

PREPARATION, CHARACTERIZATION AND ELECTROCHEMISTRY OF SYNTHETIC COPPER CLAYS

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Abstract—Hydrothermal treatment of aqueous mixtures of sodium hydroxide, copper chloride and excess sodium silicate ($\text{Si/Cu} \geq 2$) at 150 °C produced blue powders. Scanning electron microscopy/energy dispersive X-ray (SEM/EDX) analysis of the products show they all had similar chemical compositions, with Si/Cu ratios of approximately 1.33, the value expected for 2:1 trioctahedral phyllosilicates. Their X-ray diffraction (XRD) patterns were consistent with that of swelling smectite-type clays. Reaction mixtures that did not contain excess Si ($\text{Si/Cu} \leq 1.33$) did not produce smectites. They gave gray mixtures of amorphous silicates and copper oxides, with some phyllosilicates. A mixture containing a Si/Cu ratio of 5.2 heated at 250 °C under 500 psi of Ar gave a pale blue solid containing a Si/Cu ratio of approximately 1, the value expected for chrysocolla. Transmission electron microscopy (TEM) showed this product had a well-ordered layered structure. Its XRD powder pattern was consistent with that of chrysocolla. This clay did not swell very much on exposure to glycol vapors. Peaks were observed in the cyclic voltammogram of electrodes modified with films of these synthetic Cu-clays. They were attributed to electrochemical activity of Cu(II) centers in the lattice of the clays. The presence of these redox active Cu(II) sites greatly improved charge transport in the films. Much larger voltametric waves were observed for $[\text{Os}(\text{bpy})_3]^{2+}$ ions (“bpy” = the ligand 2,2′-bipyridyl) adsorbed in films of the synthetic Cu-clays than in films of a natural montmorillonite. The larger peak currents obtained corresponded to 10- to 15-fold increases in the fractions of the adsorbed ions that were electrochemically oxidizable in the modified electrodes.

Key Words—Chrysocolla, Clay-modified Electrodes, Copper Smectites, Cyclic Voltammetry, Synthetic Clay.

INTRODUCTION

We report here on the preparation of synthetic Cu-clays for use in electrode surface modifications. A major limitation of clay-modified electrodes (CMEs) is poor charge transport in the clay films. Natural clay minerals are not electronically conductive (Wang et al. 1989). Electron transport in CMEs depends on a combination of diffusion of adsorbed electroactive species through the films and electron hopping between the adsorbed species. The low mobility of ions in clay films means that only a small fraction of them can reach the conductive substrate to participate in the electrochemical reaction (King et al. 1987; Villemure and Bard 1990). Also, the electron transfer processes in CMEs do not actually occur in the clay interlayer spaces. To participate in the electrochemical reaction, the intercalated species must first diffuse out of the interlayer spaces (Shaw 1989). Thus, the opportunity to exploit the geometry of the gallery spaces is lost.

Electrochemically active transition metal centers in the clay lattices can function as relays in the charge transfer process in CMEs. Oyama and Anson (1986) reported that structural iron sites in natural montmorillonites could mediate the reduction of hydrogen peroxide. Electron transfer from Fe(II) has been proposed to account for the anomalously larger first anodic wave of $[\text{Ru}(\text{bpy})_3]^{2+}$ (Rudzinski and Bard 1986) and

$[\text{Fe}(\text{bpy})_3]^{2+}$ adsorbed in CMEs (Villemure and Bard 1990; Xiang and Villemure 1992). We have shown that redox active iron sites in a synthetic smectite could relay electrons between $[\text{Ru}(\text{NH}_3)_6]^{3+}$ and $[\text{Fe}(\text{bpy})_3]^{2+}$ ions coadsorbed in CMEs (Xiang and Villemure 1995). More recently, we found that electron transfer between $[\text{M}(\text{bpy})_3]^{2+}$ ($\text{M} = \text{Os}, \text{Fe}$ and Ru) cations adsorbed in films of synthetic Co-smectites, and redox active Co(II) sites in the clays resulted in large increases in the adsorbed ions' electroactive fractions, up to nearly unity in 1 case (Xiang and Villemure 1996a, 1996b).

Natural Cu-rich clays are not common. Chrysocolla, poorly ordered minerals containing $\text{Si/Cu} \approx 1$, are the only well-known Cu-rich phyllosilicates (Petit et al. 1995). Their precise crystal structure is not well established (Brindley 1980; Carriat et al. 1994). They are believed to have sepiolite or palygorskite chain-type structures with discontinuous octahedral Cu sheets (Van Oosterwyck-Gastuche 1970). Cu(II) complexes are subject to Jahn-Teller distortions. It has been proposed that this property of copper is not compatible with a regular clay structure (Decarreau et al. 1992; Petit et al. 1995). Octahedral sites occupied by Cu(II) in phyllosilicates are distorted, with Cu-O distances of 1.95 Å for the 4 in plan oxygens, and 2.32 Å (in smectites) or 2.41 Å (in chrysocolla) for the 2

apical oxygens (Mosser et al. 1990, 1992). The Cu content of natural smectites is limited to about 2% (Mosser et al. 1990; 1992). Copper in Cu-rich clays is usually preferentially found in the interlayer spaces (Ildéfonse et al. 1986).

Petit et al. (1995) reported the preparation of kaolinite-type clay containing up to 7% Cu(II) by a hydrothermal method at 250 °C. The Cu(II) appeared to be incorporated in the octahedral sheet of the kaolinite without major perturbation of the kaolinite structure. De Vynck (1980) reported the preparation of cupriforous talcs and micas by high-temperature hydrothermal treatment (≥ 400 °C) of mixtures of silica gel and $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$. At lower temperatures, copper oxide and unreacted starting material were obtained. To the best of our knowledge, the preparation of smectites containing only Cu has never been reported. Decarreau (1980, 1981, 1983, 1985) described the preparation of pure Zn, Ni, Co and Fe(II) trioctahedral smectites. However, reaction mixtures containing only Cu gave chrysocolla. Smectites were only obtained for reaction mixtures in which $\text{Cu}/(\text{Cu} + \text{Mg}) < 0.5$ (Decarreau et al. 1992).

