Study of hydrogen adsorption properties on MCM-41 mesoporous materials modified with nickel

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ABSTRACT

MCM-41 samples were modified with different Ni loadings by wet impregnation method and characterized by XRD, ICP, EPMA-EDS, N_2 adsorption−desorption and hydrogen adsorption at 77 K at high and low pressure conditions. The hydrogen adsorption studies for the MCM-41 host and the impregnated samples showed that small amounts of Ni ions in MCM-41 improved the hydrogen storage capacity by spillover effect.

1. Introduction

Hydrogen is one of the main alternatives to replace petroleum products because it is a source of clean and efficient energy. However, there are barriers in its production, transport and storage, which prevent or delay its implementation. Many methods to store hydrogen, including gaseous or liquid form and solid-state storage are studied. Currently, there are researches under way to develop materials such as complex hydrides, carbon nanotubes, metal-organic frameworks and zeolite for hydrogen storage in large quantities at ambient temperatures [1,2]. In this sense, a new family of micelle-templated mesoporous molecular sieves known as MCM-41 has recently been proposed as a potential new hydrogen storage material when they are doped with metals [3,4]. MCM-41 presents regular pore diameters between 2 and 10 nm, large surface areas (>1000 m^2/g), well-defined mesoporous array and good adsorption properties. An important aspect to consider is to find the appropriate metal to modify the MCM-41. It has been reported that the nickel on mesoporous materials enhances the hydrogen adsorption due to the spillover effect, which implies the dissociation of the hydrogen molecules into atoms by transition metals and subsequent diffusion of these atoms to the host material. In this work, we analyze the influence of the Ni content on the structural and textural characteristics of the obtained samples and their relationship with the hydrogen storage capacity.

2.   Material and methods

2.1.   Synthesis

The pure siliceous mesoporous material (MCM-41) was synthesized as previously reported [5] following the method B, using cetyltrimethylammonium bromide (CTAB) as template, tetraethoxysilane (TEOS) (Aldrich 98%) as silicon source and Sodium hydroxide (NaOH) aqueous solution 2 M for hydrolysis and pH adjustment. The molar composition of gel was: NaOH/Si = 0.50, surfactant/Si = 0.12, water/Si = 132. In a usual synthesis, CTAB was dissolved in water–NaOH solution at 313 K; this new solution was then cooled to room temperature and TEOS was finally incorporated. The mixture was vigorously stirred for 4 h at room temperature and then for 3 h at 343 K in a closed flask. The final solid was filtered, washed and dried at 333 K overnight. To remove the template, the samples were heated (heating rate of 2 K/min) under N_2 flow up to 773 K and kept at this temperature for 6 h and then calcined at the same temperature under air flow for 6 h.

Ni/MCM-41 molecular sieves were synthesized with two Ni loadings (1 and 15 wt%) by the wet impregnation method. The MCM-41, previously calcined at 773 K for 5 h, was added to an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ with a concentration corresponding to the desired metallic loading. Then, the water was slowly removed by rotary evaporation at 323 K for about 30 min. The resulting powder was dried at 333 K and then calcined for 9 h at 773 K. The resulting materials were named: Ni/MCM-41(x), where x indicates the expected percentages of the metal loading.

