

Conditions of Formation of Copper Phyllosilicates in Silica-Supported Copper Catalysts Prepared by Selective Adsorption

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It is shown that, during the preparation of Cu/SiO₂ samples by selective adsorption of copper tetraammine complex [Cu(NH₃)₄(H₂O)₂]²⁺ on silica, two types of supported Cu^{II} species form: grafted Cu^{II} ions and copper phyllosilicate. The formation of grafted Cu^{II} ions results from electrostatic adsorption of Cu^{II} ammine complex cations in solution onto the surface of silica particles negatively charged due to the high solution pH. Grafting of Cu^{II} ions occurs during the subsequent drying step. The formation of copper phyllosilicate takes place in solution. It results from a reaction between silicic acid arising from silica dissolution and [Cu(OH)₂(H₂O)₄]⁰ complex in solution. Both Cu^{II} species lead to small metal particles after reduction. Several preparation parameters were investigated in this paper: the metal precursor concentration, the pH of the precursor solution, the solution/silica contact time, and the addition of ammonium nitrate to the precursor solution. The amount of copper phyllosilicate depends on the pH of the precursor solution; it is maximum at pH 9, that is, at the pH at which the concentration of [Cu(OH)₂(H₂O)₄]⁰ complex is maximum according to calculation of Cu^{II} speciation. The amount of copper phyllosilicate increases with the solution/silica contact time because its formation is a kinetically limited process. It was found that the addition of ammonium nitrate to the precursor solution prevents the formation of copper phyllosilicate. This can be explained by calculations of the Cu^{II} speciation in solution. The formation of Cu^{II} ammine complexes is favored in the presence of NH₄⁺ so that the concentration of [Cu(OH)₂(H₂O)₄]⁰ complex strongly decreases and its maximum of concentration shifts to pH lower than the pH's of preparation.

Introduction

Silica-supported copper materials find widespread application in catalysis such as the selective hydrogenation of alkynes into alkenes.^{1–5} They are usually prepared by deposition of a Cu^{II} precursor from aqueous solutions, followed by suitable thermal activation treatments, that is, calcination and reduction. As discussed in our previous paper,⁶ the method of copper precursor deposition and the nature of the copper precursor may strongly influence the ion dispersion onto the support, the metal dispersion on the reduced catalysts, and consequently their catalytic performances.^{7–12}

It has been shown that preparations involving equilibrium adsorption of a Cu^{II} complex, followed by discarding the excess Cu-containing solution, lead to high metal dispersion and small metal particles after reduction.^{6,13} The tetraammine copper^{II} complex [Cu(NH₃)₄(H₂O)₂]²⁺ is frequently used as a precursor for this type of preparation. This procedure has traditionally been called “cation exchange”; however, because this denomination suggests a particular adsorption mechanism for the cations at the molecular level, which may in fact not be operative in our systems, we will resort in this communication to the more neutral term of “selective adsorption” to refer to a preparation procedure involving separation of the solid from the deposition solution (by centrifugation or filtration followed by washings)

prior to thermal treatment, as opposed to “impregnation” procedures where such a separation is not carried out. In the pioneer works of Tominaga et al.,^{14,15} the formation of an inner sphere complex (≡SiO)₂Cu(NH₃)₂(H₂O)₂, where the surface ≡SiO[−] groups of the support act as ligands for the copper ion (grafted Cu^{II} species), was postulated to rationalize the spectroscopic results obtained with samples prepared at pH = 10–11. More recently, we showed that copper tetraammine complex is in electrostatic interaction with silica as long as the sample is still wet after preparation and grafts during the drying step at temperatures as low as 25 °C.¹⁶

In addition to grafted Cu^{II} ions, Shimokawabe et al.¹⁷ claimed to observe in catalysts prepared at pH = 11–12 “clustered Cu^{II} species”, which transform into CuO particles after calcination. Their results were partly confirmed by Kohler et al.,^{13,18} who also observed the same two copper species in calcined samples. However, these authors proposed that the small CuO particles arise in fact from calcination of Cu(OH)₂ precipitated during the washing steps performed after cationic exchange.

The formation of supported copper phyllosilicate was reported for the first time in Cu/SiO₂ samples prepared by selective adsorption of copper tetraammine at pH > 11,⁶ that is, in preparation conditions close to those described by Shimokawabe et al.¹⁷ and Kohler et al.^{13,18} Copper phyllosilicate, also called chrysocolla, Cu₂Si₂O₅(OH)₂, is a copper silicate with a lamellar structure that consists of layers of SiO₄ tetrahedra sandwiched between discontinuous layers of CuO₆ octahedra (Figure 1).^{19,20} Copper phyllosilicate is known to form during the preparation of Cu/SiO₂ catalysts by the method of deposition–precipita-

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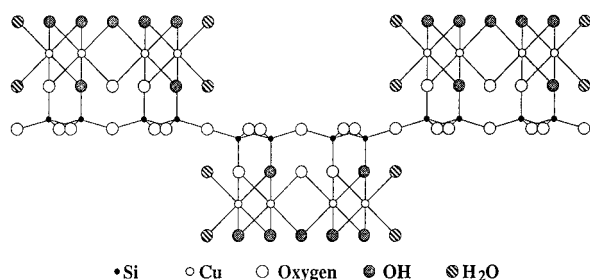


Figure 1. Schematic representation of the structure of bulk chrysocolla.

tion.^{21,22} The formation of nickel phyllosilicate was also reported in Ni/SiO₂ samples prepared by deposition–precipitation^{23–26} and by selective adsorption of nickel hexamine.^{27–34}

In the present paper, it is shown that Cu/SiO₂ samples prepared by selective adsorption at basic pH = 9 contain two types of supported Cu: grafted Cu^{II} ions and copper phyllosilicate. At lower pH, between 7 and 8.8, copper nitrate hydroxide (Cu₂(OH)₃(NO₃)₂) precipitates in solution. The presence of these two species is demonstrated by several techniques. The formation of copper phyllosilicate provides evidence for the role of silica as a reactant, and its formation mechanism will be discussed later in this paper.

The goal of this paper is also to investigate the influence of several preparation parameters on the copper loading and on the relative amount of the two Cu^{II} species. The preparation parameters investigated were the metal precursor concentration, the pH of the precursor solution, the solution/silica contact time, and the addition of ammonium nitrate to the precursor solution. It should be noted that in refs 12, 17, and 18 selective adsorption was performed without NH₄⁺ addition whereas in refs 14 and 15 NH₄⁺ was added to the precursor solution. It is generally reported that NH₄⁺ addition in the deposition step improves the final metal dispersion.³⁵ In addition, in the case of Ni/SiO₂ catalysts, it was shown that the addition of NH₄⁺ can inhibit the formation of nickel phyllosilicate.³⁶ In previous reports, ammonium is often called “competitor ion”; once again, we will avoid this term here because it conveys a probably unfounded hypothesis on the molecular mechanism of its action. One chief objective of this study was precisely to shed more light on the role of NH₄⁺, and the speciation of Cu^{II} was evaluated as a function of pH, in the presence and in the absence of NH₄⁺.

