

Highly Loaded and Thermally Stable Cu-Containing Mesoporous Silica—Active Catalyst for the NO + CO Reaction

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We report the synthesis of a highly loaded and thermally stable Cu-containing mesoporous silica, which was developed by making use of poly(acrylic acid) (Pac) assembled with surfactant (C₁₆TAB), as template. On this backbone, TEOS and Cu(II) hydrolysis takes place leading to the development of the final mesostructure. Poly(acrylic acid) is used not only as a micelle structural component but also as a complexation agent for Cu(II) species resulting in high metal loading and increased thermal stability of the mesoporous network. The original uncalcined material possesses hexagonal ordering, while upon calcination it is transformed into a wormlike mesoporous network with metal loading >14 wt % Cu. An evaluation of its performance as heterogeneous catalyst in NO reduction by CO shows catalytic activity comparable with that of noble metal catalysts. Complete NO conversion, with >90% selectivity to N₂, was achieved between 190 and 200 °C. The material retained its structure and catalytic activity after 24-h testing at the maximum catalytic conversion of NO and CO.

Introduction

Template-assisted mesoporous inorganic frameworks such as M41S,¹ SBA-n,^{2–4} HMS,^{5,6} and MSU^{7–9} loaded with various metals are very promising materials as heterogeneous catalysts for a variety of catalytic processes. The drawback of such solids is their poor thermal stability at elevated metal loadings because of sintering effects, which results in dramatic loss of their mesoporosity and surface area.

The synthetic protocols commonly implemented to achieve incorporation of transition-metal atoms into the siliceous framework include one-step pathways, where the metal source is added in the starting reaction mixture^{10–20} resulting thus in various M41S or SBA-n mesoporous frameworks. A second approach is posttreatment pathways including impregnation,^{21–24} ion exchange,^{25–29} or grafting.^{30,31}

The one-step direct synthesis methods face the possibility of trapping a degree of the total amount of incorporated metal in the bulk of the framework,³² making these sites inaccessible to reactant molecules, and thus decreasing considerably their possible catalytic activity. Such direct methods provide materials with good dispersion of metal in the structure, but a high amount of metal loading, usually about 6–7 wt %, leads to structural collapse and loss of mesoporosity because of sintering effects.

Posttreatment pathways are two-step procedures and thus more complicated. Grafting with organic molecules as amines, which are able to complexate and thus stabilize d-metal cations and result in high dispersion and accessibility of the active sites, limits their possible applications, as high working temperature will destroy the organic grafted agents. Besides, this method or the posttreatment with metal alkoxides necessitates refluxing in hazardous solvents, which should be avoided if possible, as well as acidity of the framework, which is not a strong point of

these materials. Impregnation is less complicated but offers no control over dispersion, while pore blockage and agglomeration of the metal species, especially at high loading, often results in deteriorated products.

In relation to copper-containing mesoporous silica, Hartmann et al.¹² on the basis of TPR measurements have suggested that Cu-containing MCM-48 prepared via impregnation exhibits poor dispersion of CuO_x particles which form agglomerates. In contrast, the direct introduction of the metal in the reactant mixture and subsequent hydrothermal treatment leads to highly dispersed CuO_x species, which are located on the channel wall of the framework as a result of the interaction between cupric cations with the cationic surfactant as revealed from EPR measurements.³³ The amount of copper incorporated on the framework does not exceed 3 wt %.

Pöpl et al.³³ have reported the incorporation of cupric ions into siliceous MCM-41 by making use of an additional surfactant which is able to complexate with the metal cations. However, the amount of copper on the final material did not exceed 1% with respect to silicon atoms.

Karakassides et al.¹⁵ have also prepared Cu-containing MCM-41 with 4.7 wt % total metal loading by making use of specially amine-modified silica precursors able to complexate with copper cations. The final material possesses specific surface area $S_p = 580 \text{ m}^2\text{g}^{-1}$.

Finally, Han et al.⁵³ have reported the synthesis of copper-containing mesoporous silica employing cyclodextrins as nanocasting agents instead of the typical alkyltrimethylammonium type surfactants. However, apart from the considerably higher expense of the template compared with that of common surfactants, the materials do not bare more than 1% mol copper and exhibit specific surface area that does not exceed $370 \text{ m}^2\text{g}^{-1}$.

The main conclusion derived from the available methods of synthesis of copper- or metal-containing mesoporous silica as presented above is that metal loading higher than 6–7 wt % leads to a dramatic structural degrade and loss of the mesoporosity.

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Schumacher et al.¹⁰ have reported a novel synthesis route of spherical MCM-48 and the potential of this method for developing metal-containing MCM-48 mesostructures. The proposed pathway implements common surfactants as C₁₆TAB and highly alkaline conditions in the presence of the metal species. Under these conditions, the mesophase is formed in a few minutes and the final material is isolated within 2 h. It was shown that the materials obtained by that method can incorporate a higher amount of metals and possess higher surface area compared to similar materials developed by hydrothermal methods. The same researchers state that metal content above 18 wt % leads to total structural collapse, but the morphology remains spherical. So, this approach appears to have some advantages over the other ones, as it can generate metal-containing mesoporous silica in a single step, while at the same time it ensures incorporation of a higher amount of metal and better structural characteristics. This method has been tested for the development of mesoporous silica containing several metals as Ni, Nb, Cr, V, and so forth, but it has not been tested for the preparation of Cu-containing MCM-48.

