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Cyclic Voltammetry of Tris(2,2′-bipyridyl)ruthenium(II) Cations Adsorbed in Electrodes Modified with Mesoporous Molecular Sieve Silicas

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The electrochemical behavior of $[Ru(bpy)_3]^{2+}$ was examined in electrodes modified with two mesoporous molecular sieves, HMS and Al-HMS. $[Ru(bpy)_3]^{2+}$ was adsorbed by both molecular sieves, resulting in increased peak currents for the Ru(II)/Ru(III) redox process at the HMS- or Al-HMS-modified electrodes relative to the bare ITO electrode. The peak currents obtained with the Al-HMS-modified electrode were 20 times larger than those obtained with the corresponding blank ITO electrode coated with only polystyrene. No increase in the peak currents was found for electrodes modified with a microporous NaY zeolite under the same conditions. For HMS, extensive washing of the powder prior to the preparation of the modified electrodes resulted in the complete disappearance of the voltammetric waves. This demonstrates that the electroactive $[Ru(bpy)_3]^{2+}$ ions in HMS were weakly held cations physisorbed in the neutral mesoporous silicate. In Al-HMS electrodes, however, large voltammetric waves remained, showing that unlike what was previously reported for clay-modified electrodes, the electrostatically bound ions adsorbed by cation exchange in Al-HMS were electrochemically active.

Introduction

We report here on the use of mesoporous molecular sieve silicas for the modification of electrode surfaces. These materials have regular, well-defined, and uniform channels varying from 15 to 100 Å. They were first obtained by using cationic surfactant templates to direct the condensation of silicate anions (S^+I^-).[1,2] This approach has since been extended to the use of anionic templates to direct the assembly of cationic inorganic species (S^-I^+) and to counterion-mediated assembly of surfactants and inorganic precursors having the same charge ($S^+X^-I^+$ or $S^-M^+I^-$).[3] Two other related pathways have also emerged. The first exploits hydrogen-bonding interactions between neutral amine surfactants (S^0) or nonionic polyethylene surfactants (N^0) and neutral inorganic precursors (S^0I^0 or N^0I^0).[4,5] The second is based on dative bond formation between donor groups on the surfactant and metal centers in the inorganic precursor.[6] Together, these surfactant-directed syntheses have revolutionized the field of mesoporous materials. They have proven to be simple, versatile, and reliable methods to obtain mesoporous molecular sieves with a wide range of structures and compositions.[7−9]

Several recent reports have appeared on the incorporation of potentially electrochemically active transition metal ions[10−14] and transition metal complexes[15−19]

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into the pores of mesoporous silicates, via ion exchange or by covalent attachment to the pore walls through silane bridges to surface OH groups.[19−23] Notably, Liu et al.[15] and Kim et al.[16] have reported the ion exchange of Al−MCM-41 with $[Fe(phen)_3]^{2+}$ and $[Mn(bpy)_2]^{2+}$, respectively. Transition metal bipyridyl and phenanthroline complexes have been extensively used as electrochemical probes in clay-modified electrodes.[24−28] To the best of our knowledge, the only previous report on the electrochemistry of species supported in mesoporous molecular sieves is a brief mention of the cyclic voltammetry of cobalt bound to diamine functional groups on side chains grafted to the walls of MCM-41.[29] The potential of mesoporous molecular sieves as electrode modifiers remains unexplored.

Mesoporous silicates have much larger pores than the usual microporous zeolites. It may therefore be possible for the electron-transfer reactions in electrodes modified with mesoporous silicates to occur deep within the mesopores. In zeolite-modified electrodes (ZMEs), electron-transfer almost always occurs by the so-called extrazeolite mechanism,[30] in which the electrochemical reaction takes place outside the zeolite pore system, after the electroactive species have exited the pores through ion exchange or desorption.[25,28,31,32] Intrazeolite electron transfer has only been observed in carefully designed systems where mobile, size-excluded mediators were used to transfer electron to electroactive species trapped in the zeolite pores.[33,34] Even then, however, since the mediators were size-excluded, electron transfer only occurred at the mouth of the pores. Similarly, in clay-modified electrodes (CMEs) electron transfer does not occur deep within the clay interlayer spaces.[24−28,35,36] To participate in the electrochemical reaction, the adsorbed species must first diffuse out of the clay gallery spaces to the conductive substrate.

