



# Liquid phase selective hydrogenation of cinnamaldehyde over copper supported catalysts

Victoria Gutierrez<sup>a</sup>, Mariana Alvarez<sup>b</sup>, María A. Volpe<sup>a,\*</sup>

<sup>a</sup> Planta Piloto de Ingeniería Química, PLAPIQUI (UNS-CONICET) Camino La Carrindanga km 7, CC 717, 8000 Bahía Blanca, Argentina

<sup>b</sup> Departamento de Química, Instituto de Química del Sur (INQUISUR-CONICET), Universidad Nacional del Sur, Avenida Alem 1253, 8000 Bahía Blanca, Argentina

## ARTICLE INFO

### Article history:

Received 17 July 2011

Received in revised form

19 November 2011

Accepted 25 November 2011

Available online 4 December 2011

### Keywords:

Supported copper

Selective hydrogenation

Conjugated carbonyl

Ceria

Copper oxide

$\alpha,\beta$ -Unsaturated aldehydes

## ABSTRACT

The selective hydrogenation of cinnamaldehyde is carried out in a batch reactor, at 100 °C and 1 MPa of H<sub>2</sub> using isopropyl alcohol as the solvent, over a series of copper supported catalysts: Cu/Al<sub>2</sub>O<sub>3</sub>, Cu/SiO<sub>2</sub>, Cu/MCM-48, Cu/CeO<sub>2</sub> and Cu/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The selectivity of the samples is compared with that corresponding to Pt/SiO<sub>2</sub>. Reduced Cu/Al<sub>2</sub>O<sub>3</sub> and Cu/SiO<sub>2</sub> showed lower selectivity to the cinnamyl alcohol (16–22%) than Pt/SiO<sub>2</sub> (35%), at 15% of conversion. Following a calcination at 300 °C both, activity and selectivity of copper catalysts were increased. The calcined surface would hydrogenate C=O bond by hydrogen transfer from the solvent. TPR, XRD and FTIR of adsorbed CO showed that Cu (I) species are stabilized on the mesoporous structure of MCM-48. This particular feature renders Cu/MCM-48 a selective catalyst, reaching high selectivity values (51%, at 15% of conversion). Cu/CeO<sub>2</sub> and Cu/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> showed higher selectivity than Pt based catalyst due to a promotion of the catalytic properties of copper by reduced support species.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

The selective hydrogenation of  $\alpha,\beta$ -unsaturated compounds is a reaction of paramount importance in the field of organic synthesis. The most important product is the unsaturated alcohol which is employed in the synthesis of cosmetic, pharmaceutical and fine chemicals. Metal hydrides have been employed to carry out this reaction for industrial purpose [1]. However due to environmental, economical and technical considerations, heterogeneous catalysts should be preferred. Traditionally, supported noble metal catalysts have been employed due to their relative high selectivity [1–6].

Supported copper catalysts are an interesting option to perform selective hydrogenation reactions due to the low cost of the metal combined with advantageous catalytic properties of copper for selective hydrogenation reactions [7–12]. From kinetic studies performed over Pt, Cu and Pd catalysts supported on silica, Pham et al. clearly observed that the hydrogenation of C=O bond is faster than that of C=C bond over Cu/SiO<sub>2</sub> catalysts than over Pd/SiO<sub>2</sub> or Pt/SiO<sub>2</sub> for the hydrogenation of 2-methyl-2-pentenal, though this effect is masked for high conversion level [11]. On the other hand, Marchi et al. [13] concluded that Cu/SiO<sub>2</sub> and binary Cu–Al catalysts were unselective toward the hydrogenation of carbonyl bonds,

producing predominantly hydro-cinnamaldehyde during the liquid phase hydrogenation of cinnamaldehyde on Cu-based catalysts. In the same work the author observed that ternary Cu–Zn–Al and quaternary Cu–Ni(Co)–Zn catalysts were more selective than Cu/SiO<sub>2</sub>. Cationic species of the promoter (Zn, Ni, Co) were considered to be the responsible for the creation of selective sites for the hydrogenation of C=O. In the same sense, the group of Hutchings concluded that Cu/Al<sub>2</sub>O<sub>3</sub> preferentially hydrogenates carbon–carbon double bond, though the modification by sulfur compounds leads to a selective catalyst. The creation of selective Cu<sup>0</sup>-S and Cu<sup>+</sup> sites is the origin of the high selectivity [7,8].

The present study investigates a series of copper supported catalysts for the selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes. Inert support (SiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and MCM-48) as well as supports possessing redox properties (CeO<sub>2</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) was selected for supporting copper. It is speculated that the very different nature of the support would lead to different copper species, from morphological and from chemical aspects.

The most part of the chemical catalytic reactions that are particularly important in the preparation of pharmaceutical or fine chemicals are performed in the liquid phase, under constant H<sub>2</sub> pressure. For this reason the catalysts are tested for the hydrogenation of cinnamaldehyde and crotonaldehyde, in a batch reactor using H<sub>2</sub> as the reductant and isopropanol as the solvent. The selectivity to the unsaturated alcohol (the desired product) as well as the activity of the different samples is measured. The catalytic results are discussed in the light of the characterization results, obtained

\* Corresponding author. Tel.: +54 2914861700; fax: +54 2914861600.  
E-mail address: [mvolpe@plapiqui.edu.ar](mailto:mvolpe@plapiqui.edu.ar) (M.A. Volpe).

from TEM, XRD, BET, FTIR and TPR studies. Finally the catalytic properties of supported copper are compared with those corresponding to platinum and gold catalysts tested under the same experimental conditions in previous works.

## 2. Experimental

### 2.1. Materials

Silica (SiO<sub>2</sub>), Ceria (CeO<sub>2</sub>), and alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) all from Rhone Poulenc were employed as-received for supporting for copper. MCM-48 was prepared by conventional hydrothermal synthesis, following the technique reported by Xu et al. [14]. For further details, see Ref. [15].

Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) was prepared by hydrothermal synthesis from a Fe(NO<sub>3</sub>)<sub>3</sub> solution [16].

Copper was fixed to the different supports following a wet impregnation with solutions of Cu(AcAc)<sub>2</sub> (Aldrich, 99.99%) in THF. The supports ceria, hematite, alumina and silica were calcined at 300 °C, while goethite was calcined at 120 °C. Then the oxides were put in contact with the Cu(AcAc)<sub>2</sub> solution for 48 h, at 60 °C, under constant stirring. The solids were filtered and heated at 70 °C for 24 h. Finally, all samples, but goethite supported one, were calcined at 400 °C for 4 h under air flow. For goethite the calcination was carried out at 150 °C. In this way copper supported on alumina (CuA), hematite (CuH), ceria (CuC) and silica (CuS) was obtained. For the case of MCM-48 the Cu(AcAc)<sub>2</sub> solution was put in contact with the mesoporous solid before eliminating the structure directing agent. Upon copper fixation, the mesoporous system was heated under nitrogen flow, increasing the temperature from room temperature up to 400 °C by 1 °/min. Nitrogen was switched to chromatographic air, and the sample was calcined at 400 °C for 4 h. This procedure was followed for preventing the destruction of the mesoporous structure. This sample was named as CuM.