In the past, it has been shown that metal-containing ordered mesoporous molecular sieves could be more effective catalysts than their amorphous counterparts,^{21,23,34} like metal-containing amorphous silica. Copper-containing mesoporous silica could be an effective catalyst for NO reduction, since copper promotes NO_x decomposition^{35–40} on various substrates, like zeolites, and is the most promising transition metal for de-NO_x operations, competing favorably even precious metal-based catalysts. However, there is a lack of literature concerning the catalytic evaluation of Cu-containing ordered mesoporous silica in de-NO_x operations. Such materials have been mostly tested in liquid-phase reactions of large molecules, where their mesoporosity is an obvious advantage.^{41,25,20,22} Material 5%Cu/MCM-41 synthesized by impregnation has been tested in NO reduction by CO with respect to structural modifications of the active sites during the catalytic process.²⁴ The material appears to be catalytically active in a temperature range 200–500 °C. Moreover, some noble metal containing MCM-41 materials have been tested with promising results. RhO_x/MCM-41 was proven a quite active catalyst for NO reduction by CO in the temperature range 250–350 °C.¹⁶

On the basis of these facts, it appears that there is scarce literature regarding methods of synthesis of highly copper loaded mesoporous silica with high thermal stability and surface area.

In this work, we present a preparation method of Cu-containing mesoporous silica with high metal content (>14 wt %) and enhanced thermal stability. This material shows high catalytic activity for the reduction of NO by CO which was used as a probe reaction. The material was prepared in one step without the need of any posttreatment.

The synthetic approach demonstrated in two recent publications^{42,43} involves the use of a new structural agent, namely, poly(acrylic acid), Pac in the next. Pac complexed to the cationic alkyl trimethylammonium type surfactants (C_nTAB) in the presence of a silica source (TEOS) is able to form ordered hexagonal or cubic mesoporous silica. Pac–C_nTAB complexes have been known for quite some time as a new type of highly ordered mesomorphous organic solids.⁴⁴ Their formation follows a highly cooperative zipper mechanism under a stoichiometry of 1:1, driven by Coulombic interactions between the functional groups of the anionic polyelectrolyte backbone and the cationic surfactant. Hydrophobic interactions among the surfactant chains play also an important role in the formation of the structure. We first used these complexes as template systems for the

preparation of mesoporous silica. It has been shown^{42,43} that Pac is the structural component that introduces order to the mesophase, while the surfactant chain length determines whether the hexagonal or the cubic phase is formed. The formation of the micelle template results from the complexation between the anionic polyelectrolyte and the cationic surfactant. As this complexation is controlled by the pH, it can be stopped at any pH value to check the progress of the mesophase formation.

In the present work, poly(acrylic acid) possesses an additional role as it can also complexate with Cu²⁺ cations. The underlying idea is to take advantage of the potential of Pac to act as a structural agent in a first place while at the same time to act as a carrier of Cu(II) cations via complexation along its chain. In this way, incorporation of copper species into the inorganic framework takes place almost simultaneously with the condensation and polymerization of silica precursors on the micelle template.

Experimental Section

Materials and Methods. At ambient temperature, 0.7 g of poly(acrylic acid) (Aldrich) of MW = 2000 au (Pac2) was dissolved in 100 g of deionized water under stirring. The pH of the solution measured online was typically 3.2. Hydrochloric acid (HCl) was then introduced to set pH at 1.5 to avoid uncontrolled complexation of the polyelectrolyte with the surfactant added next. Then cetyl-trimethylammonium bromide (C₁₆TAB, Merck) was added at a stoichiometric amount with respect to polyelectrolyte functional groups (3.5 g), and a clear solution is obtained. The next step was the addition of 0.56 g of Cu(NO₃)₂·3H₂O (Merck). Finally, 4.5 mL of TEOS (Merck) was added to the mixture. The molar composition of this starting mixture was TEOS/Cu/C₁₆TAB/Pac2/H₂O ≈ 1/0.115/0.48/0.0176/278 (Si/Cu = 8.70, 10.31% Cu). Then, dropwise addition of NaOH 0.1 M took place in two stages: At the first stage, the pH is gradually increased over approximately 1.5 h up to pH = 4.0, where the precipitate remained for 24 h. Then, the pH was further increased up to 10.5 and the mixture was kept under these conditions for another 24-h period. Intermediate samples are isolated at any desired pH or time during the process for examination and characterization. The time of isolation of each intermediate sample and the chosen pH for isolation are crucial parameters regarding the reproducibility and the quality of the final product. For example, when the precipitate was kept only for 1 h at the first stage or at pH higher than 4.0 (see above), the mesoporous network exhibited lower thermal stability.

All products were then subject to filtration, washing, and drying at 90 °C (*T_g* = 106 °C for poly(acrylic acid)). To remove the template, the final material was calcined at 600 °C for 6 h with a heating rate of 2 °C min^{−1} under atmospheric conditions. This material will be designated as Pac2C₁₆Cu in the text (Pac2 + C₁₆TAB + TEOS + Cu). The pure mesoporous silica sample, Pac2C₁₆ (Pac2 + C₁₆TAB + TEOS), was prepared according to a similar process described elsewhere.^{42,43}

Instrumentation. Simultaneous TG/DTA analyses were carried out on a Netzsch STA 449 C instrument under air flow (10 mL min^{−1}) with a heating rate of 10 K/min. Nitrogen adsorption measurements were performed at 77 K on a Sorptomatic 9000 Fisons instrument after outgassing for 12 h at 473 K. X-ray diffraction measurements were acquired on a Bruker Advance D8 system using Cu Kα radiation (*λ* = 1.5418 Å) and a step of 0.01°. Scanning electron microscopy (SEM) and energy-dispersive spectrometric analysis (EDS) were performed on a JEOL JSM 5600 at 20 kV equipped with an Oxford EDS X-ray