2.2.   Characterization

The X-ray diffraction (XRD) patterns were recorded in a Philips PW 3830 diffractometer with Cu K α radiation (λ = 1.5418 Å) in the range of 2θ from 1.5 to 7° and from 10 to 80°. The interplanar distance (d_{100}) was estimated using the position of the first X-ray diffraction line. The lattice parameter (a_0) of the hexagonal unit cell was calculated as $a_0 = (2^*d_{100})/\sqrt{3}$. The Ni content was determined by Inductively Coupled PALSMA Atomic Emission Spectroscopy (ICP-OES) using a spectrophotometer VISTA-MPX CCD Simultaneous ICP-OES-VARIAN. The specific surface area, the pore size distribution and the total pore volume were determined from N_2 adsorption–desorption isotherms obtained at 77 K using a Micromeritics ASAP 2000. The samples were previously degassed at 300 °C for 12 h. The specific surface area was determined by the Brunauer–Emmett–Teller (BET) method in the pressure range of P/P_0: 0.01–0.25. The pore size distributions were determined by NLDFT method. The surface elemental Energy-dispersive x-ray analysis (EMPA-EDS) was conducted in an electron microprobe Jeol JXA 8230. Hydrogen (99.995%) adsorption capacity at 77 K and pressures to 10 bar were measured in an automated manometric system ASAP 2050 (Micromeritics Instrument Corporation). Previous to all the adsorption experiments, the samples were degassed at 300 °C during 12 h under vacuum conditions (5×10^{-3} mmHg).

3.   Results and discussion

The low-angle XRD patterns of the materials synthesized in this study are shown in Fig. 1a. Three diffraction peaks are clearly observed for the MCM-41, indexed as (100), (110) and (200) reflections, characteristic of a highly ordered mesoporous structure with hexagonal pore array [7]. The low angle XRD patterns of the nickel loaded samples are similar to that of the MCM-41 host, indicating that the structure was preserved after the nickel loading. Thus, this structure allowed a Ni loading of up to ≈12 wt% without collapsing. However, increasing nickel loading, the peaks broaden and their intensities decreased, which again indicates a loss of periodicity concerning to the mesopores.

Fig. 1a inset shows the high-angle XRD patterns of the Ni/MCM-41 samples, which exhibit a broad amorphous silica peak at around 23°. The XRD patterns of Ni/MCM-41(15) showed four narrow and intense peaks at 2θ = 37°, 43°, 64° and 75°, which were assigned to the presence of crystalline nickel oxide NiO [8]. These peaks were difficult to observe on the Ni/MCM-41(1) catalyst, which suggests that the oxides are amorphous clusters or particles too small to be detected by XRD.

All the samples exhibited type IV isotherms typical of mesoporous structure (Fig. 2) with hysteresis loops with parallel and almost horizontal branches, classified as H4-type according to IUPAC. Moreover, all samples exhibited a distinct inflection in the P/P_0 range from 0.1 to 0.25, characteristic of capillary condensation inside the mesopores, and a uniform pore size distribution. These results are in agreement with those previously reported in the literature [6–9]. However, whereas the inflection is sharp for the MCM-41 host (giving account for the narrow pore size distribution), it
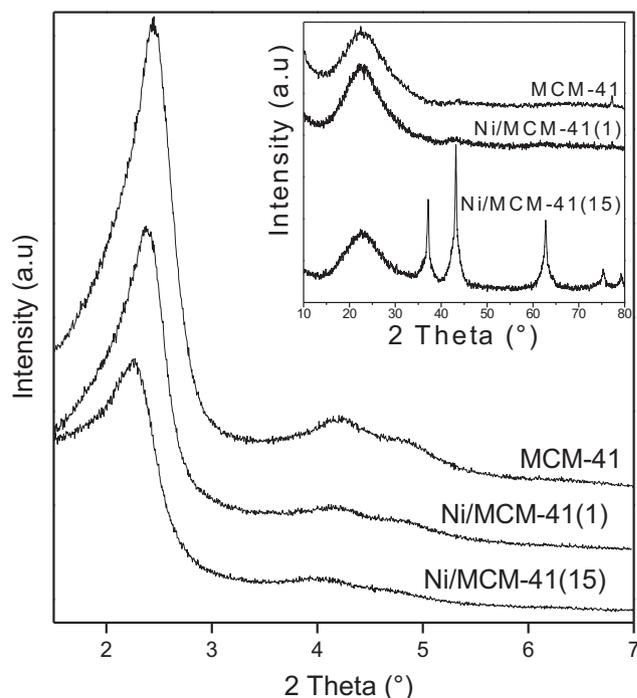

