TGA/DTG) curves of as-synthesized MOF-74, Co10MOF-74, Cu10MOF-74 and Mg10MOF-74 samples are shown in Figure 2. The first weight loss produced around 115 ºC can be attributed to the solvent (DMF/H_2O) removal from the cavities. The next main weight loss in the range 300 - 375 °C, (precise temperatures are explicitly indicated in Figure 2), corresponds to the organic ligand decomposition and thus provides an indication of the thermal stability of MOF-74 framework in air atmosphere. The thermal stability is different for each MOF-74 sample, which indirectly confirms the incorporation of the doping metal into the framework.

The porosity of these materials was measured by nitrogen adsorption-desorption at 77 K. All of them exhibit permanent microporosity, as evidenced by the reversible type I N_2 adsorption isotherms, according to IUPAC, which correspond to microporous materials [11]. Textural properties estimated from N_2 isotherms of all MOF-74 samples, summarized in Table 2, are very similar, which is not surprising when the metal ions are incorporated in MOF-74 instead of forming extra-framework species. As an exception, Co10-MOF-74 exhibits slightly better textural properties than the rest, probably because the activation treatment was somehow more effective.

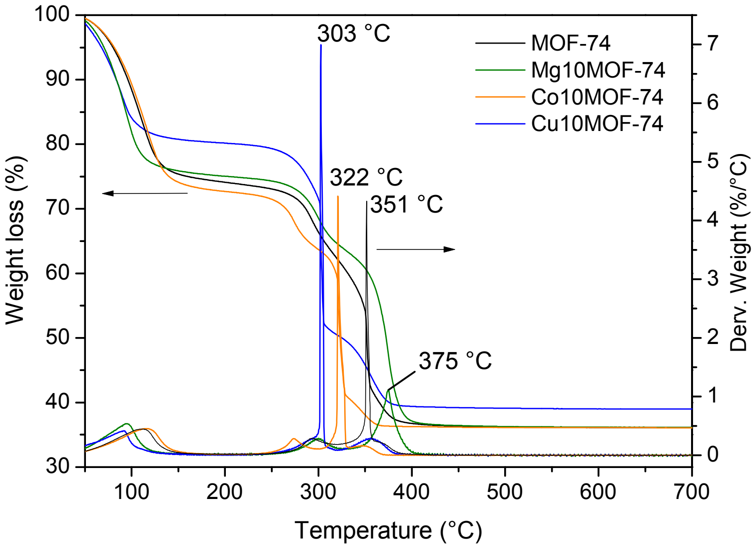

Figure 2: TGA/DTG in air atmosphere curves of MOF-74 samples.

Table 2: Textural properties and H_2 adsorption capacity of activated MOF-74 samples.

Sample	S_{BET} ± 40 (m^2/g)	S_{Lang} ± 50 (m^2/g)	Vm_{NL-DFT} ± 0.04 (cm^3/g)	H_2 adsorbed (wt. %) 77 K	Q_{st} H_2[a] kJ/mol
MOF-74	850	960	0.34	2.16	7.9
Co10-MOF-74	1111	1270	0.49	3.08	9.3
Cu10-MOF-74	822	935	0.41	1.62	9.6
Mg10-MOF-74	900	1024	0.44	3.01	8.2

[a] Q_{st} was measured for 0.3 wt. % of H_2 coverage.

Gravimetric hydrogen adsorption capacities for doped and non-doped MOF-74 materials were measured at 77 K and up to 10 bar (Table 2 and Figure 3). All doped samples adsorb significantly higher amount of hydrogen than the non-doped MOF-74 under the same conditions of temperature and pressure, except for Cu10-MOF-74 material, which is the only doped MOF-74 with hydrogen uptake lower than the Zn-based MOF-74. This low H_2 uptake value could be related to the presence of the unidentified phase observed by powder XRD, whose proportion increases along the adsorption process, as it was made clear by an XRD study after this treatment. The magnitude of interaction between hydrogen molecules and MOF framework was checked by measuring the isosteric heat of hydrogen adsorption, Q_{st} (Table 2), estimated from the hydrogen adsorption isotherms at 77 and 87 K. It is noteworthy that despite of the lower porosity of Cu10-MOF-74 compared to the other samples, the Q_{st} value of this material appears to be the highest. Therefore, the low H_2 uptake is a question of phase purity rather than simple gas affinity. The hydrogen uptakes of the materials was in the decreasing order Co10-MOF-74 > Mg10-MOF-74 > Zn10-MOF-74 > Cu10-MOF-74, whereas for Q_{st} was Cu > Co > Mg > Zn, a result which agree with the results published for CPO-27 (isostructural to MOF-74) prepared with Co, Mg and Zn [8a].

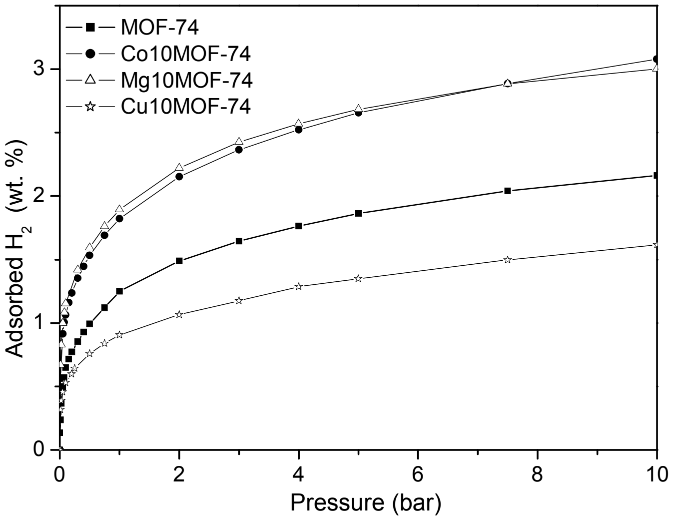

Figure 3: Hydrogen adsorption of MOF-74 materials at 77 K and up to 10 bar.

4 Conclusions

Partial doping of the open-metal-sites of a MOF-74 framework was carried out. Evidence for metal substitution of Zn sites by other divalent metals in the MOF-74 framework was provided by PXRD (unit cell parameters), TGA and N_2 adsorption at 77 K. MOF-74 materials doped with Co and Mg showed a significant enhance in H_2 uptake at 77 K and 10 bar, compared to the non-doped material. Nevertheless, Cu10-MOF-74 was not purely crystallized, so its H_2 uptake is much lower. Additionally, doped MOF-74 homologues exhibited higher affinity to H_2 molecules than Zn-based MOF-74, particularly for the sample doped with copper, a result that suggests the challenge of preparing all-Cu or pure Cu-doped MOF-74 materials. The important differences in hydrogen affinity and uptake, as well as the difference in thermal stability, support the assumption that metal ions are actually incorporated into the MOF-74 framework. This study opens the possibility of doping different MOFs materials, and particularly those which have exposed centers, thorough a non-post-synthesis strategy, for improving their adsorption properties as well as for catalysis applications.

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