We report here the preparation of pure Cu-smectites by hydrothermal treatment at 150 °C of mixtures of NaOH, CuCl_2 and Na_2SiO_3 containing Si/Cu ratios of 2 or more. Mixtures containing lower Si/Cu ratios did not produce smectites. At higher temperature (250 °C), a well-ordered layered material, believed to be a chrysocolla, was obtained. Preliminary results on the use of these synthetic Cu-clays for electrode modifications will also be presented.

EXPERIMENTAL

Preparation of the Cu-Clay

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ were obtained from Fisher Scientific (Fair Lawn, New Jersey.) All other chemicals were obtained from Aldrich (Milwaukee, Wisconsin) and used without further purification. The natural montmorillonite, STx-1 (Gonzales County, Texas) was obtained from the Source Clay Minerals Repository (University of Missouri, Columbia, Missouri). Its Na form was prepared, and its $< 0.2 \mu\text{m}$ (esd) fraction separated by literature procedures (Tanner and Jackson 1947; Jackson et al. 1949).

The reaction mixtures were prepared by dissolving enough $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ in 100 mL of distilled water to give solutions having silicate concentrations ranging from 0.025 M to 0.15 M. The pH of the solutions was adjusted to 3 with H_2SO_4 . Then 50.0 mL of a 0.050 M solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was added to give mixtures having Si/Cu ratios between 1 and 6. Next 3.0 M NaOH was added dropwise (50.0 mL, $\text{OH}^-/\text{Cu} = 15$). The dark blue mixtures were stirred at room temperature for 1 d, transferred to stainless steel cylinders and heated at 150 °C for 50 h.

One mixture, containing a Si/Cu ratio of 5.2, was transferred to a Pressure Product Industries locking autoclave, charged with 500 psi of Ar, and heated at 250 °C for 15 h with mechanical shaking.

The products were washed with distilled water to remove excess silicates (analysis of the product mixtures prior to washing gave large amounts of silicates, presumably excess unreacted sodium silicate), stirred in 1 M NaCl solution overnight to ensure complete conversion to the Na homoionic forms, washed with distilled water and dialyzed through Spectra/por 3 membranes until negative chloride tests were obtained. The sized fractions were separated by centrifugation (Jackson 1949) and freeze-dried.

Characterization of the Clays

The XRD data were obtained on a Philips X-ray diffractometer equipped with a graphite monochromator and a vertical goniometer, using $\text{CuK}\alpha$ radiation. Samples were oriented films prepared by evaporation of small volumes of suspensions of the clays on glass supports.

The TEMs were recorded on a Philips 400T transmission electron microscope operated at 120 kV. Bright-field images were recorded onto Kodak EM film (3.25×4.25 in). Clay samples were embedded in LR White (Hard formula) in gelatin capsules which were filled and capped. The resin was polymerized in an oven at 60 °C for 2 to 3 d. Sections (60–120-nm thickness) were cut with a diamond knife and collected onto carbon formvar-coated Cu or Ni grids (Malla et al. 1993).

The elemental analyses of the clays were done by SEM/EDX on a JEOL JSM-6400 scanning electron microscope equipped with a LINK eXL EDX analyzer. Samples were evaporated films of the clays on graphite supports.

The cation exchange capacities (CECs) were estimated by adding the clays to solutions of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ and measuring the amounts of the cation adsorbed by UV-Visible spectroscopy. The UV-Visible spectra were recorded on a Hewlett-Packard model 8452A diode array spectrophotometer.

Electrochemical Methods

The clay-modified electrodes consisted of approximately 300-nm-thick clay films deposited onto 1-cm² pieces of In-doped SnO_2 -coated glass. They were prepared by spin coating drops of 10 g/L clay gels at 3000 rpm as described previously (Villemure and Bard 1990). The electrochemical measurements were made with a Princeton Applied Research PARC model 270-1 electrochemical analysis system utilizing an undivided 3-electrode cell. The counter electrode was a Pt screen and the reference was a saturated calomel electrode (SCE). The electrolyte solutions were degassed by bubbling with N_2 prior to the measurements.

Table 1. Si/Cu ratios, structural formulas and estimated CECs of the synthetic clays (<0.2 μm fraction).

Clay	Si/Cu reaction mixture	Si/Cu product	Formula [†]	CEC [‡] (meq/g)
Cu-1	6.0	1.35	$[(\text{Si}_{7.93})(\text{Cu}_{5.89})\text{O}_{20}(\text{OH})_4]\text{Na}_{0.50}$	0.43
Cu-2	5.2	1.31	$[(\text{Si}_{7.86})(\text{Cu}_{6.01})\text{O}_{20}(\text{OH})_4]\text{Na}_{0.54}$	0.46
Cu-3	4.0	1.32	$[(\text{Si}_{7.92})(\text{Cu}_{6.00})\text{O}_{20}(\text{OH})_4]\text{Na}_{0.31}$	0.30
Cu-4	2.0	1.31	$[(\text{Si}_{7.85})(\text{Cu}_{5.98})\text{O}_{20}(\text{OH})_4]\text{Na}_{0.62}$	0.55
Cu-5	1.33	1.13§	$[(\text{Si}_{7.52})(\text{Cu}_{6.76})\text{O}_{20}(\text{OH})_4]\text{Na}_{0.40}$	—
Cu-6	1.0	1.09§	$[(\text{Si}_{7.49})(\text{Cu}_{6.86})\text{O}_{20}(\text{OH})_4]\text{Na}_{0.32}$	—
Cu-H	5.2	0.97	$[(\text{Si}_{7.25})(\text{Cu}_{7.35})\text{O}_{20}(\text{OH})_4]\text{Na}_{0.32}$	0.25

[†] Calculated based on $\text{O}_{20}(\text{OH})_4$ expected for 2:1 layer silicates (Newman 1987). The elemental ratios of Si and Cu were determined by SEM/EDX, the Na contents from the measured CECs.

[‡] Estimated from the amounts of $[\text{Ru}(\text{bpy})_3]^{2+}$ adsorbed by suspensions of the clays as determined by UV-visible spectroscopy.

