

SUPPORTED Pt AND Pd CATALYSTS AS ADDITIVE FOR HYDROGEN ADSORPTION ENHANCEMENT IN MOFs

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Hydrogen adsorption in Metal-Organic Frameworks is improved by using platinum and palladium on different carbon support: activated carbon or carbon nanofibres. Although, hydrogen adsorption is directly dependent of the specific surface area of the material, it is not the only factor contributing to the hydrogen adsorption, as presented in this work. Direct synthesis of metal-organic frameworks on supported Pt and Pd catalysts, reduces the surface area significantly, but the presence of the catalysts overcomes this drawback by improving hydrogen adsorption by a factor of 2.2, in case of platinum and by a factor of 1.4 in the case of palladium, compared to the metal-organic framework without catalysts.

INTRODUCTION

Metal-Organic Frameworks, MOFs, are a class of materials with low density, high crystallinity and porosity, and high surface areas (500 – 5500

m²/g). Among different composites, their structures may include metallic clusters bonded with polydentate organic linkers.¹ Their high porosity makes these materials suitable for hydrogen adsorption, up to 7.4 wt. % H₂ at 77 K.

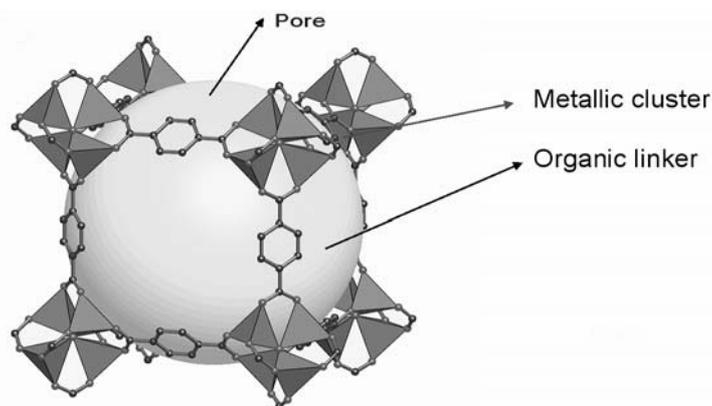


Fig. 1 – Structure of MOF-5.

One of the most studied MOF is Zn₄O(OOC-C₆H₄)₃ also known as MOF-5 or IRMOF-1. The

oxo-centered metallic cluster Zn₄O has a tetrahedral structure, with Zn ions in the tetrahedral

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corners. Structure of MOF-5 consists of metallic centers in every corner of a cube, linked by terephthalic acid residues (Fig. 1). However, the main disadvantage of these structures is that, at room temperature, do not adsorb more than 0.6 wt. % H₂. A way to improve hydrogen adsorption could be the use of different catalysts, able to catalytic dissociate the hydrogen molecule.² These catalysts are of metal/support type, where metal is a transitional one (Pt, Pd) and the support is carbon based (activated carbon, AC, or carbon nanofiber, CNF).

RESULTS AND DISCUSSION

Metal supported catalysts were prepared using carbon support of high surface area, 1200 m²/g for activated carbon (AC), and also a moderate surface area, 228 m²/g for carbon nanofiber (CNF).

Functionalization of the support with –OH and/or –COOH groups was done for the purpose of anchoring MOF with the carbon support through chemical bonds, rather than weak physical bonds. Also, the oxygen content on the surface of carbon materials, in the presence of Pt or Pd improves the spillover phenomena. Metal concentration on the support is 10% in case of Pt/AC-OH and 15% in the case of Pd/CNF-COOH.

Direct synthesis of MOF on the functionalized support may increase the number of contacts between these two materials, facilitating the spillover mechanism. Pressure-concentration isotherms made for MOF-5@Pt/AC-OH, MOF-5@Pd/CNF-COOH and MOF-5 (for comparison), at room temperature, gave a maximum adsorption capacity of 1.05 % H, 0.90 %H and 0.55 %H respectively at 90bar.

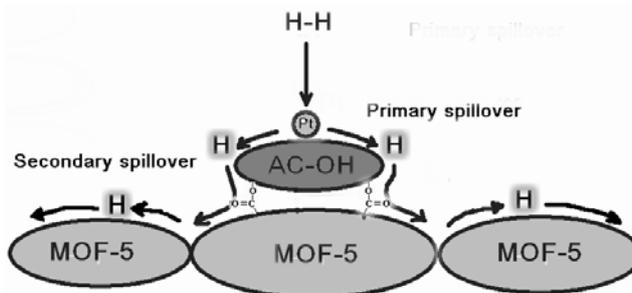


Fig. 2 – Spillover of hydrogen atoms from metal to support to MOF-5.

