

Copper incorporated mesoporous materials: synthesis, characterization and catalytic activity in benzaldehyde reduction

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Abstract Copper substituted mesoporous silica materials (Cu–HMS-n), with a variety of Si/Cu atomic ratios (*n*) ranging from 50 to 100, were synthesized by the one-pot sol–gel method using dodecylamine as template. These materials were characterized by X-ray diffraction, N₂ adsorption-desorption, transmission electron microscopy, ultraviolet and visible diffuse reflectance spectroscopy, H₂ temperature-programmed reduction, inductively coupled plasma-optical emission spectrometry, thermal analysis and X-ray photoelectron spectroscopy. All the samples showed worm-like mesoporous structures with surface areas higher than 700 m² g⁻¹ and pore volumes higher than 0.75 cm³ g⁻¹. The catalytic activity of these materials in the reduction of benzaldehyde was evaluated. Effects of the Si/Cu atomic ratio in the catalyst and the influence of time and reaction temperature on the catalytic activity were investigated. Best catalytic performance was obtained with Cu–HMS-50 with a benzaldehyde conversion of 56% and a selectivity of 28% to benzyl alcohol.

Keywords Cu-incorporating mesoporous materials \cdot Copper \cdot Benzaldehyde \cdot Benzyl alcohol \cdot Hydrogenation

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Introduction

Benzyl alcohol is the most important aromatic alcohol used in industry. Its remarkable properties such as strong polarity, low toxicity and volatility are at the origin of its use in a wide range of industries such as food and beverages, paints and coating, pharmaceuticals [1], textiles, perfumes and flavor and in the production of a large number of fine chemicals [2–4]. More recently, it has found other applications in chromatography and in the conception of photodeveloper systems and nanowires [5, 6]. At present, there are only two important industrial processes for the production of benzyl alcohol namely, the hydrolysis of benzyl chloride and the hydrogenation of benzaldehyde [7]. Depending on the reaction conditions, benzaldehyde once hydrogenated leads to the formation of benzyl alcohol, toluene, benzene and other products. In addition, it was found that in the presence of suitable reaction conditions and catalysts, very high yields of benzyl alcohol can be obtained [7]. For this purpose, a large number of catalysts have been used in the recent past such as various transition metals (Ni, Cu, Co, etc.), noble metals (Au, Pt, Pd, etc.) and monoliths [8–10]. Dispersed on supports such as alumina and silica, catalytic performance of these species was improved. Cu/SiO₂ catalysts exalting good catalytic activity and selectivity in hydrogenation reactions are reported in the literature [11-15]. Usually, the more the dispersion of the active phase, the better the catalytic performance. Consequently, increasing attention has been paid to the design of novel catalysts with large surface areas leading to the emergence of mesoporous materials supports. Many kinds of mesoporous materials including hexagonal mesoporous silica (HMS), MCM-n and SBA-n were synthesized by using various organic templates. This family of materials has exceptional properties, such as high specific surface areas of at least 700 m² g⁻¹, pore volumes larger than $0.7 \text{ cm}^3 \text{ g}^{-1}$, narrow size distributions, etc. [16–23]. Among these nanomaterials, HMS presenting a wormhole framework structure is the most easily synthesized according to the neutral assembly pathway reported by Pinnavaia and coworkers that uses a cheap primary alkylamine as the template agent at room temperature. Its thicker framework walls, small crystalline size of primary particles and textural porosity permit better transport for reactants and products via its channels [24, 25]. The organic template can be totally removed from the HMS samples either by simple calcination or by solvent extraction. The silicon atoms constituting the HMS framework can be easily substituted by transition metal cations like copper species giving rise to more active materials. Indeed, several studies showed that copper containing HMS materials often exhibit remarkable catalytic activity, probably due to the easy availability of catalytic active sites and the good dispersion of copper species [13, 26, 27]. No work on the hydrogenation of benzaldehyde in gas phase over copper substituted mesoporous silica materials has been reported thus far, even in liquid phase [8]. Herein, we present an experimental investigation of the synthesis and characterization of Cu-HMS mesoporous materials with various atomic ratios, with specific focus on their behavior in the reduction of benzaldehyde into its corresponding benzyl alcohol.

