



## Short Communication

## Effect of the cerium loading on the HMS structure. Preparation, characterization and catalytic properties

Maria Luisa Saladino <sup>a,\*</sup>, Delia F. Chillura Martino <sup>b</sup>, Elka Kraveva <sup>c</sup>, Eugenio Caponetti <sup>a,b</sup><sup>a</sup> Centro Grandi Apparecchiature-UniNetLab, Università di Palermo, Via Marini 14, Palermo I-90128, Italy<sup>b</sup> Dipartimento di Scienze e Tecnologie Biologiche Chimiche e Farmaceutiche and INSTM Udr - Palermo, Università di Palermo, Parco d'Orleans II, Viale delle Scienze pad.17, Palermo 90128, Italy<sup>c</sup> Leibniz Institute for Catalysis, University of Rostock (LIKAT), Albert-Einstein-Str. 29 a, D-18059 Rostock, Germany

## ARTICLE INFO

## Article history:

Received 20 December 2012

Received in revised form 20 February 2013

Accepted 22 February 2013

Available online 4 March 2013

## Keywords:

Mesoporous

HMS

Cerianite

Catalytic evaluation

## ABSTRACT

Ce–HMS mesoporous materials were prepared by incipient wetness method starting from HMS synthesized in acid condition. The effect of cerium quantity, in the range of Ce/Si atomic ratio 0.02–0.3, on its structure and properties was investigated. Results showed that the HMS hexagonal structure was maintained after the cerium adding. Furthermore, the surface area and the pore volume were reduced. The presence of the *cerianite* nanoparticles located within the HMS channels up to 0.05, thus covering the HMS surface at higher Ce/Si atomic ratio, was observed. The catalytic performances of the materials were tested in ethanol partial oxidation reaction.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Since it was first reported by Mobil Company in 1992 [1], mesoporous materials, such as MCM-41, SBA-15 and hexagonal mesoporous silica (HMS), play a significant role in several fields such as adsorption, medication, catalysis, etc. Their high specific surface area and tuneable pore size make them very attractive supports; in fact, they are capable of holding metal oxides in nanodimensions that, due to interactions with the host structure, can infer redox and acid catalytic properties and high catalytic activity [2–4].

In catalysis the rare earths were mainly used as promoters but can be used as the active components of catalyst in the oxides or in the microporous materials [5, 6]. In particular, cerium containing MCM-41 material has been used for many catalytic applications [7, 8]. The cerium incorporation into the mesoporous silica network or the adding of its oxides on the surface makes a mesoporous material a bifunctional catalyst in heterogeneous acid as well as redox catalysis.

Catalyst precursor, support, preparation method and metal loading can influence the behavior of cerium catalysts [9]. Most of the papers report the incorporation of cerium in the MCM-41 framework during

the synthesis. At our knowledge, only few papers report the adding of cerium oxides on the surface [10].

Partial oxidation is a very interesting process for hydrogen production because the system can be auto-thermally run, thereby eliminating the need for external heat. Moreover, it is much faster than catalytic steam reforming, which allows a quick start-up and short response times. Ethanol partial oxidation follows a very complex pathway, including several reaction intermediates formed and decomposed on both, the supports and active metals, making up the catalytic systems. The nature of the support directly influences the product distribution and catalyst stability during ethanol conversion reactions [11, 12]. Several active phases have been proposed to serve as a good supports of catalyst for this reaction [13–15]. Since HMS exhibits high surface area and highly ordered mesopores in the range 20–100 Å, the synthesis of Ce containing HMS mesoporous materials will definitively open up a new possibility for the catalysts with uniform pores in the mesoporous region so that large molecules can freely diffuse through their pores [16].

In this paper, the preparation of a new material, the Ce–HMS, is reported. HMS was synthesized in acid conditions, and then, the cerium oxide was added by using the incipient wetness method. Small angle X-ray scattering, X-ray diffraction, N<sub>2</sub> adsorption and <sup>29</sup>Si Cross Polarization–Magic Angle Spinning NMR are carried out to investigate the effect of cerium/silica molar ratio on the characteristics of mesoporous Ce–HMS. Finally, the catalytic activity of the prepared samples was evaluated in the bio-ethanol partial oxidation reaction.

