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Catalytic autoxidation of 1-decanethiol by cobalt(II) phthalocyaninetetrasulfonate intercalated in a layered double hydroxide

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A hydrotalcite-like layered double hydroxide (LDH) interlayered by cobalt(II) phthalocyaninetetrasulfonate, $[Mg_5Al_2(OH)_{14}][CoPcTs]_{0.5}.6H_2O$, has been prepared in 92% yield by reaction of $Mg_{0.63}Al_{0.25}\square_{0.12}O$ ($\square$ = vacancy) with the $[CoPcTs]^{4-}$ ion in aqueous solution. The intercalated complex was twice as active for the catalytic autoxidation of aqueous 1-decanethiol at 35 °C and pH 9.25 than the homogeneous complex under equivalent reaction conditions. More importantly, the homogeneous catalyst was completely deactivated after one catalytic cycle involving only ~ 150 turnovers, whereas no loss in activity was observed for the intercalated catalyst after five consecutive reaction cycles for a total of more than 770 turnovers. Thus, layered double hydroxide intercalation compounds appear to be exceptionally promising support materials for improving the longevity of certain types of biomimetic metallo macrocyclic catalyts.

Keywords: Thiol autoxidation; cobalt; phthalocyaninetetrasulfonate; layered double hydroxide

1. Introduction

Hydrotalcite-like layered double hydroxides of the type $M^{II}_{1-x}M^{III}_{x}(OH)_2][A^{n-}]_{x/n}.yH_2O$, wherein the A^{n-} anion is intercalated between brucite-like hydroxide sheets, have been utilized as precursors for the preparation of mixed metal oxide catalysts for a variety of organic chemical conversions [1]. However, there are relatively few examples of reaction systems wherein the LDH structure is retained during the catalytic cycle. Recent advances in the pillaring of LDHs by polyoxometalate anions may lead to new applications of these microporous materials as oxidation catalysts [2].

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As part of an effort to design LDH-based oxidation catalysts with biomimetic properties, we have been investigating the intercalation of metallo derivatives of sulfonated phthalocyanines and related macrocycles. The present work reports the preparation of a new $Mg_{2.5}Al$-LDH intercalate containing a cobalt(II) phthalocyaninetetrasulfonate anion, $[CoPcTs]^{4-}$, and describes the properties of the immobilized complex as a catalyst for the autoxidation of 1-decanethiol. The ability of $[CoPcTs]^{4-}$ to catalyze the oxidation of thiols by dioxygen is of considerable practical interest. Thiols, even when present in small quantities, are environmentally undesirable contaminants of certain petroleum distillates and industrial effluents [3]. However, $[CoPcTs]^{4-}$ as a homogeneous catalyst is readily deactivated and difficult to recover from the reaction medium. We show here that the immobilization of the complex by intercalation into a LDH host substantially improves catalyst reactivity, recoverability, and, especially, longevity.

2. Experimental

The tetrasodium salt of cobalt(II) 4, 4′, 4″, 4‴-tetrasulfonate phthalocyanine was prepared and purified by previously described methods [4]. Chemical analyses showed the Na/Co ratio to be 4.2, in accorded with the expected ratio of 4.0. The electronic spectrum of a 2×10^{-5} M solution of $Na_4[CoPcTs]$ in water at room temperature was coincident with the spectrum previously reported by Yang et al. [5]. A hydrotalcite-like layered double hydroxide of the type $[Mg_5Al_2(OH)_{14}][CO_3].yH_2O$ was prepared by the coprecipitation of stoichometric amounts of Mg^{2+} and Al^{3+} in the presence of carbonate at pH 12.7 using methods analogous to those described earlier [6]. Magnesium, aluminum, and carbon analyses were in agreement with the idealized composition. The $Mg_{2.5}Al$-LDH was converted to the metal oxide solid solution of composition $Mg_{0.63}Al_{0.25}\square_{0.12}$ ($\square$ = vacancy) by heating the LDH carbonate at 500 °C for 24 hours under an argon atmosphere. The solid solution was then reconstituted into a LDH-$CoPcTs^{4-}$ intercalation compound by reaction of the sodium salt of the complex in 10% excess with the oxide at 60 °C for seven days under an argon atmosphere to minimize contamination by atmospheric CO_2. The blue $[Mg_{2.5}Al]$-$[CoPcTs]^{4-}$ LDH product was washed free of excess salt and dried in a desiccator over calcium chloride.