Experimental

The Cu-hexagonal mesoporous solid (HMS) catalysts

Cu-HMS-n, with different Si/Cu atomic ratios (n = 50, 75 and 100), were synthesized starting from hexadecylamine (Aldrich 95%), tetraethyl orthosilicate (Aldrich 99%), Cu(NO₃)₂·3H₂O (Merck, 99.5%), and ethanol 96% v/v (Sharlau, analytical grade, ACS, Reag. Ph Eur, USP). The precursor gel has been prepared following the neutral assembly pathway protocol reported by Tanev and coworkers [20]. It consists in mixing two solutions, one containing hexadecylamine (HDA) (4.10⁻² mol) to which a mixture of water/ethanol (100 mL/160 mL) was added under agitation until obtaining a homogeneous solution and the other one, containing TEOS (0.2 mol) with an appropriate amount of Cu(NO₃)₂·3H₂O. The obtained milky solutions of light blue color were then vigorously stirred at the temperature range (30-40 °C) for 24 h. The solids were recovered by filtration, repeatedly washed with water and air-died at 393 K. The remaining organic molecules of the template in the mesopores were first removed by solvent extraction and then after drying, the so-dried materials were dispersed in a solution of ethanol (5 g/100 mL) containing 1 g of NH₄Cl and refluxed under agitation. Addition of NH₄⁺ cations ensure the exchange of protonated amines formed during the synthesis and the balance of the excess negative charges resulting from the substitution of Si⁴⁺ by Cu²⁺. The solids were recovered by filtration and washed with hot EtOH. The extraction procedure was repeated three times, and the obtained samples were dried at 120 °C, then calcined at 550 °C for 6 h with a heating rate of 1 °C/min to remove any residual organic template material. For comparison, HMSsupported copper catalyst with atomic ratio "n = 50" was prepared by a conventional impregnation of the synthesized HMS using an aqueous solution of $Cu(NO_3)_2$ ·3H₂O. The solid was collected by evaporation on a water bath to remove the solvent, washed with water, then dried at 120 °C overnight and finally calcined under the same conditions as the samples prepared by the one-pot sol-gel method. This solid was labeled as Cu/HMS-50_{imp}.

Physicochemical analysis

A number of physico-chemical methods were used for the characterization of the materials. The copper content in the final solids was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) using a Varian vista instrument. XRD patterns were collected in air at room temperature on a Bruker D8 Advance diffractometer using monochromatized Cu K α radiation of wavelength 0.15418 nm. Diffraction data were recorded in the 2θ 0–10°/10–80° ranges at an interval of 0.02° and a scanning speed of 0.3°/min. The interplanar distance (d_{100}) was obtained by the Bragg law using the position of the first X-ray diffraction line. The lattice parameter (a_0) of the hexagonal unit cell was calculated by the formula $a_0 = [2/(3)^{1/2}] \times d_{100}$. The crystalline size of the CuO species was calculated by applying the Scherrer equation using the full width at half-maximum value of the