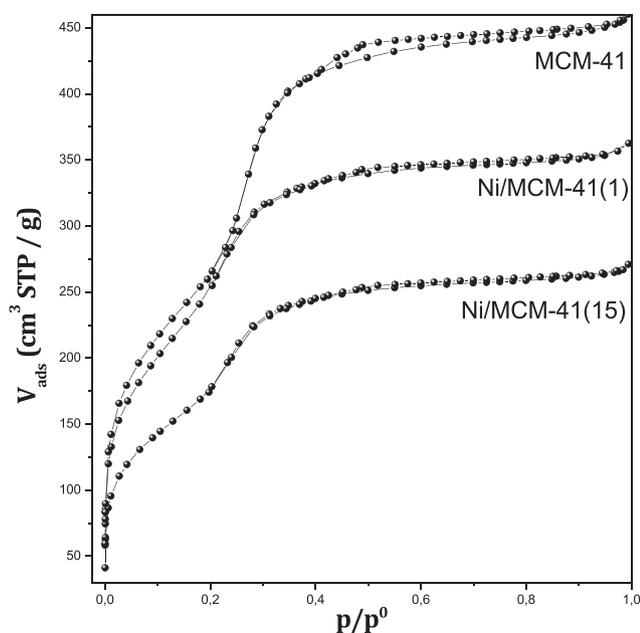**Fig. 1 – Low-angle XRD patterns of samples.**

Fig. 2 – High-angle XRD patterns of samples.

Fig. 3 – Low-pressure adsorption–desorption isotherms of H$_2$ at 77 K.

becomes less pronounced when metal loading increases, in agreement with the loose of structural order detected by XRD. The results obtained from the N$_2$ isotherms and other physicochemical and structural parameters are collected in Table 1. All the samples showed high surface areas and pore volume, which are typical of mesoporous materials; nevertheless, a slight decrease in these values is observed with increasing the Ni content. Thus, the presence of clusters and/or small particles of metal oxides finely dispersed inside the channels as well as large particles (detectable by XRD) on the external surface, could affect the pore structure provoking a decrease in the values of the specific surface area and the pore volume. The highest Ni content would promote the growth of oxides particles on the external surface of the samples, causing the highest structure deterioration. Finally, a wall thickness increase is observed with increasing Ni content which could give account for the increased presence of different Ni species inside the channels.

In order to analyze the capacity of the synthesized materials for the hydrogen storage, the low-pressure H$_2$ adsorption isotherms at 77 K of the bare MCM-41 and the Ni modified MCM-41 sieves were determined and they are shown in Fig. 3. It is important to note that hydrogen is a supercritical gas at 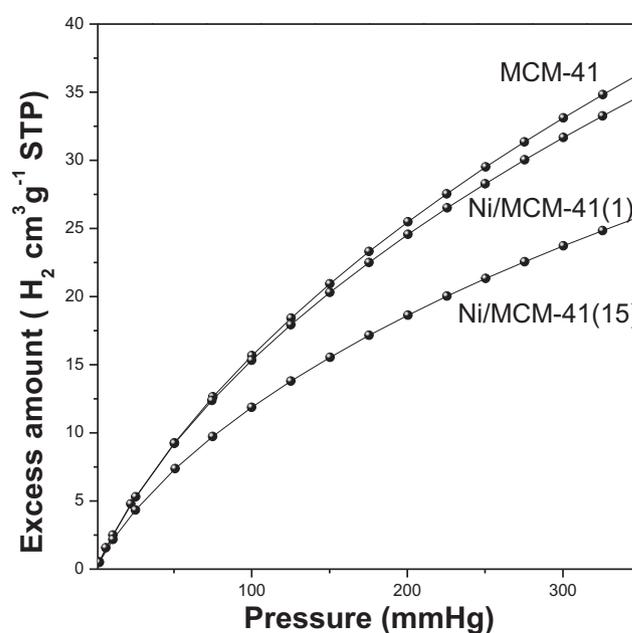the temperature of engineering interest and follows a different adsorption mechanism compared to the sub-critical gases. Thus, here it was observed that the hydrogen storage capacity at low pressure for the samples modified with different Ni contents is lower than the MCM-41. This fact could be inferred from the shape of the isotherms in Fig. 3, which have broad knees and show low interaction between H$_2$ and the adsorbents. This low interaction of the samples with H$_2$, is equal in the Ni/MCM-41(1) sample and the MCM-41, and is similar for the Ni/MCM-41(15). For its part, the high pressure adsorption excess isotherms obtained at 77 K for all of the samples are shown in Fig. 4. Unlike the typical isotherms, in which the maximum working pressure is 1 atm; in the high pressure isotherms is vitally important to differentiate between the excess adsorption and the absolute adsorption. The excess storage capacity is defined as the difference between the quantity of gas which is stored at a temperature, T, and a pressure, P, in a volume containing the adsorbent and the quantity which would be stored under the same conditions in the absence of gas–solid interactions. The absolute adsorption (N_{abs}) is the amount of hydrogen which is adsorbed in the porous material, not considering the gas phase. The relation between the excess adsorption (N_{exc}) and the absolute adsorption (N_{abs}) is defined by the expression:

