



Liquid phase hydrogenation of crotonaldehyde over copper incorporated in MCM-48

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ABSTRACT

A series of Cu/MCM-48 catalysts is studied for the liquid phase hydrogenation of crotonaldehyde. Copper is incorporated in MCM-48 following a classical hydrothermal synthesis or by wet impregnation of the MCM-48 precursor (before eliminating the directing agent) with Cu(AcAc)₂. The copper loading is in the 2–20 wt% range. Characterization results from TPR and XRD indicate that copper crystals supported on MCM-48 surface coexist with copper incorporated in the MCM-48 walls. The presence of Cu⁺ in MCM-48 is concluded from characterization with FTIR of adsorbed CO. This species would be the responsible for the relatively high selectivity of Cu/MCM-48. These catalysts show approximately 50% of selectivity against 7% of Cu/SiO₂ (both values measured at 10% of conversion).

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1. Introduction

Copper on MCM-41 has been widely employed as catalysts for different reactions [1–11]. On the contrary copper supported on MCM-48 has been much less studied, though this system should be preferred to the one supported on MCM-41 in the basis of the three dimensional structure of MCM-48. Probably this is due the fact that it is rather difficult to incorporate a high copper loading to the mesoporous structure of MCM-48 [12].

In a previous work [13] we have studied a series of copper catalysts employing MCM-48 as the support for the selective hydrogenation of cinnamaldehyde in liquid phase. Some of these samples were found to be more selective than copper supported on silica or alumina. It is well known that is very difficult to hydrogenate carbonyl bond in α , β -unsaturated compounds, due to kinetic and thermodynamic difficulties. In this context, our previous results encouraged us to further investigate on the catalytic properties of Cu/MCM-48 for selective hydrogenation reactions.

In the present work we study a series of Cu/MCM-48, for the liquid phase hydrogenation of crotonaldehyde. This α , β -unsaturated compound has been selected since it presents a low steric protection of the olefinic bond, then, hydrogenation of crotonaldehyde is still a big challenge for researchers.

The samples are studied by FTIR of adsorbed CO, XRD, TPR and BET. Finally, the samples are tested in the liquid phase hydrogenation of crotonaldehyde, in a Batch reactor. The catalytic patterns are discussed in the light of the characterization results.

2. Experimental

2.1. Catalyst preparation

2.1.1. Synthesis of MCM-48

The silicon source was tetraethyl ortho-silicate (TEOS, Aldrich). The structure-directing agent was cetyltrimethylammonium bromide (CTAB, Aldrich). MCM-48 was prepared by hydrothermal synthesis, following the technique reported by Xu et al. [14]. 10 mL of TEOS were added to a solution of CTAB in water (8.8 g/79.2 mL). 10 mL of NaOH 2 M were added at 308 K. The mixture was stirred for half an hour. The gel was heated to 373 K for 72 h under static hydrothermal conditions in a steel/Teflon autoclave. The product was filtered, washed with water, and dried at room temperature. Finally the solid was heated up 673 K at 0.5 K min⁻¹ under N₂ flow, afterwards the flow was switched to chromatographic air, and the temperature was kept constant for 6 h.

2.1.2. Synthesis of Cu/MCM-48

Two series were prepared, one of them following a hydrothermal synthesis and another one by wet impregnation of MCM-48 with Cu(AcAc)₂.

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The first series was prepared by following a classical hydrothermal method. The samples are named as CuH_x, where *x* corresponds approximately to the copper wt%. A solution of Cu(NO₃)₂ (in 27% aqueous ammonia) was added to a solution of CTAB, NaOH and TEOS. Copper nitrate solutions with different concentration were employed in order to vary the metal content. The mixture was stirred for 4 h, before loading the sample into a Teflon-steel autoclave. The solution was heated for 3 days at 373 K. The product was then filtered and washed and finally treated for eliminating the structure directing agent, in the same way as in the preparation of pure MCM-48. The copper metal loading was measured by AAS. Three samples were obtained: CuH₂, CuH₃ and CuH₅.

The other series, Cu_x (where *x* corresponds approximately to the copper wt%) was prepared by wet impregnation of MCM-48, before performing the elimination of CTBA as it is conventionally carried out (with a calcination pre-treatment). This solid was put in contact with different solutions of Cu(AcAc)₂ in tetrahydrofuran for 24 h. The concentration of the solutions was varied in order to obtain a copper concentration of approximately 5, 10 and 20%. The solids were filtered, and dried at 343 K during 4 h. Afterwards the temperature was increased at 1°/min up to 673 K, under N₂ flow. At this temperature, the gas flow was switched to chromatographic air and the sample was calcined for 6 h. Three samples were obtained: CuI₄, CuI₉ and CuI₂₀.

