Preparation and characterization of zinc containing MCM-41 spheres

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Abstract

A series of pure siliceous and Zn-modified MCM-41 spheres were synthesized at room temperature, atmospheric pressure and at short reaction times. Mesoporous molecular sieves were characterized by a number of techniques: XRD, N_2 adsorption, TEM, XPS and NH_3–TPD. Pure siliceous MCM-41 exhibits the typical hexagonal array of well-defined pores with a mean pore diameter of 3.0 nm. Addition of a small percentage of Zn (Zn/Si ratio 0.02) into the synthesis gel produces a material with increased lattice parameter (a_o), pore diameter and total adsorption capacity. These results suggest the incorporation of zinc, with a larger ionic radius, into the silica framework. Unfortunately, higher zinc contents (Zn/Si ratio 0.04) produce a deterioration of the long-range order of the material, together with a decrease in the surface area and total pore volume. In this sample, the presence of small ZnO nanoparticles embedded into the silica matrix can be envisaged. From a catalytic point of view, these Zn-modified MCM-41 mesoporous molecular sieves appear as quite interesting materials to be used as a catalyst by themselves or as a support for noble metal catalysts.
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1. Introduction

Mesoporous molecular sieves with an ordered porous structure are becoming very promising materials for a wide range of industrial applications [1–3]. The most popular example is the silica-based MCM-41 [4]. The extended use of MCM-41 is based on a well-defined hexagonal array of cylindrical unidimensional pores which provides to the material with excellent textural properties. In fact, these mesoporous molecular sieves exhibit a high surface area and a high pore volume, together with the absence of diffusional restrictions in the pore channels.

Pure siliceous MCM-41 possesses limited applications in catalytic processes due to its poor acidity and redox properties. However, the catalytic behavior can be improved by incorporation of metal cations into the silica matrix. In fact, the isomorphous substitution of Si by other metal ions such as Al [4,5], Ti [6], V [7], Cu [8,9] and Sn [10] have pro-

vide excellent catalysts for a wide range of organic reactions. In this sense, Corma et al. reported an improved catalytic activity and selectivity in Sn modified MCM-41 materials for the Baeyer–Villiger oxidation of ketones with hydrogen peroxide [11]. The promoting effect was attributed to the newly created Sn Lewis acid centers incorporated into the silica framework. These structural sites were able to activate the carbonyl group of cyclic ketones, thus favoring the nucleophilic attack of hydrogen peroxide to the more electrophilic carbonyl carbon atom.

Zn-based catalysts are also very important systems for many organic reactions dealing with carbonyl species [12,13]. However, Zn incorporation into the structure of MCM-41 materials is more difficult and only a few studies can be found in the literature [14–16]. In fact, incorporation of a limited amount of Zn was achieved by direct synthesis of Zn/Si molecular sieves, the final material showing a decreased ordered structure with an increase in the amount of Zn [15]. Higher Zn loadings (Zn/Si ratio 0.04–0.15) were achieved by post-synthesis grafting. However, the structure of these MCM-41 materials was drastically

deteriorated (total amorphization) even after incorporation of a small amount of Zn [16]. Recently, these studies have been extended to bimetallic substitutions such as those involving ZnAl [5] and CuZn [8,9]. In all cases, the long-range hexagonal ordering of the MCM-41 structure is only preserved for low metal contents.

Synthesis of high quality mesoporous molecular sieves with a well-defined morphology is highly desirable for a wide range of industrial application, e.g. high performance liquid chromatography (HPLC) and supercritical fluid chromatography (SFC). However, the majority of the studies reported in the literature deal with MCM-41 materials with no defined morphology. With this in mind, this manuscript reports the high pH synthesis of pure silica and Zn-modified MCM-41 spheres at room temperature, atmospheric pressure and at short reaction times. The textural and chemical properties of these mesoporous materials have been characterized by X-ray diffraction (XRD), N_2 adsorption at 77 K, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption of ammonia (TPD–NH_3). These Lewis acid molecular sieves (Zn-MCM-41) will be used in a subsequent work as a support of noble metal catalysts for chemo-selective hydrogenation reactions.