The properties of $[CoPcTs]^{4-}$ as a catalyst for the autoxidation of 1-decanethiol was studied in quantitative detail for the ion in both the homogeneous and intercalated state. Reactions were carried out at pH 9.25 in the presence of a borate buffer. Each experiment was conducted under a constant oxygen pressure in the range 730 to 735 Torr. Dioxygen depletion was monitored with a gas buret. An amount of catalyst containing 0.010 mmol of $[CoPcTs]^{4-}$ in a vigorously stirred suspension or solution was allowed to equilibrate for two hours under an oxygen atmosphere prior to the injection of 1.54 millimoles (0.32

mL) of 1-decanethiol. Oxygen uptake by both the homogeneous and heterogeneous catalyst was preceded by an induction period.

3. Results and discussion

$Mg_{0.63}Al_{0.25}\square_{0.12}O$ ($\square$ = vacancy), prepared by the thermal decomposition of $[Mg_5Al_2(OH)_{14}][CO_3].xH_2O$ at 500 °C, was found to react at 60 °C with aqueous $[CoPcTs]^{4-}$ in 10% stoichiometric excess to afford $[Mg_5Al_2(OH)_{14}][CoPcTs]_{0.5} \cdot 6H_2O$ in 92% yield. The infrared spectrum of the intensely blue product contained bands characteristic of the brucite-like $Mg_{2.5}Al$-LDH sheets and the intercalated $[CoPcTs]^{4-}$ anion. A weak band at 1371 cm^{-1} due to the ν_3 stretching mode of CO_3^{2-} suggested that the product contained a trace of carbonate ion as an impurity. Elemental analyses gave a Co/Al ratio of 0.23, indicating that 92% of the LDH exchange sites were balanced by $[CoPcTs]^{4-}$ anions.

The X-ray diffraction pattern for an oriented film sample of the $Mg_{2.5}Al$-$[CoPcTs]^{4-}$ LDH intercalate exhibited six orders of 001 harmonics corresponding to a basal spacing of 23.3 ± 0.3 Å. Since the van der Waals thickness of the brucite sheets is ~ 4.8 Å, the observed spacing was indicative of a gallery height of ~ 18.5 Å, a value very near the van der Waals width of the sulfonated phthalocyanine ring. It may be concluded, therefore, that the $[CoPcTs]^{4-}$ ion has been intercalated with the plane of the phthalocyanine ring perpendicular, or nearly so, to the brucite sheets of the host, as illustrated in fig. 1. A similar "edge-on" orientation recently has been reported for a non-metalated tetrasulfonated prophyrin anion intercalated into an LDH structure [7].

$[CoPcTs]^{4-}$ is known to catalyze the autoxidation of thiols under homogeneous reaction conditions according to the following reaction sequence:

$$2RS^- + O_2 + H_2O \rightarrow RSSR + HO_2^- + OH^- \quad (1)$$

$$2RS^- + HO_2^- + H_2O \rightarrow RSSR + 2H_2O + 3OH^- \quad (2)$$

where eq. (1) is rate limiting. Mechanisms involving formation of mononuclear [8] and RS^- bridged dinuclear [9] complexes have been proposed. We have examined the behavior of $[CoPcTs]^{4-}$ for the autoxidation of 1.5×10^{-2} *M* 1-decanethiol at 35 °C under homogeneous reaction conditions and have compared the results with those obtained for the anion supported on the basal surfaces of a $Mg_{2.5}Al$-LDH host. The reactions were carried out in the presence of a borate buffer at pH 9.25 to promote formation of the thiolate anion, which is believed to be the reactive species involved in the oxidation mechanism. The initial thiol: $[CoPcTs]^{4-}$ molar ratio was 151 : 1.

