

IMMOBILIZATION OF METAL SALTS IN MIL-101(Fe)

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ABSTRACT

Metal-Organic Frameworks (MOF) represents an emerging class of materials that offer a new opportunity for effective hydrogen storage. We report here on a highly-crystalline iron-terephthalate MIL-101(Fe) impregnated with nickel and magnesium to improve the sorption of hydrogen at operating conditions (temperature, pressure). The initial MIL-101(Fe) material showed highly porous nature, while the immobilization of nickel and also magnesium salts decreased the surface area of the products. Spectroscopic analyses of Ni-MIL-101(Fe) indicated the absence of metal oxides within the pores, nickel is in the pores present as aqua-complex. Hydrogen storage capacity measurements show higher final uptake of H₂ for nickel-impregnated sample comparing to non-modified and magnesium modified samples.

Keywords: hydrogen storage materials, MIL-101(Fe), metal-impregnation.

INTRODUCTION

Hydrogen is an attractive alternative energy carrier of the future because of its high energy content and clean burning, but its storage is still a technological challenge [1, 2]. Metal-Organic Frameworks (MOF) are relatively new class of materials that appeared as promising hydrogen storage materials. Their structures are built of covalently bonded metal clusters and organic linkers and exhibit low density, high porosity and high specific surface area. Additionally, the H₂ sorption process in MOFs is quick and reversible, which is crucial for on-board applications; the disadvantage is that the process requires too low temperatures and too high pressure for an effective storage [3]. The incorporation of under-coordinated metal centres in MOFs (the metal can form additional bonds with ligands to achieve its preferred or most common coordination number) by the impregnation of a given framework with excess metal ions aims to improve sorption of hydrogen at operating conditions (temperature, pressure) [4]. We report here on the immobilization of metal-organic framework structure MIL-101(Fe) with nickel and magnesium salts and on the characterisation of the obtained products emphasised on the nature of metals in the structures.

EXPERIMENTAL

MIL-101(Fe) was synthesised by using FeCl₃·6H₂O (Aldrich, 99 %) and terephthalic acid H₂BDC as a ligand (Acros, 99 %) in N,N-dimethyl-formamide (Aldrich, 99,8 %) with molar ratios of 1.8 : 1 : 137, following a slightly modified procedure for the preparation of amino-terephthalic analogue of MIL-101 [5]. After thermal treatment in Teflon-lined autoclaves (30 mL total volume) at 110 °C for 24 h, the final product (orange powder) was recovered by filtration, washed with DMF, and then dried at ambient conditions. MIL-101(Fe) was impregnated by stirring it for 4 hours at room temperature in either 0.5 M Ni(NO₃)₂·6H₂O (Kemika, 99 %) or 0.5 M MgCl₂·6H₂O (Aldrich, 99 %). The products MIL-101(Fe), Ni-MIL-101(Fe) and Mg-MIL-101(Fe) were initially characterised by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The amount of metal was detected by energy-dispersive X-ray spectroscopy (EDX). The thermal behaviour was investigated by thermogravimetric analysis and high-temperature XRD. X-ray absorption spectra (XAS) were measured in the transmission detection mode at C beamline of the HASYLAB synchrotron in

Hamburg, Germany, to determine the local structure of the present metals. The porosity of the structures was studied by using H₂ adsorption isotherms on HTP1-V volumetric analyzer. The same analyser was used to determine the hydrogen uptake at 77 K in the pressure range from 1 to 32 bar).

RESULTS AND DISCUSSION

SEM images of octahedral crystals of MIL-101(Fe) show one-phase product (Fig. 1). The EDX analysis revealed average content of immobilized metal in the final product to be 1,77 atomic % in Ni-MIL-101(Fe) and 1,15 atomic % in Mg-MIL-101(Fe).

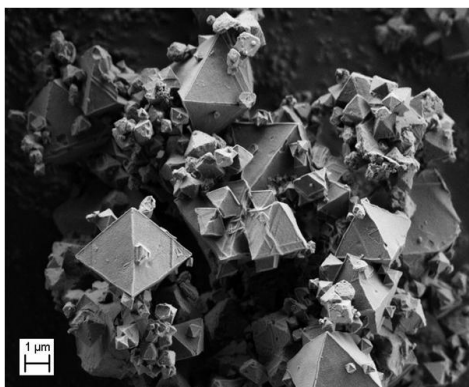


Figure 1. Octahedral crystals of MIL-101(Fe).

The structural changes indicated by TG were also confirmed by HT-XRD. The results show that the products were stable at least up to 300 °C (Fig. 2.a). Mass loss attributed to water desorption is enhanced after nickel and magnesium deposition in Ni-MIL-101(Fe) and Mg-MIL-101(Fe) suggesting the presence of additional water sorption sites (Fig. 2.b, 2.c).