Experimental Section

1. Catalyst Preparation. The samples were prepared with a nonporous silica, Aerosil Degussa AD380 (*S*_{BET} = 380 m² g^{−1}; it may be noted that the AD380 surface area is smaller than that reported by the manufacturer (380 ± 30 m² g^{−1}). It was checked that the calibration of the BET equipment was correct). Commercial copper nitrate (Cu(NO₃)₂·3H₂O; 99.999% Aldrich) was used.

The samples were prepared from precursor solutions containing copper nitrate (0.2 and 0.025 M) and NH₃ (it will be shown later that most Cu^{II} is in the form of [Cu(NH₃)₄(H₂O)₂]²⁺ complexes). The pH was adjusted by addition of solutions of NH₃ to values higher than 9 to inhibit the precipitation of Cu^{II} from the solution as nitrate hydroxide. In some preparations, NH₄NO₃ was also added to the precursor solutions with various NH₄⁺/Cu^{II} molar ratios (denoted *r* = 0.12, 1, or 10). When the *r* value is not mentioned, it means that preparations were performed without addition of NH₄NO₃ (*r* = 0).

The color of the starting solutions was dark blue or pale blue, depending on the Cu concentration. After dissolution of the copper nitrate, 2.5 g of silica were suspended into 70 mL of

these solutions. This induced a slight pH decrease. The suspensions were continuously stirred at 25 °C in a closed thermostated vessel during variable times (15 min to 1 week). The suspensions were then centrifuged. The supernatants arising from the 0.2 M exchange solutions were still dark blue, while those arising from the 0.025 M solutions were very pale blue. The samples were then washed for 10 min with 50 mL of distilled water and then centrifuged. This washing procedure was repeated four times. All of the supernatants of the 0.025 M preparations were colorless. For the 0.2 M preparations, only the last supernatant was colorless. The samples were then dried at room temperature. We checked that, in contrast with the impregnation method,¹³ the drying temperature, RT or 100 °C, has no influence on the nature of the supported phase and on the metal particle size after reduction. The samples are hereafter referred to as Cu_{*x*}M where *x* stands for the copper concentration of the precursor solution (in mol L^{−1}).

Copper phyllosilicate, also called chrysocolla, was used as a reference for the characterization of the Cu/SiO₂ samples. It was synthesized by A. Decarreau (HydrASA, URA 721 CNRS, Université de Poitiers, France) according to a hydrothermal process described in ref 37.

2. Techniques. The chemical analyses were performed by inductive coupling plasma in the CNRS Center of Chemical Analysis (Vernaison, France). In the following, the Cu weight loading of the samples is expressed in wt % of Cu per gram of sample calcined in air at 1000 °C:

$$\text{wt \% Cu} = \frac{m_{\text{Cu}}}{m_{\text{CuO}} + m_{\text{SiO}_2}} 100$$

X-ray diffraction (XRD) patterns were recorded on a Siemens diffractometer (D500) using Cu Kα radiation. Phase identification was performed by comparison with the tabulated Joint Committee on Powder Diffraction Standards (JCPDS) d-spacing files.

For the IR characterizations, the samples were finely ground and dispersed in KBr to make pellets. IR spectra were recorded at room temperature using a Bruker FTIR Vector 22 spectrometer equipped with a DTGS detector. The spectral resolution was 4 cm^{−1}, and 20 scans were recorded for each spectrum.

Electron spin resonance (ESR) spectra of Cu^{II} (d⁹, *I* = 3/2) were recorded at 77 K on a Bruker ESP 300 spectrometer operating at 9.3 GHz (X band). A field modulation of 100 MHz, a modulation width of 10 G, and a microwave power of 10 mW were used.

After drying, the samples were reduced by temperature-programmed reduction (TPR) in home-built equipment from room temperature to 700 °C with a heating rate of 7.5 °C min^{−1} under 5% v/v H₂ in argon (25 mL min^{−1}). Some of the samples were reduced after calcination under dry oxygen at 450 °C for 14–18 h.

The average size of the metal copper particles obtained after reduction by TPR was measured from the electron micrographs obtained by transmission electron microscopy (TEM, JEOL 100 CXII). Depending on the samples, 600–1700 particles were counted. The detection limit of the particles is ~10–15 Å. The average particle diameter was inferred from the following formula: $d_m = \sum n_i d_i / \sum n_i$, where *n_i* is the number of particles of diameter *d_i*. The standard deviation was calculated from the formula $\sigma = [(\sum (d_i - d_m)^2) / \sum n_i]^{1/2}$.

The BET surface area measurements were performed with Micromeritics ASAP 2010 equipment after sample evacuation at 250 °C overnight.

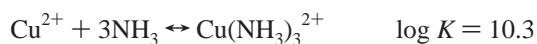
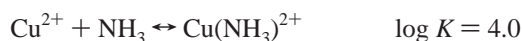
The speciation of the various Cu^{II} complexes (ammine, aqua, ammine–aqua complexes and hydroxo complexes) in a copper nitrate solution (0.2 M) was calculated for various pH's using the program ChemEQL.³⁸ The pH was varied by addition of NH₃. The influence of the addition of NH₄⁺ (2 M, which corresponds to $r = 10$ for the Cu0.2M preparations) on the Cu^{II} speciation was also investigated. The theoretical curves were calculated without taking into account hydroxynitrate precipitation because of the lack of equilibrium data for this reaction, and in the region of intermediate pH values, they correspond to solutions supersaturated with respect to this phase. However, as already mentioned, in the range of pH higher than 9, which is relevant for our preparations, precipitation is not observed.

In addition to the autoprotolysis of water, the following equilibria were taken into account in our calculations:

Ammonium Deprotonation



Cu^{II} Ammine Complexes Formation



Cu^{II} Hydroxide Complexes Formation



Dimerization



(log K values taken from the standard ChemEQL library).

As usual, water ligands are not written explicitly in the above equations so that, for instance, “Cu(NH₃)²⁺” should be understood as the [Cu(NH₃)(H₂O)₅]²⁺ complex assuming six coordination. Also, mixed (NH₃)/OH[−] complexes (such as [Cu(NH₃)(H₂O)₄(OH)]⁺) are not considered as separate species.

Results

1. Characterization of Supported Copper Phyllosilicates.

a. XRD. The XRD pattern of sample Cu0.2M (Figure 2b) prepared at pH 11 mainly shows the same features as amorphous silica (Figure 2a), that is, one broad diffusion line centered at $\theta = 22^\circ$, $d \approx 4$ Å, with perhaps very weak lines at higher θ . In samples prepared at pH 9 (Figure 2c,d), these weak lines are more clearly apparent and may be due to the presence of copper phyllosilicate: the diffraction pattern of reference bulk copper phyllosilicate (chrysocolla) shown in Figure 2e is consistent with that published in ref 20 (in contrast to nickel phyllosilicates,^{25,32} the copper phyllosilicate used as reference, even though synthesized under optimal conditions at 120 °C, is ill-crystal-