An extra copper supported alumina sample was prepared by impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with aqueous solution of Cu(NO<sub>3</sub>)<sub>2</sub>.

For all the samples, the target copper loading was 5 wt.%, while the actual metal concentration was measured by AAS.

### 2.2. Sample characterization

Adsorption/desorption isotherms of the supports and the corresponding catalysts were measured in a Nova 1200e Quantachrom equipment. From these measurements, BET surface area was obtained.

Some catalysts were analyzed by FTIR of adsorbed CO with a Nicolet 20 DXB FTIR spectrometer at 4 cm<sup>-1</sup> 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. The holder was placed in the beam path of a stainless-steel cell, sealed with CaF<sub>2</sub> windows, and coupled to a vacuum system for evacuation to 10<sup>-6</sup> Torr. It was possible to perform heat treatments up to 300 °C in air and H<sub>2</sub> and to dose small amounts of CO. CO adsorption spectra were obtained 77 K under a gas phase pressure of 5 Torr.

The reducibility of the catalysts was studied by Temperature Programmed Reduction (TPR) using a home made apparatus. The temperature of the sample was increased linearly at 10 K min<sup>-1</sup> in 5% H<sub>2</sub>/Ar at a flow rate of 20 cm<sup>3</sup> min<sup>-1</sup>, from ambient to 773 K. A thermal conductivity detector was used to measure variation in H<sub>2</sub> concentration in the gas stream. The apparatus was calibrated by performing the reduction of known amounts of CuO.

Copper particle size was determined in some cases by TEM measurements, on a Jeol 100 CX2 (Tokyo, Japan) apparatus.

X-ray diffraction (XRD) spectra were obtained *ex situ* using a Philips PW1710 BASED diffractometer equipped with a Cu-K $\alpha$  radiation source. Cu crystallite sizes were calculated from the linewidth at half height of the primary CuO peak using the Scherrer equation with Warren's correction for instrumental line broadening.

### 2.3. Catalytic testing

Liquid phase hydrogenation of cinnamaldehyde and crotonaldehyde was conducted in a batch reactor, at 373 K, and 1 MPa of H<sub>2</sub> using isopropyl alcohol (Sintorgan, 99+%). The reactive liquid mixture was 0.1 M. Before testing 0.150 g of the copper based catalyst were reduced under flowing H<sub>2</sub> at 300 °C for 1 h. The catalysts were handled without exposing to the air. Care was taken to avoid trace of oxygen in the reactor. For some samples, another pretreatment was carried out: a calcination under chromatographic air at the same temperature and for the same period of time as for the reduction pretreatment. The stirring rate was varied in the range 300 rpm. The progress of the reaction was followed by sampling a sufficient number of microsamples. The composition of the samples was analyzed by means of a Perkin Elmer gas chromatograph, equipped with a 30 m DB-WAX capillary column and a flame ionization detector. The conversion and selectivity toward the different products were measured.

## 3. Results

### 3.1. Catalysts characterization

The catalysts, the metal loading and BET surface area are listed in Table 1.

Considering that the target copper concentration was 5 wt.%, a relative high metal loading was achieved for all the samples.

The BET results show that impregnating the supports with the solution of Cu(AcAc)<sub>2</sub> and decomposition of the supported copper precursor did not result in a loss of surface area of the carriers.

The catalysts were examined by XRD to identify the phases present. In all cases, CuO (tenorite phase) diffractions peaks corresponding to  $2\theta = 35.37, 38.58$  and  $43.14$  can be observed, indicating that the cupric oxide agglomerates are present.

The tenorite (002) diffraction peak was selected for determining copper particle size from Scherrer equation. It was assumed that no lattice distortions take place. The crystallite sizes, as measured from XRD, are reported in Table 1 for all the catalysts. Since an overlapping of some of the diffraction of peaks of alumina with those corresponding to CuO exists, certain uncertainty in the determination of crystal size of the CuA sample should be considered. TEM analysis of this sample showed a low contrast between copper particles and the support, turning the measurement of particle size by this technique unreliable. In order to further investigate on copper supported on alumina by XRD analysis, and extra sample was prepared from Cu(NO<sub>3</sub>)<sub>2</sub> (the CuAN sample). The XRD pattern of this catalyst showed that CuO is more crystalline and gives more intense pattern, compared with CuA (see Fig. 1). In this way the determination of copper particle size for CuAN was reliable, with a value of 19 nm. From the comparison between CuA and CuAN it could be concluded that copper crystals are, at least, smaller than 19 nm for the former sample.

For copper supported on silica and on hematite (CuS and CuH respectively) the XRD analysis of crystal size (reported in Table 1) indicated that the copper particle size values are 18.5 nm for the silica supported sample and 21.3 nm for the hematite supported one. These results are in quite good agreement with the size obtained from TEM which indicated that the mean particle size is 20 and 23 nm for CuS and CuH, respectively.

**Table 1**  
Physicochemical properties of Cu/support catalysts.

Sample	Support	Cu (wt.%)	BET area (m <sup>2</sup> /g)	Particle size (nm) <sup>b</sup>	Copper dispersion (%)	T <sub>max</sub>	H <sub>2</sub> /Cu
CuA	γ-Al <sub>2</sub> O <sub>3</sub>	3.0	174	6.2	16	230	0.98
CuAN <sup>a</sup>	γ-Al <sub>2</sub> O <sub>3</sub>	5.2	174	19.3	5	–	–
CuS	SiO <sub>2</sub>	8.1	210	18.5	5	240	1.1
CuM	MCM-48	4.1	942	20.1	5	220	0.6
CuC	CeO <sub>2</sub>	3.8	240	9.5	10	180	1.8
CuH	α-Fe <sub>2</sub> O <sub>3</sub>	4.4	26	21.3	5	175	2.2

<sup>a</sup> Sample prepared from Cu(NO<sub>3</sub>)<sub>2</sub>.

<sup>b</sup> Calculated from Scherrer approximation from XRD diffraction peaks.

The crystal size of CuO corresponding to CuM was 20 nm, as measured by XRD. Few particles were observed by TEM for CuM. The number of particles is too low to obtain a histogram and the corresponding mean particle size. Due to the high specific surface area of the mesoporous oxide, the surface concentration of copper particles is low, the examination of this sample by TEM being difficult. On the contrary, the mesoporous channels network is clearly observed in TEM images (see Fig. 2).