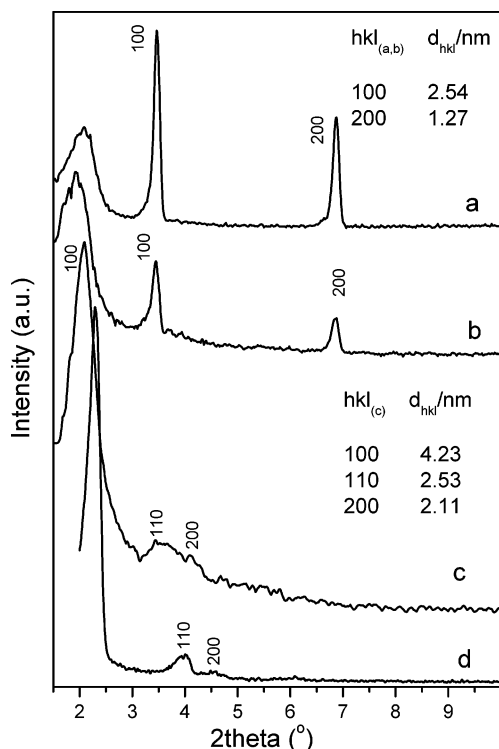


Figure 1. X-ray diffractograms of various uncalcined Pac2C₁₆Cu samples isolated from the reaction mixture as pH and time increase: (a) at pH 4.0 after 24-h reaction, (b) at pH 10.5 after 1-h reaction, and (c) at pH 10.5 after 24-h reaction; (d) XRD of the pure Pac2C₁₆ uncalcined silica sample at pH 5.5 after 24-h reaction.

microanalysis apparatus. TEM photos were recorded in a JEOL 120CX instrument equipped with CeB6 filament. Finally, pH was measured on an Inolab Terminal 3 by WTW.

Catalytic Test. Catalytic tests were performed in a lab scale plug flow reactor using 200 mg of the solid Pac2C₁₆Cu catalyst. The total flow rate of the reactant mixture (NO/CO/He, 2%/2%/96%) was 100 mL min⁻¹, which corresponds to a GHSV of 16 000 h⁻¹. The effluents were analyzed on a Carlo Erba GC using a combination of Porapac Q and Molecular Sieve 13X columns. Prior to measurements, the catalyst was treated for 1 h under the reaction mixture at 300 °C. Then, the reactor was cooled and acquisition of the temperature profiles started at increasing steps of 5–20 deg. The conversion rates (R_{NO} , R_{CO}) were calculated as $R_i = F \cdot X_i / m$, where $F = 1.36 \mu\text{mol/s}$ and is the feeding rate of NO and CO, X_i is the degree of conversion ($X_i = (\text{mass}_{\text{in}} - \text{mass}_{\text{out}}) / \text{mass}_{\text{in}}$) at each temperature i , and m is the catalyst mass.

Results

In Figure 1, the X-ray diffractograms of the pure uncalcined silica sample Pac2C₁₆ (Figure 1d) as well as of the copper-containing uncalcined hybrid materials Pac2C₁₆Cu (Figure 1a–c) are shown. Those data were recorded from samples obtained at various pH values and were kept at those pH values for various times, as indicated. In Figure 2, the X-ray diffractograms of the calcined Pac2C₁₆Cu are shown both at low as well as at high angle range (inset).

TEM images of the uncalcined and calcined Pac2C₁₆Cu sample are shown in Figure 3.

Figure 4 shows the TG/DTG and DTA diagrams of Pac2C₁₆-Cu and Pac2C₁₆ precursors.

In Figure 5, the N₂ adsorption–desorption isotherms, and the corresponding pore size distribution calculated according to the Horvath–Kawazoe method, are shown for Pac2C₁₆Cu solid.

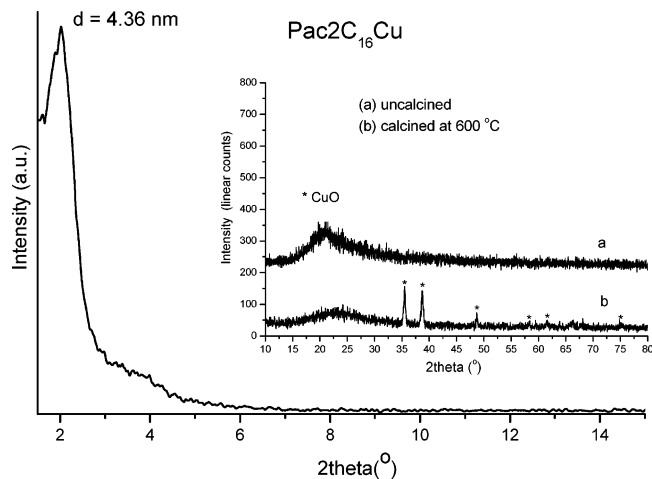


Figure 2. X-ray diffractogram of the sample Pac2C₁₆Cu calcined at 600 °C. In the inset, the high angle diffractograms of the uncalcined (a) as well as of the calcined (b) sample are shown. The peaks indicated with (*) correspond to CuO species.

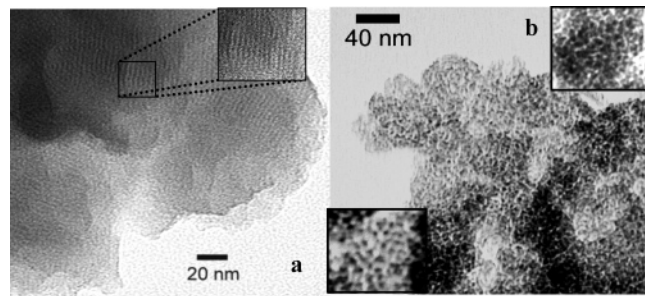


Figure 3. TEM photos of (a) the uncalcined Pac2C₁₆Cu sample exhibiting hexagonal channel ordering. In b, the same sample after calcination exhibits a wormlike mesoporous network.

Figure 6 shows a SEM image and the corresponding EDS spectra of Cu microanalysis for the Pac2C₁₆Cu solid.

In Figure 8, the conversion profiles for the catalytic conversion of NO (X_{NO}) and CO (X_{CO}) are shown as a function of temperature for the Pac2C₁₆Cu catalyst. Figure 9 shows the % selectivity of N₂ and N₂O produced during the reaction. The estimation of the apparent activation energies E_{app} at conversion <20%, from the corresponding Arrhenius plots $\ln R = f(1000/T)$, is shown in Figure 10. In Figure 11, a structural and catalytic stability test is shown for the catalyst Pac2C₁₆Cu, run for 24 h at 260 °C, where 100% conversion of both NO and CO to N₂ and CO₂ is achieved. In Figure 12, the corresponding X-ray diffractogram and N₂ sorption measurements of the same catalyst after the stability test are finally shown.