Table 1 – Structure properties and chemical composition of the synthesized samples.

Sample	Area[a] (m^2/g)	a_o (nm)	Surface Ni (wt%)[b]	Bulk Ni (wt%)[c]	D_p (nm)[d]	V_{TP} (cm^3/g)	t_w[e] (nm)
MCM-41	940	4.09	–	–	3.5	0.70	0.667
Ni/MCM-41(1)	910	4.18	0.83	0.81	3.2	0.56	1.052
Ni/MCM-41(15)	695	4.25	10.54	11.35	3.2	0.41	1.308

[a] Determined by BET.
[b] Determined by EPMA-EDS.
[c] Determined method ICP.
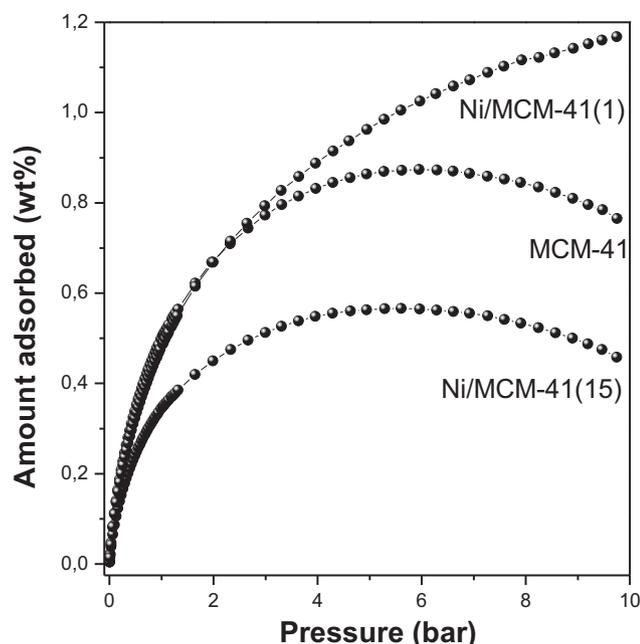[d] N$_2$ adsorption–desorption.
[e] $t_w = a_0 - D_p$.

