

# Catalytic properties of biomimetic metallomacrocycles intercalated in layered double hydroxides and smectite clay: the importance of edge-site access

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## Abstract

Anionic and cationic forms of two biomimetic macrocyclic metal complexes, namely, Co(II)–tetrasulphthalocyanine anions, [CoPcTs]<sup>4-</sup>, and Co(II)–tetra(*N*-methyl-4-pyridiniumyl)porphyrin cations, [CoTMPyP]<sup>4+</sup>, have been intercalated in Mg/Al layered double hydroxides (LDH) and a fluorohectorite smectite clay, respectively. The catalytic activities of the intercalated complexes for the dioxygen oxidation of 2,6-di-*tert*-butylphenol have been compared with those for the corresponding complexes under homogeneous reaction conditions. [CoPcTs]<sup>4-</sup> intercalated in Mg<sub>2</sub>Al- and Mg<sub>4</sub>Al-layered double hydroxides exhibit dramatically enhanced catalytic activity and longevity relative the homogenous metal complex. In contrast, [CoTMPyP]<sup>4+</sup> intercalated in F-hectorite reduces the activity of the metallomacrocycle. The activities are correlated with the orientation of the macrocyclic complex in the galleries of the layered host. In the LDH intercalates, the plane of the complex is perpendicular to the host layers, whereas in F-hectorite the plane is inclined at an angle of 27°. The vertical orientation of the macrocycle in LDHs optimizes the accessibility of the metal complex centers near the external edge sites of the crystallites, which are the most important sites for reaction with the substrate. Metallomacrocycles bound at intracrystal gallery sites or at the external basal planes of the host are not readily accessible for reaction and do not contribute greatly to the overall catalytic activity.

**Keywords:** Intercalated metallomacrocycles; Phthalocyanine; Porphyrin; Phenol oxidation; Smectite clay; Layered double hydroxides

## 1. Introduction

Metalloporphyrins and metallophthalocyanines both in homogeneous solution and in the solid supported state are capable of carrying out redox catalysis under ambient conditions [1–16]. In general, supported rather than homogeneous forms of metallomacrocycles are desired in order to immobilize and stabilize the complexes

against deactivating dimerization and other destructive processes under oxidizing conditions in homogeneous solution. Molecular sieves are attractive support systems for catalytically attractive cationic species. Zeolites, for instance, possess a well defined architecture that could be useful for shape selectivity, as initially demonstrated by Herron et al. [8,9]. These latter workers used zeolite encapsulated iron phthalocyanine catalysts for the oxidation of cycloalkanes such as cyclododecane.

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We have reported the synthesis and characterization of intercalated layered double hydroxides (LDH) and smectite clays interlayered by Co(II)–tetrasulfophthalocyanine anions,  $[\text{CoPcTs}]^{4-}$ , and Co(II)–tetra(*N*-methyl-4-pyridiniumyl) porphyrin cations,  $[\text{CoTMPyP}]^{4+}$ , respectively [10,11]. A combination of electron spin resonance (ESR), UV–Vis spectroscopy and X-ray diffraction (XRD) was used to characterize the wet and dry states of the intercalation products. We found that  $[\text{CoTMPyP}]^{4+}$ , when intercalated in the low charge density clay hectorite, adopted an orientation with the plane of the porphyrin parallel to the silicate layers with no axially water coordinated to the cobalt. However, intercalation of the complex in the high charge density clay fluorohectorite, caused the porphyrin to be oriented at a  $27^\circ$  angle relative to the clay layers with water molecules coordinated axially to Co(II). In the LDH– $[\text{CoPcTs}]^{4-}$  system a basal spacing of 23.7 Å indicated an ‘edge-on orientation’ of the phthalocyanine. ESR showed that water was axially coordinated to Co(II). This edge-on orientation is not affected by dehydration, unlike the F-hectorite system where vacuum dehydration caused rearrangement of the  $[\text{CoTMPyP}]^{4+}$  into a ‘staggered’ bilayer orientation.