most intense peak. Specific surface area, pore size distribution and total pore volume were determined from N₂ adsorption/desorption isotherms obtained at - 196 °C using a Micromeritics ASAP 2010 instrument. The surface area was determined by the Brunauer, Emmett, and Teller (BET) method and the pore size distribution was determined by the Barrett, Joyner, and Halenda (BJH) method. Thermal analyses (TGA/DSC) were carried out with a SDT Q600 V20.9 (TAI instruments, Inc.). Measurements were carried out in a constant (10 mL/min) air flow with a heating rate of 10 °C/min. Diffuse reflectance (UV-vis) was recorded on a Varian Carry-5000 spectrophotometer equipped with a diffuse reflectance accessory. The spectra were taken in air at room temperature in the range 200-900 nm. Hydrogentemperature-programmed reduction (TPR) was performed with a quartz tube fixedbed microreactor equipped with a thermal conductivity detector (TCD). Prior to the TPR measurement, each 30 mg catalyst sample was pretreated in argon at 300 °C for 30 min. After being cooled to ambient temperature in the same atmosphere, the sample was exposed to flow (30 mL/min of 5 vol% H₂/Ar and ramped to 1000 °C at a heating rate of 10 °C/min. The consumption of H₂ was monitored by the TCD. The XPS spectra were taken using an Omicron (ESCA+) X-ray photoelectron spectrometer. The base pressure in the experimental chamber was in the low 10^{-9} mbar range. The spectra were collected using a monochromatic Al K α (hv = 1486.6 eV) X-ray source with an accelerating voltage of 14 kV and a current intensity of 20 mA, and the overall energy resolution was about 0.8 eV. The pass energy was 20 eV for the high resolution spectra and 100 eV for the surveys. Survey spectra were recorded for the samples in the 0–1100 eV kinetic energy range by 1 eV steps while high resolution scans with 0.1 eV steps were conducted over the following regions of interest: C 1 s, O 1 s, Si 2p, and Cu 2p. Surface charging effects were compensated by referencing the BE (binding energy) to the C 1 s line of residual carbon set at 284.7 eV BE. Spectral decomposition assumed mixed Gaussian-Lorenzian curves and was performed by using background subtraction and a least square fitting program. High resolution transmission electron microscopy (HRTEM) was carried out on a JEOL TEM 100 CXII electron microscope operating at an acceleration voltage of 100 kV.

Catalytic testing

The catalytic hydrogenation of benzaldehyde was carried out in a glass tubular fixed-bed reactor using 30 mg of sample powder at atmospheric pressure and in the 100–300 °C range for temperature. Pure hydrogen was fed at a total flow rate of 50 cm³ min⁻¹. Gaseous benzaldehyde (4.8 Torr) was delivered by bubbling N₂ (250 Torr) in liquid benzaldehyde maintained at constant temperature (50 °C) in a saturator. The gaseous reactant and products were heated up-stream and out-stream to avoid condensation. They were analyzed online by a FID gas chromatograph (Delsi IGC 121 ML) equipped with a 10% CP-SIL 8 CB/Chromosorb W column. Each reaction temperature was maintained constant until the corresponding steady-state was reached as indicated by the gas chromatograph analysis of the exit gases (ca. 2 h). Before testing, the catalyst was in situ pre-treated for 2 h at 300 °C in hydrogen flow at 20 cm³ min⁻¹.

Results and discussion

Thermal analysis

The curves of weight loss of the HMS, Cu/HMS-50_{imp} and Cu-HMS-50 samples before calcination are given in Fig. 1. The molecules of free water remaining in the pores without any special interaction with the surface escape from the material in the temperature range from 16 to 100 °C. A few of them are retained in the pores up to the temperature of 150–220 °C, which is probably due to the formation of hydrogen bonds between them and the surface of the material. The slight turning point in the process rate depicted in the zone of 500–600 °C reflect a change in the steric conditions of the (Si–OH) groups interaction [28].

XRD and TEM

The powder XRD patterns of the calcined mesoporous HMS and copper containing HMS are shown in Fig. 2. It must be noted that the diffractograms of the different samples have been shifted in the y-axis to make easier comparison. All the materials exhibit an intense single low-angle reflection between 1.5° and 2.5° , characteristic of a wormhole framework [13]. The higher order Bragg reflections are resolved as a weak reflection between 3.5° and 4.5° corresponding to the overlapping of the diffraction peaks of the (110) and (200) planes [13]. These can be imputed to the hexagonal regularity of the porous structure of the HMS, denoting that the long-range order of the HMS framework was well retained after copper introduction and calcination processes. Regarding the Cu–HMS-50 sample, the (100) peak located at $(2\theta \approx 2^{\circ})$, is a little bit deformed, indicating a de-organisation at long range of the mesoporous structure [29]. It is worthy to note that the diffraction peak of the copper containing HMS samples shifts to a lower angle comparing with the pure



Fig. 1 Thermal analyses (TG) in air of the samples before calcination



Fig. 2 XRD patterns of the calcined samples before the catalytic test: filled diamond CuO tenorite