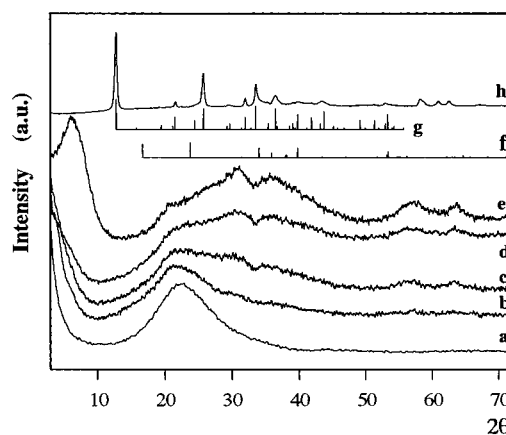


Figure 2. XRD diffractograms of (a) AD380 silica, (b) Cu0.2M ($r = 0$, pH = 11, adsorption time = 24 h, washed with water and dried at 25 °C), (c) Cu0.2M ($r = 0$, pH = 9, adsorption time = 24 h, washed with water and dried at 25 °C), (d) Cu0.2M ($r = 0$, pH = 9, adsorption time = 1 week, washed with water and dried at 25 °C), (e) bulk chrysocolla, (f) copper hydroxide, JCDPS file 80-0656, (g) copper nitrate hydroxide, Cu₂(OH)₃(NO₃), JCDPS file 15-0014, and (h) copper nitrate hydroxide obtained by precipitation of copper nitrate with ammonia.

TABLE 1: Frequencies of Structural Groups in Bulk Cu Lamellar Compounds

sample	δ_{OH} (cm ^{−1})	ν_{NO_3} (cm ^{−1})	ν_{SiO} (cm ^{−1})
Cu(OH) ₂	938 694		
Cu ₂ (OH) ₃ (NO ₃)	880 784 677	1422 1384 1349 1048	
Cu ₂ Si ₂ O ₅ (OH) ₂ (chrysocolla)	670		1027

lized). Line assignments are based on ref 20; broad and intense lines are observed at 12.2 (001) and 15.2 Å (nonattributed) and weak and broad lines at 4.4 (040), 2.8 (060), 2.5 (070), 1.6 (01,10), and 1.4 Å (01,20). It may be noted that in our Cu/SiO₂ samples, the (001) line of chrysocolla is absent while the ($hk0$) lines and (hk) bands may be present; in addition, the lines of Cu(OH)₂ and of copper nitrate hydroxide (Figure 2f,g) are absent even from the XRD patterns of the Cu0.2M samples (Figure 2b–d).

b. IR Spectroscopy. Cu(OH)₂, copper nitrate hydroxide, and copper phyllosilicate exhibit a lamellar structure and have structural OH groups. The structure of the nitrate hydroxide salt is derived from that of Cu(OH)₂ with 1/4 of the OH groups of Cu(OH)₂ replaced by O atoms of the nitrate ions.³⁹ IR spectroscopy is well-adapted to discriminate between these three lamellar compounds the spectra of which are shown in Figure 3. Cu(OH)₂ exhibits two δ_{OH} bands characteristic of structural hydroxyl groups at 938 and 694 cm^{−1} (Figure 3a), whereas chrysocolla is characterized by a single δ_{OH} band at 670 cm^{−1} and a strong ν_{SiO} band of SiO₄ tetrahedra at 1027 cm^{−1} (Figure 3b).⁴⁰ The spectrum of copper nitrate hydroxide shows three δ_{OH} bands of structural hydroxyl groups at 677, 784, and 880 cm^{−1} and four sharp bands corresponding to molecular vibrations of nitrate ions at 1048, 1349, 1384, and 1422 cm^{−1} (Figure 3c). Table 1 summarizes the frequencies of these structural OH and NO₃ groups.

For silica-supported copper materials, the discrimination between copper hydroxide and copper phyllosilicate can be made from the frequencies of the δ_{OH} bands and the presence

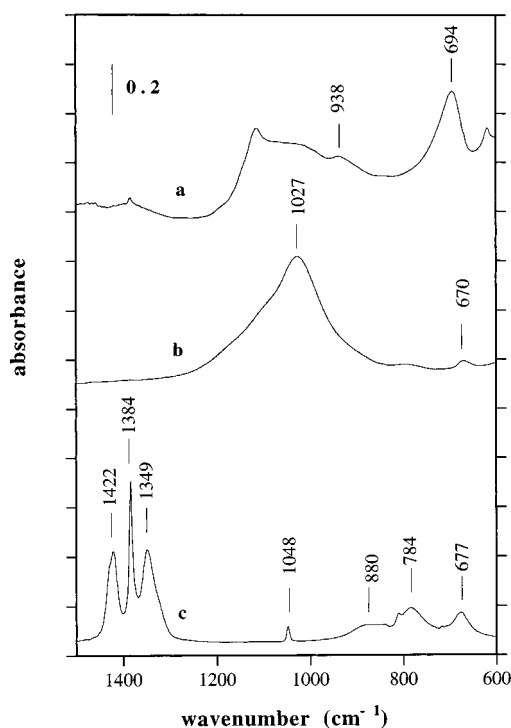


Figure 3. FTIR spectra of (a) commercial copper hydroxide, (b) bulk chrysocolla, and (c) copper nitrate hydroxide obtained by precipitation of copper nitrate with ammonia.

or absence of ν_{SiO} bands. The presence of copper nitrate hydroxide would translate in strong and sharp NO_3 bands. In fact, in the spectra of Cu0.2M samples prepared at various pH's, the presence of supported copper phyllosilicate is attested by the δ_{OH} band at $\sim 670 \text{ cm}^{-1}$ and the ν_{SiO} shoulder at $\sim 1040 \text{ cm}^{-1}$ on the low-frequency side of the asymmetric stretching ν_{SiO} band of silica at 1100 cm^{-1} (Figure 4). The IR spectra of Cu0.2M samples shown in Figure 4 and discussed later on clearly show that copper phyllosilicate forms in these samples and not copper hydroxide or copper nitrate hydroxide.

The relative amount of supported phyllosilicate in these samples can be evaluated by considering the integrated intensity of the δ_{OH} band at 670 cm^{-1} normalized to the integrated intensity of the symmetric ν_{SiO} band of amorphous silica at 800 cm^{-1} , which we will call I_{670}/I_{800} . The intense asymmetric ν_{SiO} band at 1100 cm^{-1} cannot be taken into consideration because it overlaps the ν_{SiO} band of the phyllosilicate at $\sim 1040 \text{ cm}^{-1}$. The I_{670}/I_{800} ratio only gives a qualitative evaluation of the amount of copper phyllosilicate because the extinction coefficients of the corresponding IR bands are not known (Table 2). The accuracy of the measurement of the integrated intensities is estimated to $\pm 15\%$. As for the Cu0.025M sample prepared at pH 11, it only exhibits very weak bands of copper phyllosilicate (not shown).

c. ESR Study. The ESR spectrum of Cu0.2M recorded at 77 K exhibits two superimposed signals, a very broad isotropic one (peak-to-peak line width, $\Delta H_{\text{pp}} > 2700 \text{ G}$) and a much thinner and stronger signal at $g \approx 2$ (Figure 5a). According to a previous ESR study,¹⁶ the thin signal arises from isolated Cu^{II} species grafted on the silica surface, $(\equiv\text{SiO})_2\text{Cu}(\text{NH}_3)_2(\text{H}_2\text{O})_2$. The broad signal is assigned to supported copper phyllosilicate by comparison with the spectrum of bulk chrysocolla, which shows the same broad isotropic signal (Figure 5b). It cannot be attributed to the signal of copper nitrate hydroxide, which is much thinner (Figure 5c).

