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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 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 1s, 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

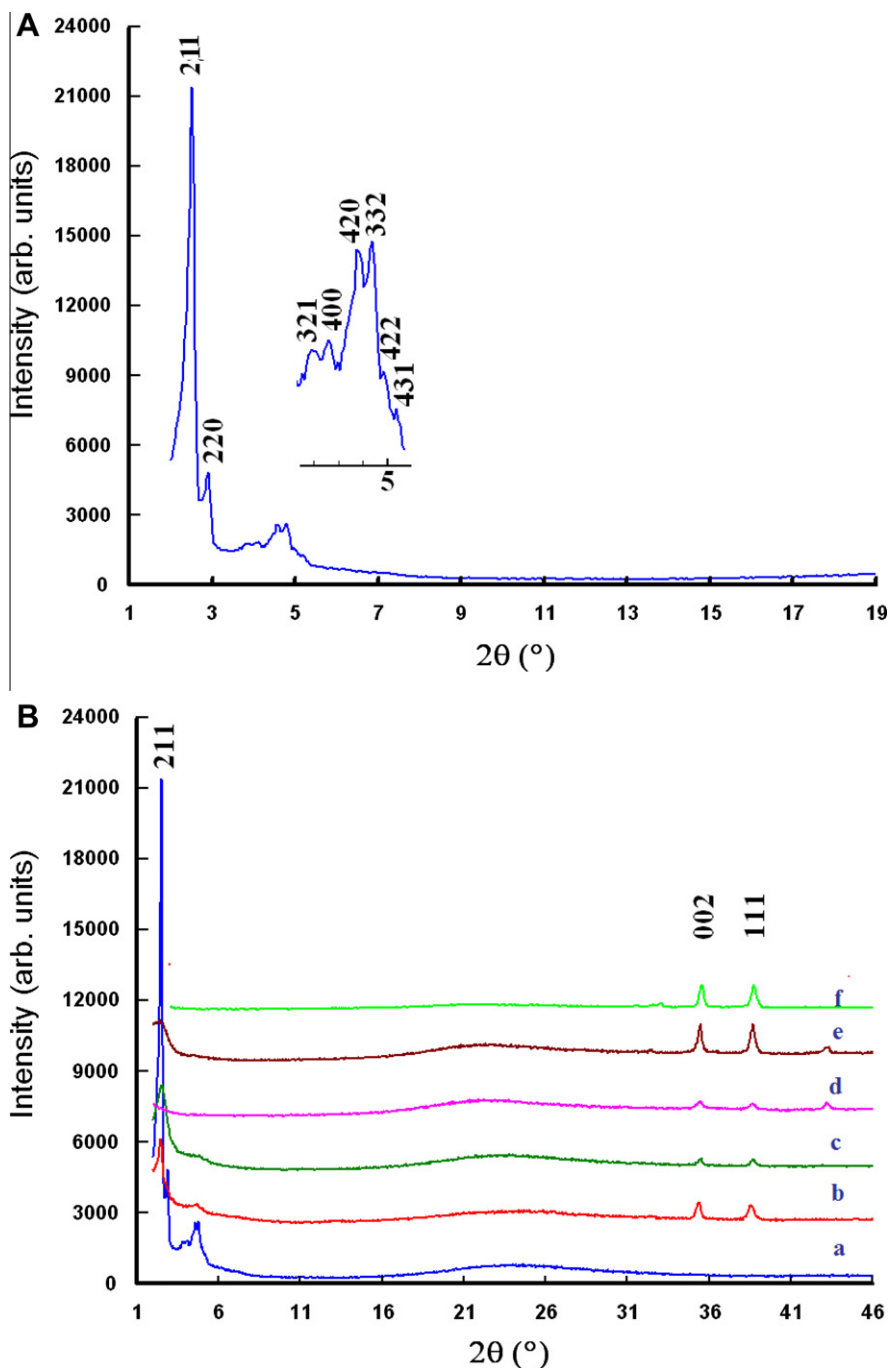


Fig. 1. (A) XRD pattern of pure MCM-48. In detail: a magnification for lower diffraction peaks. (B) XRD patterns (a) MCM-48, (b) Cu10, (c) CuH2, (d) CuH4, (e) CuH8, (f) CuH20.

hysteresis loop was obtained. This could be ascribed to a uniform distribution of particle sizes. Similar isotherms were obtained for pure MCM-48 as well as for the CuH1, CuH8, Cu10 and Cu20 catalysts. On the other hand for the samples prepared from the hydrothermal synthesis, CuH4 and CuH20, the type of the isotherm corresponds to a nonporous system.