[§] Composition was not uniform throughout the samples. Si/Cu varied by $\pm 15\%$.

RESULTS AND DISCUSSION

Characterization of the Cu-Clays

The products' Si/Cu ratios determined by SEM/EDX analysis of the clays and the formulas obtained by fitting the results to smectite unit cells are given in

Table 1. When the reaction mixtures contained excess Si, light blue solids were obtained (Cu-1 to Cu-4). Their compositions were almost independent of the initial Si/Cu ratio. They all contained Si/Cu ratios of approximately 4 to 3, close to what is expected for 2:1 trioctahedral clays. Their calculated formula fitted well to the unit cell of smectite-type minerals (Newman 1987). Their chemical compositions were also uniform. At least 3 spots of each sample were analyzed. The Si/Cu ratios obtained were reproducible within $\pm 2\%$. To test the validity of the analyses, the reaction mixture used for the preparation of sample Cu-5 was also analyzed. The measured Si/Cu ratio, 1.31, was only 1% lower than the value of 1.33 calculated from the weights of the reagents used to prepare the mixture.

Table 1 also contains estimates of the clays' CECs determined from the amounts of $[\text{Ru}(\text{bpy})_3]^{2+}$ adsorbed by the solids. Results were somewhat lower than values commonly found for natural smectites, especially for Cu-3 (Jaynes and Bigham 1986).

Figure 1 shows the XRD patterns of an oriented film of Cu-4, the blue solid obtained from the Si/Cu = 2 reaction mixture. The air-dried film showed an intense reflection at 12.5 Å, the expected basal spacings of Na-smectites (Brindley and Brown 1980), and a small-

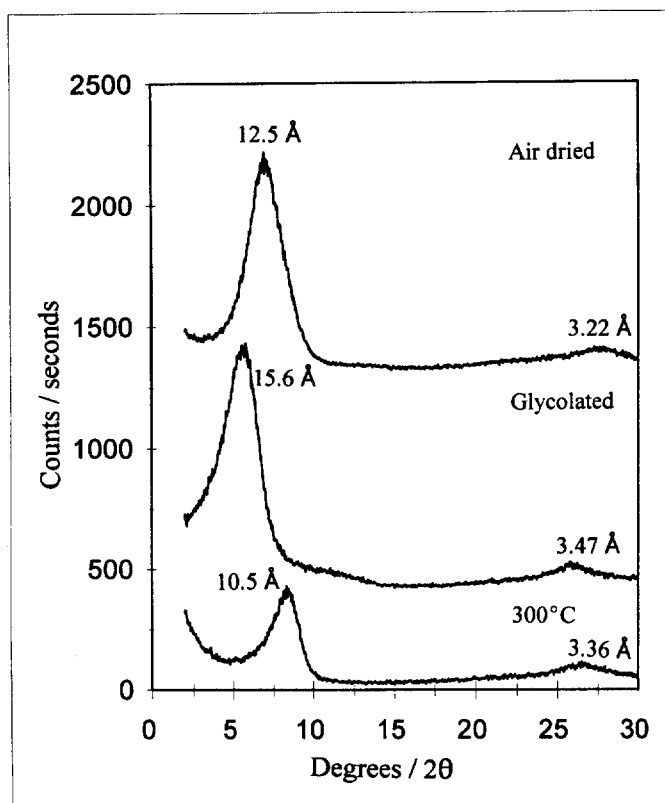


Figure 1. XRD patterns of an oriented film of the synthetic clay Cu-4 (<2.0 μm fraction).

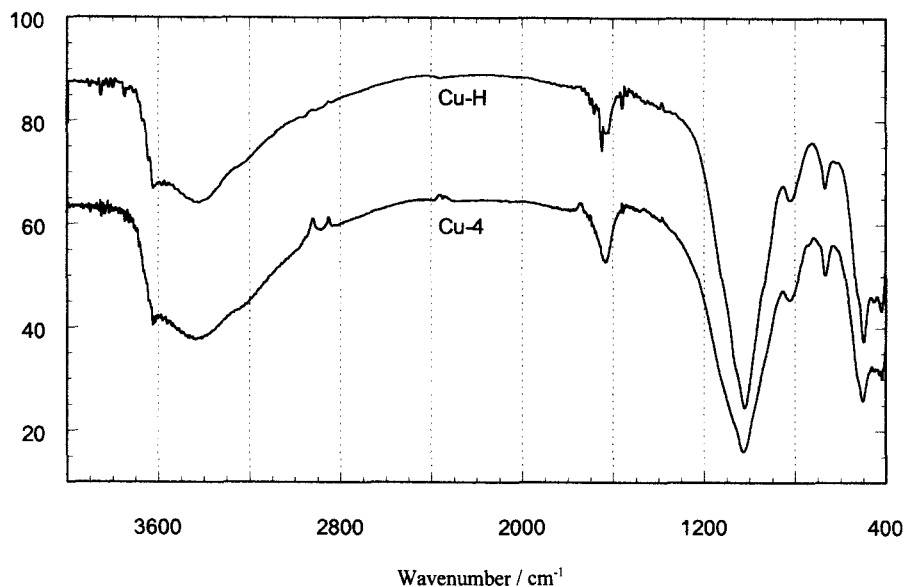


Figure 2. IR spectra of the synthetic Cu-clays.

er broad peak near 3.2 \AA . On exposure to glycol vapors, the main reflection shifted to 15.6 \AA , somewhat less than the $16.8\text{--}17 \text{ \AA}$ found for glycolated natural smectites. This incomplete swelling may indicate a mixed-layer structure with some nonexpandable talc-like layers. This would be consistent with the relatively low CEC of the clay. Heating the film to $300 \text{ }^\circ\text{C}$ caused the main reflection to shift to 10.5 \AA , not quite as low as the ≈ 9.6 to 10 \AA observed for collapsed smectites (Brindley and Brown 1980). Cu-1, Cu-2 and Cu-3 had very similar XRD patterns. The air-dried films gave intense reflections at 12.4 or 12.5 \AA that shifted up to between 15 and 15.6 \AA on exposure to glycol, and down to between 10.5 and 10.9 \AA after heating to $300 \text{ }^\circ\text{C}$. The XRD pattern of a film of Cu-4 soaked in $[\text{Ru}(\text{bpy})_3]^{2+}$ gave basal spacings of 17.2 \AA , showing that intercalation of the cation occurred. The basal spacings of $[\text{Ru}(\text{bpy})_3]^{2+}$ intercalated in natural smectites has been reported to be between 17.4 and 18 \AA (Traynor et al. 1978; Villemure et al. 1985; Villemure 1991; Breu and Catlow 1995).

