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## Influence of the Synthesis Time in the Textural and Structural Properties of Ni-Containing Mesoporous Materials.

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### Abstract

MCM-41 materials have been synthesized by hydrothermal synthesis, and the influence of the synthesis time variation on the structural and textural properties of the final solids was studied. Nickel-modified samples were synthesized with a molar ratio Si/Ni of 60 and increased days of synthesis from 0 to 7 days. The structures obtained were characterized by X-ray diffraction (XRD) and UV-vis diffuse reflectance (UV-Vis DRS) spectroscopy.

XRD patterns of samples are typical of MCM-41 structure, which improves with increasing the time of hydrothermal treatment. XRD and UV-vis studies revealed that the short synthesis times do not allow the proper incorporation of nickel in the structure. It was corroborated that, the synthesis time has an important influence on the properties of mesoporous material modified with Ni.

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*Keywords:* Mesoporous materials; synthesis time; nickel; MCM-41.

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### 1. Introduction

The global energetic demand is growing at a fast pace together with the decrease the reserves of fossil fuels. The situation will not be sustainable in the medium term, so it is necessary a transition to a new production form that is clean, safe and reliable. In this context, hydrogen widely is considered as one of the main alternative, because it is an

ideal energetic resource due to lightweight, highly abundant, high calorific power and that can be easily converted to a desired form of energy without releasing harmful emissions [Park, 2010; Züttel, 2003].

Hydrogen is a very light element, which means that the energy stored per unit mass is high, while that per unit volume is low. This is a problem, particularly in transportation applications and portable type [Jena, 2011; Satyapal, 2007].

The mesoporous materials with high specific area and pore volume are currently studied as an alternative for hydrogen storage by adsorption. Among the best known porous solids, MCM-41 silica emerges as one of the more suitable, because of its well-defined mesoporous array, regular pore diameters between 2 and 10 nm and large surface areas ( $>1000 \text{ m}^2/\text{g}$ ). Mesoporous silica doped with metals, which generates the active sites in the framework, is used to catalyst or as adsorbent of voluminous molecule. For this reason, there are many methods for synthesis mesoporous materials and the isomorphous substitution of heteroatoms in the structure [Yakamoto, 2011; Elías, 2011].

The aim of work was investigated the possibility to improve the structure of these materials modified with nickel for hydrogen storage.

## 2. Experimental procedure

### 2.1. Catalyst preparation

The nickel-containing mesoporous materials were prepared by hydrothermal synthesis [Elías et al., 2009] using decyltrimethyl ammonium bromide (CTAB) as a template, tetraethoxysilane (TEOS) (Aldrich 98%) as a Si source, nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) as Ni source and sodium hydroxide (NaOH) aqueous solution for pH adjustment. The molar composition of gel was: Si/Ni = 60, OH/Si = 0.50, surfactant/Si = 0.12, water/Si = 120. In a typical synthesis, the gel was vigorously mixed for 7 h at room temperature, and the result gel was transferred into Teflon-lined stainless-steel autoclave and kept in an oven at 373 K for 0-7 days under autogeneous pressure (0 day, material without hydrothermal treatment). The solid was then filtered off, washed with distilled water at pH 7 and dried at 333 K overnight. To remove the template, the samples were heated (heating rate of  $2 \text{ }^\circ\text{C}/\text{min}$ ) under  $\text{N}_2$  flow up to 773 K maintaining this temperature for 6 h and subsequently calcined at 773 K under air flow for 6 h.

### 2.2. Characterizations

The X-ray diffraction (XRD) patterns were recorded in a Philips PW 3830 diffractometer with Cu K  $\alpha$  radiation ( $\lambda=1.5418 \text{ \AA}$ ) in the range of  $2\theta$  from  $1.5$  to  $7^\circ$  and from  $10$  to  $80^\circ$ . 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  $a_0 = (2 d_{100}) / \sqrt{3}$ . A profile fitting was made to each maximum in the high angle range, and the mean grain size [D] of the corresponding phase was estimated using the Scherrer formula:  $[D]=0.9 \lambda / \beta \cos \theta$ , where  $\beta$  (in radians) is the peak intrinsic breadth after subtraction of the instrumental contribution,  $\lambda$  is the X-ray wavelength and  $\theta$  the diffraction (Bragg) angle. The UV-Vis diffuse reflectance spectra (UV-Vis DRS) were recorded using an Optronic OL 750-427 spectrometer in the wavelength range of 200-900 nm. The specific surface was calculated by the BET method in the pressure range of  $P/P_0$ : 0.01-0.25, using a Micromeritics ASAP 2000.

## 3. Results and Discussion

Table 1 summarizes the synthesis parameters and physical properties of the samples prepared in this study with Si/Ni molar ratio 60 in the synthesis mixture and synthesis times of 0-7 days. The  $a_0$  value was calculated using the first peak in the XRD pattern.