We report here on the electrochemical behavior of $[Ru(bpy)_3]^{2+}$ in electrodes modified with the mesoporous molecular sieves HMS and Al-HMS. $[Ru(bpy)_3]^{2+}$ was adsorbed in both mesoporous silicates, resulting in large increases in the voltammetric peak currents relative to those obtained with an unmodified ITO electrode. The absence of significant differences between the responses in the neutral HMS and the negatively charged Al-HMS indicates that unlike what is found in clay-modified electrodes, in Al-HMS-modified electrodes both the physisorbed and the ion-exchanged cations are electrochemically accessible.

Table 1. Sorption Properties of the Mesoporous Materials.

samples	d_{100} (nm)	S_{BET} (m^2/g)	HK pore size (nm)
HMS	4.2	910	3.0
Al-HMS	5.14	960	3.8

Experimental Section

Materials. The NaY zeolite (SN3-39I11) was obtained from Gulf Research and Development. All other chemicals were obtained from Aldrich and used without further purification.

HMS was prepared by the neutral surfactant templating procedure, using TEOS as the source of silicon and dodecylamine as structure directing agent, as previously described.[7] Briefly, 7.5 g (36 mmol) of TEOS was added to a vigorously stirred micelle solution of 1.48 g (8 mmol) of dodecylamine in 10 mL of ethanol and 90 mL of H_2O (water-rich solvent mixture[37]) and the mixture was stirred overnight. Al-HMS is a mesoporous aluminosilicate in which about 5% of the silicon atoms in the framework is replaced by aluminum. It was obtained by the postsynthesis alumination of a HMS, using $NaAlO_2$ as the source of aluminum.[38] Briefly, 4.5 g (3.75 mmol) of trimethylbenzene was added to a stirred micelle solution of 1.63 g (8.75 mmol) of dodecylamine in 10 mL of ethanol and 70 mL of H_2O. After 30 min, 8.82 g (32.7 mmol) of TEOS in 10 mL of EtOH was added, and the mixture was stirred for 4 days. During the stirring, three aliquots of 20, 20, and 10 mL of a 0.0327 M $NaAlO_2$ solution were added to the reaction mixture after 24, 48, and 72 h, respectively.

The products were filtered, washed with distilled water, and dried in air. The surfactants were removed by Soxhlet extraction over ethanol for 48 h. The products were then calcined at 650 °C for 4 h and characterized by powder X-ray diffraction (XRD) and N_2 sorptometry. Results are summarized in Table 1.

The XRD patterns were measured on a Rigaku Rotaflex diffractometer equipped with a rotating anode using Cu Kα radiation. The N_2 adsorption−desorption isotherms were measured at −196 °C on a Micromeritics ASAP 2010 instrument using a static adsorption procedure. The BET surface areas were calculated from the linear part of the BET plots according to IUPAC recommendations.[39] The pore size distributions were calculated from the N_2 adsorption branch using the Horvath−Kawazoe model.[40]

Preparation of the Electrodes. Simple evaporation of suspensions of the mesoporous silicates did not produce robust films. Polystyrene had to be added in order to obtain films that adhered well to the conductive substrates and were robust enough for handling. Polystyrene has been used extensively in the preparation of zeolite-modified electrodes.[26,28,31−34,41,42] The porous polystyrene layers provide good mechanical stabil-