HMS. At high diffraction angles as can be seen in Fig. 2b, no diffraction peaks of any crystalline phase of copper species were observed when the atomic ratio Si/Cu was higher than 50, denoting that the Cu species in the matrix are well dispersed. However, in the case of Cu–HMS-50, the characteristic peaks of CuO are well resolved at 35.4° and 38.62° , assignable to (11-1) and (111) diffractions, respectively, confirming the presence of a minor tenorite phase of copper on the HMS surface. The two diffraction peaks of CuO in the Cu–HMS-50 catalyst are less intense compared to those of Cu/HMS-50_{imp}, which means that CuO species aggregating on the HMS surface of Cu–HMS-50 have smaller crystalline size (21 vs. 24 nm) and are more dispersed [13]. On the other hand, no diffraction peaks of Cu₂O phase and Cu⁰ could be depicted in the samples. The particle sizes estimated from XRD data are listed in Table 1.

The HRTEM images of all the samples show worm-like mesoporous structures, which are similar to that of HMS mesoporous materials reported by Pinnavaia and

Before catalytic te	st	After catalytic test			
Sample	$d(_{100})^{a}(nm)$	$a_0^{\rm b}$ (nm)	$D_{\text{CuO}}^{\text{c}}(\text{nm})$	$d (100)^{a} (nm)$	$a_0^{\rm b} (\rm nm)$
HMS	4.22	4.85	-	_	_
Cu-HMS-100	4.97	5.26	_	4.65	5.26
Cu–HMS-75	4.86	5.54	_	4.80	5.41
Cu-HMS-50	4.41	5.12	21	4.48	5.00
Cu/HMS-50 _{imp}	4.37	5.03	24	4.42	5.03

Table 1 DRX data of samples before and after the catalytic test

^aInterplanar spacing (100)

^bLattice parameter

^cSize of CuO particles from the Scherrer equation

co-workers [23]. A typical HRTEM image of Cu–HMS-75 is shown in Fig. 3. The absence of any bulk CuO crystallites condensed on its surface further confirm that the copper species are finely and uniformly dispersed [29].

XRD patterns of the catalyst samples after the catalytic test are shown in Fig. 4. After the catalytic test, diffraction peaks of copper species were still invisible when the atomic ratio of Si/Cu is higher than 50. However, for Cu–HMS-50, a few diffraction peaks can be observed. In fact, in the 2θ region between 40° and 60°, the peak appearing at 42.63° is assigned to Cu₂O, whereas the one resolving at 50.42° is attributed to Cu⁰. For Cu/HMS-50_{imp}, the two detected diffraction peaks at 32.64° and 36.58° are attributed to Cu⁰ and Cu₂O species, respectively. It is worthwhile to note that the values of the lattice parameter a₀ for the two catalysts Cu-HMS-50 and Cu-HMS-75, decreased slightly after the catalytic test.

Nitrogen physisorption

The nitrogen physisorption isotherms and the corresponding pore size distributions of the different materials are given in Fig. 5. All samples studied exhibit Langmuir type IV isotherms with a H1-type hysteresis loop characteristic of a typical largepore mesoporous material with 1D cylindrical channels [30]. The increase in nitrogen uptake in the characteristic relative pressure (P/P_0) range of 0.2–0.5 for the different samples is due to the occurrence of a capillary condensation of nitrogen within uniform mesopores. Such behavior suggests typical mesoporous structures with uniform pore diameters. Generally, the sample with higher copper content presents a less steep slope at P/P_0 ranging from 0.2–0.5 suggesting that the pore size uniformity becomes worse. This is in agreement with the pore size distribution of samples (Fig. 5b) and the decrease of the amount of adsorbed nitrogen with increasing copper content in the different materials. The additional hysteresis loop observed for all the synthesized samples in the adsorption branch at relative pressure > 0.9 is associated to the textural inter-particle mesoporosity [22, 24]. All the catalysts prepared by one-pot sol-gel method possess large BET surface areas above 714 m² g⁻¹ (Table 2), which is one of the features characteristic of HMS materials. We notice that the catalyst prepared with higher Cu content, namely Cu-HMS-50, has the lowest surface area which is likely due to the incorporation of a higher



Fig. 3 HRTEM image for calcinated Cu-HMS-75. a 30000X and b 120000X



Fig. 4 XRD patterns of the reduced samples after the catalytic test. Opencircle Cu^0 metallic copper, open rectangle Cu_2O cuprite, filled diamond: SiO₂ silica