It is interesting to note that diffraction peaks due to Cu<sub>2</sub>O were not observed in any sample, but for CuM. In Fig. 3 the XRD pattern of this sample is shown. Both CuO and Cu<sub>2</sub>O are detected. Another interesting feature found for CuM is that the diffraction peaks corresponding to the (2 1 1) plane of MCM-48 are kept upon copper introduction, showing that the mesoporous cubic order is not destroyed in CuM. However, the fine structure of the minor peaks of the (4 2 0), (3 3 2), etc. planes (shown in the inset of Fig. 3), disappears due to copper being incorporated in the network. Following XRD analysis of CuM, it can be concluded that three copper phases exist: crystalline oxidic species of Cu(I) and Cu(II) as well as highly dispersed copper incorporated in the mesoporous structure.

CuA, CuS and CuM samples were analyzed by FTIR of adsorbed CO. The characterization by means of FTIR employing CO as the probe molecule was previously reported for studying the different oxidation state of supported copper [17,18]. The catalysts were previously submitted to a reduction pre-treatment or to calcination pre-treatment. The infrared spectrum of CO adsorption on following an *in situ* reduction at 300 °C is shown in Fig. 4(a). The CuA

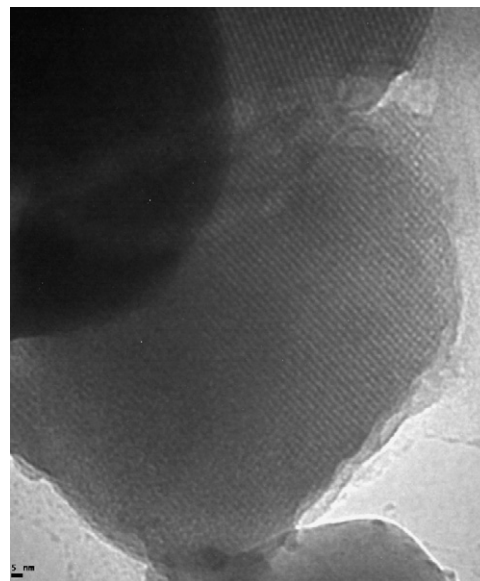


Fig. 2. TEM image corresponding to CuM (Cu/MCM-48).

catalyst presents an intense band at 2106 cm<sup>-1</sup> due to CO adsorbed on Cu<sup>0</sup>. The spectrum corresponding to the same sample, but after an *in situ* oxidizing pre-treatment at 300 °C (see Fig. 4(b)), shows a low intensity band at 2149 cm<sup>-1</sup> that could be assigned to CO on

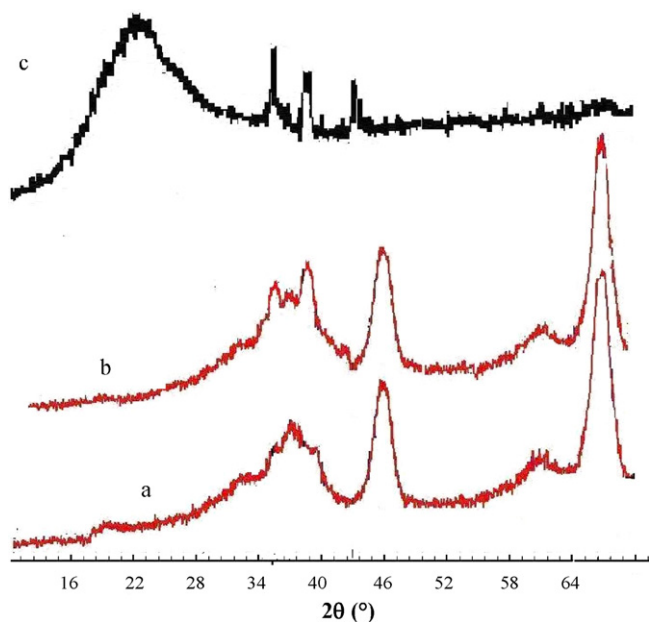


Fig. 1. XRD pattern for: (a) CuA (Cu/Al<sub>2</sub>O<sub>3</sub> prepared from Cu(AcAc)<sub>2</sub>), (b) CuAN (Cu/Al<sub>2</sub>O<sub>3</sub> prepared from Cu(NO<sub>3</sub>)<sub>2</sub>), and (c) CuS (Cu/SiO<sub>2</sub> prepared from Cu(AcAc)<sub>2</sub>) samples.

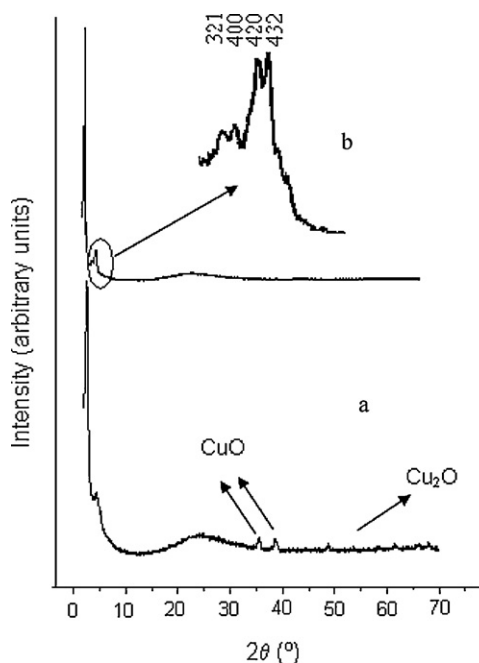
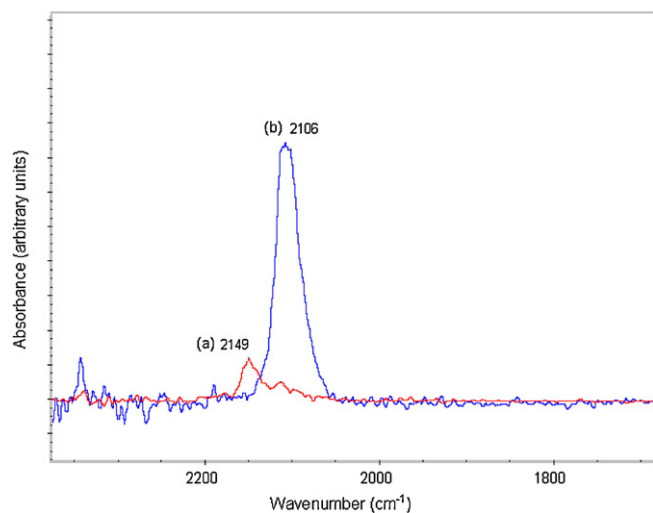
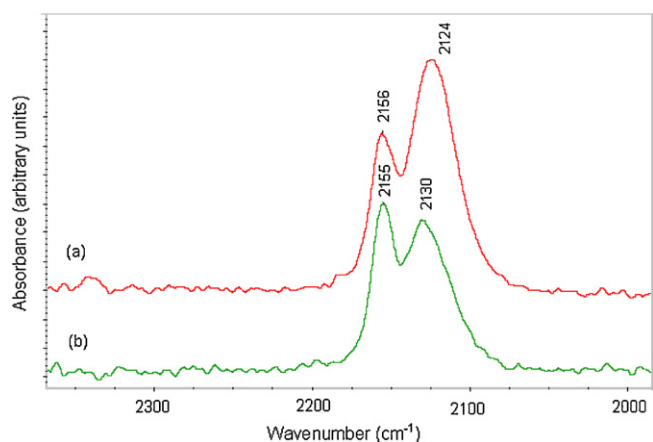


