

Highly selective copper nanoparticles for the hydrogenation of α,β -unsaturated aldehydes in liquid phase

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ABSTRACT

Unsupported copper nanoparticles (CuNPs), 3–4 nm in size, are obtained from the reduction of the corresponding metal chloride through an electron transfer from a lithium arenide. CuNPs are tested for the liquid phase hydrogenation of cinnamaldehyde in batch conditions by using H₂. High activity and selectivity to cinnamyl alcohol (87%, at high conversion) are reached. When CuNPs are supported on MCM-41 and on high surface area CeO₂, TEM and XRD characterization shows that the nanometric size of copper is retained. For the hydrogenation of crotonaldehyde or of cinnamaldehyde, CuNPs/MCM-41 and CuNPs/CeO₂ are less active and less selective than unsupported nanoparticles. However the selectivity levels reached by these catalysts are higher than those obtained over noble metal (Au and Pt) based catalysts, tested under the same reaction conditions. The catalytic properties of supported and unsupported CuNPs would be related to the nanometric size of copper.

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1. Introduction

The synthesis of unsaturated alcohols from α,β -unsaturated aldehydes by heterogeneous processes is a challenge since the hydrogenation of the C=O bond, while leaving the C=C intact, is not favored from a thermodynamic point of view [1]. Due to the fact that this reaction is of paramount importance in the field of fine chemicals, large efforts have been devoted to the design of suitable heterogeneous catalysts [2]. In traditional industrial processes, metal hydrides are employed to carry out this transformation. However, heterogeneous catalysts should be preferred because of environmental concerns and for technical and economical considerations.

Noble metal based catalysts have been largely studied for the hydrogenation of α,β -unsaturated compounds, and high selectivities to the unsaturated alcohol were reported in some cases [3–7]. On the contrary, supported copper catalysts have remained less explored, and it was postulated that this metal would be rather unselective and poorly active for semihydrogenation reactions [8–10]. However, some of us have observed that certain copper catalysts are highly selective for the hydrogenation of cinnamaldehyde in liquid phase [11,12]. This previous result, along with the consideration of the low cost of copper, encouraged us to further study this metal as a catalyst for selective hydrogenation reactions.

Unsupported Ni, Fe and Cu nanoparticles, synthesized by chemical reduction of the corresponding metal (II) chloride with lithium sand and an arene as electron carrier, are quite interesting systems [13–15]. These unsupported nanoparticles (NPs) are uniform in size (3.0 ± 1.5 nm) and possess no protective agent. NPs are highly reactive and efficiently promote a variety of organic transformations.

In the present study, naked copper unsupported nanoparticles (CuNPs) are tested for the liquid phase hydrogenation of cinnamaldehyde. Besides, CuNPs are prepared over mesoporous MCM-41 and high surface area ceria (HAS-CeO₂), giving rise to the supported systems CuNPs/MCM-41 and CuNPs/CeO₂. These catalysts are characterized by XRD, TEM, TPR, and N₂ isotherms at 77 K measurements and then they are tested for liquid phase hydrogenation of cinnamaldehyde and crotonaldehyde, for comparing the properties of the supported and unsupported CuNPs. Besides, the reuse of the samples is also analysed. The catalytic results of the copper based catalysts are compared with those of other noble metal catalysts tested under the same operational conditions.

2. Experimental

2.1. Catalysts preparation

2.1.1. Naked unsupported copper nanoparticles (CuNPs)

The unsupported CuNPs were prepared by reaction of 0.5 mmol of anhydrous CuCl₂ (99.9% from Aldrich) and 4.0 mmol of lithium sand, in the presence of a catalytic amount of 4,4'-di-*tert*-butylbiphenyl (DTBB) as the electron carrier and 3 mL of THF

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(anhydrous, freshly distilled from sodium/benzophenone ketyl). The CuNPs preparation was carried out in a Parr reactor (100 mL), under 1 atm of N_2 .

When the formation of CuNPs was achieved (30 min after putting in contact the reactants, based on previous work [13]), 2 mL of isopropanol were injected into the reactor under N_2 flow, for eliminating the excess of lithium.

2.1.2. Supported copper nanoparticles

The supports were SiO_2 (210 m²/g, from Davison), high surface area CeO_2 (240 m²/g, from Rhône Poulenc) and MCM-41, which was synthesized following the hydrothermal route reported in ref [16]. For supporting the CuNPs, the reduction of copper chloride was carried out, in the presence of 600 mg of the support. At the end of the reaction, the solids were washed with bidistilled water and diethyl ether and dried in oven (313 K, 1 h). In this way three catalysts were obtained: CuNPs/ SiO_2 , CuNPs/MCM-41 and CuNPs/ SiO_2 with nominal copper loading of 20 wt%.

