Stabilization of a Cobalt(II) Phthalocyanine Oxidation Catalyst by Intercalation in a Layered Double Hydroxide Host

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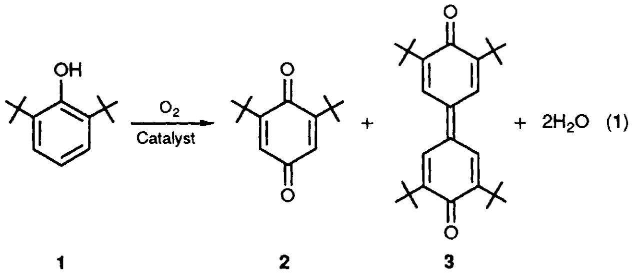
Cobalt(II) phthalocyaninetetrasulfonate $[Co(pcts)]^{4-}$ intercalated into a $Mg_5Al_{2.5}$-layered double hydroxide (LDH) exhibited greatly enhanced catalytic stability compared to the homogeneous catalyst for the autoxidation of 2,6-di-*tert*-butylphenol to the corresponding diphenoquine at 35 ± 2 °C; under homogeneous reaction conditions the complex deactivated within 25 catalytic turnovers, whereas the LDH-supported species remained fully active even after more than 3200 turnovers.

Several redox active metalloporphyrins, metallophthalocyanines and other macrocyclic complexes can function as biomimetic catalysts for the autoxidation of organic molecules in aqueous solution.[1–3] This property is of potential interest for applications in the remediation under ambient conditions of contaminated ground water and industrial effluents. However, the complexes typically have limited longevity and suffer the disadvantage of high recovery costs. In an effort to improve their catalytic longevity and recylability, macrocyclic complexes have been immobilized on a variety of supports that include charcoal,[4–7] polymers[8] and zeolites.[9–12]

One especially promising class of supports currently under investigation is the layered double hydroxides (LDHs) of the general type $[M_{1-x}^{2+}M_x^{3+}(OH)_2]$ $[A^{n-}]_{x/n}\cdot yH_2O$, where A^{n-} is an intercalated gallery anion. Various A^{n-} anions, including catalytically active polyoxometallates can be intercalated into LDH structures by a variety of synthetic routes.[13–21] More recently, the anionic macrocyclic complex cobalt(II) phthalocyaninetetrasulfonate, $[Co^{II}(pcts)]^{4-}$, was intercalated with the plane of the macrocycle orthogonal to the LDH sheet, and the intercalated complex was shown to be active for the autoxidation of a thiolate to a disulfide.[22] The longevity of LDH-intercalated metallophthalocyanine and related macrocyclic complexes is of considerable importance, especially if such materials are to be designed for the remediation of polluted aqueous environments. In the present work we report the activity of an LDH–$[Co(pcts)]^{4-}$ catalyst over several thousand catalytic turnovers using the autoxidation of 2,6-di-*tert*-butylphenol as a probe reaction. The enzymatic peroxide oxidation of phenols has been proposed as means of removing such toxicants from aqueous environments.[23] A biomimetic pathway based on dioxygen as the oxidizing agent might provide an even more viable decontamination process.

An LDH carbonate of approximate composition $Mg_6Al_2(OH)CO_3\cdot yH_2O$ was prepared by the co-precipitation of stoichiometric amounts of Mg^{2+}, Al^{3+} and CO_3^{2-} as described elsewhere.[24] The preparation of the sodium salt of cobalt(II) 4,4′,4″,4‴-tetrasulfonatophthalocyanine followed closely the method described by Weber and Busch.[25] The LDH-carbonate was heated at 450 °C for 18 h in air to form a mixed-metal oxide solid solution.[19] The solid solution then was reconstituted into an LDH–$[Co(pcts)]^{4-}$ intercalation product by hydrothermal reaction (100 °C) of the oxide with the sodium salt of the complex.[22] The amount of the $Na_4[Co(pcts)]$ salt used was in 8–10 fold stoichiometric excess. From elemental analysis the LDH composition was found to be $[Mg_5Al_{2.5}(OH)_{14.9}][Co(pcts)]_{0.6}\cdot 4H_2O$. As shown in Fig. 1 an oriented thin film of the intercalated LDH displayed seven orders of X-ray harmonics indicative of a layered structure with a basal spacing of ~23.7 Å and an edge-on orientation of the macrocycle within the LDH galleries.



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In order to obtain rate data for the oxidation of 2,6-di-*tert*-butylphenol the O_2 concentration was monitored by using a Clark-type O_2 electrode (Orion model 98-07). The electrode was attached to a Fisher Accumet Selective Analyzer Model 750 pH meter for readout of dioxygen concentration in ppm. The depletion of phenol was monitored by gas chromatography.