Fig. 3. XRD patterns: (a) CuM (Cu/MCM-48) and (b) MCM-48.

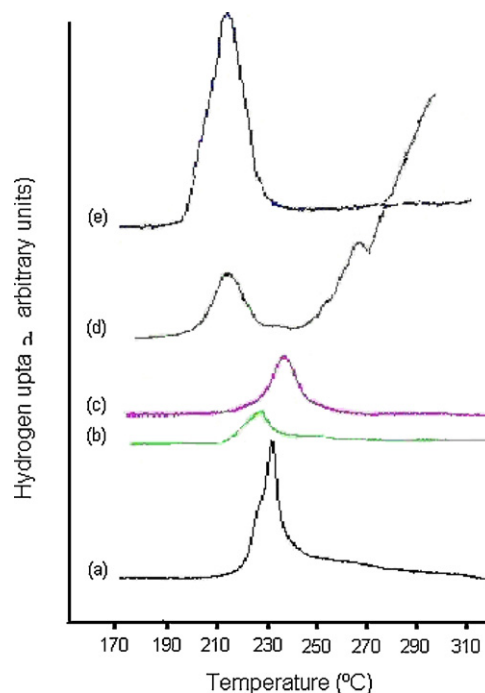


**Fig. 4.** FTIR spectra of CO adsorbed at 77 K on CuA (Cu/Al<sub>2</sub>O<sub>3</sub>). Equilibrium CO pressure of 5 Torr. (a) Sample reduced *in situ* at 300 °C, and (b) sample calcined *in situ* at 300 °C.

Cu(II). It is generally accepted that Cu(II) species does not form stable carbonyls species, even at low temperatures. The low intensity of this band is due to the fact that the interaction between Cu<sup>2+</sup> and CO is of electrostatic nature [19,20]. The FTIR results of CuS are similar to that observed for CuA: the reduced sample shows a band assigned to metallic copper, while the pre-calcined showed only a minor band. It is important to note that for both cases, the CO on cupric species easily disappears after evacuating the analysis chamber. On the other hand, for CuM the spectra of calcined or reduced samples (see Fig. 5(a and b)) are both different from those of CuS and CuA. Two bands are observed for the sample reduced *in situ*: one at 2124 cm<sup>-1</sup> due to CO on metallic copper and another at 2156 cm<sup>-1</sup> assigned to CO on the silanol groups of the mesoporous support. Following an evacuation of the chamber up to 10<sup>-6</sup> Torr, both bands disappear, showing the lability of these species. The spectrum corresponding to pre-calcined CuM shows an intense band at 2132 cm<sup>-1</sup>, besides the signal due to the silanol groups. This band is assigned to CO on Cu<sup>1+</sup> [18–20]. Following an evacuation of the chamber, the signal remains, showing that the CO–Cu<sup>1+</sup> interaction is particularly strong. The low charge and the high d density of cuprous species is the reason for the high interaction between the probe molecule and Cu<sup>1+</sup> [18].



**Fig. 5.** FTIR spectra of CO adsorbed at 77 K on CuM (Cu/MCM-48). Equilibrium CO pressure of 5 Torr. (a) Sample reduced *in situ* at 300 °C, and (b) sample calcined *in situ* at 300 °C.



**Fig. 6.** TPR profiles for Cu/support catalysts. (a) CuA, (b) CuM, (c) CuS, (d) CuH, (e) CuC.

The TPR profiles of the copper supported catalysts, as well as the corresponding to some of the supports are shown in Fig. 6. The temperature at each peak maximum and the specific hydrogen consumption (expressed as the ratio between the moles of H<sub>2</sub> consumed and the moles of copper) for each catalyst are given in Table 1.

The TPR profiles for CuA and CuS consist of a single reduction peak at 230–240 °C corresponding to the complete reduction of CuO to metallic copper. CuM is also reduced in one step, at 220 °C, but the reduction process is incomplete, and the measured hydrogen consumption is lower than the one corresponding to the total reduction to CuO. This diminished reducibility of copper on MCM-48 was previously observed for a series of Cu/MCM-48 samples [15]. In line with XRD pattern, showing the presence of Cu<sub>2</sub>O, the lower uptake of hydrogen could be attributed to a stabilization of Cu(I) species in the mesoporous oxide.

The hydrogen consumption of copper supported on the reducible oxides, ceria and hematite, was relatively high. The enhanced consumption would be due to support species (Ce<sup>4+</sup>, Fe<sup>3+</sup>) engaged in the reduction process at temperatures lower than the ones observed for the bare supports. The higher reducibility of support species observed over metal supported catalysts was previously observed for Pt/CeO<sub>2</sub> [21], Au/CeO<sub>2</sub> [22], Au/Fe<sub>x</sub>O<sub>y</sub> [23].

Besides, for the supports with redox properties, the reduction of copper species is shifted to lower temperatures, as compared to species supported on inert oxide (see *T*<sub>max</sub> in Table 2). Summing up, from TPR results it could be concluded that ceria and iron oxides supports notably enhances the reducibility of copper species.

### 3.2. Catalytic test

Catalyst weights in the 0.1–0.6 g were used to check that the reaction was not diffusion limited under the experimental conditions used. The conversion measured after 3 h of reaction time was found to increase linearly with the amount of catalyst used, indicating the absence of external diffusion control under the experimental conditions used in the present work. Weisz–Prater



**Table 2**

Catalytic properties of Cu/support catalysts for the liquid phase hydrogenation of cinnamaldehyde.