The surface areas and the pore diameters calculated from the N_2 isotherms are reported in Table 1. It can be observed that large surface areas were obtained, except for the two samples without the mesoporous structure, CuH4 and CuH20. For the other samples, the general trend is that the introduction of copper lowers the specific surface area of MCM-48.

Fig. 3 a and b show the FTIR spectra of MCM-48 and CuH2. For all the cases, the broad band centered at approximately 3500 cm^{-1}

is due to hydroxyl groups; while the bands at 1080 (with a shoulder at 1230), and 462 cm^{-1} are assigned to symmetric stretching and bending of "Si–O–Si". The band at 950 cm^{-1} is attributed to defect sites ("Si–OH") [41]. No bands at 2920 and 2848 cm^{-1} appear, indicating the absence of hydrocarbons. Thus this result shows that the calcination pretreatment has completely removed the template compound. Besides the amount of residual C was measured by Elemental analysis for both MCM-48 and CuH2. The concentration of C was relatively low and for the case of the CuH2 catalysts, the C loading (0.56%) was much lower than the amount of copper in the sample.

In Fig. 4 the TPR profiles of the following samples are shown: CuH2, CuH4, CuH8, Cu10, and Cu20. For the sake of comparison the TPR result of Cu/ γ - Al_2O_3 is also shown.

Table 1
Characterization of MCM-48 and Cu-MCM-48 by XRD, AAS and N₂ sorption analysis.

Catalyst	Cu (wt%)	Pore diam. (nm)	BET area (m ² /g)	H ₂ /Cu ^a	T _{max} ^b
MCM-48	–	4.2	1150	–	–
CuH2	2.5	3.8	942	0.60	220
CuH4	4.7	9.2	103	0.81	240
CuH8	7.2	3.8	423	0.43	245
CuH20	17.0	–	56	0.98	–
CuI1	0.5	3.7	1010	–	–
CuI10	9.0	3.8	1119	0.52	235
CuI20	17.6	2.0	650	0.70	220
Cu/γ-Al ₂ O ₃	2.8	8.3	174	1.10	230

^a Molar ratio between hydrogen consumed by the catalyst and the copper loading.

^b Temperature corresponding to the maxima of the reduction peak in TPR.

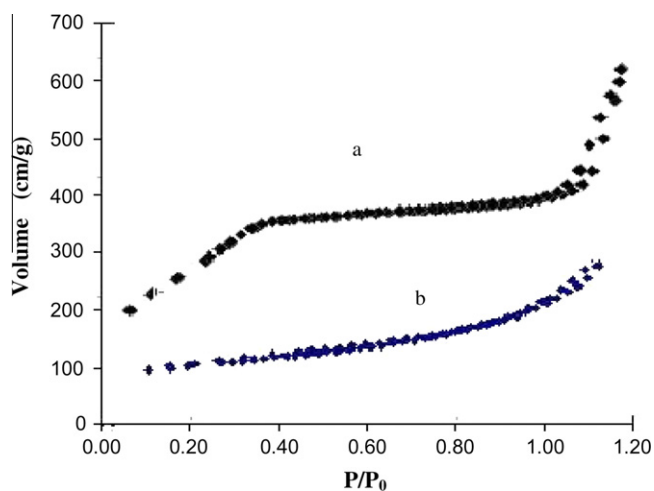


Fig. 2. Nitrogen sorption isotherms of: (a) CuH2 and (b) CuH20.

For all the cases only one peak is observed. The temperature corresponding to the peak maximum is reported in Table 1. The reduction of copper in the different samples occurs approximately at the same temperature (220–240 °C). Regarding the amount of hydrogen engaged in the TPR reduction process, the molar ratio between consumed H₂ and the total amount of copper in the catalyst is reported in the last column of Table 1. If a complete reduction from Cu II to Cu 0 is considered, the theoretical ratio is the unity. For Cu/γ-Al₂O₃ the measured ratio is quite close to 1, showing that almost all copper species are being reduced. On the contrary the ratio is lower than the unity for Cu/MCM-48 (CuH2, CuH8, CuI2 and CuI20). It could be suggested that highly dispersed copper is resistant to reduction and concomitantly low H₂ consumption are detected in TPR.