Discussion

The pure uncalcined silicate sample Pac2C₁₆ isolated at pH range 4.0–5.5 possesses a hexagonal mesostructure^{42,43} as shown in Figure 1d for the sample isolated at pH = 5.5 and in Figure 7a (inset) for the sample isolated at pH = 4.0. In the same, the X-ray diffractograms of various Cu-containing uncalcined Pac2C₁₆Cu samples are shown. These materials were isolated from the same mixture at different pHs and times as follows: (a) at pH = 4.0 after 24 h, (b) at pH = 10.5 after 1 h, and (c) at pH = 10.5 after 24 h reaction. It is clear that in the first case, namely, at pH 4.0, a lamellar phase of repeating distance 25.4 Å coexists with another mesostructure of ambiguous identity (Figure 1a). As pH rises up to 10.5, the lamellar mesophase is gradually transformed to the hexagonal one as a function of time or pH (compare Figure 1b and Figure 1c). This

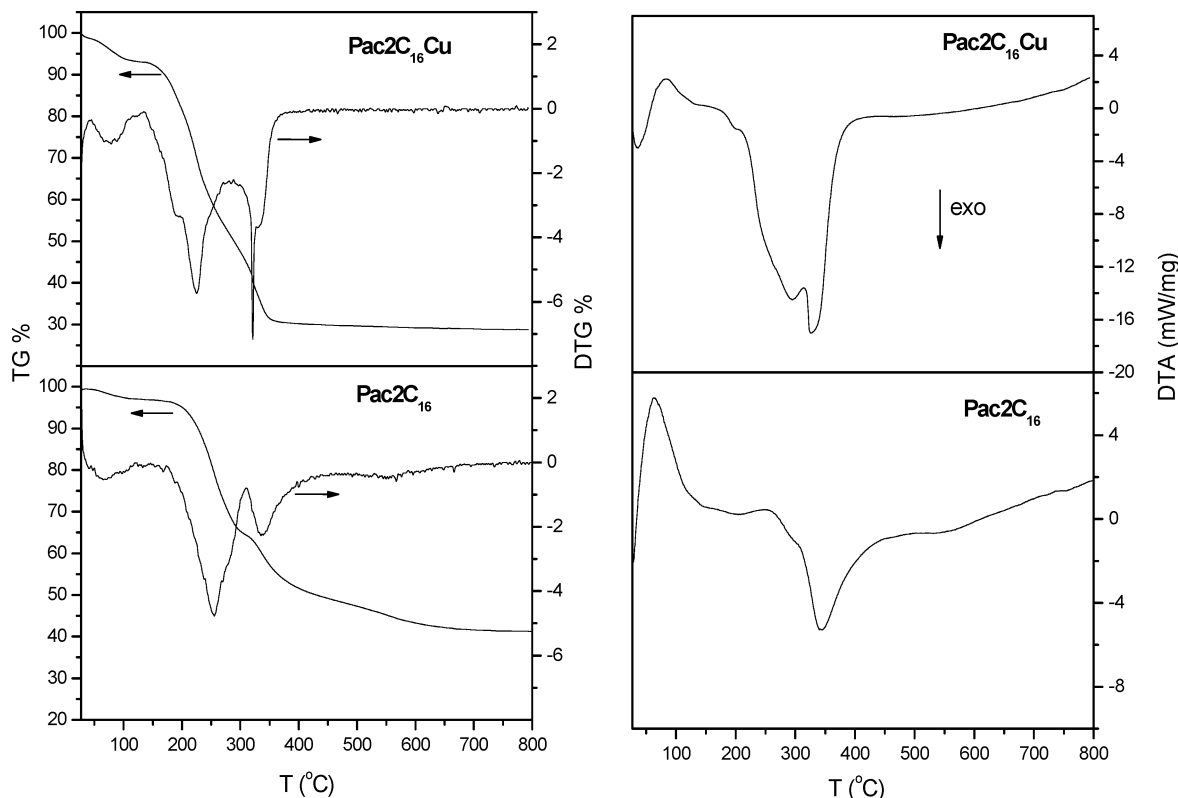


Figure 4. TG/DTG (left) and DTA (right) curves of the copper-containing precursor Pac2C₁₆Cu (upper part) and of the precursor Pac2C₁₆ containing just silica (lower part).

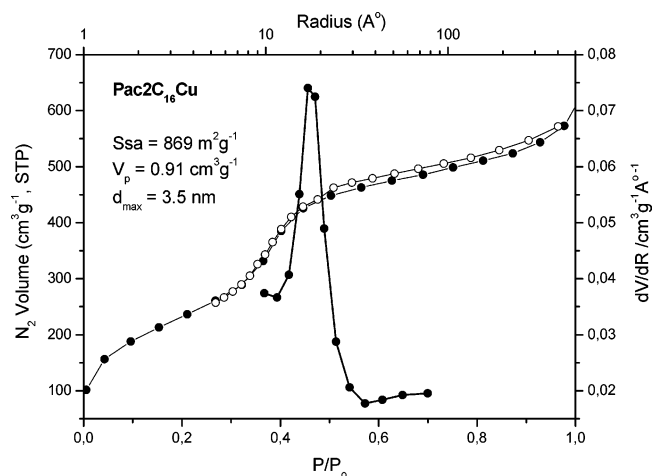


Figure 5. N₂ adsorption-desorption isotherms at 77 K and the corresponding pore size distribution calculated according to the Horvath-Kawazoe method for the calcined Pac2C₁₆Cu sample.

transformation is clearly indicated by the decreasing intensity of the Bragg reflections at $d = 2.54$ nm and 1.27 nm (Figure a, b) and the increasing intensity of the reflection at about 4.23 nm. The indexing of the three characteristic peaks according to the hexagonal symmetry is also indicated on Figure 1c, from which a unit cell of $a_0 = 4.88$ nm is derived ($a_0 = 2d_{100}/3^{1/2}$). However, the higher order peaks 110 and 200, of the hexagonal mesostructure of Pac2C₁₆Cu sample, appear broader compared to the Pac2C₁₆ sample of pure silica, a fact indicating loss of order.