Sample	Activity ( $\mu\text{mol s}^{-1} \text{gCu}^{-1} \text{Pt}^{-1}$ )	TOF ( $\text{s}^{-1}$ ) $\times 10^3$	S% <sup>b</sup>	S% <sup>c</sup>
CuA	6.3	2.5	16	15
CuA <sub>cal</sub> <sup>a</sup>	12.7	5.0	73	51
CuS	2.7	2.7	22	15
CuS <sub>cal</sub> <sup>a</sup>	4.8	4.5	75	48
CuM	1.1	1.3	51	46
CuC	16.5	7.4	45	35
CuH	3.2	4.0	38	36
PtS <sup>d</sup>	51.6	22.3	35	37

<sup>a</sup> Samples previously calcined at 300 °C.<sup>b</sup> Selectivity toward cinnamyl alcohol measured at 15% of conversion.<sup>c</sup> Selectivity toward cinnamyl alcohol measured at 30% of conversion.<sup>d</sup> Pt (2%)/SiO<sub>2</sub>, 45% of dispersion.

criterion was considered in order to evaluate the absence of pore diffusion limitations. A value of WP less than 0.15 can be considered a sufficient condition for the absence of significant pore diffusion limitation [24]. The WP number corresponding to the catalysts supported on MCM-48, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> were lower than 0.15, both for H<sub>2</sub> and for cinnamaldehyde. These values verify the absence of transport limitation for both the gas and the aldehyde. Though the WP number corresponding to the transport of H<sub>2</sub> in CeO<sub>2</sub> indicated that diffusion limitation can be neglected, the cinnamaldehyde diffusion within the ceria pore would be restricted.

The product of the decarbonylation of cinnamaldehyde (styrene) was not observed for the reaction performed over the copper supported catalysts, but for CuC. This is an important difference between some of the copper catalysts and gold or platinum ones: the cinnamaldehyde hydrogenation over Pt/Al<sub>2</sub>O<sub>3</sub> or Au/Al<sub>2</sub>O<sub>3</sub> catalysts (performed under the same reaction conditions as the one of the present work) produced styrene [23].

The percentage of selectivity to the three products of hydrogenation (cinnamyl alcohol, hydrocinnamaldehyde, phenyl propanol) as a function of reaction time is plotted for some of the copper catalysts and for Pt/SiO<sub>2</sub> previously reduced at 300 °C in Figs. 7–11.

For all the cases the aldehyde concentration decreased linearly with reaction time, indicating that the reaction is of zero order overall. The gradients of conversion against time were used to determine rate constants, *k*, for each of the catalysts. These values are listed in Table 2 as  $\mu\text{mol}$  of cinnamaldehyde converted per second and per g of copper. The copper dispersion (see Table 1) was estimated considering both, the surface density of copper ( $1.35 \times 10^{19} \text{Cu/m}^2$  [25]) and the particle size as determined from XRD, following the relation described by Scholten et al. [26].

The Pt/SiO<sub>2</sub> catalyst shows a much higher TOF than the copper based catalyst due to the high intrinsic activity of Pt against Cu for hydrogenation reactions. The comparison of TOF number of the dif-

ferent copper catalysts indicates that hematite, alumina and silica supported ones show similar values. On the other hand, Cu/MCM-48 was less active, while Cu/CeO<sub>2</sub> shows a relatively high TOF. For the latter sample a promotion of the support species on copper activity could be postulated.

Table 2 also lists the percentage of selectivity to cinnamyl alcohol at 15 and 30% of conversion levels. For CuA, it was found that the selectivity to the desired product is low (25–15% range) for all the reaction time period, as could be observed in Fig. 7. For CuS the trend was similar, though the selectivity to cinnamyl alcohol was slightly higher (see Table 2). This difference could be assigned to the higher copper particle size found for silica support (18.5 nm) than for alumina (6.2 nm).

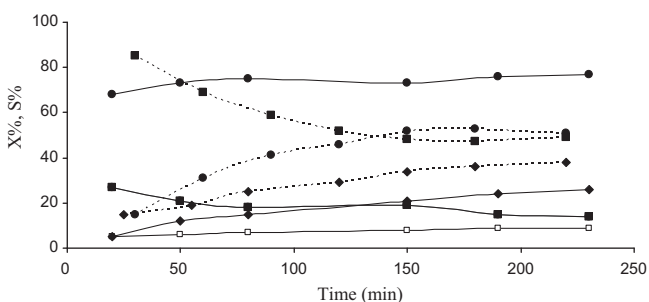
In Fig. 11 the catalytic pattern corresponding to Pt/SiO<sub>2</sub> is shown. The reaction yields other products than the primary hydrogenation ones, as styrene, condensation products, etc., thought that their concentration is relatively low. For the sake of simplicity in Fig. 11, only the products of the hydrogenation of cinnamaldehyde are shown, and the selectivities were calculated on the basis of only these products.

It could be observed that the noble metal based sample showed a higher selectivity to cinnamyl alcohol than the ones corresponding to copper catalysts supported on SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>.

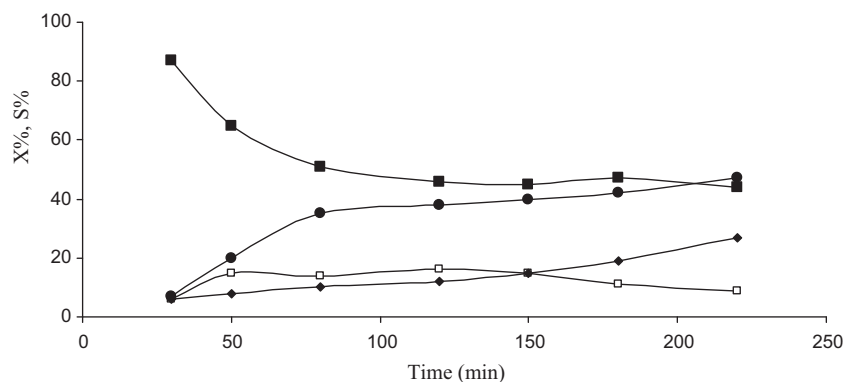
MCM-48 should be considered as an inert support, like silica or alumina. However the catalytic pattern of the CuM catalyst (see Fig. 8) is completely different from those of the CuS or CuA samples. The selectivity toward cinnamyl alcohol measured over CuM is much higher than the ones corresponding to the latter samples, at the same level of conversion. For low conversion level, at initial reaction time, the catalyst is highly selective, but it turns rather unselective with time, due to a higher production of hydrocinnamaldehyde than that of cinnamyl alcohol. Anyway CuM is more selective than CuS or CuA during the entire reaction time. The existence of Cu<sup>1+</sup>, stabilized on MCM-48 would be related with the high selectivity of copper species on the mesoporous support. Previous works proposed that the fraction of cuprous ions plays an important role in the catalytic activity of copper catalysts employed for selective hydrogenation reactions [8,9,27].