The selective autoxidation of 2,6-di-*tert*-butylphenol **1** in the presence of the homogenous[26] and polymer supported[27] $[Co(pcts)]^{4-}$ has been reported previously to afford mainly the corresponding diphenoquinone **3** and some of the benzoquinone **2**. An analogous catalytic conversion can be accomplished with the LDH-intercalated catalyst at 35 °C as shown in eqn. (1).

Fig. 2(*a*) and (*b*) provides the initial O_2 uptake curves for the homogeneous and LDH-intercalated catalysts. In the absence of the catalyst no dioxygen uptake occurred. Almost no induction period was observed for the LDH-supported catalyst, whereas about 7 min was required for the onset of the reaction for the homogeneous species. Significantly, the homogenous reaction exhibited an initial rate of dioxygen uptake [51.8 mmol O_2 (mol complex)$^{-1}$ min^{-1}] that was substantially lower than the rate for the intercalated catalyst [109 mmol O_2 (mol complex)$^{-1}$ min^{-1}]. More importantly, the homogeneous catalyst was deactivated almost completely after only 25 catalytic turnovers of $[Co(pcts)]^{4-}$. Deactivation was accompanied by a change in catalyst colour from blue to

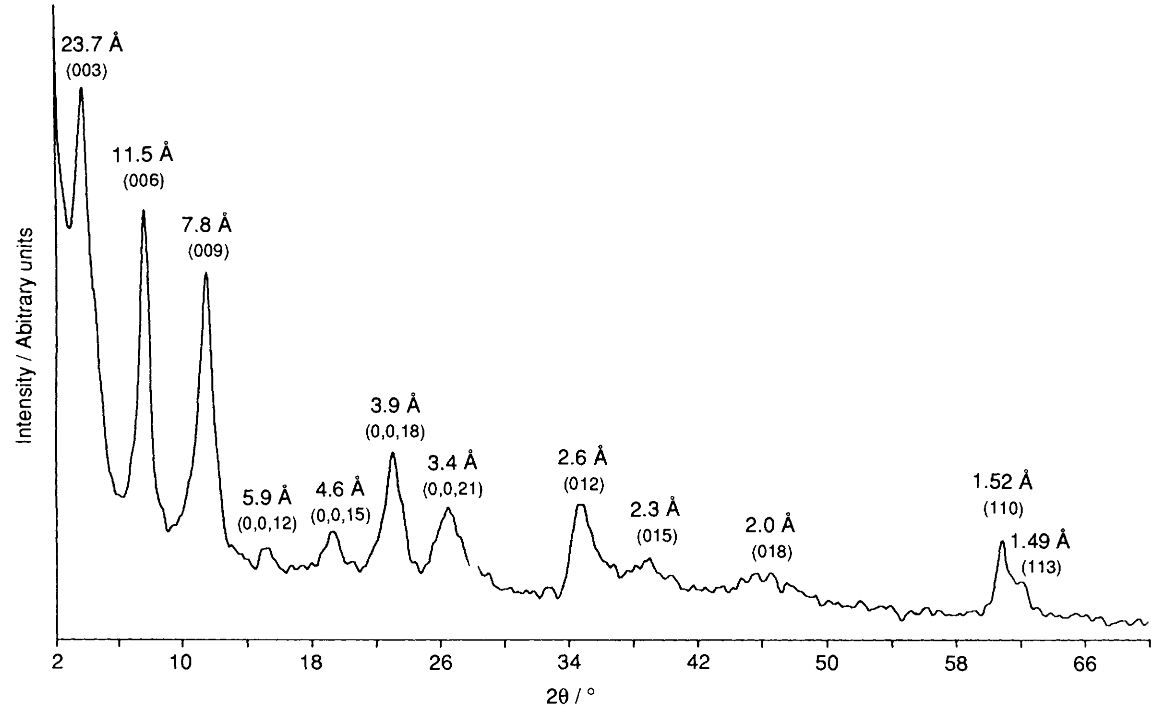

Fig. 1 X-Ray diffraction pattern (Cu-Kα) of an orientated thin film sample of a $[Mg_{2.5}Al]$–$[Co(pcts)]$-LDH intercalate