The infrared (IR) spectrum of Cu-4 is shown in Figure 2. It is similar to that reported by De Vynck (1980) for a Cu-talc. A broad band attributed to the interlayer H_2O is observed at 3420 cm^{-1} . The sharp band attributed to O-H stretching of the structural OH appears at 3620 cm^{-1} , lower than the 3656 cm^{-1} found for a synthetic mix Mg-Cu-talc (Wilkins and Ito 1967). A medium intensity band at 675 cm^{-1} , assigned to a deformation mode of OH linked to 3 Cu atoms, is observed between the Si-O stretching and bending vibrations (Sun 1963; Farmer 1974; Decarreau et al. 1992). However, an additional band is observed near 820 cm^{-1} . De Vynck (1980) observed a band near 830 cm^{-1} in

a Cu-mica, but it was attributed to tetrahedral AlO_4 . Bands in this region are also typically found for dioctahedral minerals (Farmer 1974). Decarreau et al. (1992) reported bands near 800 cm^{-1} in the IR spectra of synthetic chrysocolla. The IR spectra of Cu-1, Cu-2 and Cu-3 were very similar to that of Cu-4.

When the reaction mixtures did not contain excess silicon, the products obtained were gray powders (Cu-5 and Cu-6), indicating the presence of some copper oxide. Their average Si/Cu ratios were significantly lower than the 1.33 expected for $2:1$ phyllosilicates. Their calculated formula did not fit the unit cell of smectites. They contained far too much Cu and not enough Si. Also, unlike the first 4 clays, the chemical compositions of Cu-5 and Cu-6 were not uniform. The measured Si/Cu ratios varied by as much as $\pm 15\%$ when different spots of the samples were analyzed. For example, darker regions of Cu-5 gave Si/Cu ratios as high as 1.30 , close to those obtained for the first 4 clays, while lighter grainy areas give Si/Cu ratios as low as 0.96 . The XRD pattern of Cu-5 had 1 sharp reflection at 19.2 \AA , while that of Cu-6 had 2 sharp reflections at 13.2 \AA and 2.82 \AA . In addition, broad humps in the XRD baselines, between 20 and 35° , were observed for both Cu-5 and Cu-6, indicating the presence of significant amounts of amorphous silicates.

The last product in Table 1 was obtained from a reaction mixture containing $\text{Si/Cu} = 5.2$ by hydrothermal treatment at $250 \text{ }^\circ\text{C}$ under 500 psi of Ar. The light blue product obtained differed significantly from Cu-2 obtained when the same reaction mixture was heated at $150 \text{ }^\circ\text{C}$. It contained significantly less Si and more Cu. The average Si/Cu ratio in Cu-H was ap-

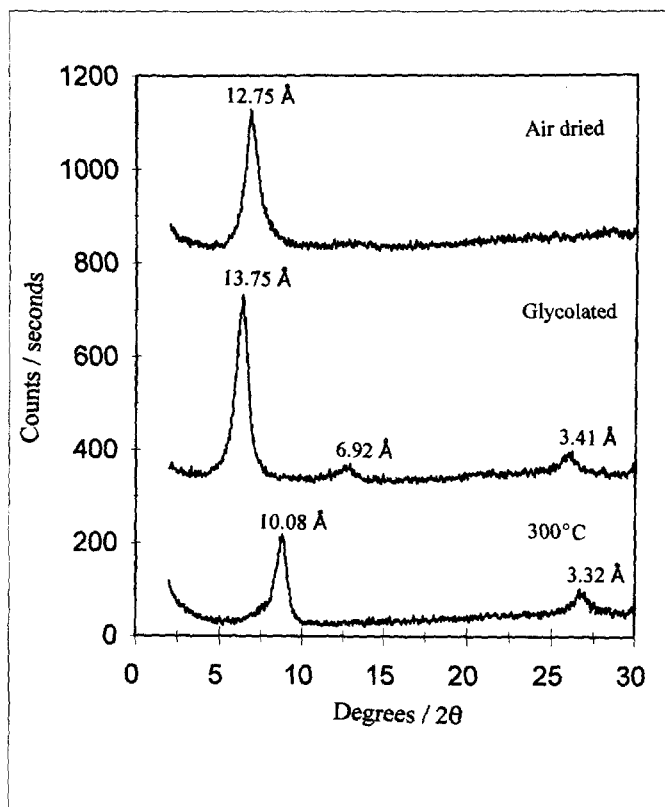


Figure 3. XRD patterns of an oriented film of the synthetic clay Cu-H (<2.0 μm fraction).

proximately 1, the ratio found in chrysocolla (Van Oosterwyck-Gastuche 1970). The composition of Cu-H was also much less uniform than that Cu-2. The Si/Cu ratio in Cu-H varied by almost $\pm 10\%$ when different spots of the sample were analyzed.

Figure 3 shows the XRD patterns of an oriented film of Cu-H. The air-dried film gave a single sharp peak at 12.75 Å, sharper than the reflection obtained for the first 4 clays (see Figure 1). Cu-H did not swell very much on exposure to glycol vapors. The main reflection shifted to only 13.75 Å. Small peaks also became visible at 6.92 Å and 3.41 Å. Heating to 300 °C caused the basal spacings to decrease to 10.08 Å. The XRD of a powder sample of Cu-H gave peaks at 13.3, 2.94 and 2.47 Å, smaller reflections at 7.33 and 1.63 Å, and very weak reflections at 4.42 and 1.44 Å, consistent with the reported XRD reflections of chrysocolla (Oosterwyck-Gastuche 1970; Decarreau 1981; Carriat et al. 1994).