The variation of the selectivity toward cinnamyl alcohol with time, for CuM, would be related with a decrease in the concentration of Cu<sup>1+</sup> species. The characterization of the spent CuM catalyst by XRD showed that the intensity of the diffraction peaks due to Cu<sub>2</sub>O is lower than the one corresponding to peaks of the fresh sample.

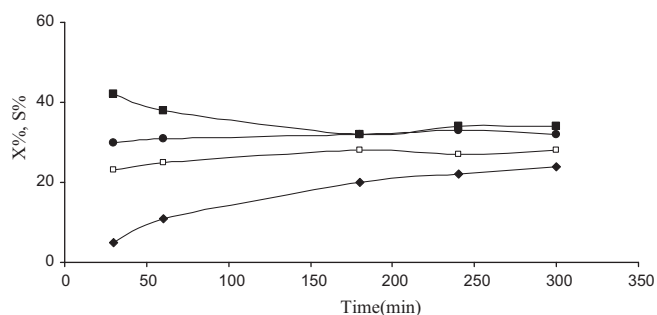
Considering that copper species in the +1 oxidation state would notably influence on the catalytic properties of copper based catalysts, it was decided to perform a calcination treatment to the samples previously to the catalytic test. It could be speculated that such a treatment would modify the relative concentration of Cu<sup>0</sup>, Cu<sup>1+</sup> and Cu<sup>2+</sup>. The dependence of the conversion and the selectivity to the different products for CuA following calcination pre-treatment is plotted in Fig. 7. When a comparison of the catalytic pattern of CuA submitted to a calcination treatment at 300 °C with that of the same catalyst following a reduction is performed, remarkable differences arise. Firstly, the conversion attained by the previously calcined sample is higher than the one obtained over the reduced one. Concomitantly, the TOF number of CuA previously calcined is higher than the TOF of the sample previously reduced. Besides the selectivity to cinnamyl alcohol notably increases following the calcination pre-treatment. Thus a much higher yield of the desired product is obtained for the pre-calcined CuA sample than for the reduced CuA catalyst. The same trends were observed for CuS previously calcined: a notable improvement of the selectivity and an increase in the activity (see Table 2). It is interesting to



**Fig. 7.** Dependence of the conversion of cinnamaldehyde, (◆) and of the selectivities to cinnamyl alcohol (■), to hydrocinnamaldehyde (●), and to phenyl propanol (□) on time for CuA (Cu/Al<sub>2</sub>O<sub>3</sub>). Samples previously reduced (—) and previously calcined (---).



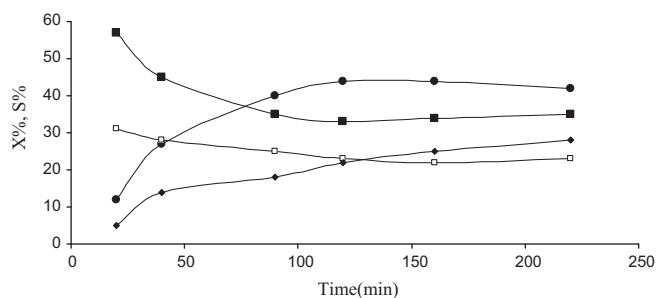
**Fig. 8.** Dependence of the conversion of cinnamaldehyde (◆) and of the selectivities to cinnamyl alcohol (■), to hydrocinnamaldehyde (●), and to phenyl propanol (□) on time for CuM (Cu/MCM-48).



**Fig. 9.** Dependence of the conversion of cinnamaldehyde (◆) and of the selectivities to cinnamyl alcohol (■), to hydrocinnamaldehyde (●), and to phenyl propanol (□) on time for CuH (Cu/α-Fe<sub>2</sub>O<sub>3</sub>).

note that over the calcined samples, CuS or CuA, no phenyl propanol was detected.

The higher activity of the calcined CuA and CuS would be related with a higher availability of hydrogen species. To investigate on the origin of such species, the hydrogenation of cinnamaldehyde was carried out in the absence of H<sub>2</sub>, under N<sub>2</sub> pressure. The other experimental parameters (mass of the catalysts, stirring speed, temperature, etc.) were kept constant. Under the inert gas atmosphere, the catalyst remained active, though the conversion attained was lower than when H<sub>2</sub> is employed. Considering this result it is postulated that the solvent isopropanol is responsible for the hydrogenation of cinnamaldehyde. Isopropanol would transfer hydrogen to C=O group in the presence of calcined copper catalyst. Finally it is important to note that neither in the absence of isopropanol (using THF as the solvent) nor in the absence of the catalyst, hydrogenation reactions were observed.



**Fig. 10.** Dependence of the conversion of cinnamaldehyde (◆) and of the selectivities to cinnamyl alcohol (■), to hydrocinnamaldehyde (●), and to phenyl propanol (□) on time for CuC (Cu/CeO<sub>2</sub>).

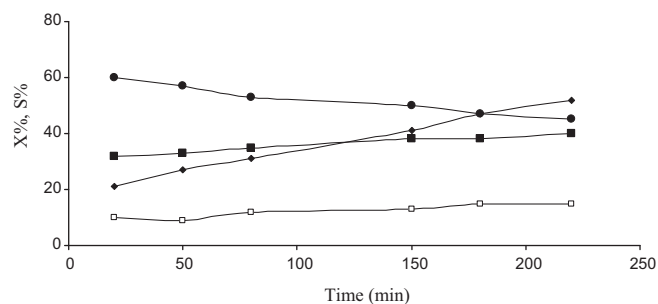
On the other hand the calcination performed over CuM does not modify both the activity and the selectivity of this sample. This result is rather difficult to explain. Probably the calcination pretreatment carried out over CuM does not deeply change the relative concentration of the different copper species.

Turning the attention to the catalysts in which copper is supported on reducible oxide, *i.e.* the CuH and CuC samples, the selectivity is relatively high in these cases. For CuH the selectivity to cinnamyl alcohol is nearly constant with conversion (see Fig. 9). This catalyst is more selective than the catalysts supported on inert oxides, CuA and CuS. The existence of Fe<sup>2+</sup>/Fe<sup>3+</sup> species would promote the selectivity of copper for the selective hydrogenation of C=O against C=C.

On CuC (see Fig. 10) a high selectivity level is measured at low conversion, which decreases with time mainly due to an increase in the production of hydrocinnamaldehyde. The origin of the high initial selectivity would be related with support sites. In an additional test, the hydrogenation of cinnamaldehyde was carried out over the bare support. A low conversion (5%) was attained at initial reaction time, but the activity was completely lost after a short period of reaction time. The selectivity to the cinnamyl alcohol was extremely high (90%), showing that ceria possesses sites for the selective hydrogenation of C=O, though they become deactivated. Thus, the variation of the selectivity toward cinnamyl alcohol with time observed for CuC could be explained: highly selective ceria sites become deactivated.