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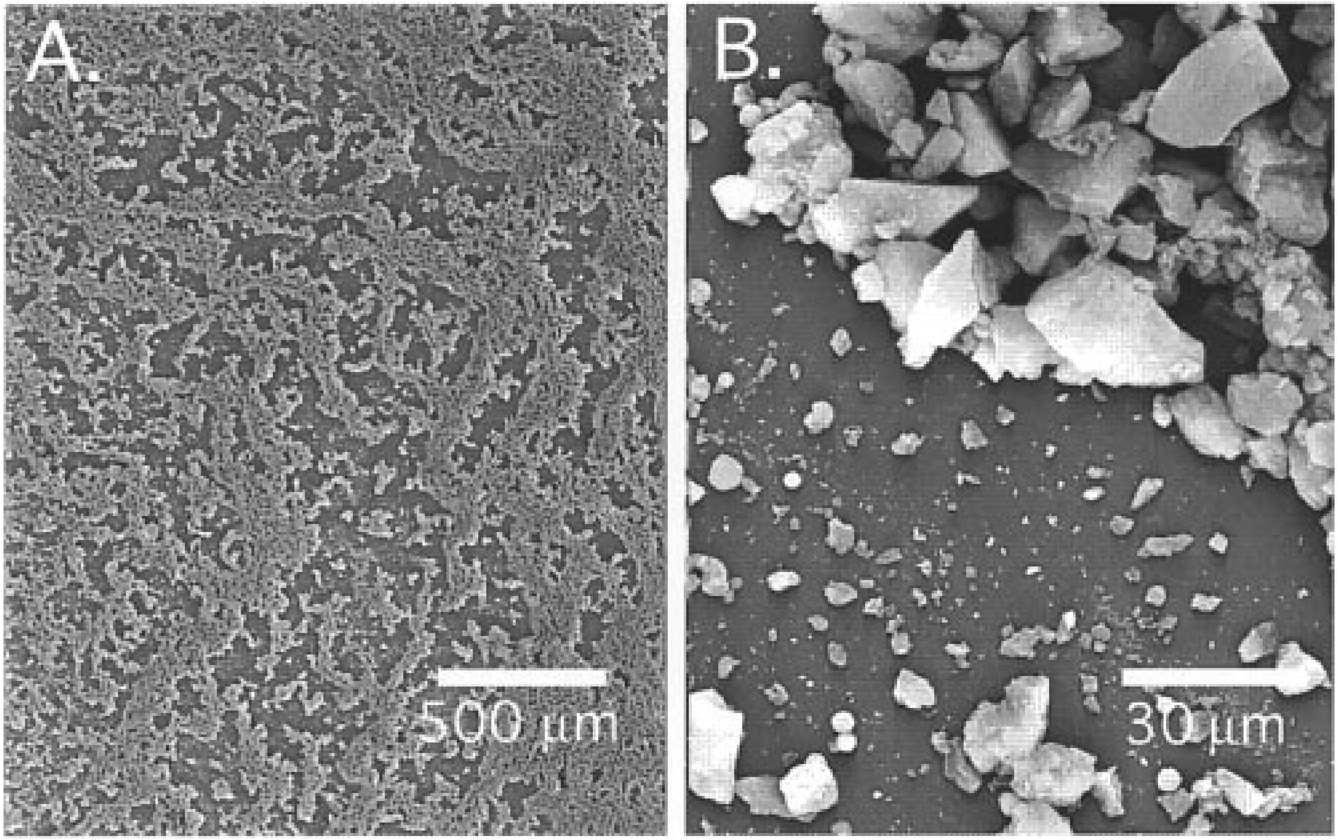

Figure 1. Scanning electron micrographs of a 1 cm^2 piece of ITO coated with 0.25 mg of Al-HMS and 0.05 mg of polystyrene.

ity and do not appear to interfere with the diffusion of the electroactive species.

The HMS-modified electrodes used in this study consisted of HMS particles dispersed in polystyrene films deposited on indium-doped tin oxide coated glass substrates (ITO; Delta Technologies, Limited Stillwater MN). In a typical preparation, 100 μL of a suspension containing 5 mg of HMS and 1 mg of polystyrene (MW 280 000) per milliliter of THF was spread on a 1 × 2.5 cm piece of ITO, and the solvent was allowed to evaporate. Part of the whitish film obtained was rubbed off, leaving a ~1 cm^2 film. The Al-HMS- and NaY zeolite-modified electrodes were prepared by the same procedure.