Figure 3a shows a TEM image perpendicular to the pore tunnel axis, where parallel channels are clearly visible. Calcination of the final Pac2C₁₆Cu sample, shown in Figure 1c, at 600 °C results in a loss of the higher order reflections as revealed by XRD and formation of a wormhole mesoporous structure

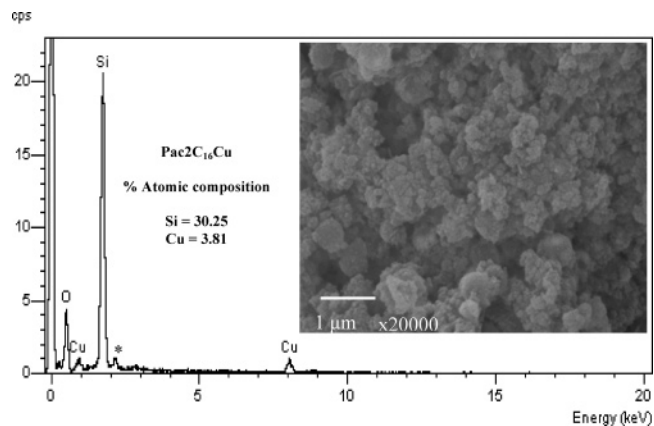


Figure 6. SEM photo, EDS spectra, and atomic percent composition for Pac2C₁₆Cu sample calcined at 600 °C (* corresponds to Au that was used to coat the sample thus avoiding charging effects on the image).

(Figure 2a) as confirmed by TEM (Figure 3b). Nevertheless, the characteristic d_{100} value related to the pore-to-pore distance of the uncalcined sample, which equals 4.23 nm (Figure 1c), appears to be almost equal to that of the calcined Pac2C₁₆Cu sample, which is 4.36 nm (Figure 2). This indicates that no contraction of the channel wall takes place. This is rare in metal-containing mesoporous silicas and indicates a mesoporous network of high thermal stability. This result is also of greater value if we consider the exceptionally high amount of copper, which as determined by EDS microanalysis is around 14 wt % (Figure 6).

Some useful indications concerning the way copper is spread through the material can be provided by a closer observation of the TEM images (Figure 3). The TEM image in Figure 3a corresponds to the uncalcined material. The high angle portion of the XRD pattern (see inset a in Figure 2) of this solid does

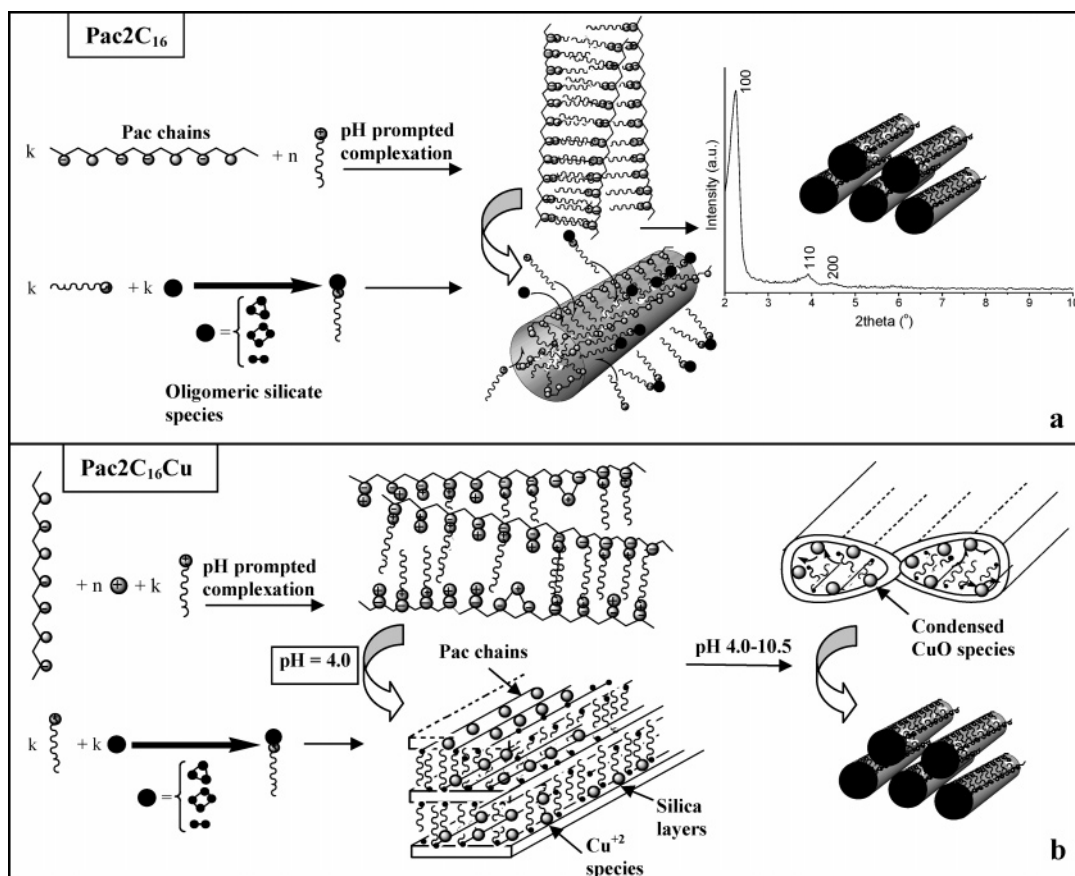


Figure 7. A schematic illustration of the pathway of phase evolution on the basis of the experimental data and the literature for (a) the pure silica Pac2C_{16} system (inset shows an X-ray diffractogram of a preliminary Pac2C_{16} sample isolated at $\text{pH} = 4.0$ after 10 min of reaction) and (b) in the presence of Cu^{2+} ions. In b, monodentate and bidentate $(\text{COO})_x\text{Cu}$ complexes are shown to compete with $(\text{COO})_{16}\text{TA}$ complex formation.