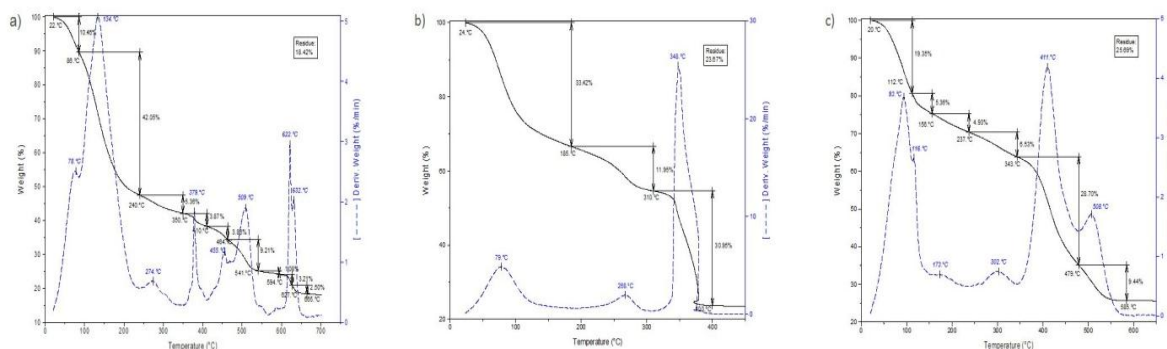


Figure 2. TG measurements of (a) MIL-101(Fe) show weight loss in four major steps and the indicated structural changes by TG were also confirmed by HT-XRD (Fig. 3). Weight loss attributed to water desorption is enhanced after nickel and magnesium deposition in (b) Ni-MIL-101(Fe) and (c) Mg-MIL-101(Fe) suggesting the presence of additional water sorption sites.

By analyzing EXAFS spectra we can obtain the coordination number and the nearest neighbors of the observed; in the case of Ni-MIL-101(Fe) there are 6 oxygen atoms in the first coordination sphere. The EXAFS analysis indicated the presence of well-distributed metal sites, i.e. the absence of NiO clusters in Ni-MIL-101(Fe) sample (Fig. 3).

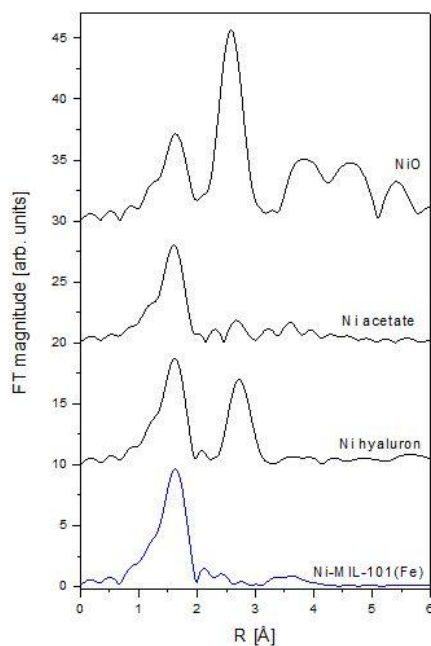


Figure 3. FT XAFS spectre of Ni-MIL-101(Fe) sample compared with different reference compounds.

N₂ adsorption isotherms of non-modified nickel and magnesium modified MIL-101(Fe) samples show that nitrogen uptake is lower after impregnation. Hydrogen adsorption isotherm of nickel modified MIL-101(Fe) show higher final uptake of H₂ comparing to non-modified and magnesium modified sample.

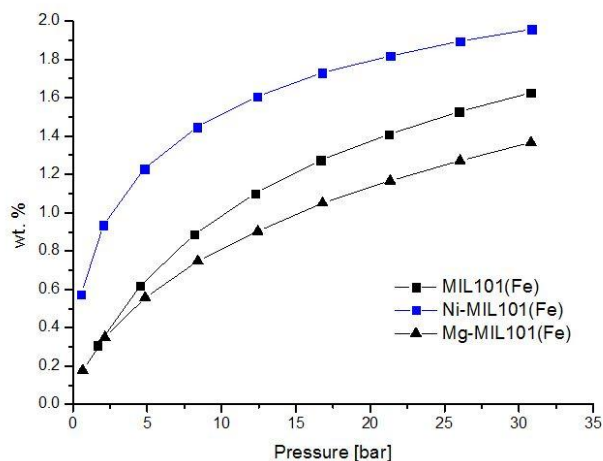


Figure 4. Hydrogen adsorption isotherms of non-modified and nickel and magnesium modified MIL-101(Fe) samples.

CONCLUSION

We synthesised highly-crystalline iron-terephthalate MIL-101(Fe) and additionally immobilised it with nickel and magnesium salts. The initial material showed highly porous nature. Nickel and also magnesium impregnation of MIL-101(Fe) decreased the surface area of the products. Spectroscopic analyses indicated the absence of metal oxides within the pores. The nickel sites are well distributed over the material, which is beneficial for hydrogen storage applications. Hydrogen adsorption measurements for the three samples show the best hydrogen uptake for Ni-MIL-101(Fe).

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