\* Corresponding author. Tel.: +39 091 23897921; fax: +39 091 590015.  
E-mail address: [marialuisa.saladino@unipa.it](mailto:marialuisa.saladino@unipa.it) (M.L. Saladino).

## 2. Experimental section

### 2.1. Materials

Cetyltrimethylammonium bromide (CTAB, Aldrich), cerium nitrate esahydrate (Aldrich), hydrochloric acid (Aldrich, 37%), and tetraethoxysilane (TEOS, Fluka) were used as received. Solutions were prepared by weight adding conductivity grade water.

### 2.2. Sample preparation

#### 2.2.1. HMS

Mesoporous silica was prepared by adding the silica precursor tetraethoxysilane to an aqueous solution containing cetyltrimethylammonium bromide (CTAB) as template in acid environment. The reactants molar ratios were: CTAB/SiO<sub>2</sub> = 0.21, HCl/SiO<sub>2</sub> = 2.1 and H<sub>2</sub>O/SiO<sub>2</sub> = 146. The obtained precipitate was recovered after 2 h by filtration, washed, dried at room temperature and calcined on air at 600 °C for 4 h.

#### 2.2.2. Ce-HMS

Five samples with Ce/Si atomic ratio *R* equal to 0.02, 0.05, 0.1, 0.2, and 0.3 were prepared by impregnation. Calcined mesoporous silica samples were treated with ethanol solutions containing the adequate amounts of cerium nitrate, following the incipient wetness method [17]. Samples were treated for 24 h at 60 °C in order to move away the ethanol. The dry materials were thermally treated at 350 °C for 1 h and, then, at 400 °C for 2 h. At the end of the impregnation process the material color changed from white to yellow wherein its intensity depends on cerium loading. An aliquot of non-impregnated HMS was treated at the same conditions in order to be used as *reference* sample (*R* = 0).

### 2.3. Characterization methods

*Small Angle X-ray Scattering* measurements were taken using a Bruker AXS Nanostar-U instrument wherein its source was a Cu rotating anode working at 40 kV and 18 mA. The X-ray beam was monochromatized at a wavelength  $\lambda$  of 1.54 Å (Cu K $\alpha$ ) using a couple of Göbel mirrors and was collimated using three pinholes with diameters of 500, 150 and 500  $\mu$ m. Samples were directly mounted on the sample stage to avoid additional scattering of the holder. Data were collected at room temperature for 1000 s, and were recorded in a two-dimensional multiwire proportional counter detector placed at 24 cm from the sample. The measurements were carried out in two different portions of each sample to check its homogeneity.

*X-ray diffraction* (XRD) patterns were recorded with a Philips diffractometer in the Bragg–Brentano geometry using a Ni filtered Cu K $\alpha$  radiation ( $\lambda$  = 1.54056 Å) and a graphite monochromator in the diffracted beam. The X-ray generator worked at 40 kV and 30 mA; the instrument resolution (divergent and antiscatter slits of 0.5°) was determined using standards free from the effect of reduced crystallite size and lattice defects. The diffraction patterns were analyzed according to the Rietveld method [18] using the program MAUD [19].

*N<sub>2</sub> absorption-desorption isotherms* were registered at 77 K using a Quantachrome Nova 2200 Multi-Station High Speed Gas Sorption Analyzer. Samples were outgassed for 3 h at 573 K in the degas station. Adsorbed nitrogen volumes were normalized to the standard temperature and pressure.

<sup>13</sup>C *Cross Polarization–Magic Angle Spinning Nuclear Magnetic Resonance* (<sup>13</sup>C {<sup>1</sup>H} CP–MAS NMR) spectra were obtained at room temperature through a Bruker Avance II 400 MHz (9.4 T) spectrometer operating at 79.4 MHz for the <sup>29</sup>Si nucleus with MAS rate of 5 kHz, 4096 scans, contact time of 8 ms and repetition delay of 8 s. The optimization of the Hartmann–Hahn condition [20] was obtained using a

Q<sub>8</sub>M<sub>8</sub> (Si[(CH<sub>3</sub>)<sub>3</sub>Si<sub>8</sub>O<sub>20</sub>) standard. All samples were placed in a 4 mm zirconia rotor sealed with KEL-F caps.

