



Influence of the Brönsted and Lewis acid sites on the catalytic activity and selectivity of Fe/MCM-41 system

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ARTICLE INFO

Article history:

Received 26 March 2012

Accepted 2 June 2012

Available online 9 June 2012

Keywords:

POX isomerization

Lewis acid sites

MCM-41

Mössbauer spectroscopy

ABSTRACT

The system Fe₂O₃/MCM-41, with high iron dispersion, was synthesized in order to introduce Lewis acid sites into the MCM-41 structure. Two calcination atmospheres (inert and oxidant) were used to produce iron nanoclusters with different structural properties. Besides, a silylation treatment was realized on both solids with the aim of neutralizing the Brönsted acidity associated with the MCM-41 silanol groups. The samples were characterized by atomic absorption spectroscopy, X-ray diffraction at low angles, N₂ adsorption, temperature-programmed reduction, Fourier transform infrared spectroscopy, nuclear magnetic resonance of ²⁹Si, and Mössbauer spectroscopy. The influence of the structural changes of the nanoclusters and the effect of the simultaneous presence of Lewis and Brönsted acid sites were evaluated studying the product distribution from the α -pinene oxide isomerization reaction. It was determined that the Brönsted acidity of the Fe/MCM-41 system has not the sufficient acid strength to modify the product distribution which is mainly governed by the Lewis sites.

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1. Introduction

In order to replace the conventional homogeneous acid catalysts (such as metal halides, HF and H₂SO₄) in many fine chemical reactions, numerous researches with solid acids had been made in the last decades. Solid acid catalysts with protonic acidity (Brönsted acid sites) have been better developed than Lewis acid containing catalysts [1–3], in particular zeolite materials. Many oxides containing dispersed metal centers on different supports appear good candidates as Lewis acid catalysts and they have been displayed interesting catalytic performances in reactions where Lewis acid centers are concerned [4,5]. Among them, the Fe₂O₃/SiO₂ system, with the high degree of coordinative unsaturation of the nanosized Fe₂O₃ clusters gives excellent catalytic properties in acid reactions, such as Friedel–Crafts alkylations [6,7]. A method to obtain such samples with the required Lewis acid sites is supporting “nanoclusters” of iron oxides on silica materials. In order to avoid the diffusional hindrance of large reactive molecules, mesoporous

silicas with tuneable pore size could be used as supports for highly dispersed iron species. In this perspective, the Fe/MCM-41 system was selected in order to produce active and selective catalysts with Lewis acid sites associated with the Fe presence. However, it must be considered that the bare surface of MCM-41 has a great number of silanol groups, which have Brönsted acidity that adds up to the introduced Lewis acid sites of the Fe species [8].

To investigate on the acid properties and catalytic performances of the Fe/MCM-41 system, the α -pinene oxide (POX) isomerization reaction was taken into account; information on the Brönsted or Lewis catalytic action can be inferred from the obtained product distribution [9]. Moreover, the POX isomerization is an interesting reaction of fine chemistry, because one of the main products, campholenic aldehyde (CPA), is a very important intermediate used for the manufacture of sandalwood fragrances, currently being investigated together with macrocyclic musks, as possible substitutes for nitro and polycyclic musks, which are widespread used as fragrances in laundry detergents, fabric softeners, cleaning agents and cosmetic products, and are recognized as damaging chemical species to the environment.

Taking into account the co-presence of both the two kinds of acid sites (Brönsted and Lewis type) on the Fe/MCM-41 system, one aim of this work is to study the product distribution from the POX isomerization obtained on different Fe/MCM-41 samples with presence or suppression of the Brönsted acid sites of MCM-41, by evaluating the acid-strength of the different site-types, too. In order

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to get this purpose, the surface silanol groups were replaced by trimethylsilyl groups using a silylation treatment. On the other hand, the possibility of generate different iron Lewis acid sites in the Fe/MCM-41 system, changing the calcination atmospheres (inert and oxidant), was studied too. The consequences produced by these treatments on the sample properties were studied by different characterization techniques and evaluated analyzing their influence on the selectivity and the activity on POX reaction.

2. Experimental

2.1. Catalyst preparation

MCM-41 support was prepared according to the methodology proposed by Ryoo and Kim [10] using sodium silicate as silica source, cetyl-trimethyl-ammonium chloride as surfactant under controlled pH during the hydrothermal synthesis. For the preparation of 16 g of sample, 40 g of sodium silicate (26.1% SiO₂) was dissolved into 74 g of water. The solution was then slowly added to 38 ml of cetyl-trimethyl-ammonium chloride and 0.65 ml of NH₃ under vigorous stirring at room temperature. This mixture was heated at 373 K for 24 h in a polypropylene bottle without stirring. Afterwards, it was cooled at room temperature. Then, the pH value was regulated to approximately 11 by drop wise addition of acetic acid under vigorous stirring. The reaction mixture was heated again at 373 K for 24 h. This procedure for pH control and subsequent heating was repeated twice. The resulting solid was filtered, washed and dried in air at room temperature. The surfactant was removed by calcination in N₂ flow (150 cm³/min) heating the solid from room temperature to 783 K (8 K/min) maintaining the final temperature for 1 h. Finally, the N₂ flow was replaced by air, and the solid remained at 783 K for 6 h under air flowing.