Besides, TEM characterization of Cu/γ-Al₂O₃ showed that copper particles are in the 6–10 nm size range. Unfortunately, copper particle could not be observed with TEM in the case of Cu/MCM-48, probably because highly dispersed copper crystallites are below the detection limit of the instrument.

3.1. Catalytic testing: hydrogenation of cinnamaldehyde

Catalyst weights ranging from 200 to 600 mg were employed to check that the reaction was not diffusion limited. The absence of external diffusion control was confirmed since the conversion increased linearly with the mass of the catalyst. Besides, it was confirmed that the bare support, MCM-48, is inactive for the reaction.

Other tests were performed in order to determine the possibility of hydrogen transfer from the solvent to the aldehyde. This was

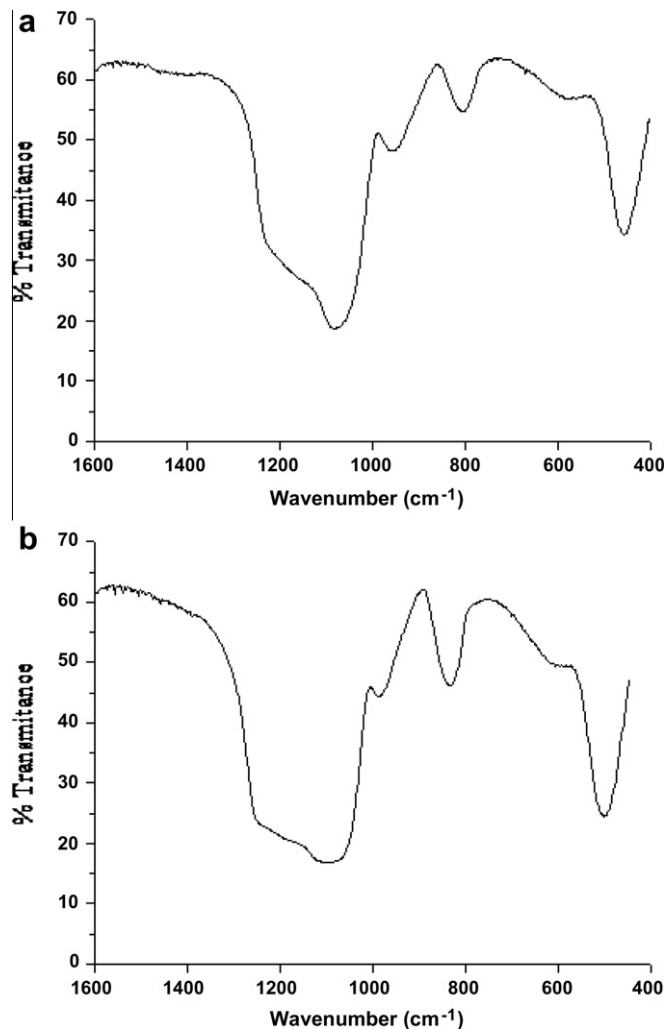


Fig. 3. (a) FTIR of MCM-48 (b) FTIR of CuH2.

disregarded since the conversion of cinnamaldehyde was nil for the catalytic test carried out in the absence of H₂.

In a typical experiment, the three hydrogenation products (see Fig. 5), cinnamyl alcohol, hydrocinnamaldehyde and phenyl propanol were detected. Besides, ethylbenzene was also observed, showing that the decarbonylation of cinnamaldehyde occurs. On the other hand, products from cracking or condensation reactions were not produced.

In Table 2 the selectivity towards the three hydrogenation products and the conversion levels attained by the different catalysts following 3 h of reaction are reported. For the sake of comparison the results corresponding to a Cu/γ-Al₂O₃ catalyst are also shown. While the Cu/γ-Al₂O₃ catalyst is completely unselective towards the cinnamyl alcohol, CuH2, CuH4, CuH8, CuI10 and CuI20 are quite selective, showing a selectivity higher than 40%. It is worth noting that MCM-48 should be considered as inert support, thus no promotional effect of this support on the catalytic properties of copper should be expected. The relative high selectivity towards the desired product measured over MCM-48 based catalysts would be originated in high dispersion of copper species on the mesoporous support. On the other hand, on γ-Al₂O₃ bulky copper particles are formed, the reactive sites being unselective metallic copper. The same consideration is valid for the unselective CuH20 for which bulky copper particles are present. The CuI1 sample attained extremely low levels of conversion, for this reason no reliable value of selectivity could be measured.