Recently Meunier and his co-workers [12] reported that metalloporphyrins are excellent homogeneous catalysts for the oxidative destruction of chlorinated aromatics in aqueous solution. The immobilization of such macrocyclic complexes on a readily recyclable solid support, such as an LDH or a smectite clay, would greatly enhance the usefulness of such macrocyclic complexes for environmental pollution control. But having supported metal centers that are accessible to large organic substrates is an essential prerequisite for the biomimetic catalytic applications of supported metallomacrocyclic systems, especially if these systems are to be useful for the remediation of contaminated ground waters and industrial effluents.

In this report we investigate the role that accessibility plays in determining the heterogeneous catalytic activity of intercalated

$[\text{CoPcTs}]^{4-}$  and  $[\text{CoTMPyP}]^{4+}$  in LDHs and smectite clay. The dioxygen oxidation of 2,6-di-*tert*-butylphenol is used as a model reaction. Our earlier studies suggested that the ‘edge on’ orientation of metallophthalocyanines in LDHs should facilitate access of reactants and products in the interlayers more readily than in  $[\text{CoTMPyP}]^{4+}$ –F-hectorite, wherein the metallomacrocycles are packed more densely in a less accessible inclined orientation. We compare the catalytic activities of the intercalated LDH and smectite clay systems and investigate the influence of LDH charge density on intercalation and activity. Also, we include the homogeneous metallomacrocycles in the investigation for comparative purposes.

## 2. Experimental

### 2.1. Materials and physical characterization

All chemicals were analytical reagent grade and were used as received.  $[\text{CoTMPyP}]^{4+}$  was obtained as tetrachloride salt from Mid-century Co. (Posen, IL).  $[\text{CoPcTs}]^{4-}$  was synthesized as the tetrasodium salt by a published procedure [13]. The  $[\text{CoTMPyP}]^{4+}$  concentration in solution was determined by dissolving the complex in deoxygenated water under nitrogen and measuring the absorbance at 429 nm ( $\epsilon = 1.38 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ).

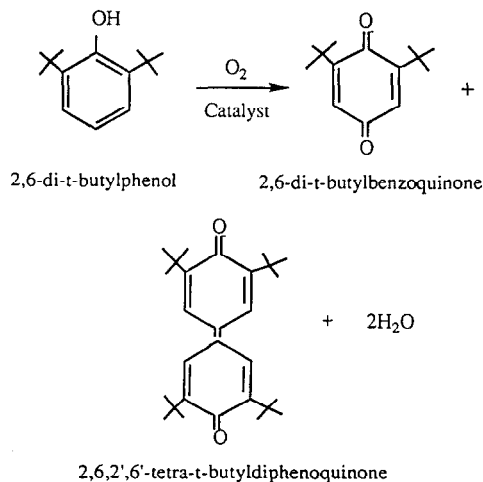
A layered double hydroxide of the type  $[\text{Mg}_5\text{Al}_2(\text{OH})_{14}][\text{CO}_3] \cdot y\text{H}_2\text{O}$  was prepared by co-precipitation. The LDH carbonate was calcined at  $500^\circ\text{C}$  to form a Mg–Al–O solid solution, which was then reconstituted into a  $[\text{CoPcTs}]^{4-}$  intercalated LDH by methods reported earlier [6,7]. Elemental analysis showed the LDH composition to be  $\text{Mg}_5\text{Al}_{2.5}(\text{OH})_{14.9}(\text{CoPcTs})_{0.6} \cdot 4\text{H}_2\text{O}$ . Analogous methods were used to form a Mg<sub>4</sub>Al– $[\text{CoPcTs}]^{4-}$  intercalate wherein the layer charge density is half that of the Mg<sub>2</sub>Al intercalate. Synthetic F-hectorite,  $\text{Li}_{1.6}(\text{Mg}_{4.4}\text{Li}_{1.6})\text{Si}_8\text{O}_{20}\text{F}_4$ , was obtained from Corning, Inc. and used without further modification.

$[\text{CoTMPyP}]^{4+}$  was intercalated in F-hectorite by reacting 0.1 g of clay as a 0.1 wt.-% aqueous suspension with 47.5 ml of  $10^{-3}$  M aqueous solution of  $[\text{CoTMPyP}]^{4+}$  to fully saturate the cation exchange capacity (CEC) of the clay. The exchange reaction was performed under a  $\text{N}_2$  atmosphere. After 4 h reaction time the  $[\text{CoTMPyP}]^{4+}$  exchanged clay was centrifuged. The supernatant liquid was colorless, indicating that all the porphyrin had been intercalated. The  $[\text{CoTMPyP}]^{4+}$ -F-hectorite used for catalytic studies was stored as an aqueous suspension.