Some of the modified electrodes were examined by scanning electron microscopy (SEM) on a JEOL JSM 6400V microscope. The electrodes were mounted on graphite stubs and sputtered with gold prior to the measurements.

The electrochemical measurements were taken with a BAS CV50 Voltammetric Analyzer in an undivided three-electrode cell. The counter electrode was a Pt wire and the reference was a Ag/AgCl reference electrode (SSCE). All measurements were made in 0.05 M Na_2SO_4 supporting electrolyte in deionized distilled water.

Results and Discussion

Figure 1 shows the scanning electron micrographs of a typical Al-HMS/polystyrene-modified electrode. The coverage of the ITO substrate by the Al-HMS particles was not complete. The film appears to consist of aggregates of Al-HMS particles separated by areas covered only with polystyrene. The coating is perhaps best described as a dispersion of Al-HMS particles in a polystyrene film. Note, however, that the appearance of the film was uniform throughout the sample. The Al-HMS particles were uniformly dispersed on the surface of the ITO substrate. More complete coverage of the ITO could be obtained by evaporation of larger volumes of the Al-HMS/polystyrene suspension. However, increasing the Al-HMS contents in the films did not have a major effect on the behavior of the modified electrodes toward solution $[Ru(bpy)_3]^{2+}$ ions, while it made the films much more fragile. The thicker films tended to crack and peel off the substrates during drying.

The appearances of the HMS/polystyrene- and NaY zeolite/polystyrene-modified electrodes were similar to that of the Al-HMS/polystyrene electrodes.

Cyclic Voltammetry in $[Ru(bpy)_3]^{2+}$ Solutions. Figure 2 shows cyclic voltammograms taken in a 0.05 M Na_2SO_4 solution containing 0.05 mM $[Ru(bpy)_3]^{2+}$. Curve a shows the voltammogram obtained with a bare ITO electrode. As expected, a small voltammetric wave ($I_{pa} = -4.3$ μA) for the reversible oxidation of $[Ru(bpy)_3]^{2+}$ was observed. Curve b shows the voltammogram obtained in the same solution with an ITO electrode coated with polystyrene (0.04 mg/cm^2). The peak currents decreased by almost 50% ($I_{pa} = -2.2$ μA), while the peak positions and the peak separation were unchanged. The voltammetric waves obtained with polystyrene-coated ITO electrodes were independent of the time the films spent in the electrolyte solution. The peak currents obtained for an ITO electrode coated with only polystyrene, 24 h after the film was placed in the $[Ru(bpy)_2]^{2+}/Na_2SO_4$ solution, were the same as those obtained immediately after the film was first placed in the solution.

Curves c and d show voltammograms obtained with an Al-HMS/polystyrene-modified electrode taken 1 min and 4 h, respectively, after the film was placed in the solution. Initially, only a broad, poorly defined wave was seen (curve c). The initial peak currents were even

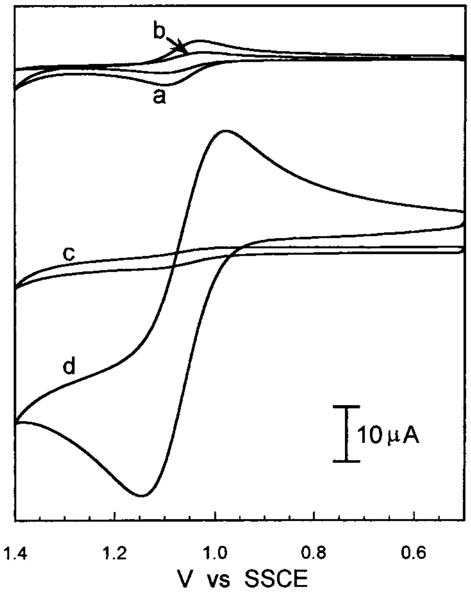

Figure 2. Cyclic voltammograms recorded at 50 mV/s in 0.05 M Na_2SO_4 electrolyte containing 0.05 mM $[Ru(bpy)_3]^{2+}$: (a) bare ITO, (b) ITO coated with 0.04 mg/cm^2 of polystyrene, and Al-HMS/polystyrene-modified electrode (c) 1 min and (d) 4 h after the film was placed in the solution.