2.2. Catalysts characterization

The samples were characterized by Transmission Electron Microscopy (TEM), in a JEOL 100CX2 (Tokyo, Japan) Instrument. CuNPs were characterized immediately following their preparation. The supported samples were characterized following a pre-treatment, which consisted of a reduction under H_2 flow at 523 K for 30 min; the solid was then cooled down to room temperature. Under H_2 flow the solid was introduced into a vessel containing hexane (previously purged with N_2 to eliminate air in the liquid). Immediately afterwards, a drop of this mixture was put in a TEM grid and the analysis was carried out. Approximately one hundred metal 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: $d = (\sum n_i d_i) / n_i$.

Copper content of the supported catalysts was determined by atomic absorption spectroscopy.

The specific surface area of the bare supports and the catalysts were calculated by BET method, from the N_2 isotherm at 77 K measured in a Quantachrom NOVA 1200e apparatus.

The reducibility of the supported catalysts was analysed by temperature programmed reduction (TPR) in a home-made equipment. The samples were pre-treated with chromatographic air at 300 °C. Then, a flowing mixture (20 mL/min) of 10% H_2 /Ar was introduced, raising the temperature from room temperature up to 773 K, with a heating rate of 8°/min. The TPR profile was obtained following the H_2 consumption with a TCD detector.

X-ray diffraction (XRD) spectra were obtained using a Philips PW1710 BASED diffractometer equipped with a Cu K α radiation source. Copper crystallite sizes were calculated from the line width at half height of the corresponding peaks using the Scherrer equation with Warren's correction for instrumental line broadening.

2.3. Catalytic tests: hydrogenation of cinnamaldehyde and of crotonaldehyde.

The catalytic test of naked CuNPs was carried out over the particles immediately following their preparation (as described in Section 2.1.1). The Parr reactor containing recently prepared naked nanoparticles, under N_2 atmosphere, was filled with a solution of cinnamaldehyde (Carlo Erba, 99.9%) in THF, in order to obtain a 0.1 M solution with a volume of 30 mL. The pressure was increased to 1 MPa and the temperature was raised to 373 K. The magnetic stirring was set in 800 rpm and the reaction was considered to be started. Aliquots of the reaction mixture were analysed by gas chromatography with a ZB wax semicapilar column in order to measure conversion and selectivity along with time.

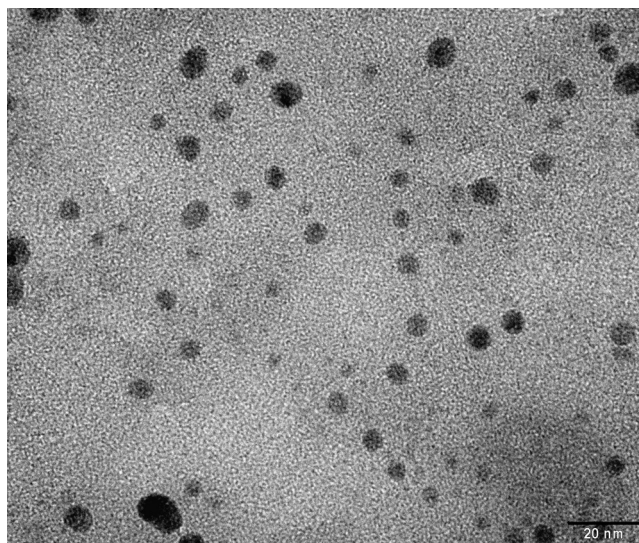


Fig. 1. TEM image of unsupported copper nanoparticles, CuNPs.

The test of the CuNPs/support catalysts was carried out with a mass of 100–200 mg prepared as described in Section 2.1.1. In a typical experiment, the catalyst was reduced for 30 min at 523 K in the reactor under H_2 (99.99%) flow. Afterwards, the reactor was cooled down to 373 K and a solution of crotonaldehyde or cinnamaldehyde (0.1 M) was introduced avoiding contact with air. The same procedure as in the case of CuNPs was followed for testing supported catalysts. The absence of external diffusion limitation was checked by varying the catalyst weights in the 0.1–0.6 g range, as well as the stirring rate in the 200–900 rpm range. Weisz–Prater criterion was considered in order to evaluate the absence of pore diffusion limitations.

The concentration of the reactive solution was varied in the 0.05–0.5 M range and it was observed that the reaction is a pseudo-first order one regarding the aldehyde.

For evaluating the reuse of the supported samples the following procedure was carried out: the spent catalysts were separated filtering the reactive mixture, and washed with fresh solvent. The used sample was reduced again for 30 min at 523 K in the reactor under H_2 flow and a new catalytic run was carried out, following the same protocol as in the case of the fresh samples.

