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Cu incorporated MCM-48 for the liquid phase hydrogenation of cinnamaldehyde

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ABSTRACT

A series of copper/MCM-48 mesoporous samples is prepared and characterized following two methods: a traditional hydrothermal synthesis and an impregnation with Cu(AcAc)₂ before eliminating the structure-directing agent. The samples are characterized by XRD, BET, FTIR, TPR and TEM. Only for certain cases the morphological aspects of MCM-48 are not modified by the incorporation of copper into the mesoporous framework. The samples are tested as catalysts for the liquid phase hydrogenation of cinnamaldehyde in a Batch reactor, employing H₂ as the reductant. Some Cu/MCM-48 catalysts were more selective than copper supported on alumina (Cu/ γ -Al₂O₃) tested under the same reaction conditions. The reason for the better catalytic performance would be that copper is finely dispersed and highly uncoordinated.

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1. Introduction

The selective hydrogenation of α,β -unsaturated compounds is an important class of reaction in organic synthesis. The desired product from an industrial viewpoint is the unsaturated alcohol which is a reactant in the synthesis of cosmetic, pharmaceutical and specialty chemical products. The industrial process is carried out over metal hydrides [1,2]. Due to environmental concerns and for technical and economical considerations, heterogeneous catalysts should be preferred to conventional methods. However, it is very difficult to preferentially hydrogenate the C=O bond over the C=C bond using classical hydrogenation catalysts [2–6]. A large variety of Pt based catalysts have been employed with certain success for the selective hydrogenation of α,β -unsaturated compounds [7–30]. On the other hand, few reports deal with copper catalysts for this reaction [31–36].

Employment of mesoporous materials in catalysts preparation is highly convenient, since these oxides combine a high specific surface area with an order structure of wide pores. Thus a high concentration of active sites and, at the same time, free diffusion of reactants and products can be achieved over mesoporous supports.

In the present work, the mesoporous silicate MCM-48 is substituted with copper to obtain a series of catalysts to be employed in the liquid phase hydrogenation of cinnamaldehyde. Taking into account that free diffusion of reactants and products is searched for liquid phase reactions, the tridimensional pore network of MCM-

48 should be preferred to the mono-dimensional structure of MCM-41. However, research works regarding MCM-48 based catalysts are much lesser than those corresponding to MCM-41. This is probably due to the technical difficulties associated with the synthesis of MCM-48 materials [37].

In this study copper incorporated MCM-48 catalysts, with copper loading in the 2–20 wt% range, are prepared and characterized by BET, XRD, TEM, TPR and FTIR. The samples are tested for the selective hydrogenation of cinnamaldehyde. The reaction is carried out in Batch conditions, employing H₂ as the reductant. To our knowledge, it is the first time that the copper/MCM-48 system is tested for this reaction.

The catalytic patterns are analyzed in the light of the characterization results. Comparison with conventional copper, platinum and gold catalyst tested under the same operational conditions [38,39] are carried out.

2. Experimental

2.1. Synthesis of MCM-48

Tetraethyl ortho-silicate (TEOS) was used as source of silicon. The structure-directing agent was cetyltrimethylammonium bromide (CTAB). The chemicals were used as purchased (Aldrich). MCM-48 was synthesized by the conventional hydrothermal pathway, following the technique reported by Xu et al. [40]. Ten milliliters of TEOS were added to an aqueous solution containing 8.8 g of CTAB in 79.2 mL of H₂O and 10 mL NaOH 2 M at 308 K. The mixture was kept under mechanical stirring for half an hour. The gel was heated to 373 K for 72 h under static hydrothermal conditions

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in a steel/Teflon autoclave. The obtained product was filtered, washed with distilled water, and then dried at ambient conditions. In order to remove the surfactant the following procedure was carried out: the sample was heated from room temperature up to 673 K at a slow heating rate (0.5 K/min) under N_2 flow (15 ml/min), afterwards the inert gas flow was switched to chromatographic air for calcination treatment for 6 h.

Finally the sample was cooled down in air. The total elimination of organic species was confirmed by FTIR.

2.2. Synthesis of Cu/MCM-48

The catalysts are named as CuH x or CuI x , where x indicates the copper loading (wt%, as determined by AAS) and H or I indicate that samples were prepared by classical hydrothermal synthesis and by impregnation with $Cu(AcAc)_2$, respectively.

2.2.1. CuH2, CuH4, CuH8 and CuH20

A cuprammonia solution composed of $Cu(NO_3)_2$ and 25% aqueous ammonia was added to a solution of CTAB, NaOH and TEOS. The Si/Cu varied in the 70–10 range. The stirring was continued for further 4 h, before loading the sample into a Teflon-steel autoclave, where the synthesis solution was heated for 3 days at 373 K. The product was then filtered and washed with water. Finally, the same treatment as for other catalysts was performed in order to eliminate CTAB.