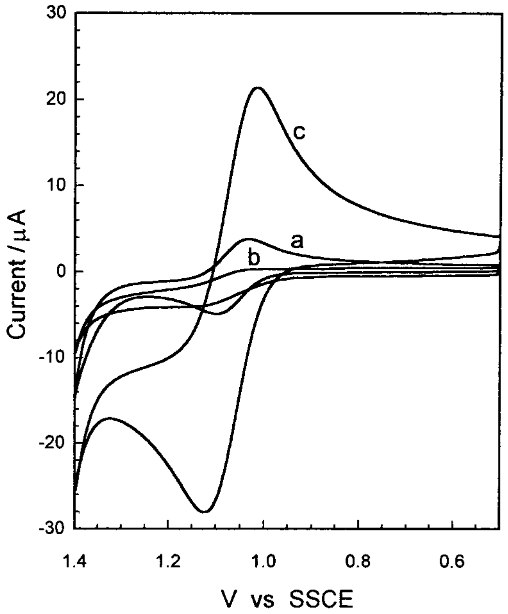

Figure 3. Cyclic voltammograms recorded at 50 mV/s in 0.05 M Na_2SO_4 electrolyte containing 0.05 mM $[Ru(bpy)_3]^{2+}$: (a) bare ITO and HMS/polystyrene-modified electrode (b) 1 min and (c) 5 h after the film was placed in the solution.

smaller than those obtained with the blank polystyrene film. It took more than 1 h before the peak currents became comparable to those obtained with the bare ITO electrode. Curve d shows the stable voltammetric wave obtained after 4 h. By this time, the anodic peak current had grown to −46.6 μA, more than 10 times larger than for the bare ITO, and more than 20 times larger than for ITO coated with only polystyrene. The position of the wave ($E_{1/2} = 1.066$ V) was the same as for the bare ITO. The peak currents were not linearly dependent on the square root of the scan speed. The peak separation (155 mV) was larger than for the bare ITO (65 mV), and it increased with the scan speed.

In many ways, the behavior of the Al-HMS/polystyrene-modified electrodes toward $[Ru(bpy)_3]^{2+}$ cations in solution was similar to that of clay-modified electrodes. This was not surprising. $[Ru(bpy)_3]^{2+}$ was expected to be concentrated, by ion exchange, in the negatively charged Al-HMS, in much the same way as in clay films.[24−28,35,36] An increase in the local concentration of the cation in the films would accounts for the increase in the peak currents, despite the greatly reduced mobility of the adsorbed cations.

To determine how much $[Ru(bpy)_3]^{2+}$ could be adsorbed by Al-HMS, suspensions of the mesoporous solid in water were mixed with solutions of the cation. After 2 days, the mixtures were centrifuged, and the decrease in concentration of $[Ru(bpy)_3]^{2+}$ in the supernatant solutions was determined by UV−visible spectroscopy.[43,44] Al-HMS was found to adsorbed an average of 0.47 mequiv/g of $[Ru(bpy)_3]^{2+}$. This was slightly more than half the maximum cation exchange capacity of Al-HMS, ∼0.82 mequiv/g, estimated by assuming one negative charge for each Al atom in the framework, suggesting that some Al(III) sites in the framework walls were not accessible for ion exchange. Unlike the pores in microporous crystalline zeolites, the pores in M41S type mesoporous silicates are separated by relatively thick amorphous walls. From the HK pore size and d_{100} spacings (Table 1), the wall thickness in the Al-HMS used in this study was estimated to be 2.1 nm.[7] Some of the Al(III) sites in Al-HMS may be buried deep in the walls.