3. Results

3.1. Catalysts preparation and characterization

Table 1 shows the list of the copper catalysts, as well as the corresponding metal loadings and BET surface areas.

The MCM-41 supported catalyst presents a metal loading quite similar to the nominal one (20 wt%), showing that the whole of the synthesized CuNPs in contact with the support can be retained. On the other hand, for silica and ceria-supported catalysts, the loading of the metal fixed is lower than the target concentrations, indicating that certain amount of CuNPs are lost during the preparation.

The mean particle size of the different samples, as calculated from TEM, is reported in Table 1. In Fig. 1, a TEM image corresponding to CuNPs is shown. The mean particle size of unsupported copper is 3.1 nm and a narrow distribution of size was obtained.

The mean particle size corresponding to CuNPs/MCM-41 is 3.8 nm as measured by TEM (Fig. 2a and Table 1). This result indicates that the nanometric scale of the naked CuNPs is retained upon supporting on MCM-41. On the contrary, in the case of CuNPs/ SiO_2 the mean particle size is relatively large (see Table 1 and Fig. 2b).

Table 1
Physicochemical properties of copper and gold catalysts.

Sample	Cu or Au wt%	BET surf. area (m ² /g)	TEM part. size (nm)	D% ^a
CuNPs	100	–	3.1	32
CuNPs/SiO ₂	12	210	18.5	7
CuNPs/CeO ₂	18	240	3.1 ^b –1.1 ^c	29–85
CuNPs/MCM-41	21	810	3.8	26

^a Metal dispersion calculated from the average particle sizes determined by TEM, using the formula $D = 10^{21} \times M \times \rho_{\text{site}} / (d \times \rho_{\text{metal}} \times N)$ from Ref. [19].

^b Estimated from the TEM size of naked CuNPs.

^c Determined from H₂ chemisorption measurements.

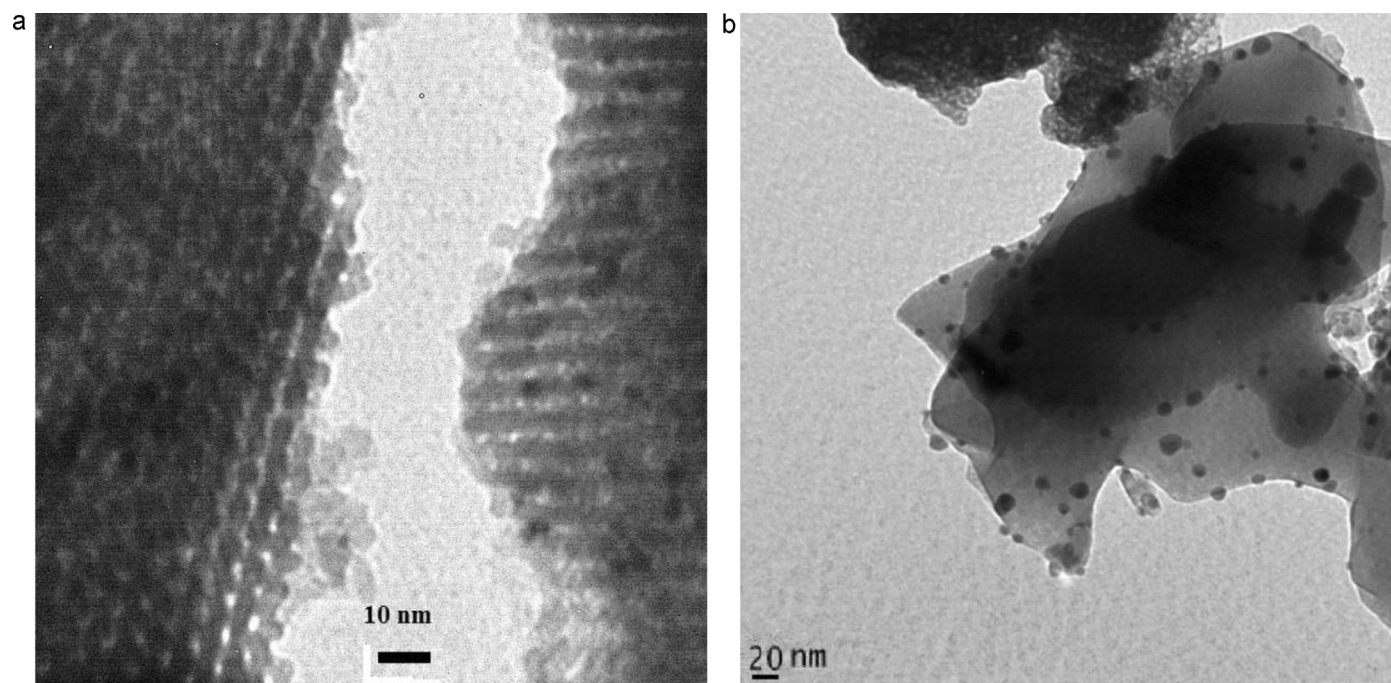


Fig. 2. TEM images of supported copper nanoparticles. (a) CuNPs/MCM-41 and (b) CuNPs/SiO₂.