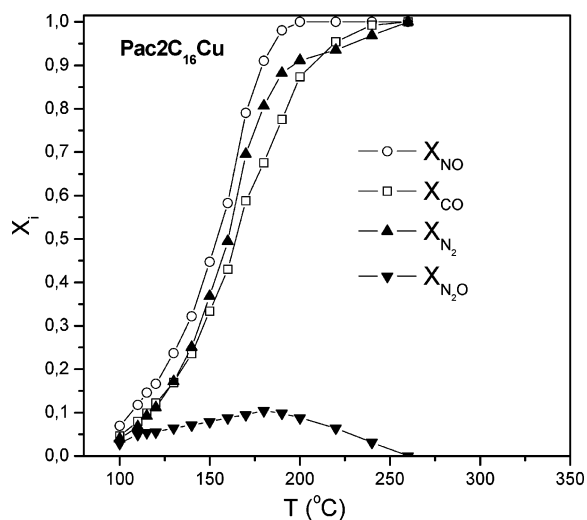


Figure 8. Conversion profiles of NO and CO and the corresponding ones of N_2 and N_2O for the $\text{Pac2C}_{16}\text{Cu}$ catalyst.

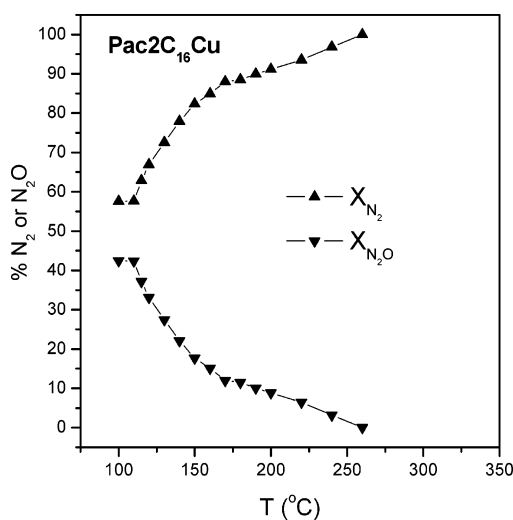


Figure 9. Selectivity toward N_2 and N_2O as a function of temperature for the $\text{Pac2C}_{16}\text{Cu}$ sample.

not show any Bragg peaks suggesting the absence of any crystalline phase. This can be well understood since the silica framework is amorphous and copper is expected to be in the form of Cu^{2+} forming a complex with poly(acrylic acid). A representative TEM image of this solid is shown in Figure 3a where there is a smooth contrast throughout the entire particle without any evidence of a separate dense phase. In other words, only the mesostructured network is visible. In marked contrast, the TEM image of the calcined solid shows the presence of wormhole-type mesoporous network that appears with light gray

color and dark dense spots that presumably correspond to CuO nanoparticles.

The inset of Figure 2 shows the X-ray diffraction diagram of the same sample $\text{Pac2C}_{16}\text{Cu}$ at higher angles before and after calcination at 600 °C. The observed peaks correspond to CuO species formed upon calcination. Moreover, the corresponding Bragg peaks are broad indicating the formation of CuO nanoparticles. Using the Scherrer equation, the calculated crystallite size is approximately 15 nm. The existence of CuO nanoparticles also explains the high thermal stability of the network. These results are in agreement with the TEM image

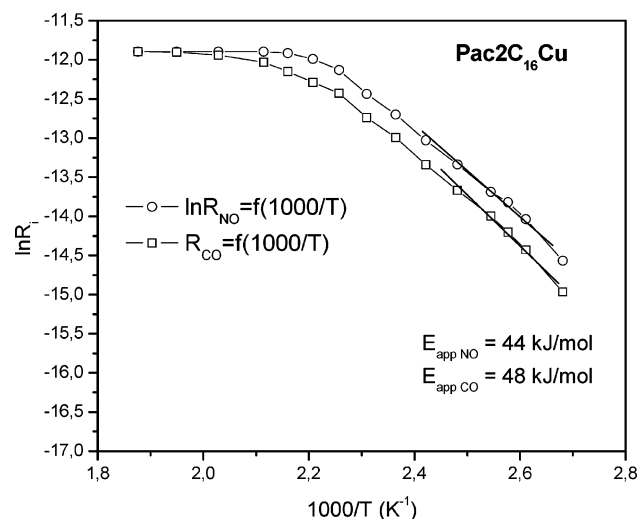


Figure 10. Arrhenius plots ($\ln R_i = f(1000/T)$) and the apparent activation energies E_{app} .

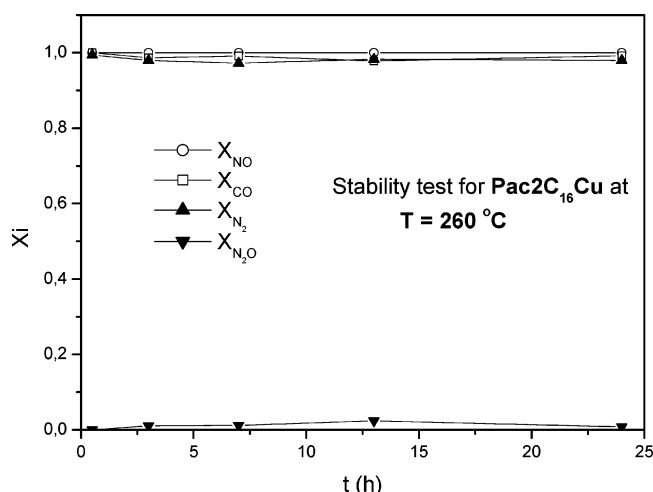


Figure 11. Structural and catalytic stability test for Pac2C₁₆Cu material at 100% conversion of NO and CO to N₂ and CO₂, for 24-h period.

