



## Magnetic properties and catalytic performance of iron-containing mesoporous molecular sieves

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### ABSTRACT

Fe-containing mesoporous molecular sieves were synthesized by the wet impregnation method with two different metallic loadings. The resulting iron oxide/silica composites were then submitted to a reduction treatment for 6 h at 873 K, under H<sub>2</sub> flow. The microstructure of both, the Si-MCM-41 host and the impregnated composites were characterized by XRD, N<sub>2</sub> adsorption, DRUV-vis and Mössbauer spectroscopy. The magnetic behavior of each microstructure was characterized by the magnetization dependence on the magnetic field (up to 1.5 T) and temperature (between 5 and 300 K). The catalytic performance was tested for cyclohexene oxidation by hydrogen peroxide and further correlated with the observed magnetic properties. It was found that the reduction treatment largely affects the selectivity to reaction products, leading to catalysts exhibiting a selectivity of 80% towards the allylic oxidation products. This is attributed to a large free radical generation arising from the interaction between the hydrogen peroxide and the partially reduced iron species (mainly Fe<sup>0</sup> and Fe<sub>3</sub>O<sub>4</sub>), exhibiting superparamagnetic and/or ferromagnetic character.

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### 1. Introduction

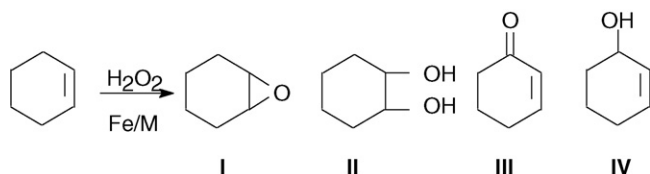
Since their discovery, the MCM-41 molecular sieves have been the basis of different catalysts of spread use in industrial processes. Their special features of high surface areas (>1000 m<sup>2</sup>/g) and highly ordered porous structure (with pore diameter between 2 and 10 nm) confer these materials a high adsorption capacity even for large molecules. The surface of the MCM-41 materials may be modified by inserting different transition metals, and the resulting catalysts are applied to numerous chemical reactions, among which special attention has been paid to the oxidation of organic substrates [1–4]. In the fine chemical industry, the selective oxidation reactions are carried out with significant amounts of transition metals and organic peroxyacids as reactive; the use of modified MCM-41 type molecular sieves emerged as an interesting option for the development of environ compatible processes. In addition, the diluted hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is one of the most conve-

nient oxidants in use due to its easy manipulation, high active oxygen content and the absence of by-products [5]. In this context, the oxidation reactions of organic compounds, mainly bulky olefins, have gained interest [1]. Among the studied olefins, the cyclohexene is frequently used to evaluate the redox ability of modified MCM-41 using H<sub>2</sub>O<sub>2</sub> as oxidant [6]. Scheme 1 shows the typical products of this reaction. The cyclohexene oxide (**I**), generated by the heterolitic epoxidation of the cyclohexene double bond and the 1,2-cyclohexanediol (**II**) side product formed by hydrolysis of the epoxide ring, generally reflect a concerted process. The allylic oxidation products, 2-cyclohexen-1-one (**III**) and 2-cyclohexen-1-ol (**IV**), are often ascribed to a homolytic radical path [7,8].

The introduction of Fe into the molecular sieves has received much attention because of its activity in alkylation and oxidation reactions [1,2,9]. The mesoporous molecular sieves are generally constituted by diamagnetic units as carbon or silica [2] and the incorporation of magnetic ions/species in different oxidation states may lead to special catalytic behavior. In this sense, the development of molecular sieves with magnetic properties found wide application in processes of magnetic separation, transport of adsorbed compounds in a magnetic field [3,4], in the development

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**Scheme 1.** Products of cyclohexene oxidation by hydrogen peroxide. Cyclohexene oxide (I), 1,2-cyclohexanediol (II), 2-cyclohexen-1-one (III) and 2-cyclohexen-1-ol (IV).

of magneto-chemical sensors [10–12], as high density magnetic recording supports and other nano-devices [13]. In particular, the catalytic activity of mesoporous molecular sieves modified with Fe and its relationship with their magnetic properties have been reported [14,15] for the selective reduction of NO<sub>x</sub>.

In this work, mesoporous molecular sieves Si-MCM-41 have been synthesized and modified with Fe by the wet impregnation method. In addition, these materials were submitted to a high temperature reduction process to generate Fe-containing species in different oxidation states on the surface. These catalysts were evaluated in the cyclohexene oxidation with H<sub>2</sub>O<sub>2</sub>. Special attention was paid to the reaction product selectivity as a function of the treatment performed on the samples, and the catalytic behavior was related with the observed magnetic properties.