Fig. 5 $\,N_2$ adsorption/desorption isotherms at - 196 $^{\circ}C$ and BJH pore size distribution of the calcined samples

Table 2	Chemical	composition	and	textural	composition	of	calcined	samples

Sample	Si/Cu ^a	$S_{\rm BET} ({ m m}^2 { m g}^{-1})$	Cu (wt%)	D ^b (nm)	$t_{\rm w}^{\rm c}$ (nm)	$V_{\rm pore}^{\rm d} \ ({\rm cm}^3 \ {\rm g}^{-1})$
HMS	_	761	_	2.9	2.0	0.56
Cu-HMS-100	140	765	0.71	3.3	2.0	0.84
Cu-HMS-75	86	716	1.16	3.6	1.9	0.89
Cu-HMS-50	64	714	1.56	3.4	1.7	0.75
Cu/HMS-50 _{imp}	56	728	1.79	2.9	2.2	0.52

^aDetermined by ICP/OES

^{b,d}Pore diameter and pore volume determined by BJH method

^cWall thickness calculated by a_0-D_p

content of Cu^{2+} ions into the HMS framework leading to an increase in density of the composites [31] and consequently creating a de-organisation at long range of the mesoporous structure. This de-organisation is well established by the XRD signal observed at low diffraction angles. On the other hand, since HMS walls are amorphous, it becomes obvious that any modification in their chemical composition by introducing a certain amount of any element different from Si, will affect the average unit cell parameter. This technique is generally considered as an additional way to confirm the incorporation of any element in the framework of the HMS [32-34]. For the mesoporous materials considered here, we notice a shift of the main peak corresponding to plane (100) toward lower diffraction angles and an increase in the unit cell parameter a_0 (Table 1), confirming the probability of introduction of Cu into the HMS framework. Hence, the substitution of Si⁴⁺ ion (0.41\AA) by the larger Cu²⁺ ion (0.87\AA) provokes a distortion of the geometry around Cu from an ideal Td. Indeed, the length of Si-O-Cu bond is different from that of Si-O-Si leading invariably to some structure deformation and a decrease of the surface area. For the catalyst prepared by the impregnation method, the reduction of the surface area is likely due to the blocking of pores of the mesoporous structure by bulky CuO oxides [29]. On the other hand, the slight increase in the pore diameter for sample Cu-HMS-75 with respect to sample Cu-HMS-50 could be attributed to the longer length of the Si-O-Cu bond with respect to the Si-O-Si bond due to the insertion of the metal into the framework [35].

Diffuse reflectance UV-visible spectroscopy

UV visible reflectance spectra of the solids prepared were recorded (Fig. 6), in order to precisely determine the coordination mode of Cu species in the HMS structure. The strong absorption band at *ca*. 250 nm is ascribed to a ligand to metal charge transfer between the surface oxygen and the isolated Cu²⁺ ions [36, 37], whereas the weak and broad band at *ca*. 700 nm can be assigned to ${}^{2}E_{g} \rightarrow {}^{2}T_{2g}$ spin-allowed



Fig. 6 UV-visible diffuse reflectance spectra of the calcined samples

transition of Cu^{2+} ions in the distorted octahedral sites of crystalline CuO species [38].

Temperature programmed reduction analysis

It has been reported that the reduction of CuO species supported on SiO₂ support occurs at lower temperatures than bulk CuO [39, 40], and that the values of the temperature maximum as well as the peak width increase with increasing CuO particle size. Also, many authors reported that the segregated CuO would be reduced to Cu⁰ by H₂ in one step at about 310 °C [31, 41]. TPR profiles in Fig. 7 revealed that there is a strong broad reduction peak, depicted at around 220-280 °C for both Cu-HMS-50 and Cu-HMS-75 samples. The shoulder observed on the Cu-HMS-50 TPR profile with maxima at ca. 223 °C, could account for the two-step reduction $(Cu^{2+} \rightarrow Cu^{+} \rightarrow Cu)$. In addition, the peak located at around 300-450 °C, is possibly due to the concurrence of bulk CuO species. It is interesting to note that among all the catalysts, Cu-HMS-50 shows the lowest reduction temperature, denoting that the copper content is an important parameter in optimizing the redox properties of a catalyst. This finding is consistent with the XRD results, exalting the presence of small sized CuO in the material. The TPR diagram of the Cu/HMS-50_{imp} sample obtained by the impregnation method shows only the second reduction peak at a temperature lower than that for the corresponding Cu-HMS-50 obtained by the one-pot sol-gel method. In the case