The comparison of the activities achieved by the different Cu/support catalysts showed that CuC is the most active sample. As commented above the high activity would be related with sites other than copper ones, probably in the metal/support interphase.

For the samples supported on reducible oxides, CuH and CuC, the calcination pretreatment also originates an improvement of both selectivity and activity, though in a much lesser extent than for



**Fig. 11.** Dependence of the conversion of cinnamaldehyde (◆) and of the selectivities to cinnamyl alcohol (■), to hydrocinnamaldehyde (●), and to hydrocinnamyl alcohol (□) on time for Pt/SiO<sub>2</sub>.

CuA or CuS. As for the case of CuM, it could be supposed that the calcination cannot significantly alter the relative concentration of the different copper species.

#### 4. Discussion

Reduced CuS and CuA catalysts showed a low selectivity for the hydrogenation of C=O against C=C bond, in the hydrogenation of cinnamaldehyde, showing that supported metallic copper is intrinsically unselective toward the hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes.

However, copper could be modified in order to increase its selectivity. Supporting copper on MCM-48 results in a selective catalyst for the hydrogenation of cinnamaldehyde. For CuM three different species coexist: highly dispersed copper in the mesoporous framework, Cu<sub>2</sub>O particles and CuO particles. It could be suggested that the selective sites in Cu/MCM-48 are highly dispersed copper and/or to Cu<sub>2</sub>O. Both sites are related with Cu(I) species, in which beneficial effect on selectivity has been previously established [28,29]. Still another interpretation should not be disregarded: highly dispersed copper presents an increase in the number of d electrons due to the loss of bulky properties should be expected. This effect would favor C=O hydrogenation. This argument was invoked previously for explaining the high selectivity achieved by gold supported catalysts for the hydrogenation of  $\alpha,\beta$ -unsaturated compounds [30]. Whatever the nature of the modification of copper which turns it selective for C=O bond hydrogenation, it arises upon supporting copper on MCM-48. Another interesting feature of copper on MCM-48 (CuM) is its low specific activity (moles of cinnamaldehyde converted per second and per g of copper) by comparison with copper supported on silica or alumina. Since the activity of the samples is due to adsorbed hydrogen species, it is likely that certain fraction of copper is inactive for activating H<sub>2</sub>. Considering the scenario of the different copper species on MCM-48, H<sub>2</sub> is not dissociated on it.

On the contrary, CuO particles would be related with unselective sites. CuO is the only copper phase in for silica or alumina (as concluded from FTIR, TPR and XRD analysis), for this reason Cu/SiO<sub>2</sub> and Cu/Al<sub>2</sub>O<sub>3</sub> are unselective catalysts.

The catalysts based on supports possessing redox properties, hematite and ceria (CuH and CuC) should also be considered as selective ones. It is likely that the promotional effect is due to support species (Ce<sup>3+</sup>/Ce<sup>4+</sup> and Fe<sup>2+</sup>/Fe<sup>3+</sup>). Metal-support interfacial sites would be responsible for the increase of selectivity toward C=O hydrogenation, as observed previously for noble metal based catalysts [5,6,31,32]. It is important to note that the mean size of copper crystals supported on ceria or hematite is in the same range as in the case of copper supported on inert oxides (CuS and CuA). Thus, a geometric effect for explaining the relative high selectivity of copper when supported on reducible oxides should be disregarded. The reduction of the supports, and concomitantly the creation of reactive sites in the metal-support interface are easily achieved for ceria and hematite due to the presence of copper crystals. TPR characterization clearly demonstrates that the reducibility of the supports is increased by the presence of the metal.

For CuC a very high selectivity to cinnamyl alcohol was measured for the first reaction times (60% following 20 min of reaction time). Undoubtedly, ceria sites are responsible for the high selectivity to hydrogenate C=O, since bare ceria showed initial activity for hydrogenating cinnamaldehyde to cinnamyl alcohol. Although the yield to cinnamyl alcohol over bare ceria was rather low, the selectivity was nearly 90%. However, for both, the bare support and the CuC catalyst, the support sites became deactivated. The deactivation is complete for bare ceria, for which the activity is null

after a short period of reaction time. On the contrary for CuC the deactivation of support sites is not complete, some of them (probably located at the Cu/ceria interphase) remain active giving rise to a higher selectivity to cinnamyl alcohol than when copper is supported on inert oxides.

The most important feature of copper catalysts supported on alumina or silica, following a calcination pre-treatment, is that they show higher selectivity as well as higher activity than the corresponding pre-reduced samples. This a surprising result, considering that copper oxides surface do not dissociate dihydrogen and that it was previously reported that the activity of copper supported on silica was completely lost, if the samples were calcined at 623 K [28]. In order to explain the activity of calcined copper catalyst it is postulated that the hydrogenation of cinnamaldehyde is carried out by a catalytic hydrogen transfer from the solvent, isopropanol. The samples previously calcined are active for hydrogenating the aldehyde under inert gas atmosphere (N<sub>2</sub>), though in a lesser extent than under H<sub>2</sub> atmosphere. This result confirms that catalytic hydrogen transfer from the solvent takes place over calcined copper surface for CuA and CuS.

A decrease of the selectivity was observed for previously calcined samples: the selectivity was higher than 80% at early reaction times and decreased to approximately 50%. A morphological modification of the catalysts under reaction conditions cannot be invoked to explain the loss of selectivity, since XRD performed over the spent catalysts showed that copper particle size was not modified. It is likely that the oxidation state of copper species varies due to the hydrogenating conditions and this modification leads to a decrease in the hydrogen transfer.

At this point it is interesting to note that the production of the total hydrogenation product, phenyl propanol was nil for calcined samples. It could be postulated that copper surface after the calcination pre-treatment is inert for the adsorption of the desired product, cinnamyl alcohol as well as for the adsorption of hydrocinnamaldehyde, preventing the formation of the total hydrogenation product, the hydrocinnamaldehyde alcohol. In this aspect the improvement of the selectivity after the calcination pre-treatment is originated in a different way to that corresponding to the CuM, CuC or CuH catalysts.