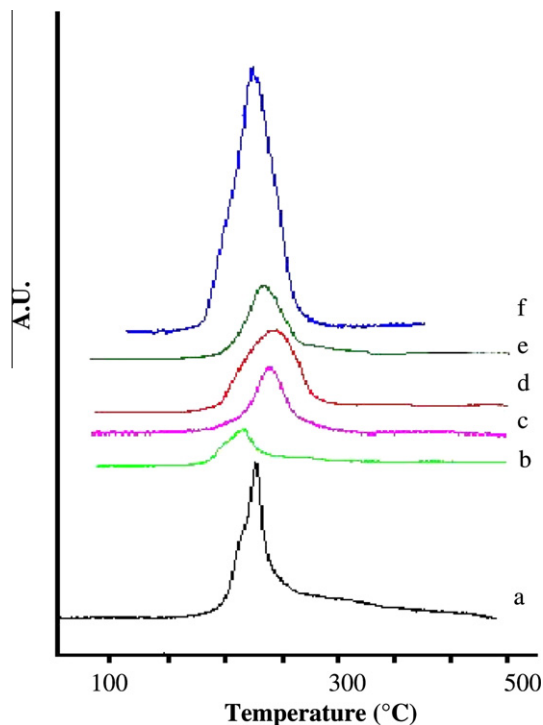


Fig. 4. TPR profiles for: (a) Cu/γ-Al₂O₃, (b) CuH₂, (c) CuH₄, (d) CuH₈, (e) CuI₁₀, (f) CuI₂₀.

At this point it is important to comment on the results obtained by Chambers et al. [43] on copper supported catalysts. The authors concluded that an influence of copper surface area on the selectivity of the samples takes place. The higher the copper dispersion the lower the selectivity to the desired product. This result would be in disagreement with the conclusion of the present work (highly dispersed copper species are more selective than poorly dispersed ones). However, Chambers et al. analyzed crystal size within the 16–25 nm range. In the samples presented in this work copper dis-

Table 2

Catalytic properties of Cu/MCM-48 catalysts: percentage of conversion (X%), percentage of selectivity to cinnamyl alcohol (%) and activity of the catalysts.

Catalysts	X%	Activity (10 ⁶) ^a	S%
MCM-48	0	–	–
CuH ₂	7.5	1.7	42
CuH ₄	11.2	1.2	44
CuH ₈	22.1	1.3	47
CuH ₂₀ ^b	15.4	4.5	0
CuI ₁₀	21.3	1.0	48
CuI ₂₀ ^b	18.3	1.6	45
Cu/γ-Al ₂ O ₃	5.3	6.0	2

^a Moles of cinnamaldehyde converted per second and per gram of copper.

^b The catalytic test was performed with half the mass of the other catalysts (100 mg).

persion is much higher, and much more uncoordinated. This would be the origin of the selectivity of copper.

Regarding the activity of the catalysts (see Table 2), the general trend is that selective samples prepared from hydrothermal synthesis or by wet impregnation are much less active than Cu/γ-Al₂O₃.

In Fig. 6 the dependence of conversion on time is shown for CuH₂. It is interesting to observe that the conversion increases linearly with time for reaction times lower than 200 min, suggesting that the reaction is zero order.

The dependence of the selectivity towards the different hydrogenation products on time on stream is shown in Fig. 6. For calculating selectivity only hydrogenation products were considered, while ethyl benzene was disregarded.