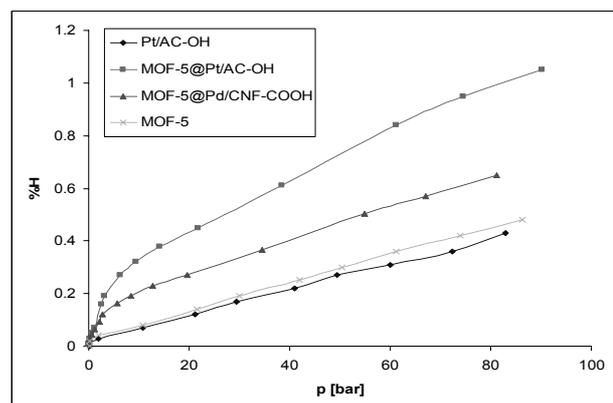
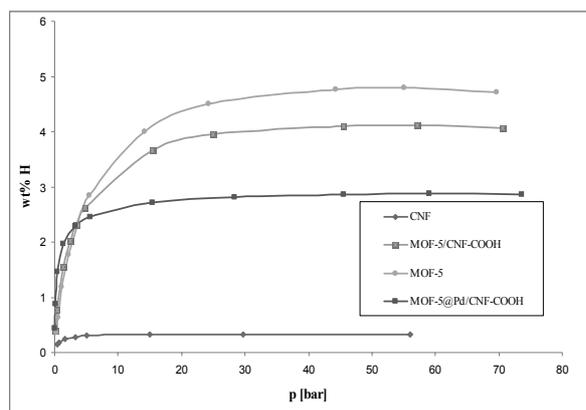


Fig. 3 – Adsorption isotherms at 77K (left) and 293K (right).

This experiment proves that, although the specific surface area is higher for MOF-5, this is not the main factor that contributes to the hydrogen adsorption. The use of Pd or Pt supported catalysts increases the hydrogen adsorption capacity, slightly higher for the latter, see Table 1 below.

Hydrogen adsorption of physical mixture can be calculated using equation 1, where x is weight fraction of the supported catalyst, 10% in case of Pt/AC-OH and 15% in the case of Pd/AC-COOH

$$Q_{\text{composite}} = xQ_{\text{Pt/AC}} + (1-x)Q_{\text{MOF-5}} \quad (1)$$

Table 1

Hydrogen adsorption capacity for different materials versus surface area at 293K

Material	S_{BET} (m^2/g)	wt % H physical mixture	wt. % H r.t.
MOF-5	2650	-	0.48
Pt/AC-OH	900	-	0.42
Pd/CNF-COOH	228	-	0.13
MOF-5@Pd/CNF-COOH	1150	0.41	0.65
MOF-5@Pt/AC-OH	1100	0.45	1.05

EXPERIMENTAL

Functionalization of Pt/AC with OH groups

Commercially available Pt/AC ($S_{\text{BET}} = 1230 \text{ m}^2/\text{g}$) was functionalized with OH groups using H_2O_2 . The reaction takes place at 150°C in H_2O_2 50% sol. for 1-2 h, filtration and drying over night at 125°C .³ Functionalized carbon supported catalyst, Pt/AC-OH, has a specific surface area $S_{\text{BET}} = 900 \text{ m}^2/\text{g}$, proving that the oxidation does not significantly affect the carbon porosity.

Functionalization of Pd/CNF with –COOH groups

Pd supported on CNF was done by wet impregnation method using $\text{Pd}(\text{NO}_3)_2$ solution, drying at 50°C , decomposition at $120\text{--}123^\circ\text{C}$ and reduction of PdO in He and H_2 (16% vol. H_2) at 125°C , for 2h.⁴ Oxidation of CNF needs more energetic conditions: sonication with HNO_3 for 30 minutes, refluxing for 20h, filtration, washing until pH=7 was achieved.

Evidence for -OH groups in AC and -COOH groups in CNF oxidation were made using IR spectroscopy.

Synthesis of MOF-5@Pt/AC-OH and MOF-5@Pd/CNF-COOH

A mixture of $\text{Zn}(\text{NO}_3)_2$, benzene dicarboxylic acid (H_2bdc) and 10% Pt/AC-OH (or Pd/CNF-COOH) in dimethyl formamide was sonicated for 20 minutes, then placed in an autoclave and kept for 2 days at 100°C . The crude product was filtered, washed with chloroform and dried at 50°C . The structure of the compound was characterized using TGA for stability, XRD for crystallographic data, BET for specific surface area.

Hydrogen adsorption measurements

Isothermal desorption curves were measured with a home made P–C–T gas storage device. About 0.3 g of sample was

placed in the reaction tube. Before sample measurements were obtained, all experiments were carried out at room temperature (approximately 293 K) and out gassed under vacuum to a final temperature of 473 K for 3-5 h. The temperature was kept constant and the pressure was increased in equal pressure steps.

CONCLUSIONS

Use of metal supported catalysts for hydrogen adsorption in MOF-5 increases the adsorption capacity by a factor of 2.2, for MOF-5@Pt/AC-OH and a factor of 1.4 for MOF-5@Pd/CNF-COOH compared to the MOF-5 without catalyst.

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