Fig. 7 TPR profiles of calcined samples

of Cu-HMS-50 and Cu-HMS-75 samples, TPR results indicate that the copper species may exist in both highly dispersed CuO and also as isolated Cu²⁺ ions, which are in interaction with silanol groups on the surfaces of the HMS matrix. However, the copper species in the Cu/HMS-50_{imp} sample seem to exist in worse dispersion and much weaker interaction with the HMS support. Furthermore, the reduction profile is almost symmetrical, indicating an homogeneous material. Finally, the absence of reduction peaks at temperatures above 450 °C confirms the strong interaction of Cu^{2+} isolated species with the framework, which are not reduced even at high temperatures. It should be noted that the sample Cu-HMS-100 did not present any significant consumption of H₂ in these experiments, which is corroborating the very low amount of Cu species, as evidenced in the ICP/OES data (Table 2). At this step, it is worthwhile to note that the observed shift in reduction temperature may be attributed, not only to the copper content, but also to the different copper particle sizes, different interactions between copper oxide and silica and different copper oxide dispersions. In order to know whether the copper could be re-oxidized, the reduction and re-oxidation of copper phase of the catalyst Cu-HMS-50 was evaluated in TPR/TPO experiments. The TPO profile, not presented here, does not exhibit any oxidation peaks, suggesting that copper species once reduced cannot be re-oxidized again.

XPS analysis

It is well known that XPS is a powerful superficial technique to explore the oxidation state of the transition metal compounds with localized valence d orbitals [42, 43]. Thereby, it is possible to evidence the coexistence or not of Cu^+ and Cu^{2+} ions in the materials synthesized. The Cu 2p core level spectra of the samples after irradiation are shown in Fig. 8. The XPS results reveal the presence of CuO in the different samples, as exhibited by the Cu $2p_{3/2}$ peaks. Cu⁺ has a single peak at 932.2 eV, whereas Cu²⁺ has one main peak at 933.5 eV and two shakeup satellites at higher binding energies. These satellite signals are assigned to an electron transfer from a ligand to a d orbital of the metal, corresponding to a np (ligand) \rightarrow 3d (metal) transition [44]. This latter is impossible for Cu^+ and Cu^0 species that have filled d levels, but is mainly characteristic of bivalent copper with d^9 character [43]. Moreover, as it can be seen in Fig. 8, the Cu^{2+} peaks are less intense than the corresponding Cu⁺ ions because under X-ray irradiation in UHV, Cu²⁺ undergoes reduction [45] leading to the formation of Cu⁺ [44]. However, it is also possible that complete reduction to Cu⁰ can take place. The fact that the binding energy of both Cu⁺ and Cu⁰ are very close makes their distinction very difficult. Nevertheless, we do not think that there is Cu⁰ in the catalyst since that calcinations process was performed under air conditions. Besides, the Cu⁰ signal is not observable in XRD patterns. The relatively big positive BE shift of the Cu $2p_{3/2}$ core level (~ 935 eV), observed for all the calcined catalysts stipulate a charge transfer from the metal ions toward the support matrix, leading to a strong interaction between the metal ions and the matrix [46]. This finding also confirms the presence of well-dispersed Cu^{2+} ions interacting with the surface of the HMS, which is in a good agreement with the TPR results. Consequently, the low-temperature and the high-temperature reduction