Table 1: Synthesis Parameters and Physical Properties of the synthesized samples

Sample	Synthesis Time (days)	Area (m <sup>2</sup> /g) <sup>a</sup>	a <sub>0</sub> (nm) <sup>b</sup>	d <sub>100</sub> (nm) <sup>c</sup>
Ni(60)0	0	1311	4.09	3,54
Ni(60)1	1	987	4.40	3,81
Ni(60)3	3	940	4.44	3,84
Ni(60)5	5	1165	4.51	3.90
Ni(60)7	7	1097	4.35	3.77

The low-angle XRD patterns of the materials synthesized with relation Si/Ni 60 in the initial gel and synthesis time of 0, 1, 3, 5 and 7 are shown in Figure 1.A. Four diffraction peaks are clearly observed for the MCM-41, indexed as (100), (110), (200) and (210) reflections, characteristic of a highly ordered mesoporous structure with hexagonal pore array. As it is known, the number of well defined peaks and their relative intensities represent the relative structural ordering of a MCM-41 structure [Elias et. al., 2011]. Therefore, the decrease in the intensity of the first peak, besides an evident broadening for all peaks, can be attributed to a lowering of the lattice order.

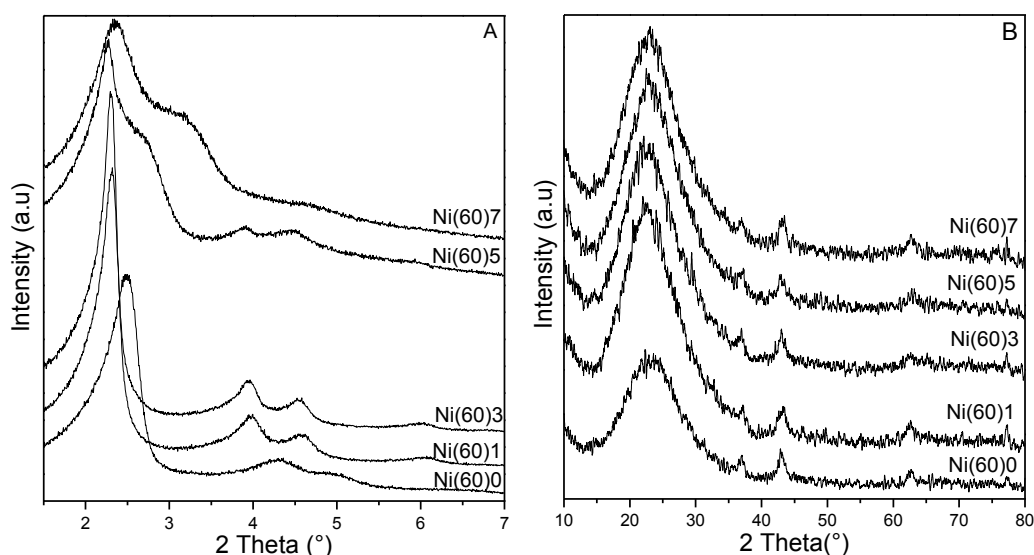


Fig. 1. Low-angle XRD patterns (A) and high-angle XRD patterns (B) of the samples synthesized with Si/Ni 60.

Even though the mesostructure was formed before the hydrothermal treatment, the structural ordering was increased when the samples were hydrothermally treated. However, a different effect of hydrothermal synthesis time on such ordering was observed for the samples. This effect was analyzed for the Si/Ni molar ratio 60, evaluating the structural ordering degree of each sample in comparison to a sample arbitrarily taken as reference with 100% (Si/Ti 60 and hydrothermal synthesis of 3 day) [Eliás, 2009; Eimer, 2008]. Figure 2 shows a degree ordering structural of the samples in function of hydrothermal treatment days. As it can be observed, at 1 day of synthesis the structural regularity was achieved. However, the structural regularity was increased when the sample was hydrothermally treated. A hydrothermal treatment time of 3 days appears optimum to obtain a good structure. Then, a longer time appears to induce some disorder in the structure. These results are in agreement with previous reports [Eimer, 2008; Eliás, 2009; Vaschetto, 2013].

On the other hand, the position of the interplanar distance ( $d_{100}$ ) and the hexagonal unit cell parameter ( $a_0$ ) of the samples, estimated by XRD, are presented in Table 1. The  $d_{100}$  values are shifted to lower angle with the increase the synthesis days, and concurrently lattice parameter ( $a_0$ ) increased when long-range order of MCM-41 diminished and introduction of Ni on silica frameworks. Consequently, this slow shift from the day of hydrothermal treatment can be attributed to the substitution of Si<sup>4+</sup> (radius 40 pm) by the larger Ni<sup>2+</sup> (radius 69 pm) in a state of tetrahedral coordination on silica MCM-41 [Park et. al, 2010].