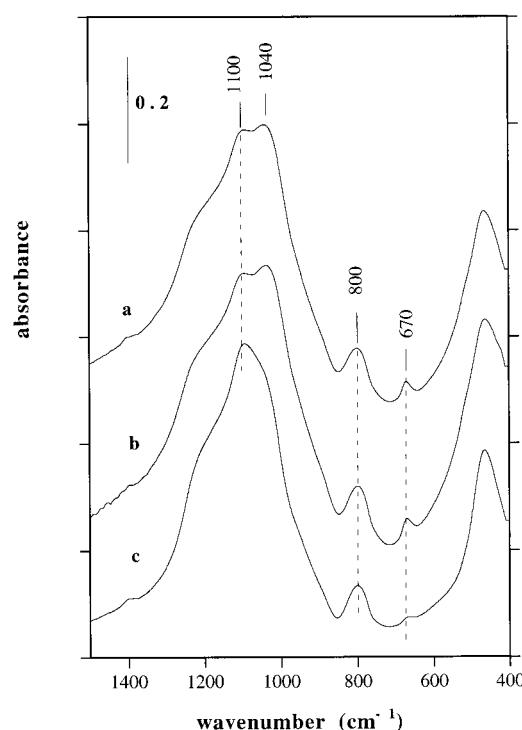


Figure 4. FTIR spectra of Cu0.2M samples prepared without added NH_4^+ ($r = 0$) as a function of the pH of the exchange solution (adsorption time = 24 h, washed with water and dried at 25°C): (a) pH 9; (b) pH 10; (c) pH 11.

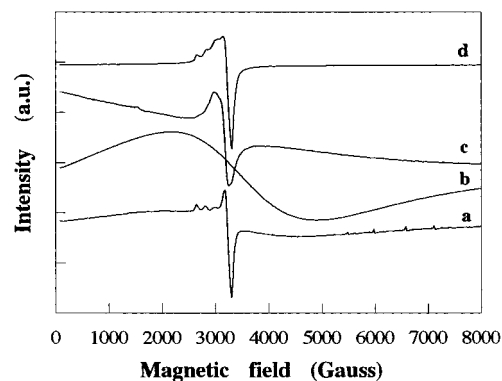


Figure 5. ESR spectra recorded at 77 K of (a) Cu0.2M ($r = 0$, pH = 11, adsorption time = 24 h, washed with water and dried at 25°C), (b) bulk chrysocolla, (c) copper nitrate hydroxide, and (d) Cu0.2M ($r = 10$, pH = 11, adsorption time = 24 h).

The ESR spectrum of the Cu0.025M sample also exhibits these two signals, attesting the presence of isolated copper species and of copper phyllosilicate, which were not detectable by XRD and hardly by IR spectroscopy.

2. Parameters Influencing the Amount of Supported Copper Phyllosilicate. *a. Influence of the Solution pH.* Table 2 and Figure 4 show the influence of the pH of the precursor solution on the copper loading and the amount of supported copper phyllosilicate for the Cu0.2M series. The copper loading is the same for samples prepared at pH 9 and 10 ($\sim 26 \text{ wt } \%$), but it is lower for the sample prepared at pH 11 ($15 \text{ wt } \%$). The amount of copper phyllosilicate (IR bands at ~ 670 and $\sim 1040 \text{ cm}^{-1}$, Figure 4) estimated from the I_{670}/I_{800} ratio follows the same evolution. These results are confirmed by XRD. The XRD pattern of Cu0.2M prepared at pH 9 (Figure 2c) exhibits more visible lines of copper phyllosilicate than that prepared at pH 11 (Figure 2b).

TABLE 2: Influence of the Preparation Parameters on the Copper Loading and the Amount of Supported Copper Phyllosilicate

samples	preparation parameters	Cu loading (wt %) ^a	relative amount of copper phyllosilicate, I_{670}/I_{800} ^b	BET surface area (m ² g ⁻¹)
silica AD380				315 ^c
Cu0.2M, $r = 0$, contact time = 24 h, water-washed, dried at 25 °C	pH of the exchange solution			
	9	26.3 (22.4)	0.15	
	10	26.2	0.16	
Cu0.2M, $r = 0$, pH 9, water-washed, dried at 25 °C	11	14.8	0.04	
	time of contact			
	15 min	16.2	0.01	
	2 h	19.7	0.06	190
	24 h	26.3 (22.4)	0.15	405
	1 week	36.6	0.30	175
Cu0.2M, $r = 0$, pH 9, contact time = 24 h, dried at 25 °C	initial pH of the washing solution ^d			
	6 (water)	26.3 (22.4)	0.15	
	11	24.9 (26.2)	0.14	
Cu0.2M, pH 11, contact time = 24 h, water-washed, dried at 25 °C	r			
	0	14.8	0.040	
	0.12	11	0.035	
	10	4.1 (4.3)	0	180 (190)
Cu0.025M, pH 11, contact time = 24 h, water-washed, dried at 25 °C	0	4.5	0.007	
	1	4.2	0	

^a The preparations are reproducible; the copper loadings of samples prepared under the same conditions are given in parentheses. ^b The accuracy of the measurement of the integrated intensities is estimated to $\pm 15\%$. ^c It may be noted that the AD380 surface area is smaller than that reported by the manufacturer ($380 \pm 30 \text{ m}^2 \text{ g}^{-1}$). ^d The pH of the water solution increased to 9 during washing.

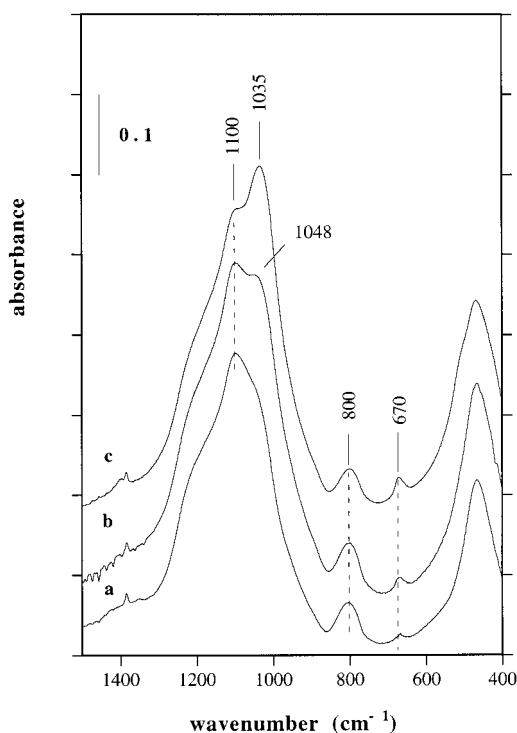


Figure 6. FTIR spectra of Cu0.2M samples prepared without added NH_4^+ ($r = 0$) at pH 9 as a function of the silica/solution time of contact and then washed with water and dried at 25 °C: (a) 2 h; (b) 24 h; (c) 1 week.