Fig. 8 Cu 2p core level photoelectron profile of the samples before catalytic test

peaks of the TPR profiles can effectively be ascribed to the highly dispersed copper species and the segregated copper particles, respectively. The two characterization techniques are in good agreement with each other. On the whole, the XPS results showed without any ambiguity the presence of copper in both oxidation states Cu^+ and Cu^{2+} . Table 3 summarizes the binding energy values, surface copper contents and surface O/Si atomic ratios considering the Cu $2p_{3/2}$ region. The O 1 s peak position at 532.8 eV and the Si 2p peak position at 103.6 eV are in agreement with SiO₂-type materials [44]. The position of these latter peaks for all the mesoporous materials remains substantially the same. On the other hand, the copper amounts are rather less than those obtained from ICP/OES (see Table 2), denoting a relative higher atomic concentration of copper species on the internal surface of the

Sample	O 1 s	Si 2p	Cu 2p _{3/2}	Cu (wt %)	O/Si
Cu-HMS-100	533.08	103.88	933.08 (30%) 935.52 (70%)	0.08	1.75
Cu-HMS-75	532.97	103.77	933.13 (36%) 935.86 (64%)	0.22	1.72
Cu-HMS-50	532.92	103.72	933.46 (42%) 935.71 (58%)	0.17	1.69
Cu/HMS-50 _{imp}	533.08	103.98	933.61 (49%) 935.91 (51%)	0.36	1.69

Table 3 BE values (in eV), surface copper content and O/Si atomic ratio before catalytic test



Fig. 9 Cu 2p core level photoelectron profile of the samples after catalytic test

materials. After the catalytic test, as it can be observed in Fig. 9, the intensity of the Cu $2p_{3/2}$ signal corresponding to Cu²⁺ (935 eV) has decreased and the two corresponding shakeup satellites peaks disappear completely. We think that the decrease in intensity of the peak of Cu²⁺ (933.5 eV) is probably due to the reduction of Cu²⁺ to Cu⁺ in the segregated CuO particles. Simultaneously, the remaining Cu²⁺, even after reaction, could be assigned to Cu²⁺ isolated species, more strongly interacting with the framework [46]. After reaction, a certain quantity of copper species is transferred to the surface thereby increasing the amount of copper in the case of Cu–HMS-50 and Cu–HMS-100 samples. Whereas for the sample Cu–HMS-75, the surface content of copper is much lower after reaction. This result suggests that a certain amount of copper species is confined in the framework of the channel walls [46].

Catalytic Activities

The evolution of benzaldehyde conversion as a function of reaction time for all the catalysts used in this work except Cu–HMS-100, which is not active, is illustrated in Fig. 10.

All the catalysts present relatively higher activity at 200 °C. The latter tends to decrease with time reaction on flow and reaches a constant value, suggesting an insitu catalyst deactivation. The benzaldehyde conversion increases with increasing copper content for the catalysts prepared by the one-pot sol-gel method and peaks over the Cu–HMS-50. However, the Cu/HMS-50_{imp} sample prepared by the



Fig.10 Benzaldehyde conversion vs. time on stream over the catalysts under a hydrogen atmosphere, pre-treated: H_2/350 $^\circ C$

impregnation method, despite its higher copper content (see Table 2), exhibits lower benzaldehyde conversion in comparison with the corresponding Cu-HMS-50. This may be explained by formation of less active crystalline CuO species [13]. The formation of such species in the latter catalyst is confirmed by the characterization studies detailed before. Also, it can be concluded that most of copper species in Cu-HMS-75 and Cu-HMS-50 are dispersed on HMS surfaces in the form of finely dispersed CuO particles and a few of them have relatively strong interactions with silica units. Results for benzaldehyde hydrogenation at a steady state over the different catalysts are reported in Table 5.

The influence of reaction temperature on the performance of the catalysts is displayed in Table 5. We notice that the reaction products are benzyl alcohol and toluene for all the active catalysts. On the other hand, it may be noted that benzyl alcohol was formed over all the catalysts whatever the reaction temperature. As it can be observed in Table 4, the benzaldehyde conversion begins at 100 °C, increases until reaching a maximum at 200 °C and decreases dramatically until getting at 300 °C. This behavior is observed for all the samples. We think that at 200 °C, some molecules of the formed products or their derivatives, either benzyl alcohol and/or toluene, remain strongly adsorbed on some of the active sites on the surface of the different catalysts, leading to the decrease of the activity. Furthermore, at this same temperature, among the Cu–HMS-50 and Cu–HMS-75