Although the copper particles in this sample are not nanosized ones, the NPs denomination is employed anyway since CuNPs/SiO₂ was prepared from naked CuNPs.

Unfortunately, copper particles cannot be observed by TEM over the CuNPs/CeO₂ sample, due to the low particle/support contrast. This fact was previously observed for gold particles supported on the same support, high surface area CeO₂ [17,18].

XRD diffractograms of the supported samples are shown in Fig. 3a–c. CuNPs/MCM-41 shows a typical diffraction profile of a hexagonal mesoporous structure. An intense peak at angles lower than 2.5° of 2θ due to the diffraction of (1 0 0) plane of MCM-41 [16] is detected. Other minor peaks due to reflections of (1 1 0), (2 1 0) and (2 0 0) planes also appear. No diffraction peaks due to copper species are observed. It can be concluded that copper is highly dispersed on MCM-41 as nanometric crystals which give no diffraction pattern. Besides, the preparation method of CuNPs does not destroy the mesoporous network of MCM-41.

The XRD pattern of the silica-supported catalyst, CuNPs/SiO₂, is shown in Fig. 3b. The diffraction peaks corresponding the CuO (tenorite) phase were observed at 2θ = 35.37 and 38.58. The calculation following Scherrer approximation shows that these copper crystals possess a size of 21 nm, in relatively good agreement with TEM measurements.

The XRD characterization of CuNPs/CeO₂ is shown in Fig. 3c, where intense ceria diffraction peaks can be observed while the diffraction of CuO was not detected due to the relative low size of the crystals.

The TPR profiles of the copper supported catalysts are shown in Fig. 4. The reduction of copper species is accomplished at different temperatures for the different catalysts. The temperature corresponding to the maximum of the reduction peak (T_{max}) is 571 K for the sample supported on SiO₂, while for CuNPs/MCM-41 the T_{max} value is 544 K. This difference between T_{max} would be

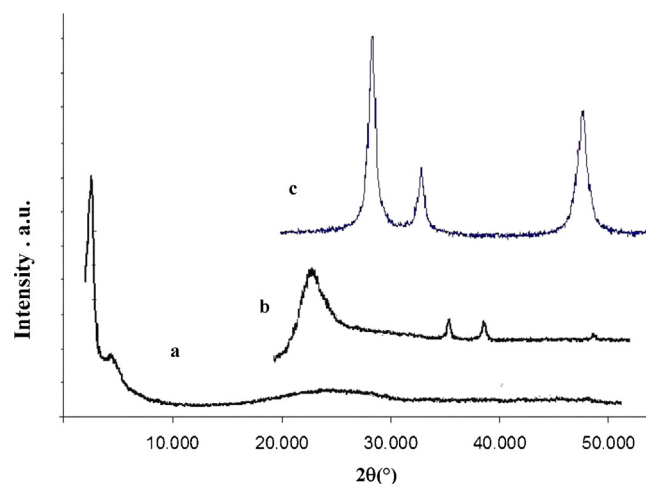


Fig. 3. XRD pattern of supported copper catalysts. (a) CuNPs/MCM-41, (b) CuNPs/SiO₂ and (c) CuNPs/CeO₂.

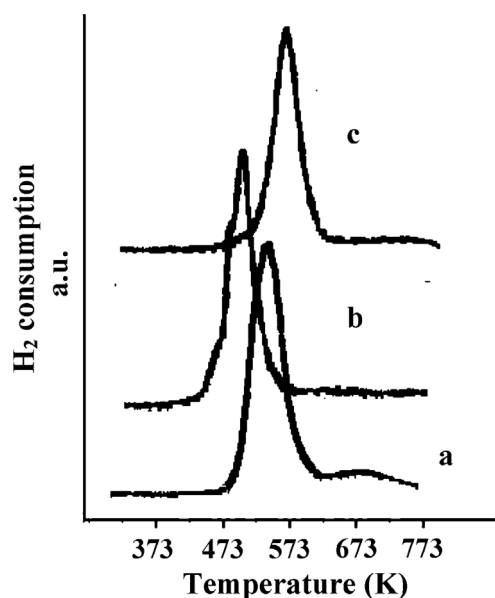


Fig. 4. TRP profiles of copper supported catalysts. (a) CuNPs/MCM-41, (b) CuNPs/CeO₂ and (c) CuNPs/SiO₂.

due to the fact that copper particle size is much lower for MCM-41 than for SiO₂, thus the reduction process is being favored over the former sample. For both, CuNPs/MCM-41 and CuNPs/SiO₂, the H₂ consumption corresponds to a complete reduction from CuO to Cu.