Powdered and thin film samples were used to collect X-ray diffraction data. The diffraction patterns were collected using a Rigaku rotating anode X-ray diffraction with  $\text{Cu K}_\alpha$  radiation.

## 2.2. Catalysis studies

The reaction shown below was carried out in a closed 200-ml round bottomed flask using 0.1 g 2,6-di-tert-butylphenol dissolved in a 14/1 (v/v) water/methanol mixture saturated by air. Dioxygen depletion was monitored using a Clark-type  $\text{O}_2$  electrode (Orion model 98-07). The electrode was attached to a Fisher Accumet selective analyzer Model 750 pH meter equipped with a plotter for readout of dioxygen concentration in parts-per-million (ppm). GC/mass spectrometry was used to identify the reaction products.



## 3. Results and discussion

### 3.1. LDH intercalates

The powder X-ray diffraction shown in Fig. 1a of an oriented thin film of  $[\text{Co}(\text{PcTs})]^{4-}$  intercalated in a  $\text{Mg}_2\text{Al}$  LDH gave multiple 001 reflections indicative of a basal spacing of  $\approx 23.7$  Å. Since the van der Waals thickness of the brucite sheets is about  $\approx 4.8$  Å, the basal spacing corresponds to a gallery height of  $\approx 19$  Å, a value very close to the van der Waals width of the sulfonated phthalocyanine ring. On the basis of this evidence an edge-on orientation is indeed indicated as illustrated in Fig. 2. A virtually identical XRD pattern and  $[\text{CoPcTs}]^{4-}$  orientation was observed for the corresponding  $\text{Mg}_4\text{Al}$ -LDH intercalate. For both layer charge densities the edge-on macrocycle orientation effectively balances the layer charge by placing the sulfate groups close to the centers of positive charge in the host layers. In contrast, a parallel orientation of the phthalocyanine ring would require unfavorable multiple layer stacking of the negatively charged  $\text{Mg}$  complex anions for both the  $\text{Mg}_2\text{Al}$ - and  $\text{Mg}_4\text{Al}$ -LDH intercalates. As shown by the diffraction pattern in Fig. 1b of the  $\text{Mg}_2\text{Al}$ -LDH intercalate after use as a heterogeneous catalyst for 2,6-di-tert-butylphenol oxidation, the catalyst is structurally stable under catalytic reaction conditions.

The initial oxygen uptake for the homogeneous  $[\text{CoPcTs}]^{4-}$  for the phenol oxidation reaction was characterized by a linear uptake with a limited induction period (Fig. 3). The turnover frequency for the homogeneous catalyst was found to be about 52 mmol dioxygen/mol  $[\text{CoPcTs}]^{4-}$ /min. However, the catalyst longevity toward the homogeneous reaction was greatly limited. Only 25 turnovers (mole substrate/mole complex) could be achieved before the homogeneous catalyst became completely deactivated. In comparison, the heterogeneous  $\text{Mg}_2\text{Al}$ - $[\text{CoPcTs}]^{4-}$  LDH catalyst showed an  $\text{O}_2$  uptake rate (shown in Fig. 4) of just about

double the turnover frequency of 109 mmol dioxygen/mol  $[\text{CoPcTs}]^{4-}$ /min and a longevity of over 3200 turnovers (mole substrate/mole complex).

The exceptional reactivity the heterogeneous  $\text{Mg}_2\text{Al}-[\text{CoPcTs}]^{4-}$  LDH catalyst was realized despite a  $\text{N}_2$  BET surface area for the LDH catalyst of only  $28 \text{ m}^2/\text{g}$ . Also, the LDH catalyst is completely non-porous toward dinitrogen with almost all of the nitrogen being adsorbed on the external surfaces of the LDH crystallites. The absence of microporosity toward dinitrogen means that the intracrystalline  $[\text{CoPcTs}]^{4-}$  sites also are inaccessible to the reactant molecule 2,6-di-tert-butylphenol, which has a much larger Van der Waals diameter of about  $10.9 \text{ \AA}$ . Thus,