When the Al-HMS films were removed from the $[Ru(bpy_3]^{2+}$ solution and cycled in blank electrolyte, the size of the voltammetric wave decreased rapidly. The peak currents decreased by about 75% in the first 90 min after the transfer. This was significantly faster than for clay films. It takes several hours before an equivalent loss of activity is observed in CMEs.[36,45−47] Leaching of the adsorbed $[Ru(bpy)_3]^{2+}$ out of Al-HMS films by the electrolyte cations appeared to be faster than what is observed for clays films. However, not all the electroactive ions could be desorbed. Significant peak currents, 15−20% that of the originals, were still observed 20 h after the Al-HMS films were transfer to blank electrolyte. Also, the films retained a yellow color at the end of the experiments, indicating that some adsorbed $[Ru(bpy)_3]^{2+}$ remained in the Al-HMS films.

Figure 3 shows the cyclic voltammograms obtained for an electrode modified with a HMS/polystyrene film. The results were very similar to those obtained with Al-HMS. Initially, only a small broad voltammetric wave was seen (curve b). This wave grew with time, stabilizing after a few hours. Curve c shows the voltammogram obtained 5 h after the film was placed in the solution. The anodic peak current is −28.5 μA, about 6 times what was obtained with the bare ITO (curve a). However, this is only 60% of the maximum peak current found for Al-HMS-modified electrodes. Also, in the HMS-modified electrodes, the peak currents in-

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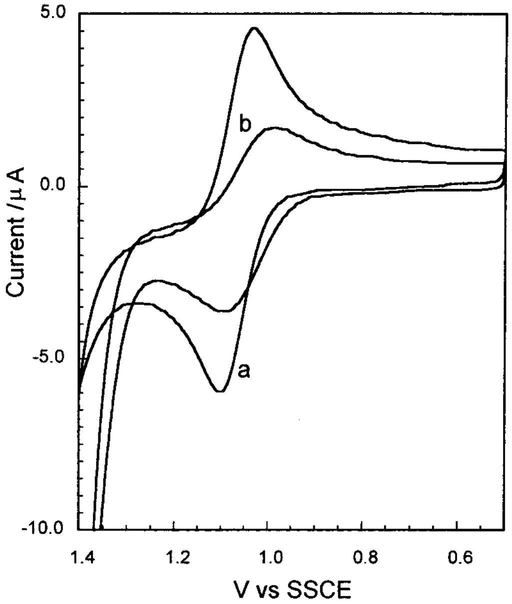

Figure 4. Cyclic voltammograms recorded at 50 mV/s in 0.05 M Na_2SO_4 electrolyte containing 0.05 mM $[Ru(bpy)_3]^{2+}$: (a) bare ITO and (b) NaY zeolite/polystyrene-modified electrode.

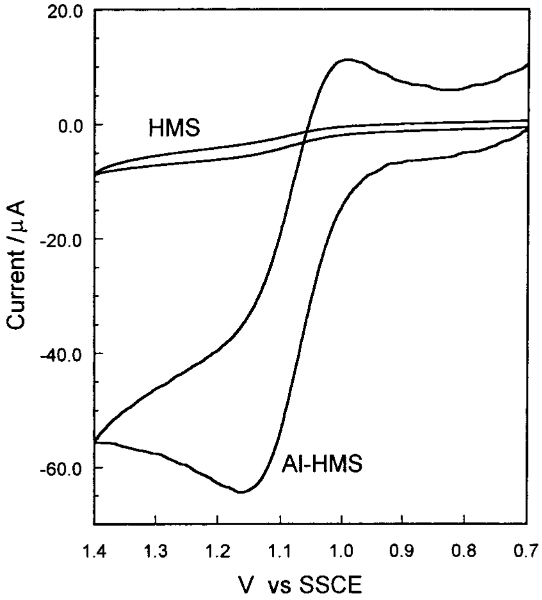

Figure 5. Cyclic voltammograms of electrodes modified with films of the two mesoporous molecular sieves preexchange with $[Ru(bpy)_3]^{2+}$ (third scans, 50 mV/s in 0.05 M Na_2SO_4).

creased linearly with the square root of the scan speed, for scan speeds of less than 100 mV/s. This was not the case for Al-HMS. The peak separation was also smaller in HMS, 98 mV at 50 mV/s, compared to 155 mV in Al-HMS.