b. Influence of Solution/Silica Contact Time. To investigate the kinetics of formation of copper phyllosilicate, the evolution of the amount of copper phyllosilicate formed was followed as a function of contact time for Cu0.2M samples prepared at pH 9. Table 2 and Figure 6 show that the copper loading and the amount of copper phyllosilicate (I_{670}/I_{800}) increase with the time of contact; the correlation between these two parameters is very good. Between 24 h and 1 week of contact time, the IR spectra

(Figure 6b,c) show that the ν_{SiO} shoulder characteristic of copper phyllosilicate (1035 cm^{-1}) has become higher in intensity than the ν_{SiO} band of silica (1100 cm^{-1}); the XRD pattern of the latter sample also shows stronger bands of copper phyllosilicate (Figure 2c,d).

c. Influence of the pH of the Washing Solutions. Whatever the pH of the precursor solution, when the Cu0.2M samples are washed with water, the pH of the washing solution, initially equal to 5–6 (distilled water), increases to pH 9–10 and remains at these values during successive washings. When an ammoniacal solution at pH 11 is used for the washings, the copper loadings do not significantly change (Table 2).

d. Influence of NH_4^+ Addition. The influence of added NH_4^+ was investigated for the Cu0.2M and Cu0.025M samples prepared at pH 11, as in most previous works.^{14,15,17,18} The amount of ammonium nitrate was adjusted so that r , the $\text{NH}_4^+/\text{Cu}^{\text{II}}$ molar ratio, was equal to 0.12 or 10 in the 0.2 M solutions and to 1 in the 0.025 M solutions. In the Cu0.2M samples, for $r = 0.12$, the copper loading and the amount of copper phyllosilicate seem to slightly decrease with respect to $r = 0$. For $r = 10$, copper phyllosilicate is no longer detected by IR and the copper loading decreases to 4 wt %. In the Cu0.025M samples, copper phyllosilicate, present only as traces in IR spectra when $r = 0$, is not observed anymore for $r = 1$ (spectra not shown).

The absence of copper phyllosilicate is even more evident in the ESR spectra because neither the spectrum of Cu0.2M, $r = 10$, nor that of Cu0.025M, $r = 1$ (Figure 5d), exhibits the broad line characteristic of copper phyllosilicate, which was visible in the samples prepared with $r = 0$ (Figure 5a). Only the signal corresponding to grafted Cu^{II} ions is observed.

To rationalize these findings, we have evaluated Cu^{II} speciation in the various precursor solutions. Because pH is regulated by NH_3 addition, it is no surprise to find that complexes with increasing numbers of ammine ligands come to predominate as the pH increases, going from $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ at the most acidic pH to $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ at the most basic pH. The addition of NH_4^+ shifts the predominance region of

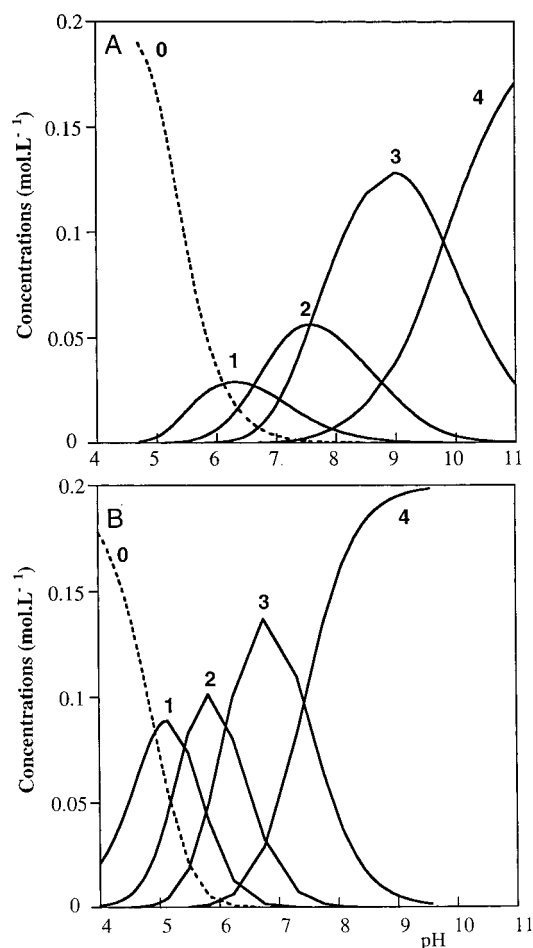


Figure 7. Cu speciation in the 0.2 M solution (A) in the absence of NH₄⁺ versus pH and (B) in the presence of NH₄⁺ 2 M (which corresponds to $r = 10$). The 0 stands for [Cu(H₂O)₆]²⁺, 1 for [Cu(NH₃)(H₂O)₅]²⁺, 2 for [Cu(NH₃)₂(H₂O)₄]²⁺, 3 for [Cu(NH₃)₃(H₂O)₃]²⁺, and 4 for [Cu(NH₃)₄(H₂O)₂]²⁺.

the ammine complexes toward lower pH's. Once again, this was expected because the ammonium deprotonation equilibrium (NH₄⁺ → NH₃ + H⁺) provides NH₃ ligands. Figure 7 compares the Cu^{II} speciations in a 0.2 M Cu solution as a function of pH, for $r = 0$ (Figure 7A) and $r = 10$ (Figure 7B). In the absence of added NH₄⁺ ($r = 0$), three different ammine complexes are significant in the pH range of our preparations ([Cu(NH₃)₂(H₂O)₄]²⁺, [Cu(NH₃)₃(H₂O)₃]²⁺, and [Cu(NH₃)₄(H₂O)₂]²⁺); in contrast, for $r = 10$, [Cu(NH₃)₄(H₂O)₂]²⁺ is overwhelmingly predominant between pH = 9 and 11.

Cu^{II} speciation, however, not only involves ammine/aqua complexes but also involves hydroxo complexes. As shown in Figure 8A, the latter can represent a significant fraction of the total Cu; in particular, for [Cu] = 0.2 M and $r = 0$, the predominant species at pH = 6–7.5 is expected to be the dimer [Cu₂(OH)₂(H₂O)₈]²⁺, while the neutral monomer [Cu(OH)₂(H₂O)₄]⁰ accounts for 2–3% of total Cu at pH = 9–10. Adding NH₄⁺ ($r = 10$) results in a dramatic suppression of all hydroxide-containing complexes and a shift of their concentration maximum to lower pH. For instance, for $r = 10$, the maximal [Cu(OH)₂(H₂O)₄]⁰ concentration never exceeds 5×10^{-6} M (at pH = 5.9) and falls down to 10^{-18} M at pH = 9 (compare with 5×10^{-3} M at pH = 9 for $r = 0$).