The T_{\max} of CuNPs/CeO₂ is relatively low (493 K). The amount of H₂ consumed exceeds the one corresponding to the reduction of CuO to Cu suggesting that reducible ceria species are also engaged in the redox process. This result is similar to the one obtained for noble metals supported on HAS-CeO₂ [6,17,18]. In this way, ceria should not be considered an inert support, and it would influence on the redox properties of copper nanoparticles. In line with this, the reduction of CuNPs/CeO₂ is accomplished at a temperature lower than the ones corresponding to the other catalysts.

3.2. Catalytic test

Firstly, the catalytic results corresponding to unsupported CuNPs will be presented.

The dependence of conversion of cinnamaldehyde on time on stream for CuNPs is shown in Fig. 5. High conversion levels are attained, and no noticeable depletion in the increase of this level is observed suggesting that no deactivation process takes place.

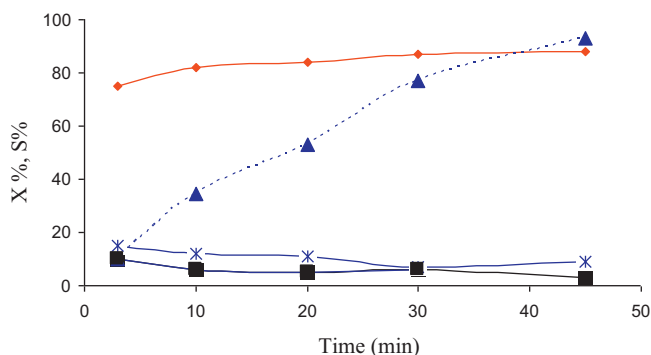


Fig. 5. Dependence on time of conversion (▲) of cinnamaldehyde and of the selectivities to cinnamyl alcohol (◆), hydrocinnamaldehyde (✱) and hydrocinnamyl alcohol (■) for CuNPs.

Table 2

Catalytic properties of CuNPs and CuNPs/support.

Sample	Activity ^a	TOF ^b	S% ^c
Cinnamaldehyde hydrogenation			
Cups	31	0.008	87
CuNPs/MCM-41	8	0.002	65
CuNPs/SiO ₂	3	0.003	16
CuNPs/CeO ₂	15		85
Cu/CeO ₂ ^d	16.5	0.007	35
Cu/MCM-48 ^e	1.1	0.001	46
Crotonaldehyde hydrogenation			
CuNPs/MCM-41	10	0.003	60
CuNPs/SiO ₂	5	0.005	16
CuNPs/CeO ₂	17	0.012	65

^a μmol converted per g of metal and per second.

^b Moles converted per mole of exposed copper (calculated from $D\%$ in Table 1) and per second.

^c Selectivity towards the unsaturated alcohol measured at approximately 30% of conversion.

^d Results from Ref. [11].

^e Results from Ref. [12].

The activity is reported in Table 2, expressed in terms of a rate related to the mass of copper (moles of aldehyde converted per second and per g of metal, calculated following 1 h of reaction time). Besides, Table 2 also reports the activity related to the surface concentration of copper (TOF, moles of the aldehyde converted per second and per mole of exposed metal). For calculating TOF, the average particles sizes of CuNPs were recalculated to dispersion values ($D\%$ in Table 1) using the formula described by Scholten et al. [19] and considering that the copper surface density was $1.35 \times 10^{19} \text{ Cu/m}^2$ [20]. High TOF values were observed, showing the high reactivity of CuNPs.

Focusing the attention on the selectivity to the desired product, cinnamyl alcohol, it is high for all the conversion levels (see Fig. 5 and Table 2), indicating that the naked CuNPs are highly selective for the hydrogenation of the C=O bond when the C=C bond is present in the same molecule. The selectivities corresponding to the different primary hydrogenation products remain nearly constant with the reaction time. No other products, such as decarbonylation or polymerization ones are detected.

In an additional experiment, naked gold nanoparticles (AuNPs) were prepared from HAuCl₄, following the same procedure as for preparing CuNPs. These naked AuNPs resulted highly active for the hydrogenation of cinnamaldehyde. Approximately the same activity than for CuNPs was observed. However, these noble metal particles were unselective towards cinnamyl alcohol, hydrocinnamaldehyde being the main product for all the reaction time. For all the conversion range the selectivity to the unsaturated alcohol did not surpass 20%.