Unlike the negatively charged Al-HMS, the neutral HMS cannot adsorb $[Ru(bpy)_3]^{2+}$ by ion exchange. The neutral HMS was not expected to adsorbed any significant amounts of $[Ru(bpy)_3]^{2+}$. Yet, the fact that the peak currents in the HMS films were much larger than for the unmodified electrodes indicates that some adsorption of the cation did occur. In fact, when a suspension of HMS was mixed with a solution of $[Ru(bpy)_3]^{2+}$, UV–visible spectroscopy of the supernatant solution showed that HMS did adsorb a small amount of $[Ru(bpy)_3]^{2+}$, about 0.07 mequiv/g. However, these cations interacted only weakly with HMS. Washing the solid with water was sufficient to extract a significant fraction of the adsorbed $[Ru(bpy)_3]^{2+}$.

That the voltammetric waves in HMS were due to weakly bound physisorbed cations is consistent with the linear I_p vs $\nu^{1/2}$ plots and with the smaller peak separations obtained for the HMS-modified electrodes. Physisorbed ion-paired species can be expected to retain higher mobility than more strongly bound cations adsorbed by ion exchange. Higher effective diffusion coefficients would explain how small amounts of physisorbed $[Ru(bpy)_3]^{2+}$ in HMS gave voltammetric waves almost as large as more numerous, but less mobile, electrostatically bound $[Ru(bpy)_3]^{2+}$ in Al-HMS.

Figure 4 shows the cyclic voltammogram obtained with an electrode modified with a NaY zeolite/polystyrene film. The voltammetric wave obtained for the zeolite-modified electrode (curve b) was smaller than the wave obtained with bare ITO (curve a). In fact, the $[Ru(bpy)_3]^{2+}$ wave in the zeolite/polystyrene-modified electrodes did not grow beyond the size of the wave obtained with ITO coated with only polystyrene. This was very different from what was obtained with the two mesoporous silicates. In zeolite Y, adsorption of $[Ru(bpy)_3]^{2+}$ is restricted to the outer surfaces of the microporous zeolite particles.[33] This was not enough to cause an increase in the size of the voltammetric waves relative to what was obtained with an unmodified ITO electrode.

Cyclic Voltammetry in Blank Electrolyte. To unambiguously establish that $[Ru(bpy)_3]^{2+}$ cations adsorbed by ion exchange in the negatively charged Al-HMS were electrochemically active, mesoporous silicates preexchanged with $[Ru(bpy)_3]^{2+}$ were prepared. Suspensions of Al-HMS and HMS were stirred overnight in solutions containing a large excess of $[Ru(bpy)_3]^{2+}$. The mixtures were then centrifuged, and the solids were washed extensively with water to remove all physisorbed cations. This was continued until no more cation could be extracted from the solids, as shown by completely clear supernatant solutions. After drying, the bright orange $[Ru(bpy)_3]^{2+}$/Al-HMS and pale yellow $[Ru(bpy)_3]^{2+}$/HMS powders were dispersed in 1 mg/mL polystyrene solutions in THF and used to prepare the modified electrodes.

In Figure 5 the cyclic voltammograms obtained with the two preexchanged mesoporous solids are compared. For the neutral HMS, only a small broad shoulder was seen where the anodic peak for adsorbed $[Ru(bpy)_3]^{2+}$ ions should appear. This demonstrates that extensive washing of the $[Ru(bpy)_3]^{2+}$/HMS powder prior to its use to prepare the modified electrodes was successful in removing essential all redox active cations from the mesoporous silicate. For Al-HMS, however, a large voltammetric wave was observed. This wave had to be due to $[Ru(bpy)_3]^{2+}$ adsorbed in Al-HMS by ion exchange, since no other types of cations were present. This is different from what is found in CMEs. Electrodes modified with clay films preexchanged with $[Ru(bpy)_3]^{2+}$ show no voltammetric activity. In CMEs, electrostatically bounded intercalated $[M(bpy)_3]^{2+}$ ions are electrochemically inactive.[24–28,35]