## 2. Experimental procedures

### 2.1. Synthesis

The pure siliceous mesoporous material (Si-MCM-41) was synthesized by using cetyltrimethylammonium bromide (CTAB) as template and tetraethoxysilane (TEOS) (Aldrich 98%) as silicon source. Sodium hydroxide (NaOH) aqueous solution 2 M was used for hydrolysis and pH adjustment. The catalyst was synthesized from gel of molar composition: NaOH/Si = 0.50, surfactant/Si = 0.12, water/Si = 132. In a typical 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 sample was heated (heating rate of 2 K/min) under N<sub>2</sub> flow up to 773 K and kept at this temperature for 6 h; it was then calcined under air flow for 6 h at 773 K.

The Si-MCM-41 host was then modified with Fe by the wet impregnation method. In order to obtain two different metallic loadings, an appropriate amount of none-hydrate iron (III) nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) aqueous solution 2 or 5 M was added to the out gassed Si-MCM-41 (5 h in oven at 773 K). Then, water was slowly removed by rotary evaporation at 323 K for 30 min. The resulting powder was dried at 333 K and then calcined for 6 h at 773 K. Some of these samples were reduced in a H<sub>2</sub> flow of 50 mL/min. The samples were placed in a quartz reactor, heated at a rate of 10 K/min under H<sub>2</sub> flow up to 873 K and kept at this temperature for 6 h. The resulting materials were named: Fe/M(x) or Fe/M(x)R, where x is the initial concentration of the impregnating solution and R indicates that the sample was reduced.

### 2.2. Characterization

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 70 $^\circ$ . 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  $a_0 = (2/\sqrt{3}) d_{(100)}$ . 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 formulae:  $[D] = 0.9\lambda/\beta \cos \theta$ , 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.

UV–vis diffuse reflectance (DRUV–vis) spectra were recorded using an Optronic OL 750–427 spectrometer in the wavelength range 200–1000 nm. The original spectra obtained were fitted by three Gaussian bands using the conventional least squares method. Curve-fitting calculations were useful in determining each band location and relative area, with confidence levels given by  $\chi^2 \leq 0.0005$  and  $R^2 \geq 0.99$ . The Fe content was determined by atomic absorption spectroscopy (AA) using a Varian SpectrAA 220. Specific surface area, pore size distribution and total pore volume were determined from N<sub>2</sub> adsorption–desorption isotherms obtained at 77 K using a Quantachrome Autosorb Automated Gas Sorption System. The surface area was determined by the BET method in the pressure range of  $P/P_0$ : 0.01–0.25. The pore size distribution was calculated by the Barrett–Joyner–Halenda (BJH) method, based on the Kelvin equation [16]. Mössbauer spectra were recorded in transmission geometry using a constant acceleration spectrometer with a 50-mCi <sup>57</sup>CoRh source at room temperature.

The room temperature magnetization curves were measured in a vibrating sample magnetometer (VSM) LakeShore 7300, with static field up to  $\mu_0 H = 1.5 \text{ T}$ . Magnetization and hysteresis loops as functions of temperature were measured in a Quantum Design SQUID magnetometer up to 6 T. The hysteresis properties as coercivity and remanence were obtained directly from the magnetization curves; these hysteresis curves were well fitted by the sum of three contributions: a linear paramagnetic or diamagnetic contribution (LM), a ferromagnetic one (FM) [17], and a superparamagnetic-like one (SPM) [18], so that the total magnetization results:  $TM = LM + FM + SPM$ , with:

$$LM = \chi \mu_0 H_i \quad (1)$$

$$FM = \frac{2M_{sf}}{\pi} \left( \arctan \left( \frac{H_i + H_{ic}}{H_{ic}} \right) \tan \frac{\pi M_r}{M_{sf}} \right) \quad (2)$$

$$SPM = M_{ssp} \left\{ \coth h \frac{\mu(H_i + H_i^*)}{k_B T} - \frac{k_B T}{\mu(H_i + H_i^*)} \right\} \quad (3)$$

here  $M_{sf}$ ,  $\mu_0 H_{ic}$  and  $M_r$  are the effective ferromagnetic saturation magnetization, the coercive field and the remanent magnetization, associated to the ferromagnetic contribution, respectively.  $M_{ssp}$ ,  $\mu_i$  and  $H_i^*$  are the effective saturation magnetization, the mean magnetic moment of the activated clusters and a mean interaction field [18], introduced to account for the effect of eventual interactions between particles on the superparamagnetic-like component of the  $M(H)$  loops.

The temperature dependence of the magnetization was measured following the conventional zero field cooling (ZFC) and field cooling (FC) protocols, under a small applied field of 10 mT.

### 2.3. Catalytic experiments

The cyclohexene oxidation reactions with H<sub>2</sub>O<sub>2</sub> were carried out at 343 K, under vigorous stirring, in a batch reactor immersed in a thermostatic bath. Typically, the reacting mixture consisted of 9.00 mg of catalyst, 91.90 mg of cyclohexene (Baker 98%), 26.60 mg of oxidant (hydrogen peroxide 35% (w/w), Riedel-de Haen) and 678.30 mg of solvent (acetonitrile, Cicarelli). The substrate to oxidant molar ratio was 4:1 or 2:1. Samples were withdrawn at different times and analyzed by gas chromatography (Hewlett Packard 5890 Series II) using a capillary column (cross-linked

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