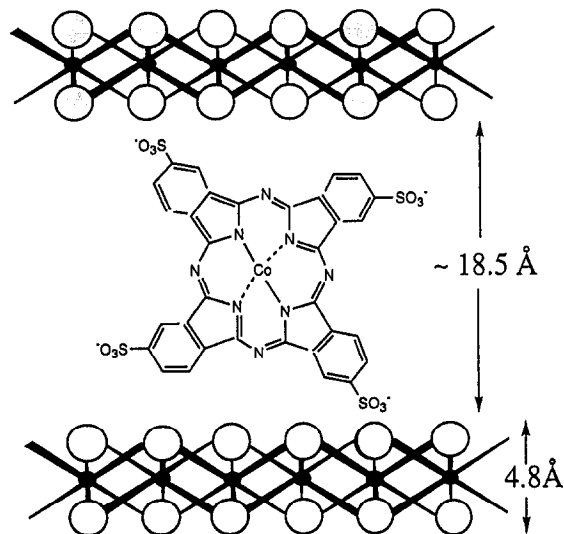


Fig. 2. Orientation of  $[\text{CoPcTs}]^{4-}$  intercalated between layered double hydroxide host.

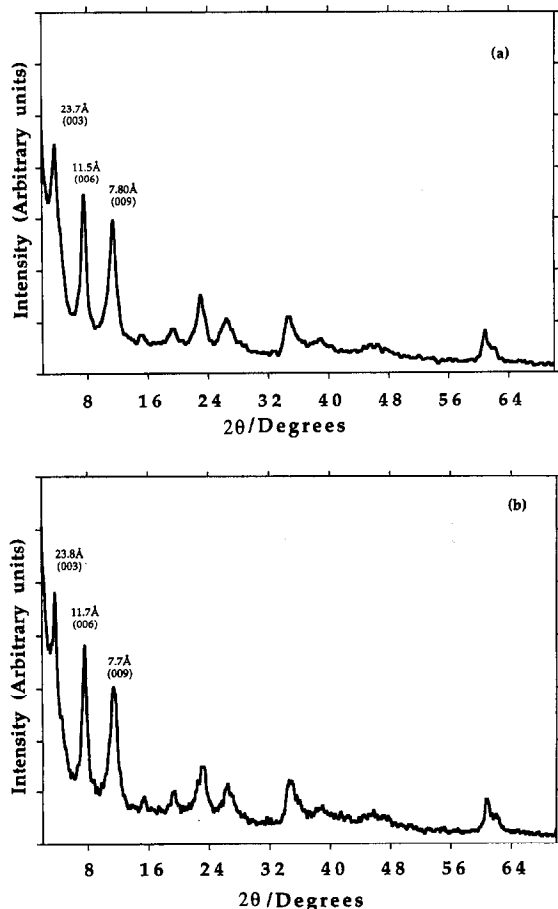


Fig. 1. X-ray diffraction patterns of a  $\text{Mg}_2\text{Al}-[\text{CoPcTs}]^{4-}$  LDH intercalate (a) before and (b) after use as a catalyst for 2,6-di-tert-butylphenol oxidation.

only  $[\text{CoPcTs}]^{4-}$  ions held at crystallite edge sites and external basal surface sites are capable of participating in the oxidation reaction.

The intercalation of  $[\text{CoPcTs}]^{4-}$  into a lower charge density  $\text{Mg}_4\text{Al}$  LDH host resulted in an almost fivefold increase in reaction rate to 519 mmol dioxygen/mol complex/min (see Fig. 4). The significant increase in the rate of dioxygen uptake by the  $\text{Mg}_4\text{Al}$  LDH system could be a result of some near edge gallery cobalt sites becoming accessible for the reaction due to the lower layer charge density and greater separation between the intercalated cobalt centers (area/charge ratio  $\approx 40 \text{ \AA}^2/e^+$  compared to  $\approx 26 \text{ \AA}^2/e^+$  for the  $\text{Mg}_{2.5}\text{Al}$  LDH). Tatsumi and his co-workers [17] have claimed intracrystalline activity for a polyoxometalate-pillared LDH for the selective epoxidation of alkenes using hydrogen peroxide as the oxidizing agent. They observed that while the epoxidation of 2-hexene in the presence of an LDH- $[\text{Mo}_7\text{O}_{24}]^{6-}$  intercalate proceeded smoothly, while that of the more spatially demanding cyclohexene did not. However, the  $\text{Mg}_4\text{Al}-[\text{CoPcTs}]^{4-}$  LDH catalyst of the present work exhibits only a slightly larger  $\text{N}_2$  BET surface area. Thus, it appears that the higher reactivity