3. Metal Particle Size. After reduction by TPR up to 700 °C, copper in the Cu0.2M and Cu0.025M samples is fully reduced as indicated by the absence of Cu^{II} signal by ESR

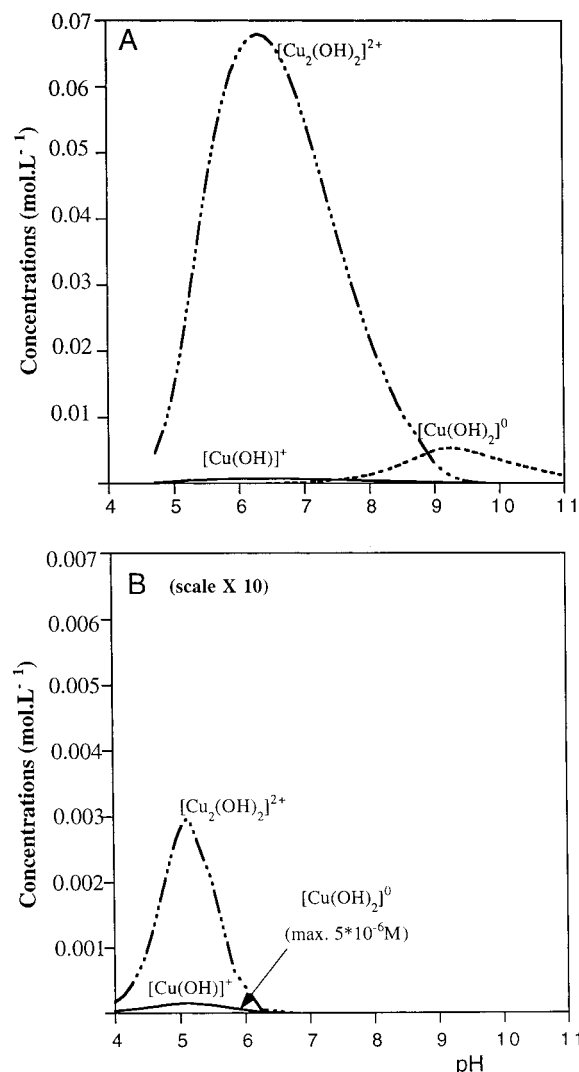


Figure 8. Cu speciation ([Cu(OH)(H₂O)₅]⁺, [Cu(OH)₂(H₂O)₄]⁰, and [Cu₂(OH)₂(H₂O)₈]²⁺) in the 0.2 M solution (A) in the absence of NH₄⁺ and (B) in the presence of NH₄⁺ 2 M (which corresponds to $r = 10$) versus pH.

spectroscopy and of Cu^I ions by photoluminescence. The electron micrographs of the reduced samples show well-dispersed metal particles of which the average sizes and size distribution are reported in Table 3. For all samples, the average particle size is small, between 27 and 45 Å. It may be noted that the differences in the average particle size and size distribution are difficult to correlate with the parameters of the preparation. It is not clear whether the differences are significant. Indeed, Table 3 also shows that the number of particles measured is different from one sample to another and that the values for the standard deviations are rather high for some samples. The most relevant results are the following: (i) the average particle size does not increase with the copper loading from 4 to 36 wt %; (ii) the average particle size does not vary significantly when the samples are calcined before reduction.

In a former paper,⁶ we showed that copper metal particles are small when Cu^{II} is in strong interaction with a silica support before reduction. This is the case when Cu^{II} is grafted or involved in copper phyllosilicate, that is, when the Cu^{II} species are bonded to SiO₂ surface or inserted in a silicate layer (Figure 1). It was also reported that calcination at 450 °C does not strongly modify the state of the Cu^{II} species: copper phyllosilicate is almost not decomposed⁶ and grafted Cu^{II} species lose

TABLE 3: Influence of the Preparation Conditions of the Cu/SiO₂ Samples on Their Metal Particle Size Measured after Reduction by TPR up to 700 °C

samples	preparation conditions	<i>r</i>	Cu loading (wt %)	thermal treatment (°C)	average particle size (Å)	size distribution (Å)	standard dispersion (Å)	number of particles
Cu0.025M	pH 11, 24 h	0	4.5	25	38	21–96	11	707
				450	36	21–106	10	822
Cu0.025M	pH 11, 24 h	1	4.2	25	37	16–85	12	985
				450	38	15–99	13	626
Cu0.2M	pH 11, 24 h	0	11	25	43	16–118	16	1407
				450	43	15–155	21	458
Cu0.2M	pH 11, 24 h	10	4.1	25	32	11–132	12	612
				450	27	11–69	8	673
Cu0.2M	pH 9, 24 h	0	26.3	25	35	15–98	12	1092
				450	30	15–70	8	1719
Cu0.2M	pH 9, 1 week	0	36.6	25	45	15–150	20	1398

their NH₃ ligands, which are later replaced by H₂O ligands on exposure to air.¹⁶ This explains the fact that, whatever the copper loading and whether a calcination treatment is performed before TPR, the particle size remains small. The same type of result was also obtained for Ni/SiO₂ samples prepared by deposition–precipitation with urea.⁴¹ This method leads to the formation of supported nickel phyllosilicate. After reduction, the samples contain particles of about the same average size, 47–53 Å for Ni loadings between 5 and 25 wt %.

Discussion

1. Identification of the Cu-Supported Phases. First, it must be noted that the copper loading in the Cu0.2M samples prepared without added NH₄⁺ (*r* = 0) (Table 2) exceeds the exchange capacity of silica. Indeed, in the case of purely electrostatic adsorption, each [Cu(NH₃)₄(H₂O)₂]²⁺ complex should compensate 2 SiO[−] surface groups. The silanol site density is reported by the manufacturer to be equal to 2.5 OH nm^{−2}.⁴² On the basis of IR data coupled with deuteration and surface functionalization. Other authors claim, from IR/deuteration and thermogravimetric results, that silanol densities are fairly constant for all kinds of silica at about 5 OH nm^{−2}.⁴³ ²⁹Si NMR of the AD380 silica that we used as support, through quantification of the Q³ and Q⁴ signals, seems to favor the latter figure.⁴⁴ One can thus calculate that the maximum cation exchange capacity of the silica surface would correspond to a copper loading of ~5 or ~10 wt %, depending on which figure is accepted. These values definitely lie under the Cu experimental loadings of the Cu0.2M samples (Table 2) (the discrepancy is no doubt even more significant because the maximum loadings reported are based on the hypothesis that all silanol groups are ionized, which is unlikely even at pH 11).

Second, two kinds of copper species were identified in the Cu samples after drying: copper phyllosilicate and grafted copper ion (≡SiO)₂Cu(NH₃)₂(H₂O)₂. Supported copper phyllosilicate the formation of which has already been reported in ref 6 is more extensively characterized by IR, XRD, and ESR in this paper. Grafted Cu^{II} ions, the presence of which is detected by ESR (Figure 5a), were deeply characterized by ESR, UV, and EXAFS in ref 16. According to this former study, Cu^{II} is initially in electrostatic interaction with two SiO[−] groups and is grafted during the drying step at 25 °C. It must be noted that our preparation conditions at pH = 9 exclude the formation of copper nitrate hydroxide because we observed experimentally that this compound precipitates at 7 < pH < 8.8.

When deposition is carried out in the presence of added NH₄⁺ (pH 11, *r* = 10), copper phyllosilicate is not formed, and the copper loading is 4.1 wt % (Table 2). It can be assumed that

this sample does not contain other Cu species than grafted Cu^{II} species because the copper loading is smaller than the theoretical value reported above (~5 or ~10 wt %).