The size of the $[Ru(bpy)_3]^{2+}$ voltammetric waves in preexchanged Al-HMS films decreased rapidly with time in the first few minutes of scanning. The anodic peak current decrease by more that 80% after only 10 min. At least initially, the displacement of the adsorbed electroactive $[Ru(bpy)_3]^{2+}$ in Al-HMS by sodium ions from the electrolyte was rapid. From then on, however, the decrease in the peak currents was much slower. After 20 h, the anodic peak current was down to 5 μA. By this time, enough $[Ru(bpy)_3]^{2+}$ had been desorbed to give the electrolyte a visible yellow color. From the concentration of $[Ru(bpy)_3]^{2+}$ in the electrolyte solution, determined by UV−visible spectroscopy, we estimated that two-thirds of the $[Ru(bpy)_3]^{2+}$ ions initially present in the Al-HMS film had been displaced by Na^+ ions from the electrolyte.

To estimate what fraction of the $[Ru(bpy)_3]^{2+}$ ions initially present in the Al-HMS film were electroactive, a voltammetric scan was taken at 1 mV/s. A very slow scan speed should allow enough time for all the redox active cations present in the film to react. This is one of the methods used to estimate the electroactive fraction of $[M(bpy)_3]^{n+}$ type ions in CMEs.[25−27,43−47] Integration of the anodic peak gave a charge of −1.6 mC. This corresponded to the oxidation of about 40% of the $[Ru(bpy)_3]^{2+}$ ions initially present in the Al-HMS film. However, scanning the potential at such a slow speed takes time. The 1 mV/s anodic half-scan was only completed 20 min after the film was first placed in the electrolyte. By this time a large fraction of the initial activity had already been lost. Another estimate of the minimum electroactive fraction can be made from the residual activity observed after 20 h. As mentioned above, a voltammetric wave was still observed 20 h after the Al-HMS film was placed in the blank electrolyte, even though by this time two-thirds of the $[Ru(bpy)_3]^{2+}$ ions initially present in the film had been desorbed. This suggests that at least two-thirds of the $[Ru(bpy)_3]^{2+}$ cations adsorbed in Al-HMS were electrochemically active. A large electroactive fraction is consistent with the electrochemical activity of cations adsorbed by ion exchange. The very low electroactive fractions found for $[M(bpy)_3]^{2+}$ type ions in CMEs are attributed to the complete inactivity of the electrostatically bound intercalated ions.[24−28,36,45−47]

The electrochemical activity of the electrostatically bound cations in the mesoporous silicates does not, however, necessarily mean that the redox reactions occurred in the mesopores. In fact, it is more likely that $[Ru(bpy)_3]^{2+}$ cations adsorbed by ion exchange in mesoporous Al-HMS were electrochemically accessible only because the cations retained enough mobility to diffuse out of the mesopores on the time scale of the electrochemical measurements. Electroactive fractions of up to 80% have been reported for $[Ru(NH_3)_6]^{3+}$ in CMEs.[46] The smaller $[Ru(NH_3)_6]^{3+}$ ions are mobile in clay films and can diffuse out of the gallery spaces. Consequently, intercalated $[Ru(NH_3)_6]^{3+}$ cations are electrochemically active in CMEs.[46]

Conclusion

The results of this work indicate that metal complex cations electrostatically bound to the framework of mesoporous molecular sieves are sufficiently mobile (exchangeable) to be electrochemically active. This behavior is unlike that of clay-modified electrodes, where large complex cations are nonexchangeable and redox inactive. The large pores in the mesoporous HMS and Al-HMS allowed the adsorption of $[Ru(bpy)_3]^{2+}$into the framework of the solids, resulting in a large increase in peak currents for the Ru(II)/Ru(III) redox process at the HMS- or Al-HMS-modified electrodes relative to the bare ITO. This was not the case for an electrode modified with zeolite Y, where adsorption of $[Ru(bpy)_3]^{2+}$ was restricted to the outer surfaces of the microporous zeolite particles. Recently, important advances have been reported for the formation of continuous films of mesoporous molecular sieves on glass[48,49] and graphite surfaces.[50] Such films should exhibit electrochemical properties analogous to those observed in the present work.

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