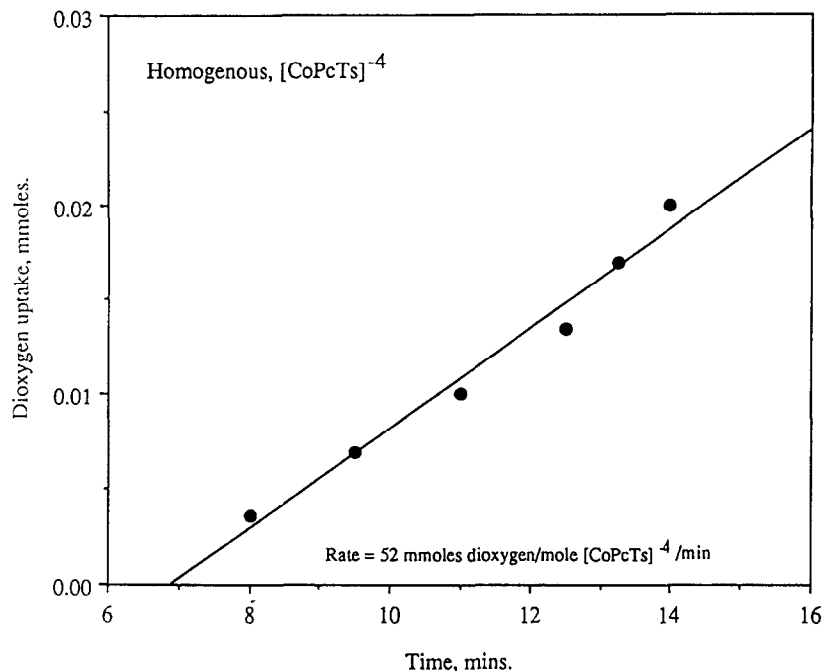


Fig. 3. Initial dioxygen uptake plots for oxidation of  $5.8 \times 10^{-4}$  mol of 2,6-di-tert-butylphenol in 15:1 (v:v) water-methanol at 35°C in the presence  $\text{Na}_4[\text{CoPcTs}]$  as a homogenous catalyst. Rate = 52 mmol oxygen/mol  $[\text{CoPcTs}]^{4-}$ /min.