The catalytic tests for the CuNPs/MCM-41, CuNPs/CeO₂ and CuNPs/SiO₂ catalysts were carried out for the cinnamaldehyde and the crotonaldehyde hydrogenation reactions.

Catalyst weights in the 0.07–0.5 g range were used to check that the reaction was not diffusion limited under the present experimental conditions. The conversion was found to increase linearly with the amount of catalyst, indicating the absence of external diffusion control. Weisz–Prater criterion was considered in order to evaluate the absence of internal diffusion limitations. The WP number corresponding to the supported catalysts were lower than 0.15, both for H₂ and for the aldehyde. These values verify the absence of transport limitation [21].

Fig. 6 shows the results of the hydrogenation of cinnamaldehyde over CuNPs/MCM-41.

The activity was lower than that of the corresponding to naked CuNPs, showing that supporting metal particles diminishes the corresponding activity. Besides the selectivity to cinnamyl alcohol is

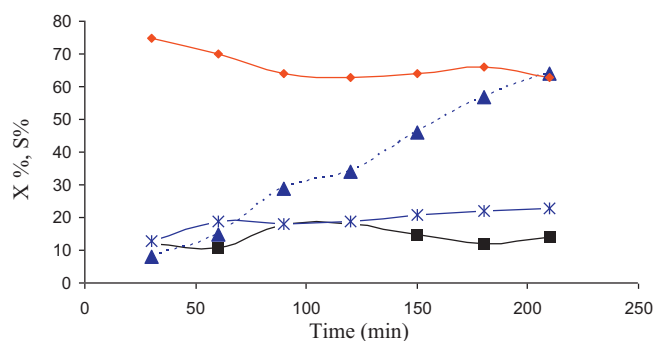


Fig. 6. Dependence on time of conversion (▲) of cinnamaldehyde and of the selectivities to cinnamyl alcohol (◆), hydrocinnamaldehyde (✱) and hydrocinnamyl alcohol (■) for CuNPs/MCM-41.

lower than the one corresponding to CuNPs. To label, for a conversion level of 10%, the selectivity of CuNPs is 80%, while that of CuNPs/MCM-41 is 63%. The lower production of the unsaturated alcohol in the supported sample by comparison with the naked unsupported particles is due to an augmentation in the production of the saturated aldehyde and not to an increase in the production to the saturated alcohol. Similar trends were observed for the hydrogenation of crotonaldehyde (see Table 2).

Spent CuNPs/MCM-41 was washed with isopropanol, submitted to a reduction pre-treatment in situ and a new catalytic test was carried out over this used sample. Approximately the same catalytic pattern as that shown in Fig. 6 was obtained, showing the possibility of reuse this catalyst.

Fig. 7 shows the results for the hydrogenation of crotonaldehyde over CuNPs/SiO₂. The specific activity of this sample was lower than the one of the unsupported catalyst (see Table 2). The selectivity towards crotyl alcohol was also lower than that obtained by using naked CuNPs for all the reaction time and this sample should be considered as an unselective one. The trends for the dependence of conversion and selectivity on time on stream for the hydrogenation of cinnamaldehyde were similar to those of the hydrogenation of crotonaldehyde (the corresponding results are reported in Table 2).

The catalytic results of the hydrogenation of crotonaldehyde and cinnamaldehyde over CuNPs/CeO₂ are shown in Fig. 8 and in Table 2. The activity of the ceria-supported sample, CuNPs/CeO₂, is higher than the one corresponding to the CuNPs/MCM-41 catalyst. As commented above, it was not possible to determine copper particle size for the ceria-supported sample neither from XRD, nor from TEM analysis. In order to calculate copper dispersion, a H₂ chemisorption dynamic measurement was performed. The copper dispersion obtained was quite high, 85%. Such a high metal dispersion would correspond to a copper particle size of 1.1 nm [19]. Considering that the method of preparation of copper

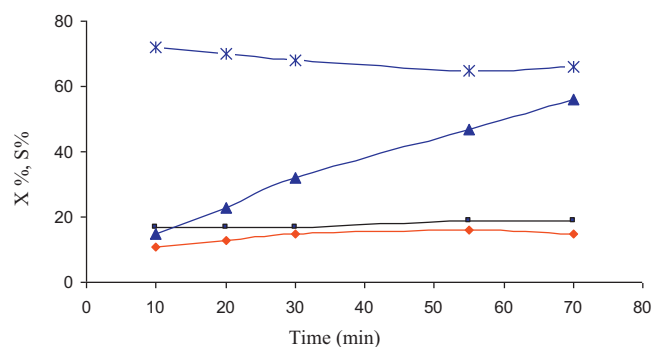


Fig. 7. Dependence on time of conversion (▲) of crotonaldehyde and of the selectivities to crotyl alcohol (◆), butanal (✱) and butanol (■) for CuNPs/SiO₂.