As shown in fig. 2A, the homogeneous catalyst exhibited a linear uptake of dioxygen following an induction period of ~ 2.3 hr. The turnover frequency

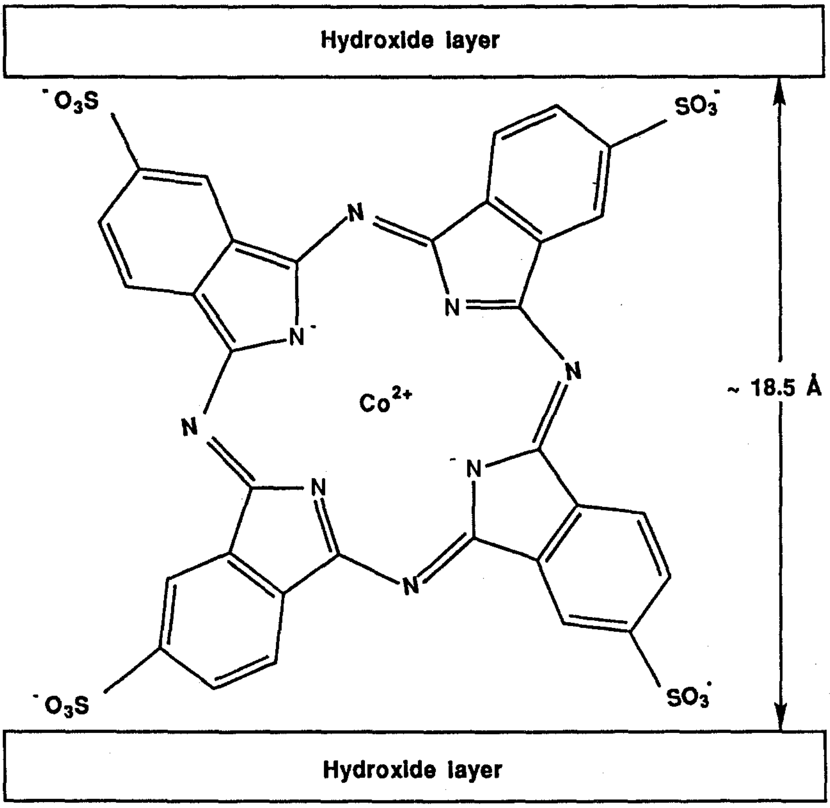

Fig. 1. Schematic illustration of the "edge-on" orientation of the $[CoPcTs]^{4-}$ anion intercalated in a $Mg_{2.5}Al$-LDH.

determined from the O_2 uptake plot was 21 mol thiol/mol $[CoPcTs]^{4-}$/hr. After one 12-hr reaction cycle the net O_2 uptake was in agreement with the overall stiochiometry given by the sum of eqs. (1) and (2) and no thiol odor was detected after this reaction period. Over the same 12-hr reaction cycle, however, the color of the solution gradually faded from the intense blue characteristic of $[CoPcTs]^{4-}$ to colorless, and a gummy red precipitate formed at the bottom of the reaction flask. The addition of a second aliquot portion of 1-decanethiol into the reaction vessel resulted in no additional O_2 uptake, indicating that the homogeneous catalyst had become completely deactivated after only one reaction cycle ($\sim$ 150 catalytic turnovers). These observations were in agreement with previous reports of the deactivation of the homogeneous catalyst [10]. Significantly, no O_2 uptake was noted over a 24 hr reaction period in the absence of $[CoPcTs]^{4-}$.

In comparison to homogeneous $[CoPcTs]^{4-}$, the LDH intercalated catalyst exhibited a substantially shorter induction period (45 min) and a larger turnover frequency of 40 mol thiol/mole $[CoPcTs]^{4-}$/hr (cf. fig. 2B). More importantly,