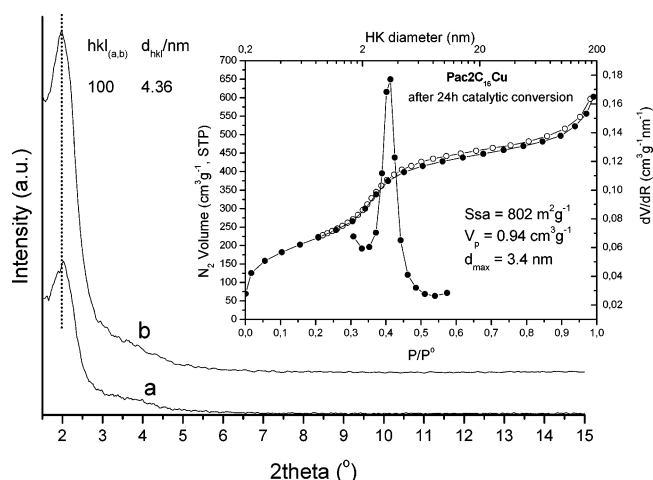


Figure 12. X-ray diffraction patterns for Pac2C₁₆Cu sample before (a) and after (b) the 24-h stability test. Inset: N₂ sorption isotherms at 77 K of b.

shown in Figure 3b where the highly dispersed CuO nanoparticles are visible as dark dense spots. A strong indication that the CuO nanoparticles are highly dispersed throughout the silica mesoporous network is provided by the thermogravimetric TG/DTG and DTA diagrams of Pac2C₁₆Cu and Pac2C₁₆ precursors,

shown in Figure 4. In these diagrams, we observe a steep weight loss and a strong exothermic peak at ~ 320 °C of the TG/DTG and DTA curves that corresponds to the burning and removal of the template from the Pac2C₁₆Cu precursor (upper part in Figure 4). These data indicate a complete elimination of the organic part at this temperature. In contrast, the corresponding curves for the Pac2C₁₆ precursor (lower part of Figure 4) show a prolonged surfactant burning taking place at a higher temperature compared to the Pac2C₁₆Cu sample, and complete decomposition of the organic part is achieved around 600 °C. This behavior is indicative of the catalytic promotion of the template burning induced by CuO nanoparticles in Pac2C₁₆Cu compared to the Pac2C₁₆ precursor.⁵² As the organic counterpart fills the space inside the pores, the above results imply that the metal sites are also in close proximity throughout the entire solid suggesting a high degree of dispersion.

The N₂ adsorption–desorption curves are shown in Figure 5. The Pac2C₁₆Cu sample possesses a specific surface area equal to $S_p = 869$ m² g^{−1}. The adsorption isotherm exhibits a relatively steep condensation step at P/P_0 0.35–0.4. The desorption step shows just a trace of hysteresis. These data indicate an open network with pores having a narrow pore size distribution (psd). Indeed, a narrow psd with a maximum diameter $d_{max} = 3.5$ nm was calculated by the Horvath–Kawazoe (HK) method and shown in Figure 5.

The Cu loading was assessed by means of EDS analysis. In Figure 6, a SEM picture of the calcined Pac2C₁₆Cu sample as well as the corresponding EDS spectra of the elemental microanalysis is shown. This analysis indicates a high amount of copper on the sample Si/Cu = 7.94 (11.19% atomic or 14.38 wt % if calculated as SiO₂/CuO). This value is close to the used one in the starting mixture Si/Cu = 8.7 (10.31%). The small difference could be due to incomplete condensation of silica.

According to the existing literature, copper content above 5 wt % results in poorly ordered mesoporous materials (wormlike materials) with surface areas less than 600 m² g^{−1}.¹⁵ Higher metal content in the silicate framework would lead to total loss of the particular structural characteristics for materials synthesized according to the direct methods mentioned in the Introduction. Considering the above, it becomes clear that Pac2C₁₆Cu porous solid possesses enhanced structural characteristics (mesoporosity, ssa, pore volume) and considerably higher copper loading compared to other similar cases. This result stems from the favorable influence of the complexation agent Pac in achieving higher metal loading.

We shall discuss now in more details the observed evolution of the various phases of the system (Figure 7).

As demonstrated previously in similar cases concerning pure mesostructured silica,^{42,43} the complex micelles resulting from the self-assembly of the complexed poly(acrylic acid) chains (Pac) with the cationic surfactant and the silicate precursors are the species which consequently determine the phase evolution. At pH 3.2, where the solid hybrid material starts to precipitate, a sufficient degree of complexation has been achieved resulting in the formation of the first micelles (Figure 7a). Moreover, it has been established that regardless of the presence of silica, the organic complex Pac-C₁₆TAB is separated from the solution at exactly the same pH 3.2, where the ionization degree of Pac (a) is less than 0.1.^{45a} The mechanism is a simple exchange of H⁺ with the CTA⁺ cations. The hybrid mesophase Pac2-C₁₆-TAB–SiO_x has a hexagonal structure at pH = 4.0 at least after reacting time 10 min (Figure 7a) and for the next 24 h (Figure 1d). In other words, if the system does not contain any copper,

but just silica, then it quickly ($t < 10$ min) self-organizes into a stable ($t > 24$ h) hexagonal mesostructure.