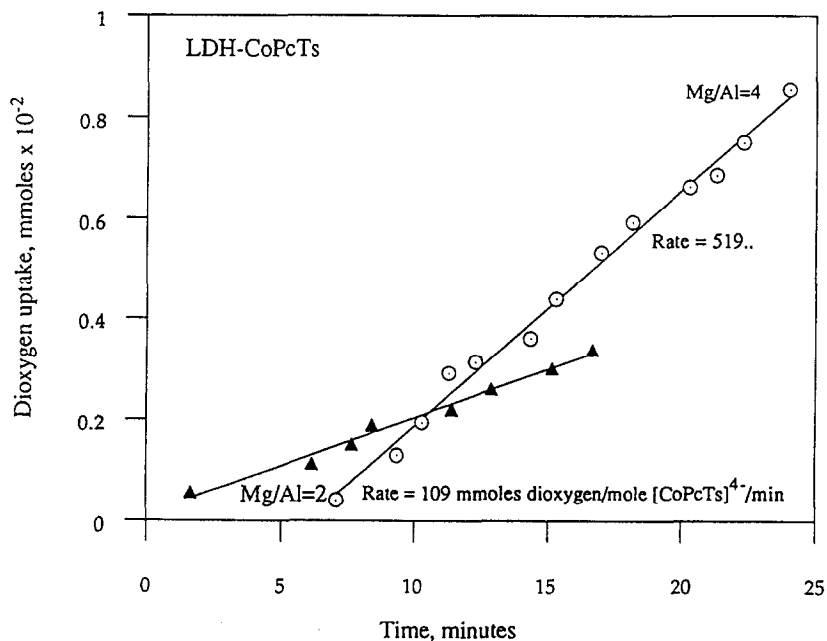


Fig. 4. Initial dioxygen uptake plots for the oxidation of 2,6-di-tert-butylphenol in 15:1 water-methanol (v:v) at 35°C in the presence of  $\text{Mg}_2\text{Al}-[\text{CoPcTs}]^{4-}$  LDH catalyst. Rate = 109 mmol oxygen/mol  $[\text{CoPcTs}]^{4-}$ /min and  $\text{Mg}_4\text{Al}-[\text{CoPcTs}]^{4-}$  LDH catalyst. Rate = 519 mmol oxygen/mol  $[\text{CoPcTs}]^{4-}$ /min.

cannot be due to substantially greater intracrystal accessibility of the macrocyclic centers. It may be that there is improved access to complex sites localized near the external edge surfaces of the  $Mg_4Al$  LDH crystallites.

### 3.2. *F*-hectorite intercalated $[CoTMPyP]^{4+}$

The immobilization of  $[CoTMPyP]^{4+}$  in the galleries of the smectite clay *F*-hectorite results in the intercalation of the porphyrin at an angle of  $27^\circ$  relative to the host layers. This orientation, which is indicated by a basal spacing of  $18.6 \text{ \AA}$  in the powder XRD pattern (see Fig. 5), differs from that of metallophthalocyanines intercalated between both  $Mg_2Al$  and  $Mg_4Al$  LDH host layers, wherein the orientation of the macrocycle is perpendicular to the host layers in both cases.

Fig. 6 and Fig. 7 show the catalytic results for homogenous  $[CoTMPyP]^{4+}$  and heterogeneous  $[CoTMPyP]^{4+}$ -*F*-hectorite catalysts, respectively. There are notable differences between the two catalyst systems. For instance, the induction period before the catalytic reaction

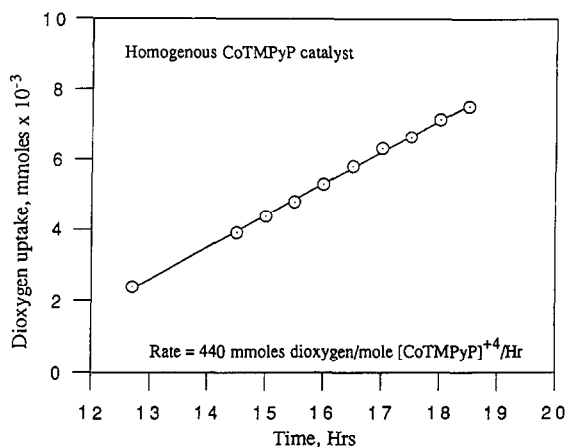


Fig. 6. Initial dioxygen uptake plots for the oxidation of 2,6-di-tert-butylphenol ( $4.84 \times 10^{-4}$  mol) in 15:1 (v:v) water-methanol at  $35^\circ\text{C}$  in the presence of a homogenous  $[CoTMPyP]^{4+}$  catalyst. Rate = 440 mmol oxygen/mol  $[CoTMPyP]^{4+}$ /min.

begins at  $\approx 10$  h for the homogenous solution and at  $\approx 13$  h for the *F*-hectorite system. In contrast to the remarkable enhancement in activity for  $[CoPcTs]^{4-}$  intercalated in LDHs, the immobilization of the  $[CoTMPyP]^{4+}$  metallo-macrocycle in the smectite galleries does not