This study also shows that the proportion of copper phyllosilicate depends on several parameters of preparation: the pH of the precursor solution, the silica/solution contact time, and the addition of NH₄⁺ (Table 2). Phyllosilicate formation is inhibited by the addition of NH₄⁺. In the absence of added NH₄⁺, the amount of copper phyllosilicate increases with the time of contact (Table 2). The highest amount of copper phyllosilicate is obtained when the precursor solution is at pH 9 or 10. At pH 11, both the copper loading and the *I*₆₇₀/*I*₈₀₀ ratio are lower, which indicates that less copper phyllosilicate is formed.

It may be noted that the copper loading of the Cu0.025M sample is the same in the presence (4.2 wt %) or in the absence (4.5 wt %) of added NH₄⁺ (Table 2). This is due to the fact that almost all of the copper of the solution is deposited on the silica. Indeed, the solution is almost colorless after deposition; quantitative Cu deposition would correspond to a maximum copper loading of 4.4 wt % (or 4.9 wt % if one assumes that silica contains 10% of water).

Now, our results can be compared with those of Kohler et al.^{13,18} These authors have reported that their Cu/SiO₂ samples prepared at pH 11 without added NH₄⁺ and washed with water contain both ion-exchanged copper (~0.9 wt %) and Cu(OH)₂ (1–10 wt % depending on the concentration of the Cu solution, 0.025–0.2 M). They claim that Cu(OH)₂ precipitates during the washing step with water because the Cu amount is lower when the sample is washed at pH 11 (NH₃ solution) and higher when it is washed at pH 7 (distilled water). Excess Cu^{II}, initially present as the [Cu(NH₃)₄(H₂O)₂]²⁺ complex, would precipitate when contacted with a low-pH washing solution. This is dubious because distilled water has no buffering capacity; contact with the washing solution is then a simple dilution, the effect of which would not cause precipitation. It would be more likely to hypothesize that Cu(OH)₂ is formed initially during the deposition step and can then be redissolved by the NH₃-containing high-pH washing solution. However, even the nature of the precipitated phase is open to doubt: the formation of copper hydroxide was not directly proven by Kohler et al. because they did not characterize the samples after drying but after calcination. They merely assessed that the presence of large particles of CuO observed by TEM arises from calcination of Cu(OH)₂.

We believe that the formation of copper hydroxide is indeed unlikely because, according to Tarte,⁴⁵ when ammonia reacts with a Cu salt, it gives rise to the precipitation of the basic salt and not to copper hydroxide. To check this point, copper was

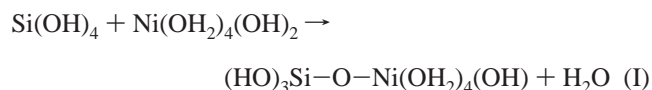
precipitated at pH 7.4 by addition of NH_3 to a solution of copper nitrate. The dried precipitate was identified by XRD (Figure 2g) and IR (Figure 3c) as a nitrate hydroxide.

Now, the question that logically follows is could the precipitated Cu in Kohler's samples be copper phyllosilicate? The answer is no. Indeed, our results are different from those described by Kohler et al.¹² (i) The copper loading in our samples remains the same whether the washing solution is water (pH 6) or ammonia solution (pH 11), and the I_{670}/I_{800} ratio is also almost the same (Table 2); this indicates that copper phyllosilicate is preformed and is not dissolved at high pH. Control experiments showed that the reference bulk chrysocolla could not be leached with an ammonia solution at pH 11, confirming this point. (ii) Washing the samples with water always led in our hands to basic supernatants (pH between 9 and 10 even in the last one, which was colorless; this indicates that although Cu ammine complexes were not released any more, free NH_3 continued to be released). Kohler et al. observed a neutral pH in the last supernatant.

For some unclear reasons, the phenomena observed by Kohler et al. and by us are different. However, the lack of identifiable copper phyllosilicate is possibly due to kinetic limitations: their samples were equilibrated with exchange solutions at pH 11 for 5 h only. This corresponds to a copper loading of 5–6 wt %, which makes copper phyllosilicate detection difficult.

2. Influence of NH_4^+ on Copper Phyllosilicate Formation.

A molecular mechanism explaining the formation of supported nickel phyllosilicate during the preparation of Ni/SiO₂ samples by deposition–precipitation was previously proposed by us.²⁶ The mechanism is based on the dissolution of silica in basic Ni-containing solution and its reprecipitation as nickel phyllosilicate. Silicic acid released in solution reacts with hydrolyzed nickel complexes containing H₂O and OH ligands through a reaction of heterocondensation of the oxolation-type, which leads to the formation of Si–O–Ni bridges:



Then, these entities polymerize and form nickel phyllosilicate onto the silica surface.

The same type of reaction probably occurs in our $\text{Cu}^{\text{II}}/\text{NH}_3/\text{SiO}_2$ systems. The events taking place upon contact of the precursor solution with the silica support would then include the following: (i) buildup of a negative surface charge on silica particles due to the high pH (fast); (ii) electrostatic adsorption of Cu-containing complex cations to compensate the surface charge (fast); (iii) eventually, silica dissolution and inception of copper phyllosilicate formation by reaction of dissolved silicic acid with some Cu^{II} complexes (slow).

We must now consider how NH_4^+ addition affects this sequence of events. It has been claimed before (see Introduction) that the use of a “competitor” ion in “ion exchange” preparations is especially useful when one tries to obtain low loadings of metal homogeneously distributed on an oxide support with a large surface area.³⁵ In a study on the preparation of Ni/SiO₂ materials by the so-called “competitive ion exchange” with nickel ammine complexes,³⁶ Carriat studied the influence of solution pH (7–10.5) and of NH_4NO_3 concentration (0.3–1 M) on the formation of nickel phyllosilicate. For samples prepared at pH 8.3, he showed that the amount of Ni in the samples increases when the concentration of NH_4NO_3 decreases because of the formation of increasing amounts of nickel phyllosilicate. In other words, NH_4^+ inhibits the formation of nickel phyllo-

silicates, just like it inhibits the formation of copper phyllosilicates in the present work.

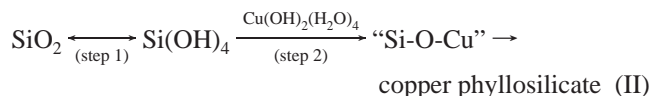
One possible rationalization of this effect of NH_4^+ addition could be that this ion prevents nickel phyllosilicate formation by inhibiting silica dissolution. Several factors are known to affect silica dissolution. Nucleophiles catalyze silica dissolution;⁴⁶ according to Stumm,⁴⁷ (anionic) ligand adsorption increases the dissolution rate of oxides or silicates while cation adsorption has an opposite effect. This is only a general trend. More precisely, Dove⁴⁸ showed that alkaline ions increase the rate of silica dissolution, whereas multivalent ions such as Zn^{2+} , Cu^{2+} , Al^{3+} , and Fe^{3+} inhibit dissolution. To the best of our knowledge, there are no data concerning silica dissolution in the presence of NH_4^+ . However, one can qualitatively compare alkali cations with NH_4^+ : Li^+ and Na^+ are small cations with a localized positive charge, which allows them to easily approach a negatively charged silica surface, to adsorb, to weaken the Si–O–Si bondings and thus to favor silica dissolution. In contrast, NH_4^+ is a much larger cation (1.43 Å against 0.68 for Li^+ and 0.97 Å for Na^+) of which the positive charge is therefore less localized. In consequence, when it approaches the silica surface, it is less strongly adsorbed, and therefore, silica dissolution is less favored.