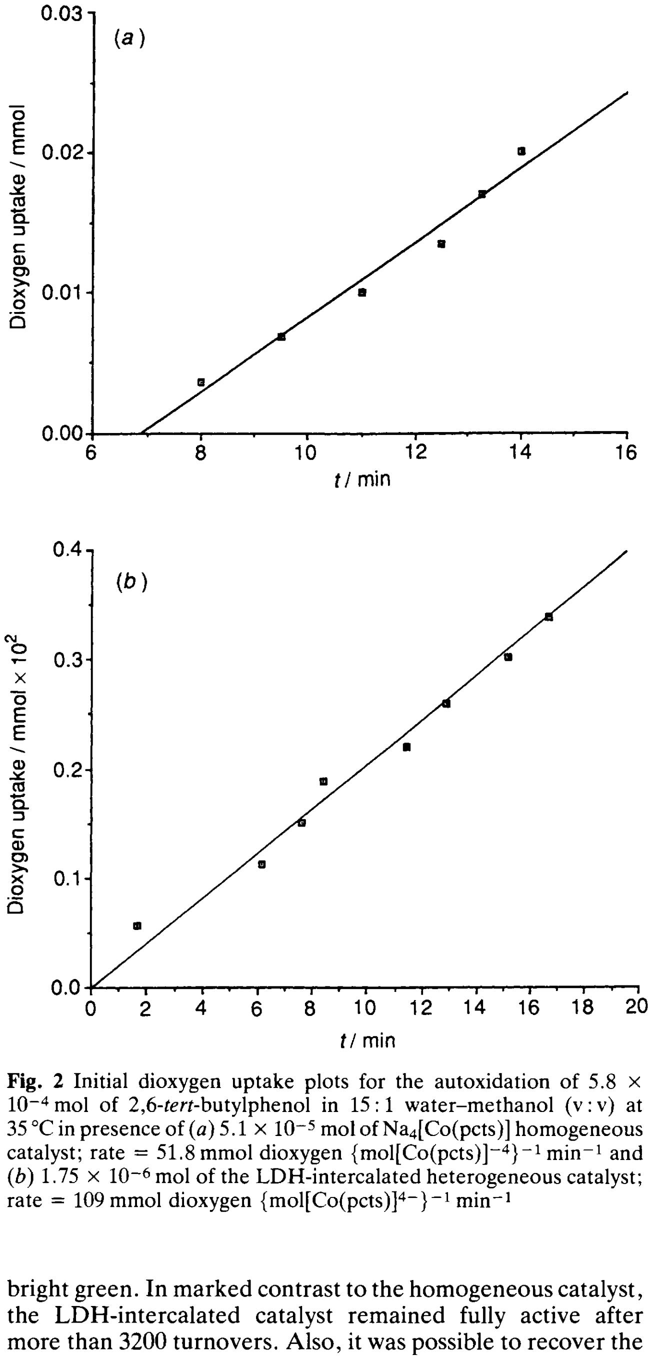

Fig. 2 Initial dioxygen uptake plots for the autoxidation of 5.8 × 10^{-4} mol of 2,6-*tert*-butylphenol in 15:1 water–methanol (v:v) at 35 °C in presence of (*a*) 5.1 × 10^{-5} mol of $Na_4[Co(pcts)]$ homogeneous catalyst; rate = 51.8 mmol dioxygen $\{mol[Co(pcts)]^{-4}\}^{-1}$ min^{-1} and (*b*) 1.75 × 10^{-6} mol of the LDH-intercalated heterogeneous catalyst; rate = 109 mmol dioxygen $\{mol[Co(pcts)]^{4-}\}^{-1}$ min^{-1}

bright green. In marked contrast to the homogeneous catalyst, the LDH-intercalated catalyst remained fully active after more than 3200 turnovers. Also, it was possible to recover the catalyst by filtration and to add more reactants without the catalyst deactivating.

The yellow reaction products obtained from both the homogeneous and heterogeneous reactions were separated by diethyl ether extraction. The presence of almost exclusively 2,6,2′,6′-tetra-*tert*-butyldiphenoquinone **3** was confirmed by GC–mass spectra. According to the mechanism proposed by Kothari and Tazuma[26] for the homogeneous autoxidation of phenol by phthalocyanines, the $[Co(pcts)]^{4-}$ forms a dioxygen intermediate that reacts with phenol to form aryloxy and hydroperoxide radicals. The deactivation of the homogeneous $[Co(pcts)]^{4-}$ catalyst is thought to arise from the formation of a peroxo-bridged dinuclear complex of the type $[(pcts)\text{-}Co^{III}O_2Co^{III}(pcts)]$, which is unable to bind and activate molecular oxygen.[28] Intercalation of the complex into an LDH host appears to be especially effective in inhibiting the dimerization process.

A nitrogen Brunauer–Emmett–Teller (BET) surface area of 21 m^2 g^{-1} was obtained for the LDH-supported $[Co(pcts)]^{4-}$, a value typical of the external surface areas of the conventional LDH intercalates containing non-pillaring anions. Thus, it is unlikely that the intracrystalline cobalt centres in the LDH intercalate are available for reaction with O_2 or phenol. More likely, only the Co centres at the external surface and edges of the LDH intercalate participate in the catalysis.

Our results for LDH-immobilized phthalocyanine complexes suggest that they possess the required stability for possible applications such as the remediation of polluted ground water and industrial effluents under ambient conditions. The same improvement in stability can be expected for complementary metallomacrocyclic complexes based on porphyrins and Schiff bases.

We acknowledge financial support of this research under NIEHS grant ES0-4911B. We also thank Alcoa for a grant in support of LDH research.

Received, 2nd November 1992; Com. 2/05848K

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