However, the IR spectrum of Cu-H differed significantly from what has been previously reported for chrysocolla (Figure 2). According to Decarreau et al. (1992), synthetic chrysocolla are characterized by 3 sharp bands in the O-H stretching zone at 3623, 3522 and 3428 cm^{-1} . Only the first of these bands is seen

here. In fact, the IR spectrum of Cu-H was very similar to that of Cu-4 (Figure 2).

The difference between Cu-H and the first 4 clays was most clearly seen when the clays were examined by TEM. Figure 4 shows electron micrographs of a sample of Cu-H. At low magnification (Figure 4A) 2 types of particles, small dark rectangular particles embedded in much more numerous large fibrous particles, can be seen. TEM/EDX analysis showed that the small dark rectangular particles were silicate impurities. They contained almost no Cu. Figure 4B shows a high magnification picture of one of the fibers. The edges of the clay layers are very clearly seen. The spacings between the layers were of the order of 12 Å. The electron micrographs of Cu-1, Cu-2, Cu-3 and Cu-4 showed much less well-defined morphologies. In particular, the well-ordered layering seen in Cu-H was not observed.

To the best of our knowledge, there are no previous reports of the successful preparation of pure Cu-smectites. However, all previous reported attempts used reaction mixtures having initial Si/Cu ratios of 4 to 3, since this is the approximate Si/Cu ratio that would be found in a 2:1 trioctahedral clay. The products obtained were chrysocolla (Decarreau 1981, 1983), or

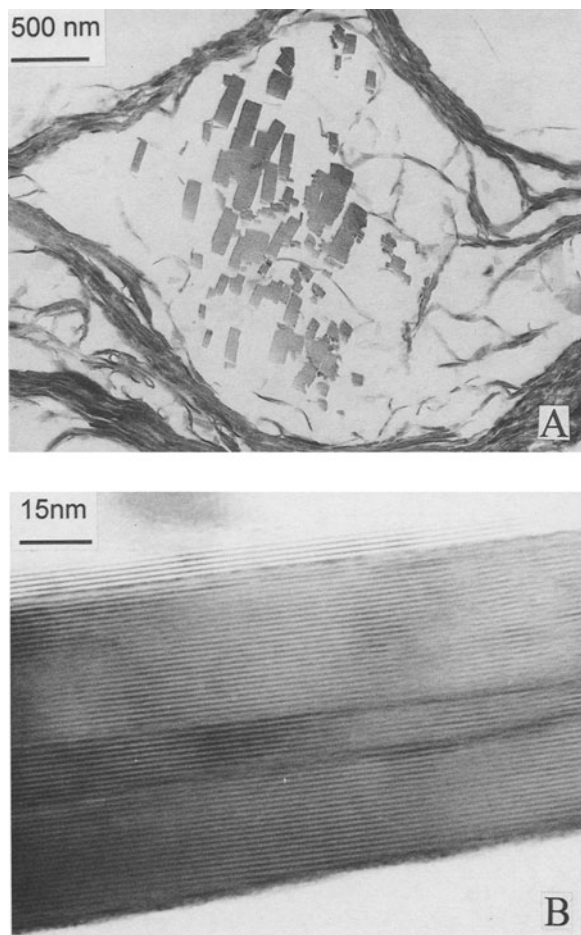


Figure 4. TEMs of a sample of the synthetic Cu-clay Cu-H.

sometimes copper oxides, unless very high temperatures were used, in which case Cu-talc was obtained (De Vynck 1980). Here, Cu-smectites were obtained, but only when the reaction mixtures contained a large excess of Si. The reaction between Cu and Si did not appear to be complete under the conditions used. When the reaction mixtures did not contain a large excess of Si, the products were mixtures of copper oxides and amorphous silicates, with perhaps some phyllosilicates.

The 2:1 layer structure was not very favorable, or very stable for Cu. When the temperature of the hydrothermal treatment was increased, the reaction proceeded further to give a product with Si/Cu \approx 1, that may be a chrysocolla. However, the true nature of this product is still not clear. Its IR spectra differed from that reported for chrysocolla (Decarreau et al. 1992), while electron microscopy showed it had a very well-ordered layer structure. Chrysocolla are reputed to be poorly ordered phyllosilicates (Brindley 1980; Carriat et al. 1994).

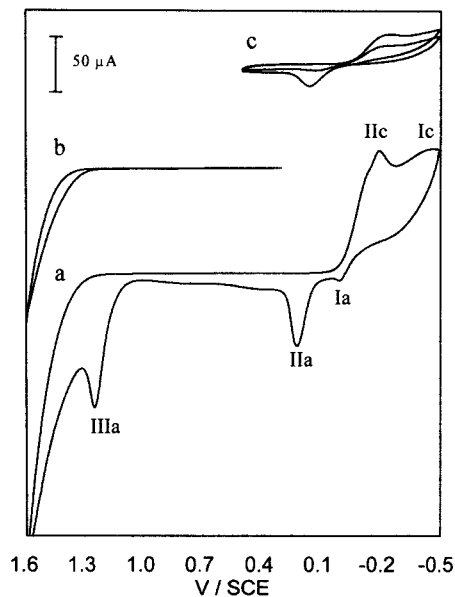


Figure 5. Cyclic voltammograms of evaporated films of the synthetic Cu-clay Cu-H. a) 20th scan, b) 2nd scan and c) 2nd and 20th scans for a freshly prepared film. Recorded at 50 mV/s in 0.05 M Na₂SO₄. The subscripts "a" and "c" refer to anodic and cathodic peaks, respectively.