2. Experimental section

2.1. Sample preparation

Mesoporous MCM-41 spheres containing different amounts of Zn (Zn/Si ratio 0.02 and 0.04) were synthesized at room temperature following the recipe described by Grün et al. for pure siliceous MCM-41 [17]. In a typical synthesis process, a solution containing 180 g ethanol and 39.6 g NH_3 (32 wt.%) was added to an aqueous solution of hexadecyltrimethylammoniumbromide (C_{16}-TMABr) (20 wt.%). For the pure siliceous MCM-41, the surfactant solution was stirred for 30 min and tetraethoxysilane (TEOS) was added resulting in a gel with the following molar composition: 1 SiO_2: 0.3 C_{16}TMABr: 144 H_2O: 58 EtOH: 11 NH_3. For the Zn containing MCM-41 materials, the appropriate amount of $Zn(NO_3)_2 \cdot 6H_2O$ was added to the surfactant solution containing ethanol and NH_3. In the ammonia media, the initial $Zn(OH)_2$ species form an amino complex which prevents precipitation and subsequent loss of metal. After 30 min under stirring, TEOS was added to the solution as described above. After stirring for 12 h at room temperature, the white precipitate was filtered and washed with 100 ml of MeOH and 100 ml of H_2O. The resulting solids were dried at 373 K for 12 h and calcined at 823 K for 5 h. The calcined samples were labelled MCM-41, for the pure mesoporous silica, and Zn(A)MCM-41 (2 wt.% Zn; Zn/Si atomic ratio 0.02) and Zn(B)MCM-41 (4 wt.% Zn; Zn/Si atomic ratio 0.04) for the zinc containing MCM-41 samples.

2.2. Sample characterization

The chemical composition of the pure siliceous and doped-MCM-41 samples was determined by X-ray fluorescence spectroscopy (XRF). X-ray diffraction patterns of calcined samples were obtained with a JSO Debye-Flex 2002 system, from Seifert, fitted with a Cu cathode and a Ni filter, and using a 2°min^{-1} scanning rate. The *d*-spacing and unit cell parameters were calculated from the XRD data. For the unit cell parameter (a_o) the following equation was used: $a_o = 2d(100)/\sqrt{3}$.

Textural characterization of the calcined samples was performed in a Coulter Omnisorb-610 equipment by nitrogen adsorption and desorption at 77 K. Before the experiment, the samples were outgassed at 523 K for 4 h under vacuum (10^{-5} Torr). The apparent surface area was obtained using the BET method. The plots corresponding to the α_s method were constructed using the N_2 adsorption data from a non-porous silica reference (Degussa TK 800) [18]. The pore diameter (d_p) was calculated from the interplanar spacing (d_{100}), obtained from XRD, and the mesopore volume (V_m), obtained from the corresponding α_s plots, using the following equation [19]:

$$d_p = c \cdot d_{100} \sqrt{\frac{(\rho_{silica} V_m)}{(1 + \rho_{silica} V_m)}} \qquad (1)$$

where $c = 1.213$ and ρ_{silica} is the density of the siliceous walls (2.2 g cm^{-3}). Eq. (1) is obtained assuming an infinite array of cylindrical pores arranged in a hexagonal pattern (geometrical approach).

TEM observations were carried out on a JEOL model JEM-2010 electron microscope working at 200 kV, equipped with a INCA Energy TEM 100 analytical system and a SIS MegaView II camera. Samples for analysis were suspended in methanol and placed on copper grids with a holey-carbon film support.

X-ray photoelectron spectra (XPS) were acquired with a VG-Microtech Multilab 3000 spectrometer equipped with a hemispherical electron analyzer and a Mg Kα ($h = 1253.6$ eV, 1 eV $= 1.6302 \times 10^{-19}$ J) 300 W X-ray source. The powder samples were pressed into small inox cylinders and then mounted on a sample rod, placed in a pre-treatment chamber, before being transferred to the analysis chamber. Before recording the spectra, the sample was maintained in the analysis chamber until a residual pressure of ca. 4×10^{-9} Torr was reached. The spectra were collected at a pass energy of 50 eV. The intensities were estimated by calculating the integral of each peak, after subtraction of the S-shaped background, and by fitting the experimental curve to a combination of Lorentzian (30%) and Gaussian (70%) lines. All binding energies (BE) were referenced to the C 1 s line at 284.6 eV, which provides binding energy values with an accuracy of ±0.2 eV. Surface Zn/Si atomic ratios were estimated from the integrated intensities corrected for atomic sensitivity factors.