The synthesized MCM-41 was impregnated by the incipient wetness impregnation method with Fe(NO₃)₃·9H₂O aqueous solution to produce a nominal Fe loading of 8% (w/w) in a single step. The solid was dried in air at room temperature, and then was split in two fractions; the first fraction was calcined in a flow of N₂ (60 cm³/min) from room temperature to 603 K (0.2 K/min), and kept at the final temperature for 1 h, so obtaining the Fe/MCM-41(N₂) sample. The second fraction was calcined under the same conditions above described, replacing the nitrogen flow by air, so obtaining the Fe/MCM-41(air) sample.

A fraction of both solids was silylated with hexamethyldisilazane (HMDS). In order to get this treatment the solids were outgassed ($p_v < 10^{-3}$ Torr) during 3 h at 573 K. Then, a solution of 1% (v/v) of HMDS in toluene was prepared in a glove box, in Ar atmosphere, and it was added to the dehydrated solids. The mixture was heated at 393 K, during 90 min under stirring. Finally, the treated solids were filtered, washed with 80 cm³ of toluene, and dried in an oven at 333 K during 16 h. The obtained solids were called Fe/MCM-41(N₂)-sil and Fe/MCM-41(air)-sil taking into account the nature of the calcination atmospheres.

2.2. Catalyst characterization

The samples were characterized by atomic absorption spectroscopy (AAS), X-ray diffraction (XRD) at low angles, N₂ adsorption at 77 K (BET), temperature-programmed reduction (TPR), Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (NMR) of ²⁹Si, and Mössbauer spectroscopy (MS) at 298 and 25 K.

The Fe content of the solids was determined by atomic absorption on an AA/AE Spectrophotometer 457 of Laboratory Instrumentation Inc. The sample was treated in a mixture of HCl and HF up to complete dissolution before measurement.

All XRD patterns at low angles were measured using a standard automated powder X-ray diffraction system Philips PW 1710 with diffracted-beam graphite monochromator using Cu K α radiation ($\lambda = 1.5406$ Å) in the range $2\theta = 0.5$ – 9° with steps of 0.02° and counting time of 2 s/step.

The textural properties, specific surface area (S_g), specific pore volume (V_p) and pore diameter (D_p), were measured in Micromeritics equipment ASAP 2020 V1.02 E.

The TPR profiles were obtained in a Quantachrome equipment, model Quantasorb Jr. The samples (≈ 50 mg) were reduced between 300 and 1273 K, at a heating rate of 10 K/min, using a 5% H₂/N₂ mixture. Taking into account the reducible amount of iron oxide in the samples, “K” (the sensitivity parameter expressed in s) and “P” (the shape and resolution parameter, expressed in K) [11] were around 75 s and 15 K, respectively.

The FT-IR absorption spectra were acquired with a Bruker IFS66 spectrometer with 1 cm⁻¹ resolution by co-addition of 32 scans. The samples were prepared mixing with potassium bromide, in a 1:100 proportion, in order to obtain the corresponding pellets.

Solid state ²⁹Si nuclear magnetic resonance spectra by direct polarization (DP) and cross-polarization (CP) ¹H–²⁹Si with proton decoupling and magic angle spinning (MAS) were recorded on a Bruker Avance II-300 spectrometer equipped with a 4-mm MAS probe operating at 300.13 MHz for protons and 59.6 MHz for ²⁹Si. Magic angle spinning rate was 5 kHz. Other experimental conditions were: cw proton decoupling at 62.5 kHz, contact time for CP 5 ms. The chemical shifts are given in ppm from H₃PO₄ (0 ppm) as standard reference.

The Mössbauer spectra were obtained in transmission geometry with a 512-channel constant acceleration spectrometer. A source of ⁵⁷Co in Rh matrix of nominally 50 mCi was used. Velocity calibration was performed against a 12 μ m-thick α -Fe foil. All isomer shifts (δ) mentioned in this paper are referred to this standard. The temperature was varied between 25 and 298 K using a Displex DE-202 Closed Cycle Cryogenic System. The Mössbauer spectra were evaluated using a commercial program with constraints named Recoil [12]. Although some spectra display magnetic relaxation, for simplicity, Lorentzian lines with equal widths were considered for each spectrum component. The spectra were folded to minimize geometric effects.

2.3. Activity and selectivity measurements

The epoxide isomerization tests using POX as substrate were carried out at room temperature (RT) in batch conditions as detailed in Refs. [9,13]. The catalyst sample (0.1 g) was activated into the glass reactor at 623 K for 30 min in air and then for 30 min under reduced pressure at the same temperature. After catalyst activation, α -pinene oxide (0.66 mmol) and toluene (8 ml) were introduced into the reactor under N₂ atmosphere. The progress of the reaction was followed by gas-chromatographic techniques (GC from Agilent 6890 with FID detector, with a 5% phenylmethylpolysiloxane column, and GC-MS from Agilent 5971 series), analyzing samples withdrawn from the reaction mixture at different times.

3. Results and discussion

3.1. Catalyst characterization and silylation effect

The ordered hexagonal structure of mesoporous MCM-41, used as support, was verified by XRD (Fig. 1) and its textural properties were measured by N₂ adsorption at 77 K (Table 1). The impregnation, calcination in different atmospheres, and silylation treatments, which lead to Fe/MCM-41(N₂), Fe/MCM-41(N₂)-sil,

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