Electrochemistry of the Cu-Clays

The cyclic voltammogram of a film of Cu-H recorded in a sodium sulfate electrolyte is shown in Figure 5 (curve a). It consists of 3 sharp anodic waves at 0.01, 0.22 and 1.25 V, labelled I_a, II_a, and III_a respectively, and 2 cathodic peaks at -0.20 and -0.48 V, labelled II_c and I_c. A shoulder on peak II_c is also seen near -0.13 V. The peaks at low potentials were similar in appearance to what we observed for a film of the natural montmorillonite STx-1, pre-exchanged with Cu²⁺ ions. Voltametric waves at similar potentials have also been reported for zeolite-modified electrodes exchanged with Cu²⁺ ions (Baker and Senaratne 1993; Li and Calzaferri 1994; Senaratne et al. 1996). They have been attributed to the reduction of Cu(II) to Cu(I), and of Cu(I) to Cu(0). The sharp peak at 1.25 V has never been reported for Cu²⁺-exchanged zeolite-modified electrodes. Small peaks at high potentials, attributed to oxidation of Cu(II) to Cu(III) have been observed in other types of Cu-modified electrodes (Prabhu and Baldwin 1989; Luo et al. 1990; Colon et al. 1993). However, these small peaks were only observed in strongly basic electrolytes, and the corresponding cathodic back waves were observed when the scan direction was reversed.

This simple picture of the electrochemistry of Cu-H is complicated when the effect of the scanning range on the voltammogram is examined. For a freshly prepared electrode that had never been oxidized, when the potential was scanned only between 0.5 and -0.5

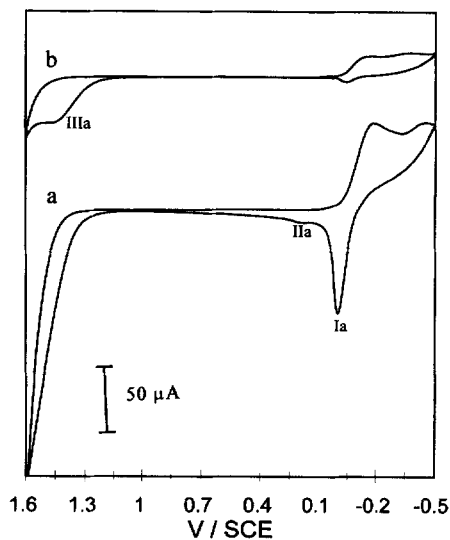


Figure 6. Cyclic voltammograms of spin-coated films of the synthetic Cu-clay, Cu-2, recorded in 0.05 M Na₂SO₄. a) 4th scan at 50 mV/s, b) 2nd scan at 5 mV/s.

V, peak I_a and II_a appeared as a single peak at intermediate potential (Figure 5, curve c). The peak currents were also smaller and the waves decreased rapidly with scanning. The large stable voltametric waves shown in curve a of Figure 5 were only obtained when the potential was scanned up to about 1.35 V, above the potential of peak III_a. Similarly, when the potential was scanned only between 0.3 V and 1.6 V, peak III_a was not observed (curve b). In fact, the sharp peak at 1.25 V was only observed in an anodic scan immediately following a cathodic scan to at least -0.4 V. Even then, if the scan was interrupted at a potential between that of peaks II_a and III_a, and then resumed in the positive direction, peak III_a only appeared as a shoulder on the oxygen evolution limit.

The cyclic voltammogram of a film of the synthetic Cu-smectite Cu-2 is shown in Figure 6. It differed for that of Cu-H in that peak III_a was only observed at low scan speed, and even then was never very sharp. Also, for the Cu-smectites (Cu-1 to Cu-4), the relative sizes of peaks I_a and II_a varied from film to film. In the example shown in Figure 6, peak II_a was very small, and the voltametric waves were not stable. They decreased with scanning.

In Figure 7, the cyclic voltammograms of [Os(bpy)₃]²⁺ adsorbed in films of the synthetic smectite Cu-2, and of the natural montmorillonite STx-1, are compared. The wave centred at 0.65 V for the oxidation of the adsorbed ions was more than 10 times larger in the Cu-clay than in STx-1. To get an estimate of the fraction of the adsorbed ions that were electroactive, the voltametric waves obtained at low scan speeds (1 mV/s) were integrated. Results are shown in Table 2, along with the total amount of [Os(bpy)₃]²⁺

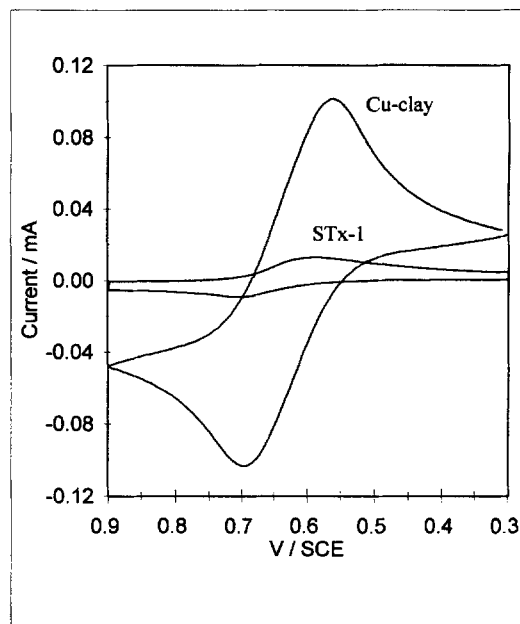


Figure 7. Cyclic voltammograms of spin-coated films of the natural montmorillonite, STx-1, and of the synthetic Cu-smectite, Cu-2, soaked overnight in a 0.1 mM solution of [Os(bpy)₃]²⁺. Recorded at 50 mV/s in 0.05 M Na₂SO₄.

adsorbed in each film as determined by UV-Visible spectroscopy. In STx-1, the charge obtained by integrating the anodic peak corresponded to the oxidation of less than 3% of the adsorbed ions. This is in agreement with what is known for this type of cations in clay-modified electrodes. The mobility of intercalated tris bipyridyl cations is too restricted for them to participate in the electrochemical reaction. Activity is restricted to more weakly bound physisorbed cations and those incorporated in the films as ion pairs (King et al. 1987; Villemure and Bard 1990; Kaviratna and Pinnavaia 1992; Petridis et al. 1994). The anodic charge obtained for Cu-2 was much larger. It corresponded to the oxidation of nearly 42% of the adsorbed ions. Sim-

Table 2. Electroactive fractions for adsorbed [Os(bpy)₃]²⁺ cations.

