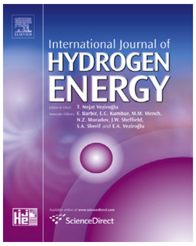
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 39 (2014) 8749–8753

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



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

P. Carraro [a,c,*], V. Elías [c,e], A.A. García Blanco [d], K. Sapag [d], G. Eimer [c,e], M. Oliva [a,b]

[a] IFEG – CONICET – Universidad Nacional de Córdoba, Medina Allende s/n C. Universitaria, 5000 Córdoba, Argentina
[b] FaMAF – Universidad Nacional de Córdoba, Córdoba, Argentina
[c] CITeQ – Universidad Tecnológica Nacional – Facultad Regional Córdoba, Córdoba, Argentina
[d] Laboratorio de Sólidos Porosos – INFAP – CONICET – Universidad Nacional de San Luis, San Luis, Argentina
[e] CONICET, Argentina

ARTICLE INFO

Article history:
Received 18 October 2013
Accepted 5 December 2013
Available online 2 January 2014

Keywords:
MCM-41
Nickel
Hydrogen storage

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.

Copyright © 2013, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

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.

---

[*] *Corresponding author.* IFEG – CONICET – Universidad Nacional de Córdoba, Medina Allende s/n C. Universitaria, 5000 Córdoba, Argentina. Tel./fax: +54 3514334054.

E-mail addresses: carraro@famaf.unc.edu.ar (P. Carraro), griseeimer@yahoo.com.ar (G. Eimer).

0360-3199/$ – see front matter Copyright © 2013, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

http://dx.doi.org/10.1016/j.ijhydene.2013.12.038

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 ($\lambda = 1.5418$ 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 $2\theta = 37°$, 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

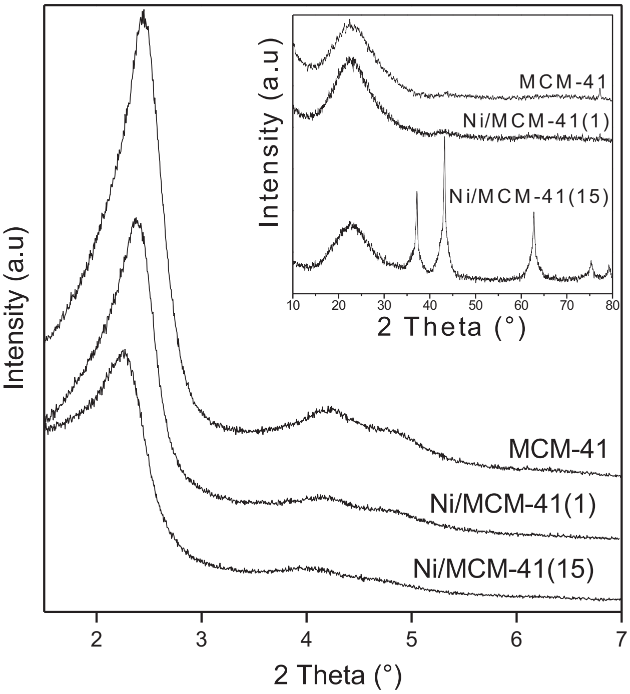


Fig. 1 – Low-angle XRD patterns of samples.

Download English Version:

https://daneshyari.com/en/article/7719460

Download Persian Version:

https://daneshyari.com/article/7719460

Daneshyari.com