Fig. 4 − High-pressure adsorption−desorption isotherms of H$_2$ at 77 K.

$$N_{exc} = N_{abs} - \rho_g V_{ads}$$

where ρ_g is the density of the gas phase, and V_{ads} is the volume of the adsorbed phase. The difference between these two quantities is more remarkable when the pressure is increased, because the amount of gas in the porous volume increases due to the pressure, it means that the ρ_g increases at high pressures. The excess isotherms tend to a maximum after which, the excess amount tends to diminish [10,11]. Thus, in our samples, the low interaction of nickel with H$_2$, was modified at high pressure for the lowest nickel content. Probably, from a certain pressure, nickel would serve as a promoter which enables the adsorption continues. In this sense, it was found in literature that the presence of Ni on mesoporous MCM-41 creates hydrogen-favorable sites that enhance the hydrogen-storage capacity by a spillover effect [9−12]. Park et al. have reported the hydrogen storage capacity of mesoporous MCM-41 modified with nickel at high pressure and temperature [9]. They observed that the presence of Ni on MCM-41 created hydrogen-favorables sites that enhanced the hydrogen adsorption by a spillover effect. Others authors presented a study of hydrogen adsorption properties of nickel-doped mesoporous silica at 77 K and 1 bar [3,4,12]. In this work we evidenced a spillover effect at 77 K and pressure up to 10 bars. At low pressure can be observed that the adsorbate−adsorbent interaction is the same for the MCM-41 and the Ni/MCM-41(1) sample, this would indicate that the adsorption sites are SiO$_2$ sites. However, at high pressure the H$_2$ adsorption in MCM-41 material reaches its saturation, and the excess isotherm tends to diminish, while the Ni/MCM-41(1) isotherm continues to increase, indicating the density of the adsorbed phase has increased. This increase of the density of the adsorbed phase could be for a spillover effect. This fact could be due to the nickel is well dispersed in the Ni/MCM-41(1)

catalyst, while the presence of clusters and/or small particles of metal oxides on the external surface in the Ni/MCM-41(15) sample, evidences the low interaction with the support.

For the Ni/MCM-41 samples, a maximum of H$_2$ adsorption of 1168 wt% was observed at 77 K and around 10 bar, corresponding to the Ni/MCM-41(1) sample, followed by the MCM-41 (0.765 wt%) and then the Ni/MCM-41(15) (0.458 wt%). It is interesting that the MCM-41 presents the higher storage capacity at low H$_2$ pressures, but low capacity at high pressures, probably due to the lack of nickel. Meanwhile, the decrease in hydrogen adsorption capacity in the sample with highest nickel content could be due to the gradual deterioration of structure evidenced by XRD, and the formation of oxide clusters or NiO nanoparticles on external surface of silicate. Generally, hydrogen adsorption strongly depends on the textural properties of the samples. Thus, from Table 1 and Fig. 4 it can be clearly seen that the adsorbed hydrogen amount over the materials with similar interaction energy with H$_2$ (MCM-41 and Ni/MCM-41(15)) follow a linear behavior with the specific surface area.

Finally, the hydrogen in the mesoporous of the sample modified with 1 wt% of Ni is more stabilized than in those of MCM-41. This last fact confirms that the nickel presence, in a suitable amount, on mesoporous materials have influence on the formation of hydrogen favorable sites. Probably a hydrogen spillover effect would allow the dissociation of hydrogen molecules on the surface nickel and the consequent adsorption of hydrogen atoms inside channels of MCM-41 [13,14]. Therefore, MCM-41 mesoporous materials modified with low nickel loading would be potentially suitable to be used in hydrogen storage.

4.   Conclusions

Nickel modified molecular sieves were successfully synthesized by the wet impregnation method, with Ni loadings of 0.8 and 12 wt% approximately. All the materials exhibit good structural regularity retaining the MCM-41 structure after the metal loading. However, a high Ni loading affects the structural ordering, the specific surface and pore volume of the material, but do not apparently changes the pore diameter. High-pressure H$_2$ adsorption isotherms at 77 K shows that the hydrogen adsorption depends on the metal loading degree in the materials. Thus, small nickel content on our MCM-41 materials had a positive effect on the hydrogen storage capacity.

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