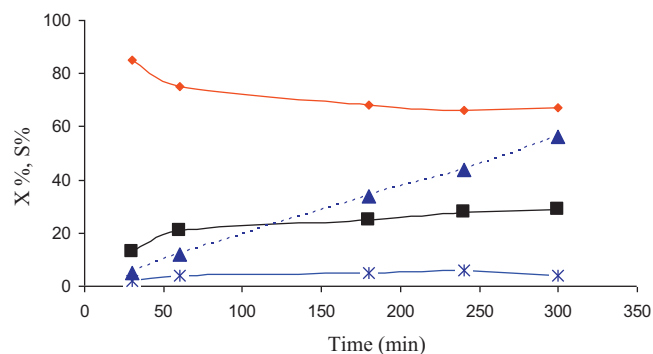


Fig. 8. Dependence on time of conversion (▲) of crotonaldehyde and of the selectivities to crotyl alcohol (◆), butanal (✱) and butanol (■) for CuNPs/CeO₂.

nanoparticles, from the fast lithium-arenide reduction of CuCl₂ leads to crystals with size of 3–4 nm, the value calculated from the H₂ chemisorption measurement would be misleading. It is likely that ceria species uptake hydrogen, giving rise to a high consumption and concomitantly not reliable copper dispersion could be measured. For this reason TOF number of CuNPs/CeO₂ has not been calculated for this sample. Anyway, the extra hydrogen consumption shows that ceria surface can activate H₂, and it is prone to provide reactive sites for hydrogenation reactions as previously observed [22]. The promotional effect of the support would be the responsible for the fact that the activity of CuNPs/CeO₂ is higher than the one corresponding to the other supported samples. Regarding the selectivity, the ceria-supported sample shows a notably high initial selectivity to the unsaturated alcohol, which is depleted to a level of approximately 70% in the case of the hydrogenation of crotonaldehyde (see Fig. 8).

The reuse of CuNPs/CeO₂ was evaluated and the same catalytic pattern as in the case of fresh sample was obtained over the spent catalyst submitted to a new pre-reduction treatment.

Finally, considering that the highest activity and selectivity among the copper supported catalysts is achieved for CuNPs supported on ceria, it is interesting to carry out a comparison of the catalytic properties of CuNPs/CeO₂ with those of noble metal based catalysts. In previous work some of us have concluded that supporting gold on hematite, gives rise to highly selective catalysts for the hydrogenation of α,β -unsaturated aldehydes. Those catalysts had been tested under the same experimental conditions than the ones reported in the present work. The comparison of the selectivity, at the same conversion, indicates that CuNPs and CuNPs/CeO₂ should be considered as selective as some gold-based samples (see Table 2).

CuNPs either supported on MCM-41 or on high surface area CeO₂, shows a higher selectivity to the desired product than Pt based catalysts, as can be concluded from the comparison of the present catalytic results with those from Ref. [23].

In previous work [11], some of us investigated on the hydrogenation of cinnamaldehyde over Cu/CeO₂ and Cu/MCM-48, prepared from wet impregnation of the mesoporous support with a copper precursor (Cu(AcAc)₂). The characterization of the supported copper particles obtained by wet impregnation showed that this method leads to relatively large crystals. Besides, it is important to note, than the specific activity and the selectivity to the unsaturated alcohol of Cu/MCM-48 are lower than the ones corresponding to CuNPs/MCM-41. As well, the production of cinamyl alcohol for Cu/CeO₂ was notably lower than the corresponding to CuNPs/CeO₂. From this point of view, the preparation of supported copper on MCM-48 and CeO₂ following the fast reduction of a copper salt should be preferred to the wet impregnation.

4. Discussion

The hydrogenation of α,β -unsaturated aldehydes with unsupported copper nano-particles, prepared by fast reduction with lithium sand and a catalytic amount of an arene was accomplished in this work, giving rise to quite high activities. Classically, copper catalysts are much less active for hydrogenation reactions than noble metals catalysts (Pd, Pt and Ru) [8,9]. The poor activation of H_2 on Cu, which is due to the high degree of filling of d-band [24], is the responsible for such a low activity. CuNPs showed a high activity, probably related with the fact that unsupported metal nanoparticles show a catalytic behaviour in the frontier of the homogeneous and heterogeneous catalysis [14]. In fact, these catalysts are often called “semi-heterogeneous”, because the active catalytic sites and the reactants are supposed to be in different phases, while showing activities and selectivities that resemble a homogeneous catalyst [14].