Sample	O 1 s	Si 2p	Cu 2p _{3/2}	Cu (wt %)	O/Si
Cu-HMS-100	532.90	103.70	932.81 (47%) 935.52 (53%)	0.20	1.75
Cu-HMS-75	532.77	103.57	933.83 (38%) 935.27 (62%)	0.14	1.67
Cu-HMS-50	532.93	103.53	932.99 (47%) 935.50 (53%)	0.28	1.66
Cu/HMS-50 _{imp}	-	-	-	-	_

Table 4 BE Values (in eV), surface copper content and O/Si atomic ratio after catalytic test

Table 5 Catalytic results for benzaldehyde hydrogenation at a steady state over the different catalysts

Catalyst	T _{reaction} (°C)	Conv. (%)	Selectivity (yield) (%)			
			Benzyl alcohol	Toluene	Benzene	
Cu–HMS-100 ^a	100	_	_	_	_	
	200	_	_	_	-	
	300	_	_	_	-	
Cu–HMS-75 ^a	100	04	100 (04)	_	-	
	200	08	57 (04.6)	43 (3.4)	-	
	300	04	87 (03.5)	13 (0.5)	-	
Cu-HMS-50 ^a	100	10	99 (09.9)	01(0.1)	-	
	200	56	28 (15.7)	72 (40.3)	-	
	300	14	45 (06.3)	55 (07.7)	-	
Cu/HMS-50 ^b _{imp}	100	05	100 (05)	_	-	
	200	07	94 (06.6)	06 (0.4)	-	
	300	05	79 (04)	21 (01)	-	

^aSamples prepared by the Tanev method

^bSample prepared by the impregnation method

catalysts, Cu–HMS-50 seems to be the most active with a conversion of 56 versus 8%. However, the selectivity towards benzyl alcohol with Cu–HMS-50 (28%) is strongly inferior to that with Cu–HMS-75 (57%). It is worthy to note that both catalysts show a total selectivity to benzyl alcohol at 100 °C. Compared to Cu–HMS-50, the corresponding Cu/HMS-50 probably arises from highly dispersed copper species with relatively high content. It is a well-known fact that the heterolytic and homolytic dissociation of hydrogen molecules on the surface of metallic oxide generate active hydrogen surface species as intermediates for direct activation of benzaldehyde molecules [47], whereas the formation of benzyl alcohol is assumed to be a 1-2 nucleophilic addition, with a high polarization of the transition state [47]. Whereas, toluene is likely formed by protonation of the alcohol function on a Brönsted acid site (H–O–Si) followed by hydrogenolysis of the protonated species on an adjacent metal site (Cu–H). The proposed reaction pathways over Cu–HMS catalysts are shown in Scheme 1.



Scheme 1 Formation pathways of both benzyl alcohol and toluene over Cu-HMS

Conclusion

In the present study, copper containing ordered mesoporous materials Cu-HMS-n, where n is the atomic ratio of Si/Cu, was synthesized by the one-pot sol-gel method and deeply characterized. The introduction of Cu^{2+} species in the framework of the HMS was confirmed by XRD which shows an expansion of the lattice parameter a₀. All the studied catalysts exhibited Langmuir type IV isotherms with a H1-type hysteresis loop that is characteristic of a typical long-mesoporous material with 1-D cylindrical channels and showed large BET surface areas above 700 m² g⁻¹ and large pore volume higher than $0.75 \text{ cm}^3 \text{ g}^{-1}$. The copper species adopting a distorted octahedral geometry are finely and uniformly dispersed on the HMS surface. Among all the samples tested, the Cu-HMS-50 sample showed the best benzaldehyde conversion of 56% at 200 °C and benzyl alcohol selectivity up to 28%. The best activity of this latter seems to be due to the highly dispersed Cu^{2+} and Cu⁺ ions coexisting on its surface, to their strong interactions with silica units and to the high content in copper compared to the other catalysts prepared by the sol-gel method. In previous work, we have found that Ni-HMS-n catalysts exhibited good performance in the catalytic reduction of benzaldehyde. We think that addition of a second metal species such as nickel or cerium into the Cu-HMS-n catalysts as promoters will improve their catalytic activity. Work in this direction is in progress.

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