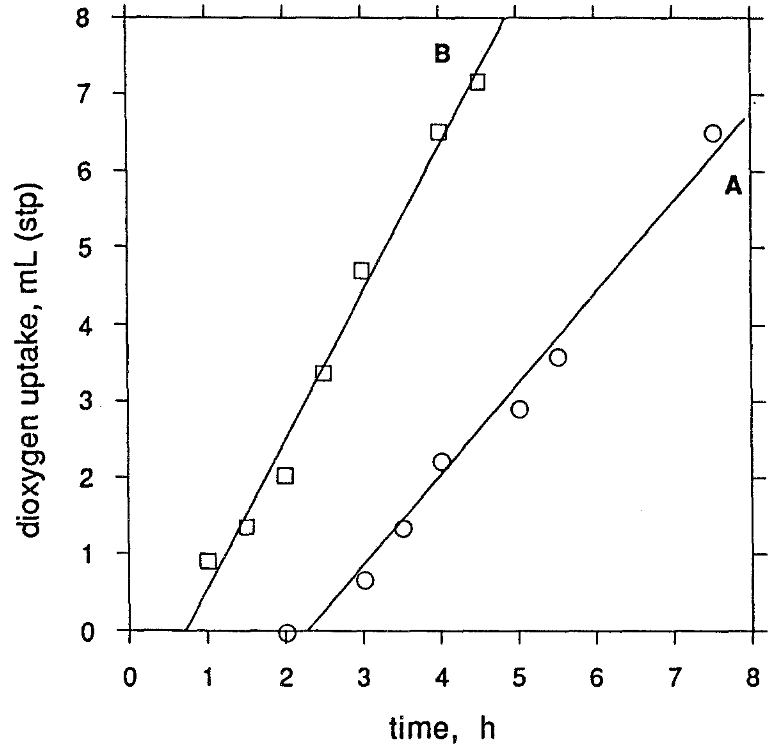

Fig. 2. Dioxygen uptake plots for the autoxidation of 1.5×10^{-2} *M* 1-decanethiol at 35 °C in the presence of the $[CoPcTs]^{4-}$ as catalyst: (A) homogeneous catalyst, (B) LDH-intercalated catalyst. The reactions were carried out at a substrate/cobalt ratio of 154 and pH 9.25.

no catalyst decomposition was noted at the end of the first catalytic cycle. The LDH intercalate retained the intense blue color of $[CoPcTs]^{4-}$, no red precipitate was observed, and the superinatent solution remained colorless. In fact, four additional catalytic cycles for a total of 770 turnovers could be carried out in the same reaction vessel without a detectable loss of activity. The recovered catalyst retained the characteristic blue color of $[CoPcTs]^{4-}$ and exhibited an unaltered basal spacing of 23.6 Å.

$[CoPcTs]^{4-}$ has been immobilized on a number of different supports, including polymers [11], amorphous oxides [12], zeolites [13] and activated carbons [12] in efforts to improve the catalytic efficiency of the complex for thiol autoxidation. Polymer colloids with particle diameters of 0.50–0.5 μm have been identified as especially promising support matrices [14]. Indeed, $[CoPcTs]^{4-}$ supported on cationic latexes [15] exhibit initial reactivities for 1-decanethiol oxidation that are more than an order of magnitude higher than our LDH-supported complex under equivalent reaction conditions. However, after only one catalytic cycle involving only ~ 150 turnovers, the latex catalyst was only 0.33 times as reactive as the fresh catalyst. This is in dramatic contrast to the stability observed for our LDH catalyst after more than 770 turnovers. Thus, the LDH intercalation compounds appear to be exceptionally promising materials for improving the longevity of certain types of biomimetic metallo macrocyclic catalysts.

The enhanced stability of the LDH-supported complex relative to the homogeneous and latex-supported species may be related to the order afforded by the crystalline LDH surfaces. Cobalt centers at external basal surfaces and crystallites edges may be accessible for reaction without being mobile. The importance of such sites for the [$Mg_{2.5}Al$] LDH system is suggested by the relatively low N_2 BET surface area of 28 m^2/g after outgassing at 190 ° C. The average separation between cobalt centers and access to the intracrystalline metal sites can in principal be mediated by controlling the fraction of M^{III} ions present in the [$M^{II}_{1-x}M^{III}_x(OH)_2$] layers.

Future studies will examine possible relationships between catalytic activity, LDH layer charge density, and pH.

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