For initial reaction times (30 min) the catalyst was rather unselective, since the production of hydrocinnamaldehyde and of phenyl alcohol were higher than the corresponding to cinnamyl alcohol. However, with time on stream the catalyst turns more selective towards the desired product. Thus, it could be speculated that modification of copper reactive sites occurs under reaction conditions that turns the catalyst more active for the production

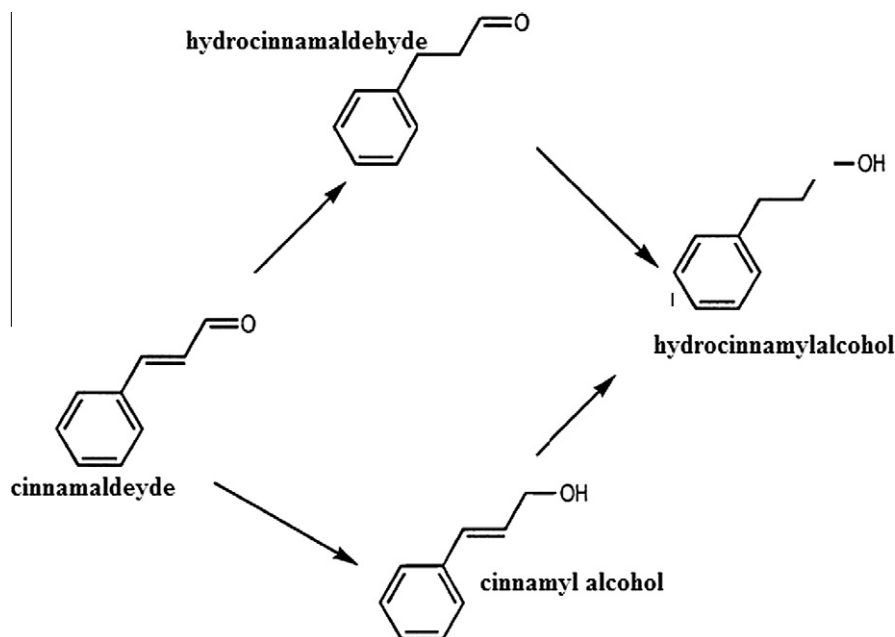


Fig. 5. Scheme for the hydrogenation of cinnamaldehyde.

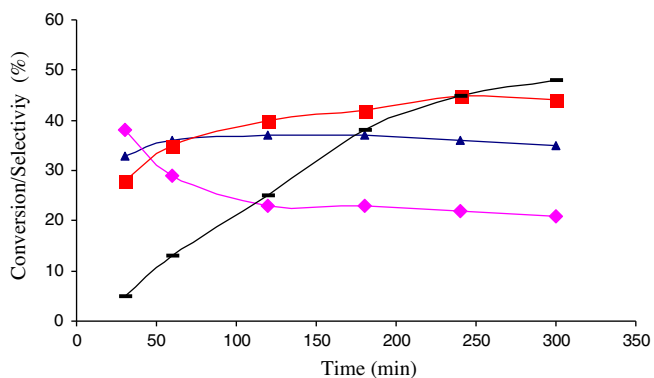


Fig. 6. Dependence of the conversion of cinnamaldehyde (+) and of the selectivities to cinnamyl alcohol (■), to hydrocinnamaldehyde (◆), and to hydrocinnamyl alcohol (▲) on time for CuH2.

of the desired product. For reaction times higher than 60 min, cinnamyl alcohol is the main product.

4. Discussion

The morphological aspects of MCM-48 are modified by the incorporation of copper. The main changes are: a diminution of the specific surface area, a decrease of pore diameter, and a reduction of the ordered mesoporous structure. Besides copper species within the MCM-48 framework, bulky copper oxide crystals are present in the samples for metal loading higher than 2 wt%.

The same trend was observed for both series (the hydrothermal one and the series prepared from $\text{Cu}(\text{AcAc})_2$): intensity of the diffraction peak (2 1 1) decreases with the copper loading. This result indicates that the cubic order phase is strongly modified by the introduction of the copper species, suggesting the inclusion of the metal into the MCM-48 walls. Copper oxide crystals are detected (by XRD) for metal loading higher than 2 wt%, though it is difficult to determine their concentration. Copper oxide crystallites are not detected by TEM, but by XRD probably due to their low size and to the low contrast between CuO and the support.

For low copper loadings the morphological modifications of MCM-48 are quite slight, whatever the preparation method, hydrothermal synthesis or impregnation with $\text{Cu}(\text{AcAc})_2$. On the other hand, when copper loading is increased the two preparation methods lead to different kind of samples. The introduction of copper from $\text{Cu}(\text{NO}_3)_2$ at the same time that the silicon source, completely destabilizes the conformation of the mesoporous structure when the ratio Cu/Si is high. Even for a ratio of 50, the mesoporous channels are not formed, and merely a physical mixture of silica and copper oxide is obtained (CuH20).