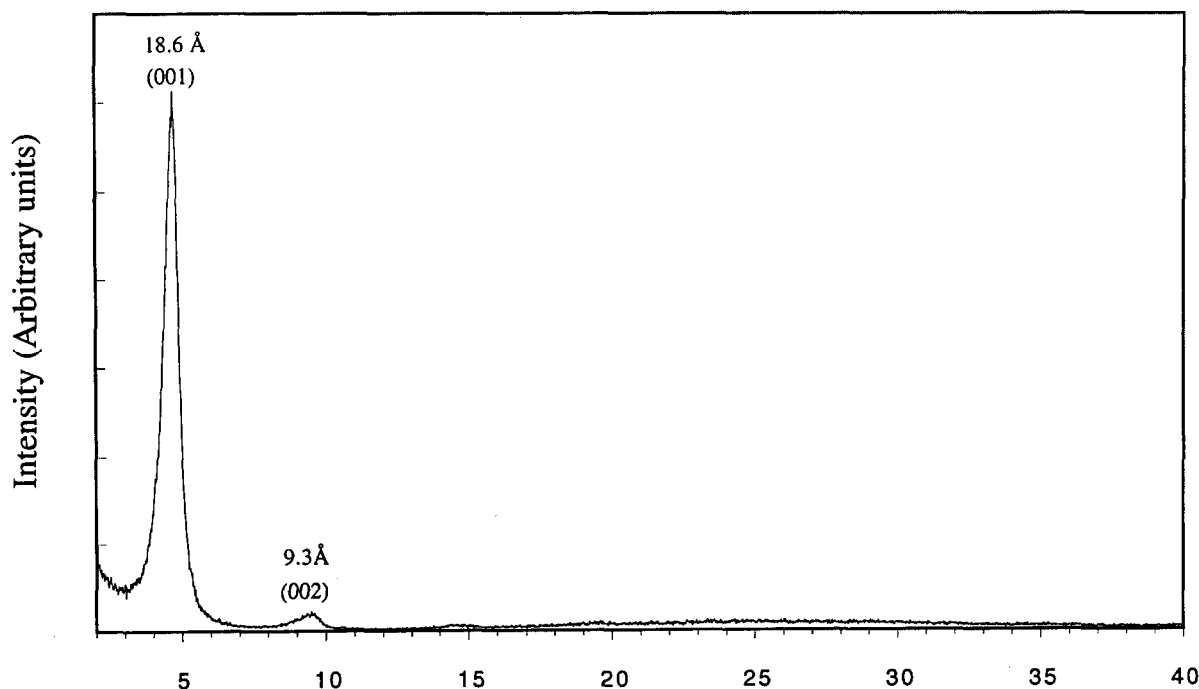


Fig. 5. Powder X-ray diffraction pattern of  $[CoTMPyP]^{4+}$ -*F*-hectorite (X-axis in degrees  $2\theta$ ).

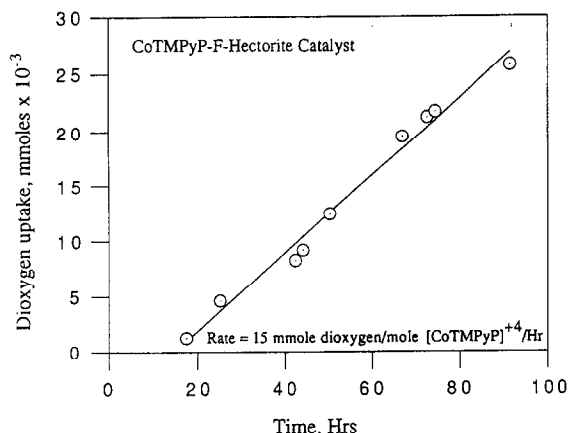


Fig. 7. Initial dioxygen uptake plots for the oxidation of 2,6-di-tert-butylphenol in 15:1 (v:v) water-methanol at 35°C in the presence of  $[\text{CoTMPyP}]^{4+}$ -F-hectorite as the heterogeneous catalyst. Rate = 15 mmol oxygen/mol  $[\text{CoTMPyP}]^{4+}$ /h.

enhance catalytic activity. In fact, there is a substantial loss in catalytic activity when  $[\text{CoTMPyP}]^{4+}$  is immobilized. The homogeneous catalyst gives a turnover frequency of 440 mmol dioxygen/mol  $\text{CoTMPyP}$ /h, whereas the F-hectorite supported complex exhibits a rate of only 15 mmol dioxygen/mol  $[\text{CoTMPyP}]^{4+}$ /h, a decrease of about 30-fold.