Clay	Q _a /mC	10 ⁹ n _a [†] /mol†	10 ⁹ n _t /mol‡	n _a [†] /n _t (%)
Cu-1	1.17	1.21	4.77	25.4
Cu-2	2.51	2.60	6.22	41.8
Cu-4	1.66	1.72	3.67	46.9
Cu-H	1.06	1.09	4.43	24.6
STx-1	0.18	0.19	7.02	2.7

† Number of moles of [Os(bpy)₃]²⁺ oxidized, calculated from the charges (Q_a) obtained by integration of the anodic peak in the 1 mV/s cyclic voltammograms.

‡ Total number of moles of [Os(bpy)₃]²⁺ adsorbed by the films, determined from the change in the absorbances of soaking solutions.

ilar 10- to 15-fold increases in the electroactive fractions were found for the other synthetic Cu-clays.

We have observed similar large increases in the electroactive fractions of metal bipyridyl cations adsorbed in synthetic Co-smectites. They were attributed to electron transfer between the adsorbed cations and redox active Co(II) sites in the clays (Xiang and Villemure 1996b). Mediation of the charge transport in films of layered double hydroxides by redox active Ni, Co or Mn sites in the modifiers was also found to result in large increase in the voltametric waves of adsorbed metal cyanide anions (Qiu and Villemure 1995; Qiu and Villemure 1997). The increases observed here can be attributed to a similar mediation of the charge transport in the films by the clays' redox active Cu(II) sites.

CONCLUSION

Cu-smectites were obtained when mixtures containing NaOH, CuCl₂ and large excesses of Na₂SiO₃ were subjected to hydrothermal treatment at 150 °C. Reaction mixtures that did not contain excess Na₂SiO₃ did not produce smectites. The 2:1 layered structure of the products was not very favorable. Increasing the temperature of the hydrothermal treatment to 250 °C gave a different product. The product had a lower Si/Cu ratio of approximately 1, the value found in chrysocolla, did not swell on exposure to glycol vapors and showed a very well-ordered layered structure under TEM.

Cu(II) sites in all synthetic Cu-clays were electrochemically active. Three oxidation peaks were found in cyclic voltammogram of a film of the chrysocolla (Cu-H). They were attributed to oxidation of Cu(0) to Cu(I), Cu(I) to Cu(II) and Cu(II) to Cu(III), respectively. For the Cu-smectites, the peak for the oxidation to Cu(III) was only observed at low scan speed, and the voltametric waves were not as stable. They decrease rapidly with scanning. [Os(bpy)₃]²⁺ ions adsorbed in films of the Cu-clays gave much larger voltametric waves than those obtained in a film of a natural montmorillonite in the same conditions. The increase in the peak currents corresponded to 10- and 15-fold increases in the fraction of the adsorbed ions that were electroactive. We are investigating the electrochemistry of the synthetic Cu-clays and their potential use for electrode surface modifications.

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REFERENCES

- Baker MD, Senaratne C. 1993. Electrochemistry with clays and zeolites. In: Ross PN, Lipkowski J, editors. *Frontiers of electrochemistry. The electrochemistry of novel materials*, vol. 3. New York: VCH. p 339–380.
- Breu J, Richard C, Catlow A. 1995. Chiral recognition among tris(diimine)-metal complexes. 4. Atomistic computer modeling of a monolayer of [Ru(bpy)₃]²⁺ intercalated into a smectite clay. *Inorg Chem* 34:4504–4510.
- Brindley GW. 1980. Order-disorder in clay mineral structure. In: Brindley GW, Brown G, editors. *Crystal structures of clay minerals and their X-ray identification*. London: Mineral Soc. p 125–195.
- Brindley GW, Brown G. 1980. X-ray diffraction procedures for clay minerals identification. In: Brindley GW, Brown G, editors. *Crystal structures of clay minerals and their X-ray identification*. London: Mineral Soc. p 305–360.
- Carriat JY, Che M, Kermarec M, Decarreau A. 1994. Influence of order-disorder parameters on the reducibility of Ni- and Cu-containing silicates: Application to talc and chrysocolla. *Catal Lett* 25:147–140.
- Colon LA, Dadoo R, Zare RN. 1993. Determination of carbonhydrates by capillary zone electrophoresis with amperometric detection at a copper microelectrode. *Anal Chem* 65:476–481.
- Decarreau A. 1980. Cristallogene experimentale des smectites magnesiennes: Hectorite, stevensite. *Bull Mineral* 103: 579–590.
- Decarreau A. 1981. Cristallogene a basse temperature de smectites trioctahedrique par vieillissement de coprecipites silico metallique de formule (Si_{1-x})₃M₃O₁₀·nH₂O. *C. R. Acad Sci Paris* 292:61–64.
- Decarreau A. 1983. Etude experimental de la cristallogene des smectites. Mesure des coefficients de partage smectite trioctaedrique-solution aqueuse pour les metaux M²⁺ de la premiere serie de transition. *Mem Sci Geol* 74:1–191.
- Decarreau A. 1985. Partitioning of divalent transition elements between octahedral sheets of trioctahedral smectites and water. *Geochim Cosmochim Acta* 49:1537–1544.
- Decarreau A, Grauby O, Petit S. 1992. The actual distribution of octahedral cations in 2:1 clay minerals: Results from clay synthesis. *Appl Clay Sci*. 7:147–167.
- De Vynck I. 1980. Synthese de phyllosilicates de cobalt, de nickel, de cuivre et de zinc. *Silicates Industriels* 3:51–66.
- Farmer VC. 1974. The layer silicates. In: Farmer VC, editor. *Infrared spectra of minerals*. London: Mineral Soc. p 331–363.
- Ildefonse P, Manceau A, Prost D, Groke MCT. 1986. Hydroxy-Cu-vermiculite formed by the weathering of Fe-biotites at salobo, Carajas, Brazil. *Clays Clay Miner* 34:338–345.
- Jackson ML, Wittig LD, Pennington RP. 1949. Segregation procedure for the mineralogical analysis of soils. *Soil Sci Soc Am Proc* 14:77–81.
- Jaynes WF, Bigham JM. 1986. Multiple cation-exchange capacity measurement on standard clays using a commercial mechanical extractor. *Clays Clay Miner* 34:93–98.
- Kaviratana P de S, Pinnavaia TJ. 1992. Electroactive Ru(NH₃)₆³⁺ gallery cations in clay-modified electrodes. *J Electroanal Chem* 332:135–145.
- King RD, Nocera DG, Pinnavaia TJ. 1987. On the nature of electroactive sites in clay-modified electrodes. *J Electroanal Chem* 236:43–53.
- Li J, Calzaferri G. 1994. Copper-zeolite-modified electrodes: An intrazeolite ion transport mechanism. *J Electroanal Chem* 377:163–175.
- Luo P, Prabhu SV, Baldwin RP. 1990. Constant potential amperometric detection at a copper-based electrode: Electrode formation and operation. *Anal Chem* 62:752–755.

