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Clay Supported Redox Catalysts

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It has been demonstrated that montmorillonite exchanged with a phase transfer catalyst (e.g. $PhCH_2NBu_3^+$) will bring about the phase transfer catalysis of several organic and organometallic reactions [1]. The method offers the advantage of facilitating work up since the clay provides both aqueous phase and catalyst. Several years ago [2] it was shown that $[Co(bipy)_3]^+$ (bipy = 2,2′-bipyridyl) would catalyse the borohydride reduction of nitrobenzene to aniline. Since, in another context, we had occasion to prepare $[Co(bipy)_3]^{3+}$/hectorite, it occurred to us that it should be possible to use this supported redox catalyst to effect organic redox reactions. It seemed sensible to evaluate the idea by consideration of the nitrobenzene to aniline reduction.

Experimental

(a) Preparation of $[Co(bipy)_3]^{3+}$/hectorite

Hectorite is a lithium–magnesium smectite clay with an ion exchange capacity in the region of 60 milliequivalents 100 g^{-1}. The clay was pretreated to remove impurities and exchanged to the sodium form prior to reaction with 0.1 M $CoCl_2$ solution (100 cm^3 solution to 12 g clay). The clay thus treated contained 15 mg cobalt g^{-1}. The cobalt exchanged clay was then treated with 2,2′-bipyridyl (2.0 g) in ethanol (100 cm^3) in air over 4 h after which it was filtered, washed with 4 × 20 cm^3 aliquots of ethanol and air dried.

The previously colourless clay was now yellow. The basal spacing, $d_{(001)}$, was determined as 18.8 Å, a value consistent with the intercalation of the large complex cation. The diffuse reflectance spectrum showed peaks at 451 and 317 nm (*cf.* literature for $[Co(bipy)_3](ClO_4)_3$: 448, 317 nm [3]) thus confirming the air oxidation of Co(II) to Co(III) in the presence of the ligand.

(b) Generation of $[Co(bipy)_3]^+$/hectorite

Two methods were used.

(i) Electrochemical generation

$[Co(bipy)_3]^{3+}$/hectorite was ground to a fine powder and allowed to flocculate from acetonitrile suspension onto the surface of a platinum electrode (1.87 cm^2) (approx. 11.4 mg). The electrode was positioned horizontally in a conical flask together with a bright platinum electrode. An acetonitrile solution, 0.1 M in tetrabutylammonium hexafluorophosphate, was introduced as supporting electrolyte. Passage of a current of 4 mA for 2 min resulted in the appearance of the deep blue $[Co(bipy)_3]^+$ on the cathode. The colour faded (~1 min) when the current was disconnected, but could be maintained for periods up to 1 h on continued passage of current.

(ii) Chemical generation

$[Co(bipy)_3]^{3+}$/hectorite (1 g) was stirred for 1 h with $NaBH_4$ (0.037 g, 1.0 mmol) in distilled water (10 cm^3) and finally filtered under dinitrogen. Diffuse reflectance measurement showed bands at 623 and 396 nm. An early report gave bands at 610 and 390 nm for a solution of $[Co(bipy)_3](ClO_4)_3$ reduced with Na/Mg or $NaBH_4$ [4].

(c) Reduction of Nitrobenzene

Two methods were used. The $NaBH_4$ reduced clay (damp) was added to nitrobenzene either with or without $NaBH_4$. In each case aniline was formed (GLC), the more effective reduction occurring in the presence of nitrobenzene (4 mmol) when added together with 40 mmol of $NaBH_4$ to the reaction flask used to generate $[Co(bipy)_3]^+$/hectorite (b(ii)). Under these conditions the conversion was 100% with no evidence for unreacted intermediates [5].

(d) Physical Methods

XRD data were obtained with a Philips instrument using Co Kα radiation with an iron filter. Traces were recorded at 1° 2θ per minute in the range 2×10^3 cps and could be observed from 3° 2θ upwards. Samples were flocculated from a pentane suspension. Diffuse reflectance spectra in the range 300–700 nm were recorded with a Pye-Unican SP 800 B instrument with an SP 890 diffuse reflectance attachment. The sample was sandwiched between quartz plates; magnesium oxide was used as reference. Reaction products were identified by GLC using a Pye-Unicam GCD gas chromatograph with a 2 m column packed with 25% silicone grease on phase prep. A.

Discussion

Clay modified electrodes have been reported, in particular montmorillonite exchanged with $[Ru(bipy)_3]^{2+}$ [6]. Given this fact, together with our earlier report of clay supported phase transfer catalysts, it seemed likely that clay supported redox catalysts could, under some circumstances, offer practical advantages particularly in terms of facilitat-

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ing work up and ease of storage of a resumable catalyst.

Hectorite was selected for this work since the very low structural iron content gives a white clay thus allowing characterization of absorbed transition metal complex ions by their absorption spectra. It was convenient to treat Co^{2+}/hectorite with bipyridyl in air. Oxidation of cobalt occurs and the final product contains $[Co(bipy)_3]^{3+}$ characterized by the absorption spectrum. Flocculation onto a platinum electrode allowed electrochemical reduction to a deep blue colour. The absorption spectrum agrees well with an earlier report, although it was at that time supposed that the blue species was a bis rather than a tris bipyridylcobalt(I) complex [4]. The electrode was fragile and work is in progress to devise a more mechanically robust system. The clay supported complex could also be reduced chemically via borohydride reduction. The addition of the damp reduced clay to nitrobenzene produced some aniline; however the best catalytic conversion was obtained when the nitrobenzene together with borohydride was added to the reaction vessel containing the reduced clay. As would be anticipated with large cations, $d_{(001)}$ does not alter (18.7 ± 0.2 Å) as a function of the oxidation state of the cobalt. Thus the complex ions also have a pillaring effect which is probably important in allowing ingress of the organics to the catalyst.

References

1 P. Monsef-Mirzai and W. R. McWhinnie, *Inorg. Chim. Acta, 52,* 211 (1981).

2 A. A. Vlcek and A. Rusina, *Proc. Chem. Soc.,* 161 (1961).

3 B. Martin and G. M. Waind, *J. Chem. Soc.,* 4248 (1958).

4 J. Csaszar, *Naturwissenschaften, 46,* 488 (1959).

5 N. Davidson, *Ph.D. Thesis,* Aston University, 1986.

6 P. K. Ghosh and A. Bard, *J. Am. Chem. Soc., 105,* 5691 (1983).