### 2.4. Catalytic test

The obtained materials were tested in the bio-ethanol partial oxidation reaction as a probe reaction.

The experiments were carried out in a fixed bed reactor at atmospheric pressure and a temperature of the reactor furnace between 400 and 600 °C in order to avoid thermal hot spot effect in catalytic levels determined real maximal temperature around 700 °C [21]. This effect, described by W.Wang et al. [22], is due to the overall exothermic nature of reactions contributing to the catalytic partial oxidation of ethanol. Typically, around 150 mg of each sample was mixed with silica as an inert material in a ratio of 1/10. The catalytic test was carried out using a constant feed composition with an oxygen:ethanol molar ratio of 0.75. Environmentally sustainable bio-ethanol (Richter GmbH) with 96.6% purity was used as fuel. A constant bio-ethanol flow rate of 10 g/h was evaporated at 120 °C and then mixed with a gas stream of Air (291 ml/min) and nitrogen (100 ml/min). The nitrogen was used as the inert component as a balance. Space velocity (GHSV), defined as the ratio of the total volumetric flow at reaction conditions to the catalytic volume, was 35,000 h<sup>-1</sup>. Composition of the inlet and outlet gases was analyzed on-line using a Shimadzu gas chromatograph equipped with FID and TCD detectors at  $\lambda$  = 0.25 nm. The carbon balance was around 100% for all samples. To evaluate catalyst performance, the following parameters were calculated:

$$\text{Conversion of ethanol } X_{\text{Ethanol}}(\%) = \frac{F_{\text{Ethanol}_{\text{in}}} - F_{\text{Ethanol}_{\text{out}}}}{F_{\text{Ethanol}_{\text{in}}}} \times 100$$

$$\text{Selectivity to hydrogen } S_{\text{H}_2}(\%) = \frac{F_{\text{H}_2}}{n_i \times (F_{\text{Ethanol}_{\text{in}}} - F_{\text{Ethanol}_{\text{out}}})} \times 100$$

$$\text{Selectivity to carbon-containing products } S_i(\%) = \frac{F_{\text{carbon-containing-products}}}{n_i \times (F_{\text{Ethanol}_{\text{in}}} - F_{\text{Ethanol}_{\text{out}}})} \times 100$$

where  $F_{i_{\text{in}}}$  and  $F_{i_{\text{out}}}$  are the molar flow of the *i* species at the inlet and outlet of the reactor respectively, and  $n_i$  is the stoichiometric factor between the carbon-containing products and ethanol. The quantity of water in the system was not calculated because of working in a dry base in gas phase.

## 3. Results and discussion

### 3.1. Structural characterization

The SAXS two-dimensional patterns of HMS and of Ce-HMS samples were isotropic. They were averaged around annular rings, thus providing the scattering intensity  $I(Q)$  in the 0.02–0.8 Å<sup>-1</sup> *Q* range. *Q*, the momentum transfer, is equal to  $4\pi\sin\theta/\lambda$ , being  $2\theta$  the scattering angle. Measurements, carried out on different portions of the samples, were overlapped thus showing that samples are homogeneous. SAXS data of Ce-HMS samples, after correction for the background, are reported versus  $2\theta$  in Fig. 1.

The presence of a strong diffraction peak around  $2\theta = 2.8^\circ$  is a characteristic of the (1 0 0) plane for the hexagonal lattice, typical of HMS [23]. The peak is also present in the impregnated samples at low cerium amount indicating that the pore structure of HMS was not modified as a consequence of the impregnation. However, by increasing the cerium amount a decrease of the intensity and a small shift of the peak were observed which indicates a disordering of the hexagonal arrangement of pores.

The interplanar distance in the (1 0 0) direction,  $d_{100}$ , was calculated by Bragg's Law ( $\lambda = 2d_{hkl} \sin \theta$ ) and the unit cell parameter ' $a_0$ ', indicating the distance between the center of two adjacent pores in the

Download English Version:

<https://daneshyari.com/en/article/50002>

Download Persian Version:

<https://daneshyari.com/article/50002>

[Daneshyari.com](https://daneshyari.com)