Another particular feature of CuNPs is their notably high selectivity to cinnamyl alcohol, even at high conversion levels. Traditionally, copper supported on inert oxides has been considered to be unselective in the hydrogenation of α,β -unsaturated compounds [8,9,12]. In this context, the peculiar behaviour of the CuNPs system, showing a high selectivity, should be ascribed to both: the nanosized dimension and to the fact that particles are unsupported.

Naked AuNPs were prepared in the present work following the sample preparation method as for CuNPs and they were also tested under the same experimental conditions. Gold nanoparticles were unselective for hydrogenating C=O against C=C, since they mainly hydrogenate cinnamaldehyde to hydrocinnamaldehyde. It has been claimed that supported gold nanoparticles are selective for the hydrogenation of C=O bond against C=C bond [3–6,26,27,7]. However the high selectivity of gold was achieved when the metal nanoparticles were supported on reducible oxides, as ZnO [3,5], α -Fe₂O₃ [4,5], CeO₂ [26]. For all these systems the authors concluded that a strong influence of the support on morphological aspect of gold particles [3,5], or on the electronic state of the noble metal [26,27] were the origin of the enhanced selectivity. Even more, interfacial gold-support sites were indicated to be the selective sites for the hydrogenation of the C=O bond [4]. The low selectivity observed for AuNPs indicates that gold is intrinsically unselective in the absence of a suitable support. In addition, it can be concluded that copper in the nanometric scale is selective for hydrogenating the carbonyl bond against the olefinic one, while gold should be considered unselective.

It is worth noting that CuNPs cannot be reused, since after removing the reaction media the metal turns inactive, due to oxidation of the active sites. Supporting this system seems to be the way to achieve one of the most important advantageous characteristics of heterogeneous catalysts: the reuse. When supporting CuNPs, the nanometric particle size is kept in the presence of MCM-41. The pore size of the support (4.2 nm, determined from the corresponding isotherms) would be the ceiling to copper particles growth. The mean particle size of copper on CuNPs/MCM-41, as measured by TEM, is quite similar to the pore diameter of the mesoporous support, suggesting that copper particles would be confined in the mesoporous network. It is important to note that the nanosized dimension of supported copper is achieved for a high loaded sample (concentration of about 20%).

On the contrary the synthesis of CuNPs on SiO₂ leads to relatively large copper crystals, which were not selective for the hydrogenation of the C=O bond.

For the case of CeO₂, the nanometric size of CuNPs was retained as in the case of MCM-41. The specific surface area of ceria is similar to that of silica, but a high interaction between copper and ceria is developed, as conclude from TPR and H_2 chemisorption results. Such an interaction would be the origin of the stability of

CuNPs. Furthermore, this interaction would be related with the high activity and selectivity of copper on ceria.

In a general way, the specific activities of the supported catalysts are lower than that of the corresponding naked unsupported metal. The diminution of the activity is not only due to a loss of the exposed metal surface (originated by the particle–support contact). The catalytic behaviour of CuNPs is in the frontier of the homogeneous/heterogeneous process [18], thus if naked copper particles are considered as a quasi-homogeneous system a change in the intrinsic activity and in the selectivity of the metal upon supporting should be an expected phenomenon.

The high selectivity of CuNPs (approximately 80%, from low to high conversion levels) is depleted upon supporting. The selectivity to cinnamyl alcohol of CuNPs/MCM-41 and CuNPs are 65% and 80%, respectively, both measured at 30% of conversion. The diminution of the selectivity cannot be ascribed to a particle size effect, since this parameter is quite similar for both samples. Once again the peculiar catalytic behaviour of unsupported CuNPs should be invoked to explain the differences in the catalytic pattern.

In turn, the ceria supported catalyst, CuNPs/CeO₂, showed a selectivity to the unsaturated alcohol of 72%, also at 30% of conversion. For this sample the promotional effect of ceria would compensate the lost selectivity upon supporting.

An important property of CuNPs/MCM-41 and CuNPs/CeO₂ is the possibility of reuse the corresponding spent catalysts, following a reduction treatment. In addition, the low cost of this metal turns copper based samples quite interesting catalytic systems.

5. Conclusions

Unsupported naked copper nanoparticles, prepared from the fast lithium-arenide of chloride salt reduction, with sizes lower than 4 nm are highly active and selective for the hydrogenation of α,β unsaturated aldehydes in liquid phase conditions. These particles retain their nanometric size upon supporting on MCM-41 or CeO₂.

Though the supported catalysts are less active and selective than the unsupported particles, they attain relatively high selectivities for the hydrogenation C=O bond when C=C is present in the same molecule. This property should be related to the nanosized dimensions of copper.

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