As expected, the intercalated macrocyclic centers in  $[\text{CoTMPyP}]^{4+}$ -F-hectorite are inaccessible to 2,6 di-tert-butylphenol molecules for oxidation to the quinone. Thus, the observed activity for the heterogeneous catalyst in the case of the LDH- $[\text{CoPcTS}]^{4-}$  systems must arise from metal complex centers at the external edges and basal surfaces of the clay tactoids. Because the external surface areas of smectite clays are similar to those found for LDH intercalates (30–60  $\text{m}^2/\text{g}$ ), the differences in the reactivity of the metallomacrocyclic in the intercalated state relative to the homogeneous complex cannot be attributed to differences in the surface areas of the layered supports.

The fundamental difference between the LDH and the smectite clay intercalates is the orientation of the complex in the gallery. Clearly, the perpendicular orientation of the complex in the LDH- $[\text{CoPcTS}]^{4-}$  systems allows the metal center to be accessible to the reagents at the

external edge sites of the galleries. However, the inclined monolayer orientation of the macrocycle in F-hectorite precludes access to the macrocyclic complex even at the edge sites. This would suggest that it is edge surface sites, as opposed to basal surface sites, that are most important in determining the catalytic activity of these intercalated macrocyclic catalysts. From our earlier study of  $[\text{CoTMPyP}]^{4+}$ -F-hectorite, we observed that upon dehydration the macrocycle rearranged from the tilted monolayer orientation into a 'staggered' bilayer structure. In contrast, the intercalated LDH catalysts retain the perpendicular orientation of the phthalocyanine even after dehydration. This is consistent with the observation that when dried before use the  $[\text{CoTMPyP}]^{4+}$ -F-hectorite is almost completely inactive, whereas the LDH- $[\text{CoPcTS}]^{4-}$  systems retain their catalytic activity.

#### 4. Conclusions

$[\text{CoPcTS}]^{4-}$  immobilized by intercalation in  $\text{Mg}_2\text{Al}$ - and  $\text{Mg}_4\text{Al}$ -layered double hydroxides exhibit dramatically enhanced catalytic activity and longevity for biomimetic oxidations relative to the homogeneous metal complex. The immobilization process presumably inhibits the deactivating dimerization and self oxidation reactions that limit the performance of the homogeneous catalysts. The 'edge-on' orientations of the intercalated  $[\text{CoPcTS}]^{4-}$  complex in both the  $\text{Mg}_2\text{Al}$ - and  $\text{Mg}_4\text{Al}$ -LDH systems allows facile access to the cobalt centers at the external edge surfaces of the LDH crystallites. The intercalated metallomacrocyclic is approximately five times more active in the  $\text{Mg}_4\text{Al}$  LDH than in the  $\text{Mg}_2\text{Al}$  host. Improved access to the edge site metal complex centers in the lower charge density host may be responsible for the greater activity.

In contrast to the LDH- $[\text{CoPcTS}]^{4-}$  intercalates, the intercalation of the  $[\text{CoTMPyP}]^{4+}$  cations in F-hectorite greatly reduces the reac-

tivity of the metallomacrocyclic complex in comparison to the homogenous complex. Owing to the 27° tilt angle and close packing of the hydrated cobalt(II) porphyrin in the F-hectorite galleries, only very limited access to external edge site centers is possible. The accessibility of edge site centers in F-hectorite is almost completely eliminated by dehydrating the complex and converting the porphyrin orientation from an inclined monolayer to a staggered lateral bilayer.

Metallomacrocyclic centers immobilized on the intragallery surfaces of LDH and the smectite clay hosts do not contribute significantly to the catalytic activities of the intercalates. It is the accessibility of the metal complex centers primarily at the external edge sites that contributes most importantly to the activity of the immobilized catalyst. Optimum accessibility to these centers is provided by a vertical orientation of the intercalated macrocycle. The vertical orientation is readily achieved in LDH hosts, probably due to the optimization of guest–host charge matching and H bonding of the sulfate groups to the hydroxyl groups of the host layers. H bonding between the layered host and intercalated guest is precluded in the analogous [CoTMPyP]<sup>4+</sup> F-hectorite system and, at best, only an inclined orientation of the metalocyclic ring is possible. Consequently, LDHs are best suited hosts for the immobilization of metallomacrocyclic complexes for biomimetic oxidation reactions. Catalytic activities even greater than those observed in the present work can be expected for intercalates formed from LDH crystallites with very small width to thickness aspect ratios. This would further increase the number of accessible metal complex centers for chemical catalysis.

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