2.1.3. Synthesis of Cu/SiO₂

The support was SiO₂, from Rhône Poulenc (99.7%, Na: 0.1%, SO₄²⁻: 0.1%, others: 0.1%), with a BET surface area of 210 m²/g. The silica was comprised of 3 mm diameter spheres. Copper was fixed to silica following a wet impregnation with solutions of Cu(AcAc)₂ (Aldrich, 99.99%) in THF. The support was calcined at 300 °C, and afterwards it was put in contact with a Cu(AcAc)₂ solution for 48 h, at 60 °C, under constant stirring. The solid was filtered and heated at 70 °C for 24 h. Finally the sample was calcined at 400 °C for 4 h under air flow

2.2. Catalyst characterization

The crystalline structure and the copper particle size of the different catalysts were determined by X-ray diffraction (XRD) in a Philips PW1710 BASED instrument operating at 45 kV and 30 mA, fitted with a graphite monochromator in order to get Cu Kα1 radiation (λ = 1.5406 Å); the angle step and counting time were 0.02° (2θ) and 1 s, respectively. The media copper crystal size was determined by applying the Scherrer equation.

The samples were characterized by TEM, employing a Jeol 100 CX2 (Tokyo, Japan) apparatus. Approximately one hundred gold particles were measured to perform the particle size distribution. The average diameter of the crystals in the different catalysts was calculated from the following formula: $d = (\sum n_i d_i) / n_i$. For all the cases a pre-treatment of the samples was carried out to allow the clear observation of the copper particles. The catalysts were reduced at 473 K for half an hour under H₂ flow. Afterwards, at room temperature the samples were thrown into a vessel fill with isopropanol, under gas flow. Immediately, a drop of the catalyst-solvent mixture was put on a grid and the TEM analysis was carried out.

The specific surface area of the catalysts was determined by adsorption-desorption of N₂ at 77 K employing a Nova 1200e Quantachrome equipment. The pre-treatment of the samples was an evacuation at 393 K for 20 h. The BET equation was employed for determining surface area. The diameter of the mesoporous of MCM-48 was measured by BHJ method. The choice of this method was based on previous combined TEM and BET characterization of MCM materials for determining pore sizes. The best agreement

between results from both techniques was attained following the BHJ approximation.

The TPR study was carried out in a conventional apparatus. Samples were previously calcined at 393 K in chromatographic air and purged in N₂. Afterwards, the samples were cooled down up to room temperature, and the inert gas was switched to the reactive mixture (H₂/Ar (10%)) with a flow of 18 cm³ min⁻¹. The hydrogen uptakes were measured by a TCD detector while the temperature was linearly increased at a rate of 8 K min⁻¹, up to 773 K.

The FTIR spectra of adsorbed CO were recorded in a Nicolet Nexus FTIR apparatus at 4 cm⁻¹ resolution. Catalyst samples of approximately 30–40 mg were pressed to form transparent disks of 13 mm in diameter that were mounted in a metal holder placed in the beam path. The metal holder is provided with CaF₂ windows, and coupled to a vacuum system for evacuation to 10⁻⁶ Torr. The spectra were recorded after contacting the sample with 5 Torr of CO, at 77 K.

2.3. Catalytic test

The catalysts were tested for the hydrogenation of crotonaldehyde in a Batch reactor at 373 K and 1 MPa of H₂ pressure. The reactive mixture was a 0.1 M solution of crotonaldehyde in isopropanol. Approximately 200 mg of catalyst reduced *ex situ* at 573 K were employed. The stirring rate was selected at 400 rpm. Previously, the stirring rate was varied in the range 300–900 rpm. Within this range the conversion of the CuH₂ catalyst was kept constant, showing the lack of external diffusion limitations.

The dependence of the conversion and of the selectivity toward the different products on time on stream was measured. The concentrations of the reactant and products were measured by gas chromatography, with a FID detector and a ZB-WAX column, at 473 K. Additionally the reaction mixture was analyzed in a PerkinElmer Clarus 500 chromatograph, provided with a mass spectrometry detector.

3. Results

The list of the Cu/MCM-48 samples is reported in Table 1.

The BET surface area of the samples is high. The lowest surface area corresponds to CuH₅, probably due to the fact that the relatively high copper loading partially destroys the mesoporous structure during the first step of the hydrothermal synthesis. In this way, CuH₅ is an heterogeneous sample, and it should be considered as a mixture of Cu/MCM-48 and Cu/SiO₂.

For the case of the hydrothermal synthesis (CuH_x), the introduction of copper from Cu(NO₃)₂ corresponding to loading higher than 5%, completely destabilizes the mesoporous structure, leading to copper supported on amorphous silica.

As a general trend, the incorporation of copper in MCM-48 decreases the pore diameter (see Table 1). This effect has been previously observed for Cu/MCM-48 [13] and it could be due to different phenomena: (i) copper inserted in the silica framework, in which the heteroatom buried in the inside the walls causes the corresponding increase in the wall width and narrows the pore diameter, (ii) copper crystals with size lower than pore diameter (4.2 nm) supported inside the pores. Anyway, whatever the origin of the distortion of pore size due to the presence of copper, it is related with a high interaction between copper and the MCM-48 support.

In Fig. 1a the XRD patterns of some Cu/MCM-48 samples are shown. The strong peak centered at 2θ = 2.5° is assigned to the (2 1 1) plane. Besides other minor peaks at low diffraction angles were detected. It is interesting to note that the profile of the low diffraction peaks (see Fig. 1b) of pure MCM-48 is strongly

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