- Malla PB, Robert M, Douglas LA, Tessier D, Komarneni S. 1993. Charge heterogeneity and nanostructure of 2:1 layer silicates by high-resolution transmission electron microscopy. *Clays Clay Miner* 41:412–422.
- Mosser C, Mestdagh M, Decarreau A, Herbillon A. 1990. Spectroscopic (ESR, EXAFS) evidence of Cu for (Al-Mg) substitution in octahedral sheets of smectites. *Clay Miner* 25:271–281.
- Mosser C, Mosser A, Romeo A, Petit S, Decarreau A. 1992. Natural and synthetic copper phyllosilicates studied by XPS. *Clays Clay Miner* 40:593–599.
- Newman ACD, Brown G. 1987. The chemical constitution of clays. In: Newman ACD, editor. *Chemistry of clays and clay minerals*. New York: Mineral Soc. p 1–29.
- Oyama N, Anson FC. 1986. Catalysis of the electroreduction of hydrogen peroxide by montmorillonite clay coatings on graphite electrodes. *J Electroanal Chem* 199:467–470.
- Petit S, Decarreau A, Mosser C, Ehret G, Grauby O. 1995. Hydrothermal synthesis (250 °C) of copper-substituted kaolinites. *Clays Clay Miner* 43:482–494.
- Petridis D, Falaras F, Pinnavaia TJ. 1994. Self-assembly of ion-paired electron-transfer centers in a clay-modified electrode. *Inorg Chem* 31:3530–3533.
- Prabhu SV, Baldwin RP. 1989. Constant potential amperometric detection of carbohydrates at a copper-based chemically modified electrode. *Anal Chem* 61:852–856.
- Qiu J, Villemure G. 1995. Anionic clay modified electrodes: Electrochemical activity of nickel(II) sites in layered double hydroxide films. *J Electroanal Chem* 395:159–166.
- Qiu J, Villemure G. 1997. Anionic clay modified electrodes: Electron transfer mediated by electroactive nickel, cobalt or manganese sites in layered double hydroxide films. *J Electroanal Chem* 428:165–172.
- Rudzinski WE, Bard AJ. 1986. Clay modified electrodes part VI. Aluminum and silicon pillared clay modified electrodes. *J Electroanal Chem* 199:323–340.
- Tanner CG, Jackson ML. 1947. Nomographs of sedimentation times for soil particles under gravity or centrifugal acceleration. *Soil Sci Soc Am Proc* 12:60–65.
- Traynor MF, Mortland MM, Pinnavaia TJ. 1978. Ion exchange and intersalation reactions of hectorite with tris-bipyridyl metal complexes. *Clays Clay Miner* 26:318–326.
- Senaratne C, Zhang J, Baker MD, Bessel CA, Rolison R. 1996. Zeolite-modified electrodes: Intra-versus extrazeolite electron transfer. *J Phys Chem* 100:5849–5862.
- Shaw BR. 1989. Modification of solid electrodes in electroanalytical chemistry 1978–1988. In: Stock JT, Orna MV, editors. *Electrochemistry past and present*, ACS Symposium Series 390. Washington, DC: Am Chem Soc. p 318–338.
- Sun MS. 1963. The natural of chrysocolla from Inspiration mine, Arizona. *Am Miner* 48:469–658.
- Van Oosterwyck-Gastuche MC. 1970. La structure de la chrysocolle. *CR Acad Sci Paris* 271:1837–1840.
- Villemure G. 1991. X-ray diffraction of montmorillonite oriented films exchanged with enantiomeric and racemic tris(2,2'-bipyridyl)ruthenium(II). *Clays Clay Miner* 39:580–585.
- Villemure G, Bard AJ. 1990. Clay modified electrodes part 9: Electrochemical studies of the electroactive fraction of adsorbed species in reduced-charge and preadsorbed clay films. *J Electroanal Chem* 282:107–121.
- Villemure G, Kodama H, Detellier C. 1985. Photoreduction of water by visible light in the presence of montmorillonite. *Can J Chem* 63:1139–1142.
- Wang D, Yu W, Zhu B. 1989. A special solid electrolyte-montmorillonite. *Solid State Ionics* 34:219–223.
- Wilkins RWT, Ito J. 1967. Infrared spectra of some synthetic talc. *Am Miner* 52:1649–1661.
- Xiang Y, Villemure G. 1992. Electron transport in clay-modified electrodes: Study of electron transfer between electrochemically oxidized tris(2,2'-bipyridyl)iron cations and clay structural iron(II) sites. *Can J Chem* 70:1833–1837.
- Xiang Y, Villemure G. 1995. Electrodes modified with synthetic clay minerals: Evidence of direct electron transfer from structural iron sites in the clay lattice. *J Electroanal Chem* 381:21–27.
- Xiang Y, Villemure G. 1996a. Electrodes modified with synthetic clay minerals: Electrochemistry of cobalt smectites. *Clays Clay Miner* 44:515–521.
- Xiang Y, Villemure G. 1996b. Electrodes modified with synthetic clay minerals: Electron transfer between adsorbed tris(2,2'-bipyridyl) metal cations and electroactive cobalt centers in synthetic smectites. *J Phys Chem* 100:7143–7147.

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