Cu^{II} speciation in the presence or absence of NH_4^+ may provide a more immediately understandable explanation of the inhibition of phyllosilicates formation by ammonium ions. Figures 7 and 8 show that the Cu^{II} speciation is very different in the presence and in the absence of NH_4^+ , as discussed in the results section. In particular, we have noted that the main species is $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ for pH = 9 and $r = 10$ (Figure 7B), while the $[\text{Cu}(\text{OH})_2(\text{H}_2\text{O})_4]^0$ ion is strongly disfavored by NH_4^+ addition in this pH range (Figure 8B).

The formation of phyllosilicates requires the presence of OH bridging ligands in the copper complex (eq I), which participate in heterocondensation reactions. This is the reason that the tetraammine copper complex, which only has nonbridging NH_3 ligands, cannot be involved in the formation of phyllosilicates. Strong chelating ligands such as ethanediamine also inhibit their formation, for the same reason.³⁰ In addition, it is generally considered that only neutral complexes can condense infinitely to give a solid phase, whereas charged precursors give only polycations.⁴⁹ Only the $[\text{Cu}(\text{OH})_2(\text{H}_2\text{O})_4]$ complex is zero-charged, and it contains two OH bridging ligands. Therefore, it can be considered as a good candidate for participation in the nucleation stage in copper phyllosilicate formation. This complex exhibits a concentration maximum at pH 9 in the absence of NH_4^+ (Figure 8A), and it is indeed at this pH that the highest amount of phyllosilicate was obtained (Table 2). In the presence of NH_4^+ , the concentration of $[\text{Cu}(\text{OH})_2(\text{H}_2\text{O})_4]$ strongly decreases and its maximum shifts to lower pH (Figure 8B); consequently, copper phyllosilicate cannot form. This is in agreement with the experimental results performed at pH 11 (Table 2). An essentially similar explanation was proposed by Carriat for the Ni/ NH_3 /SiO₂ system mentioned above; actually, he proposed the charged complex $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ as the intermediate reacting with silicic acid in solution to form nickel phyllosilicate, rather than the neutral complex $[\text{Ni}(\text{OH})_2(\text{H}_2\text{O})_4]$, because the equilibrium constants for hydroxo complex formation are low in the case of Ni^{II} (significantly lower than for Cu^{II}); he did not exclude, however, that hydroxo complex might still play a significant role in the phyllosilicate formation mechanism.

It may be noted that, although the solubility of silica is lower at pH 9 than at pH 11,⁴⁶ the heterocondensation reaction of

Si(OH)₄ with the Cu(OH)₂(H₂O)₄ complex (0.005 M) occurs and the subsequent formation of copper phyllosilicate is favored.



“Si-O-Cu” represents an oligomer obtained by the condensation of silicic acid with a Cu^{II} neutral complex, of which the simplest formula could be (HO)₃Si-O-Cu(OH)₂(H₂O)₄, in analogy with the corresponding species postulated for nickel phyllosilicate formation (eq I above).

Equation II can help us to understand the difference between the two hypotheses proposed to explain the inhibitory effect of NH₄⁺ on phyllosilicate formation. The rate-limiting step might either be step 1, silica dissolution, in which case the ammonium ion would act as a dissolution retardating agent, or it might be step 2, phyllosilicate nucleation, in which case the rate of phyllosilicate formation is expected to be proportional to the concentration of neutral Cu complex (Cu(OH)₂(H₂O)₂). The effect of NH₄⁺ addition would then be easier to understand because Cu^{II} speciation calculations show that it strongly decreases Cu(OH)₂(H₂O)₂ concentration. This second hypothesis is more economical, and we tend to favor it until more data become available.

One could also wonder whether the lower amount of copper phyllosilicate at pH 11 (*r* = 0) than at pH 9 (*r* = 0) could be due to a phenomenon of silica ripening because of the higher pH favoring silica dissolution. To evaluate this hypothesis, a few BET measurements were performed, and their results are reported in Table 2. At pH 9, competing tendencies seem to be at work. First, after short preparation times, a decrease of about one-third is observed in the surface area. Then, for longer contact times, the surface area increases and passes through a maximum, while the formation of copper phyllosilicate continues to proceed. This evolution is not unreasonable: at low loadings, the phyllosilicate layers are probably isolated and their high surface area, on the order of 750 m²/g (calculated from structural data found in ref 50), increases the global surface area of the phyllosilicate/silica mixture; at higher loadings, on the other hand, phyllosilicate layers probably start to aggregate into stacks called “tactoids”, which have a much smaller exposed surface. However, this matter would necessitate further investigations. The results on samples prepared at pH 11 are most relevant for the question of ripening: in these conditions where no phyllosilicates are formed, a decrease in the surface area is observed, but it is definitely not more pronounced than for samples prepared at pH 9. Therefore, we do not believe that the lower amount of copper phyllosilicate at pH 11 (*r* = 0) than at pH 9 (*r* = 0) is due to a phenomenon of silica ripening.

A final word of caution is in order regarding the terminology of catalyst preparation. As already mentioned in the Introduction, the term “cationic exchange” used in the literature to designate the preparation procedure that we have followed is improper because it does not account for phenomena leading to the formation of phyllosilicates. Similarly, NH₄⁺ should not be designated as a “competitor ion”: in this work, we show that its role is not to act as a competitor for Cu^{II} complexes in ion exchange but rather is to act as an inhibitor of copper phyllosilicate formation. Hence, a distinction has to be observed between catalyst preparation procedures (macroscopic level) and processes occurring at the molecular level.⁵¹ It is often misleading to refer to preparation procedures by terms such as “cation exchange” and “competitor ion” that suggest untested molecular mechanisms.

Conclusion

We have examined the nature of the Cu^{II} species formed on a silica support during the particular procedure of Cu/SiO₂ preparation starting with an ammoniacal solution containing copper ammine complexes. The molecular mechanism for Cu^{II} deposition not only consists of cation adsorption but also involves the slow formation of copper phyllosilicate (chrysocolla) of which the amount depends on the copper concentration, the pH of the precursor solution, the solution/silica contact time, and the addition of NH₄⁺ ions to the solution. After drying, the adsorbed cations are grafted on the silica surface. Both Cu^{II} species, grafted Cu^{II} and copper phyllosilicate, lead to small metal particles after reduction.

We have tried to rationalize the effect of added NH₄⁺ ions. The most conspicuous effect is the suppression of phyllosilicate formation. This can easily be explained in the generally accepted model for phyllosilicate nucleation, if the rate determining step is condensation between dissolved silicic acid and neutral Cu^{II} complexes in solution: Cu^{II} speciation calculations show that the presence of NH₄⁺ strongly decreases the equilibrium concentration of such neutral Cu^{II} complexes (Cu(OH)₂(H₂O)₂).

Thus, empirically observed effects of preparation parameters can be rationalized by a careful consideration of events taking place at the molecular level. It is hoped that this work may stimulate further research to put supported catalyst preparation on a firm chemical basis.

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