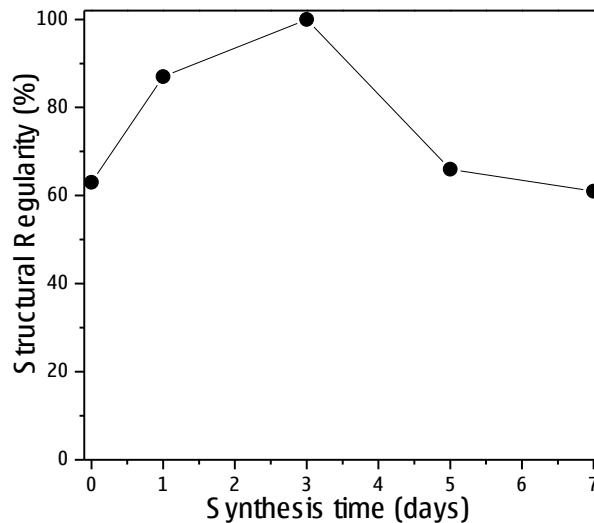


Fig. 2. Effect of synthesis time on the degree of structural regularity of the samples synthesized with Si/Ni molar ratio 60.

Figure 1.B shows the high-angle XRD patterns of the samples. All of the patterns exhibited the broad amorphous silica peak at around  $23^\circ$ . In addition, the samples showed four little peaks at  $2\theta = 37^\circ, 43^\circ, 64^\circ$  and  $75^\circ$ , which are assigned to the presence of crystalline nickel oxide (NiO) [Yakamoto, 2011; Zhao, 2011]. No peaks corresponding of Ni oxides are detected, which could suggest that the oxides are in amorphous state or are clusters / particles too small to be accurately determined by XRD.

DRUV-vis spectroscopy is a useful method to infer on the coordination environment of the different Ni species on the mesoporous samples synthesized, so it is used here to corroborate that nickel atoms are inserted into the silica network and that nickel rich species can also be formed. The DRUV-vis spectra of the samples calcined and not calcined with Si/Ni 60 in the synthesis gel and with different hydrothermal treatment times are shown in Fig. 3. The samples as calcined present a broad adsorption band, which exhibits a maximum at 260 nm with a shoulder at 296 nm and then a long tail towards longer wavelengths. The DRUV-vis spectra of the calcined samples exhibits an intense adsorption band in the 250-350 nm range, also with a maximum at 260 nm and the other at 296 nm. This zone is typically associated to the  $O^{2-}(2p) \rightarrow Ni^{2+}(3d)$  charge transfer transition of octahedral  $Ni^{2+}$  species, although a first maximum at 260 nm could also be attributed to isolated Ni incorporated in the structure [Garbarino, 2013; Liu, 2009]. We can observed that without hydrothermal treatment the second maximum exceeds the intensity of first peak, and at 7 days of hydrothermal treatment the proportion of both peaks is slightly invested. This fact could be indicated that without hydrothermal treatment there is a further segregation of clusters of nickel oxide (in a proportion greater than the isolated Ni). Increase as the days of treatment, nickel is introduced in the structure and there is a less segregation during the calcinations. Also observed in the calcined samples two adsorption bands overlapping at 378 and 420 nm, and an adsorption zone in the 700-800 nm range, which is slightly less intense with the days of hydrothermal synthesis. These absorptions in the visible region are associated to several kinds of d-d transitions, superimposed each other, of  $Ni^{2+}$  ions in octahedral local environment in NiO [Liu et. al, 1998].

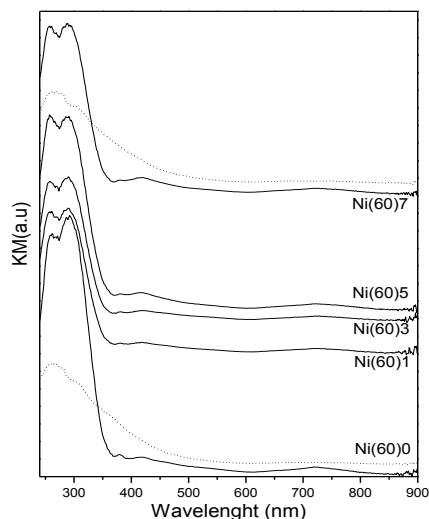


Fig. 3. DRUV-vis spectra of the samples synthesized with Si/Ni molar ratio 60 in the synthesis mixture.

#### 4. Conclusions

All the above results indicate that the synthesis time has a definitive influence in the textural and structural properties of nickel-modified mesoporous materials. For relation Si/Ni 60 in the initial gel, 1 day of synthesis time is enough to achieve a degree of structural ordering evidenced by DRX and surface area measurement. However, when analyzing the incorporation of metal in the structure by DRUV-vis techniques is observed that an increase in treatment allows an optimum incorporation of metal in the structure. Probably, a treatment more prolonged could allow reorganizing the structure and a higher incorporation of amount of nickel into the framework.

We can be concluded that a hydrothermal treatment of 3 days is necessary to achieve high structural ordering and adequate incorporation of nickel, which are important aspect to consider for these materials in the hydrogen storage.

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