When comparisons of the present results are carried out with the literature ones (mainly with those corresponding to noble metals based catalysts), it can be considered that for some of our copper samples the selectivity is relatively high. Gold based samples, tested under similar experimental conditions as the ones of the present work, presented selectivities to cinnamyl alcohol in the 26–88% range, for conversion levels lower than 20% [23]. Bus et al. tested a series of gold supported on alumina catalysts for the high-pressure liquid phase hydrogenation of cinnamaldehyde [33]. The authors reported selectivities in the 38–89% range. Plomp et al. studied the selective hydrogenation of cinnamaldehyde over carbon nanofibers supported platinum and ruthenium catalysts, and reported selectivities approximately of 60% and of 45% for Pt and Ru respectively [34]. Merlo and coworkers prepared tin-modified platinum catalysts by means of controlled surface reaction. For a certain a Pt/Sn ratio a high selectivity level (80%) was achieved in the hydrogenation of cinnamaldehyde. The general trend is that for reaching selectivities higher than 80%, sophisticated preparation method of the catalysts [23,35], or rigorous reaction conditions were employed [33].

Some of our copper samples (CuM, CuC, previously calcined CuA and CuS) showed selectivities in the 50–75% range. Thus it can be concluded that the selectivities attained over the present copper catalysts are in some cases higher than the values corresponding to noble metal based samples. This is an important result, mainly due to the low cost of copper. Even more, the relatively simple

method of preparation of the present copper catalysts is another advantage.

## 5. Conclusion

Copper is intrinsically unselective toward the hydrogenation of  $\alpha,\beta$ -unsaturated compounds to obtain the corresponding saturated alcohol. However, modification of copper based catalysts could originate selective ones. Highly dispersed copper species in the structure of MCM-48 are selective toward the hydrogenation of C=O bond in the cinnamaldehyde molecule, due to the stabilization of Cu(I) species.

Besides, supporting copper on reducible oxides also modifies the intrinsic catalytic properties of this metal, due to a promotional effect of reduced support sites.

Selective hydrogenation could also be achieved in liquid phase by employing isopropanol as a source of hydrogenating species. Hydrogen transfer occurs on certain surfaces of calcined copper, leading mainly to the unsaturated alcohol.

## References

- [1] P. Gallezot, D. Richard, *Catal. Rev. Sci. Eng.* 40 (1998) 81–126.
- [2] F. Ammari, C. Milone, R. Touroude, *J. Catal.* 235 (2005) 1–9.
- [3] M. Englisch, V.S. Ranade, J.A. Lercher, *Appl. Catal. A: Gen.* 163 (1997) 111–122.
- [4] P. Reyes, M.C. Aguirre, G. Pecchi, J.L.G. Fierro, *J. Mol. Catal. A: Chem.* 164 (2000) 245–251.
- [5] C. Milone, R. Ingoglia, L. Schipilliti, C. Crisafulli, G. Neri, S. Galvagno, *J. Catal.* 236 (2005) 80–90.
- [6] B. Campo, S. Ivanova, M. Volpe, R. Touroude, *J. Catal.* 242 (2006) 162–171.
- [7] G. Hutchings, F. King, I. Okoye, C. Rochester, *Appl. Catal. A* 83 (1992) L7–L13.
- [8] G. Hutchings, F. King, I. Okoye, M. Padley, C. Rochester, *J. Catal.* 148 (1994) 438–452.
- [9] J. Jenck, J.E. Germain, *J. Catal.* 65 (1980) 141–149.
- [10] N. Bertero, C. Apesteguia, A. Marchi, *Appl. Catal. A* 349 (2008) 100–109.
- [11] T. Pham, L. Lobban, D. Resasco, R. Mallinson, *J. Catal.* 266 (2009) 9–14.
- [12] B. Bridier, N. Lopez, J. Perez-Ramirez, *J. Catal.* 269 (2010) 80–92.
- [13] A. Marchi, D. Gordo, A. Trasarti, C. Apesteguia, *Appl. Catal. A: Gen.* 249 (2003) 53–67.
- [14] J. Xu, Z. Luan, H. He, W. Zhou, L. Kevan, *Chem. Mater.* 10 (1998) 3690–3698.
- [15] V. Gutierrez, A. Diez, M. Dennehy, M. Volpe, *Microporous Mesoporous Mater.* 141 (2011) 201–213.
- [16] K. Schwertmann, K. Cornell, *Iron Oxide in the Laboratory: Preparation and Characterization*, Wiley-VCH, 2000, p. 188.
- [17] G. Hutchings, F. King, I. Okoye, M. Padley, C. Rochester, *J. Catal.* 148 (1994) 464–469.
- [18] K. Hadjiivanov, T. Tsoncheva, M. Dimitrov, C. Minchev, H. Knözinger, *Appl. Catal. A* 241 (2003) 331–340.
- [19] G. Busca, *J. Mol. Catal.* 43 (1987) 225–236.
- [20] A. Davydov, A. Budneva, *React. Kinet. Catal. Lett.* 25 (1984) 121.
- [21] D. Andreeva, V. Idakiev, T. Tabakova, L. Ilieva, P. Falaras, A. Bourlinos, A. Travlos, *Catal. Today* 72 (2002) 51–57.
- [22] S. Ivanova, V. Pitchon, C. Petit, *J. Mol. Catal. A* 256 (2006) 278–283.
- [23] J. Lenz, B. Campo, M. Alvarez, M. Volpe, *J. Catal.* 267 (2009) 50–56.
- [24] M. Toebe, T. Nijhuis, J. Hájek, J. Bitter, A. van Dillen, D. Yu. Murzin, K. de Jong, *Chem. Eng. Sci.* 60 (2005) 5682–5695.
- [25] Th.J. Ozinga, B.G. Linsen, W.P. van Beet, *J. Catal.* 7 (1967) 277–279.
- [26] J.J.F. Scholten, A.P. Pijpers, M.L. Hustings, *Catal. Rev. Sci. Eng.* 27 (1985) 151–206.
- [27] A. Dadenkar, R. Baiker, M. Vannice, *J. Catal.* 184 (1999) 421–439.
- [28] A. Chambers, S.D. Jackson, D. Stirling, G. Webbs, *J. Catal.* 168 (1997) 301–314.
- [29] R. Hubaut, J. Bonnelle, M. Daage, *J. Mol. Catal.* 55 (1989) 170–183.
- [30] E. Bus, R. Prins, J.A. van Bokhoven, *Catal. Commun.* 8 (2007) 1397–1402.
- [31] J. Silvestre-Albero, A. Sepúlveda-Escribano, F. Rodríguez-Reinoso, J. Anderson, *J. Catal.* 223 (2004) 179–190.
- [32] M. Consonni, D. Jokic, D. Murzin, R. Touroude, *J. Catal.* 188 (1999) 165–175.
- [33] E. Bus, R. Prins, J.A. van Bokhoven, *Catal. Commun.* 8 (2007) 1397.
- [34] A. Plomp, H. Vuori, A. Krause, K. de Jong, J. Bitter, *Appl. Catal. A* (2009) 9–15.
- [35] A. Merlo, B. Machado, V. Vetere, J. Faria, M. Casella, *Appl. Catal. A* (2010) 43–49.