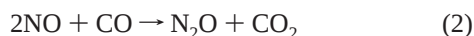
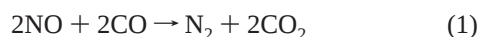
We should discuss now the influence of the addition of Cu^{2+} into the solution. The complexation of Cu^{2+} and other metals such as Zn^{2+} , Pb^{2+} , Ni^{2+} , Cd^{2+} , Ca^{2+} , and so forth, with poly(acrylic acid) has been extensively investigated in the past, as Pac is known for its chelating ability.^{45b-d,f-k} The cations Cu^{2+} form very stable monodentate complexes with Pac at low pH, < 4 , through exchange of Cu^{2+} with H^+ of the $-\text{COOH}$ groups as well as stable bidentate complexes at higher pH, > 4 .^{45b-d,k} On the other hand, the binding constant of dodecylpyridinium cations with Pac is also high.^{45e} So, we can draw from the existing literature the conclusion that in the subject system there is a competition between the cationic surfactant and Cu^{2+} species for occupation of the complexation sites $-\text{COOH}$ existing on the Pac chain. So, in the presence of Cu^{2+} , and at least up to pH = 4, beyond which the Cu^{2+} cations are hydrolyzed and precipitated,⁴⁶ we should expect several Cu^{2+} species to complexate with one or more carboxylic groups of the poly(acrylic acid) chain as shown in Figure 7b. Those Cu^{2+} cations are bound to complexation sites which otherwise would be connected to surfactant species as is the case in Pac2C_{16} . This complexation $\text{Pac-C}_{16}\text{TAB}$ is necessary for the initiation of the mesophase formation.⁴³ Thus, the presence of copper inhibits the formation of the hexagonal mesophase at pH = 4.0 (Figure 7a), where instead, at the same pH value, the main phase is the lamellar (Figure 7b) and the hexagonal is underdeveloped as seen in Figure 1a.

This is the case up to pH 4.0, where we know that precipitation of the hexagonally ordered hybrid material (Pac2C_{16}) containing just silica is achieved very quickly.

Further increase of pH up to 10.5 results in the formation of species such as $\text{Cu}_x(\text{OH})_y^{(2x-y)}$ in the range $4 < \text{pH} < 10$. At pH = 10.5, a small amount of negatively charged $\text{Cu}(\text{OH})_4^{2-}$ species appear according to literature^{46a} and polymerization reactions are initiated. It is likely that these reactions favor the transformation from lamellar to hexagonal mesostructure as observed in Figure a–c. We mention that this is just a mechanistic scenario and the reasons and details of this transformation are not quite clear.

Concluding the above discussion regarding the phase evolution, we can state that the presence of Cu^{2+} species hinders adequate degree of complexation of the surfactant with Pac and inhibits the direct formation of the hexagonal phase. This phase is, however, obtained later because of the polymerization of $\text{Cu}_x(\text{OH})_y^{(2x-y)}$, induced by the increase of pH. However, a detailed mechanism at the molecular level, through investigation of the coordination of copper species during the phase transformation and how it affects the mesostructure, is unattainable at the moment.

Catalytic Activity. In a preliminary evaluation of its redox catalytic properties, the $\text{Pac2C}_{16}\text{Cu}$ material was tested for the catalytic reduction of NO by CO, which can take place via one of the following reactions:



This reaction is of environmental interest and has been studied extensively in the past.⁴⁷ The corresponding conversion profiles are shown in Figure 8 for $\text{Pac2C}_{16}\text{Cu}$. We observe that NO conversion reaches 100% at 190–200 °C. The production of N_2 and N_2O is also shown in the same figure. N_2O is produced at relatively low percent, with a maximum of 10%. This effect

shifts the complete conversion of CO at higher temperature, compared to NO, which is around 260 °C. The selectivity to N_2 remains above 80% at 150 °C and reaches 100% at 260 °C, as indicated in Figure 9, in which the selectivity to N_2O is also shown. In Figure 10, the Arrhenius-type plots $\ln R_i = f(1000/T)$ are drawn. From them, the corresponding apparent activation energies, E_{app} , were calculated. The $\text{Pac2C}_{16}\text{Cu}$ catalyst exhibits E_{app} equal to 44 kJ mol^{-1} for NO reduction and 48 kJ mol^{-1} for CO oxidation. These values are only indicative as the drawn Arrhenius functions are approximative, but they reveal the fact that the high activity of $\text{Pac2C}_{16}\text{Cu}$ solid is due to low activation barriers for the reactions 1 and 2.

Finally, a structural and catalytic stability test of the $\text{Pac2C}_{16}\text{Cu}$ sample was performed and the results are shown in Figure 11. Namely, the catalyst was tested at 100% conversion of reactants at 260 °C for 24 h. No drop of activity was observed as shown by the steady 100% catalytic conversion for both NO and CO within the testing time period. The X-ray diffractograms and N_2 sorption profiles of the sample after this 24-h test are also shown in Figure 12. The latter indicates a 7% decrease in surface area and 3% in pore diameter. These results show that the mesoporous network exhibits a remarkable stability and it practically retains its integrity both from the structural (XRD diagram in the same Figure 12) as well as from the textural (surface area, porosity) point of view.

A literature survey shows that the catalytic activity of the tested $\text{Pac2C}_{16}\text{Cu}$ is higher compared to the corresponding ones for the same reaction on similar catalytic materials as impregnated Cu/MCM-41 (5 wt %) with an active temperature window 200–500 °C²⁴ and 2 wt % RhO_x loaded MCM-41^{16} working at 250–300 °C. These data are for the same reaction at comparable space velocity. Moreover, the $\text{Pac2C}_{16}\text{Cu}$ catalyst is favorably compared to precious metal impregnated oxide catalysts such as 1% $\text{Pt/Al}_2\text{O}_3$, 1% $\text{Pd/Al}_2\text{O}_3$, 1% Pd/CeO_2 , 1% Pt/CeO_2 , and 5% $\text{Rh/Al}_2\text{O}_3$, which achieve complete NO conversion between 190 and 270 °C,^{48–51} under similar reaction conditions.

Conclusions

A new method for the synthesis of highly loaded CuO mesoporous silica, with wormlike structure that exhibits high thermal stability and surface area, is reported. It was demonstrated that poly(acrylic acid), used as a complexation agent, favors higher CuO nanocluster loading on the final structure (approximately 14 wt %) with good metal dispersion. The material was proved to be highly active in the catalytic reduction of NO by CO achieving 100% conversion of both reactants at 260 °C with 100% selectivity to N_2 .

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