2.2.2. CuI1, CuI10, CuI20

The CuI1 sample was prepared by contacting a solution of $Cu(AcAc)_2$ in toluene with MCM-48 at 343 K under continuous stirring. The concentration of the solution corresponded to a target copper concentration in the solid of 20 wt%. Approximately 5 ml of solution and 1 g of MCM-48 were employed. The precursor of the catalyst was filtered and dried at 343 K. The CuI10 and CuI20 samples were prepared from $Cu(AcAc)_2$ solution with target copper concentration of 10 and 20 wt%, respectively. In both cases, such as for preparing CuI1 was followed, but MCM-48 was employed before performing the calcination treatment, without eliminating the structure-directing agent. The solid was filtered, and dried at 343 K during 4 h. Finally, the same treatment as for MCM-48 was carried out in order to eliminate CTAB. The amount of C after calcination treatment was measured by elemental analysis in a EXETER CE 440 equipment.

2.3. Characterization

The specific surface area of the catalysts was calculated following the BET method. Isotherms, employing a Nova 1200e Quantachrome equipment. The pore diameter was determined by BJH method. The pretreatment of the samples was an evacuation at 393 K for 20 h. For the structural characterization, X-ray data were collected on a Philips PW1710 BASED instrument operating at 45 kV and 30 mA fitted with a graphite monochromator in order to get $Cu K\alpha_1$ radiation (0.15406 Å); the angle step and counting time were $0.035^\circ(2\theta)$ and 1 s, respectively. Some samples were characterized by means of TEM, in a JEOL 100X2 (Tokyo, Japan) apparatus. The TPR study was carried out in a conventional apparatus. Samples were previously calcined at 393 K in chromatographic air and purged in N_2 . Afterwards, the samples were cooled down up to 333–353 K, and the inert was switched to the reactive mixture (H_2/Ar (10%)) with a flow of $18\text{ cm}^3/\text{s}$. The hydrogen uptakes were measured by a TCD detector while the temperature was linearly increased at a rate of 8 K/min, up to 773 K. The FTIR spectra were recorded in the $4000\text{--}400\text{ cm}^{-1}$ region in a Nicolet Nexus FTIR apparatus. Solids were diluted with KBr.

2.4. Hydrogenation of cinnamaldehyde

The catalysts were tested for the hydrogenation of cinnamaldehyde in a Batch reactor at 373 K and 1 MPa of H_2 pressure. In a typical experiment the reactive mixture (a 0.1 M solution of the aldehyde in isopropanol) was introduced in the reactor and purged with H_2 . Approximately 200 mg of catalyst reduced *ex-situ* were introduced into the reactor under H_2 flow. The stirring rate was 400 rpm. The conversion and the selectivity towards the different products were measured at 3 h of reaction time. The activity was calculated as moles of the product converted per g of copper and per second. For the CuH2 catalyst the dependence of the conversion and the selectivities on time were 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 Perkin-Elmer Clarus 500 chromatograph, provided with a mass spectrometry detector.

The stirring rate was varied in the range 300–900 rpm. Within this range the conversion/selectivity pattern of the CuH2 catalyst was the same for the different stirring rates. Thus the lack of external diffusion limitations was confirmed.

3. Results

Fig. 1A shows the XRD patterns of the MCM-48. The diffraction pattern of the pure support is typical of the mesoporous MCM-48 structure: a strong 2 1 1 peak centered at about $2\theta = 2.5^\circ$ and a minor peak at $2\theta = 2.7^\circ$, corresponding to 2 2 0 plane, were observed [42]. Besides, other lower diffraction peaks were detected (shown in the detail of Fig. 1A) which were also assigned to the structure of MCM-48. For both CuH2 and CuH8, the low angle peak was conserved, though an important decrease in the intensity was observed (see profiles c and e in Fig. 1B). The other peaks were too weak to be recognized. This might be due to the incorporation of heteroatoms (copper) into the framework of MCM-48, decreasing the ordered structure. In addition to MCM-48 peaks, characteristic peaks of CuO ($2\theta = 35.4^\circ, 38.8^\circ$) were found in high angle XRD patterns. This result indicates that besides copper in the zeolite framework, bulky metal oxide is present in the prepared materials.

XRD results of CuH4 and CuH20 (see in Fig. 1B, profiles d and f in respectively) indicated that these samples lost the mesoporous structure, since no low diffraction peaks were detected. It is difficult to explain why the incorporation of a relatively low loading of copper in CuH4 destroys the MCM-48 structure while CuH8 (a higher loaded sample) retains the mesoporous arrangement. Two copper species are present in CuH4 and CuH8 samples: (i) finely dispersed copper oxide crystals and, (ii) copper incorporated in the structure of MCM-48. It could be argued that for CuH4 the relative concentration of the latter species is high, leading to the destruction of the mesoporous framework, while for CuH8 copper is mainly present as finely dispersed crystals, and the ordered structure is maintained.

The XRD results corresponding to the samples obtained by the impregnation of MCM-48 with $Cu(AcAc)_2$ showed that this series of catalysts retain the mesoporous structure, even for relative high copper concentration. In Fig. 1B the pattern corresponding to CuI10 is shown. This sample shows a quite similar profile to MCM-48's; a strong well resolved low diffraction peak. In addition, CuO diffraction peaks were detected.

Table 1 summarizes copper contents and N_2 adsorption data of the different samples. In Fig. 2, the adsorption-desorption isotherms of CuH2 (isotherm a) and CuH20 (isotherm b) samples are shown. A typical type IV isotherm was observed for CuH2, as could be expected for mesoporous materials. No appreciable

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