Besides morphological aspects, the introduction of copper to MCM-48 originates chemical modification of this metal. A decrease in the reducibility of copper, as concluded from the low hydrogen consumption in TPR analysis was detected. Two facts could explain the diminished reduction: (i) copper oxide species are stabilized in the MCM-48 structure and their reduction is not achieved under TPR conditions or (ii) copper species are in the +1 oxidation state, giving rise to a lower H_2 consumption than in oxidation state +2. Whatever the origin of the diminution of the reducibility of Cu/MCM-48 by comparison with $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$, it could be concluded that the chemical nature of copper species is completely different when supported onto alumina surface than when incorporated to MCM-48.

The test of Cu/MCM-48 as catalysts for the hydrogenation of cinnamaldehyde indicated that copper species incorporated in the MCM-48 mesoporous structure would be the selective sites

for the hydrogenation of C=O when C=C is present. For the Cu/MCM-48 samples selectivity towards the desired products was higher than 40% at relatively high conversion levels, whatever the copper loading. It is well known that the hydrogenation of cinnamaldehyde is a reaction sensible to metal particle size of the corresponding catalyst. With this in mind one can conclude that all the selective catalysts (CuH2, CuH4, CuH8, Cu10 and Cu120) present similar copper dispersion on the MCM-48 structure.

Gold catalysts are considered to be highly selective for the hydrogenation of α,β -unsaturated compounds [39,44]. Thus it is interesting to compare catalytic results from gold supported catalysts with those corresponding to the much less expensive copper catalysts. In previous work [39], the same experimental device and the same reaction conditions were employed for testing gold supported on hematite reached 88% of selectivity to the desired product. In spite of no such high selectivity level to cinnamyl alcohol was measured for copper catalysts as for gold supported on hematite, it is worth noting that CuH2, CuH4, CuH8, Cu10 and Cu120 are more selective than $\text{Au}/\gamma\text{-Al}_2\text{O}_3$ and than Au/FeOH (comparison performed at approximately the same conversion levels).

Copper is much less active than noble metals (Pt, Au, Pd) in hydrogenation reactions [39,44]. Considering this, high copper loading should be incorporated in the support in order to attain similar levels of activity than traditional noble metal based catalysts. The wet impregnation method allows introducing a higher copper loading without completely losing the MCM-48 morphological aspects. To label, selective Cu120 catalyst stands nearly 20 wt% of copper. Certainly, this sample contains an amount of extra framework CuO. However, this phase would be finely dispersed on the surface of MCM-48 and renders a quite efficient catalyst for selective hydrogenation in liquid phase. On the other hand, CuH20 showed no mesoporous structure (XRD), a low specific surface area (BET), and poorly dispersed CuO crystallites (TPR). Concomitantly it shows an extremely low catalytic performance, showing nil selectivity towards the desired product, cinnamyl alcohol. In this context the wet impregnation from $\text{Cu}(\text{AcAc})_2$ should be preferred to the traditional hydrothermal synthesis.

From the present study it can not be fully explained which is the nature of the copper-silicon interactions that arise in the Cu/MCM-48 preparation following the wet impregnation route. Why this pathway leads to highly dispersed copper species, even for high metal loading? Further studies should be carried out, varying copper concentration is a wider range than the one of this work. However, the present results allow to conclude that wet impregnation should be preferred to traditional hydrothermal synthesis in order to obtain high active and selective catalysts for liquid phase hydrogenation reactions.

5. Conclusion

Cu/MCM-48 catalysts could be prepared following hydrothermal synthesis or wet impregnation from $\text{Cu}(\text{AcAc})_2$. However, for copper loading higher than 2 wt% the hydrothermal way may lead to a loss of the mesoporous structure. On the other hand, from wet impregnation with $\text{Cu}(\text{AcAc})_2$, the metal loading can be increased, and mesoporous samples with copper concentration as high as 18 wt% can be obtained.

Copper species in the MCM-48 framework and finely dispersed copper are selective towards the hydrogenation of the carbonyl bond in the molecule of cinnamaldehyde. The relatively high selectivity of copper mesoporous catalysts would be related with these properties of copper species.

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