

# Oxidation of cyclohexene with molecular oxygen catalyzed by cobalt porphyrin complexes immobilized on montmorillonite

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## Abstract

Composite materials were prepared by intercalating cationic porphyrinato cobalt complexes with the substituents of the quaternary ammonium salt of heterocyclic amine into a montmorillonite interlayer. Using these clay interlayer-fixed porphyrinato cobalt complexes as catalyst, the epoxidation of cyclohexene by oxygen molecules was examined. The prepared intercalation compounds have mesopores with an average diameter of about 12 nm, and their specific surface area increased in proportion to the amount of the intercalated porphyrinato cobalt complexes. It was proven that the porphyrinato cobalt complex was intercalated between montmorillonite layers functioned as a pillaring agent. A pillared clay catalyst, which was prepared by intercalating a [meso-tetrakis(1-ethyl-3-pyridinio)porphyrinato] cobalt complex into the montmorillonite interlayer, showed the highest catalytic activity forming 1,2-epoxycyclohexane preferentially in the presence of isobutyraldehyde. It is suggested that montmorillonite contributes to the stabilization of the porphyrinato cobalt complex, and also plays a role in accelerating oxidation by activating oxygen molecules by way of constructing a reaction field that is regulated three-dimensionally through electrostatic interaction with guest molecules.

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## 1. Introduction

Composite materials with fixed metal complexes in the interlamellar space of smectite clay minerals that have a combination of cation exchange, intercalation, and swelling properties are promising for application to shape selective catalysts similar to zeolites. Regarding the shape selectivity of pillared clay catalysts, there are several reports; e.g., the hydrogenation of unsaturated hydrocarbons with an intercalated rhodium complex catalyst [1], and asymmetric synthesis using a clay electrode modified with ruthenium 1,10-phenanthroline complex [2]. Pinnavaia et al. reported that a ruthenium-cluster carbonyl complex encapsulated in the galleries of an alumina pillared montmorillonite acted as an efficient catalyst for the Fisher–Tropsch (FT) reaction, and clarified that this substance had shape

selectivity different from that of the common FT catalysts [3].

In the biomimetic catalytic oxidation of olefins using metalloporphyrins [4–6], catalysts have been fixed on various supports [7–11] in order to suppress the dimerization of oxo intermediates or inactivation due to the oxidation of the porphyrin ring to inhibit this reaction [12–15]. However, in the oxidation using immobilized catalysts, the activity decreases due to suppression of the degree of freedom of the complexes or diffusion of reactants onto the catalytic sites. Aiming to develop a highly selective catalyst, we synthesized composite materials in which porphyrin complexes with various substituents were intercalated between clay layers to maintain a space on the axis of the central metal of porphyrin as a reaction field. Specifically, cationic porphyrinato cobalt complexes with the substituents of the quaternary ammonium salt of heterocyclic amine were synthesized, and these complexes were fixed between the montmorillonite layers. By using these pillared clay catalysts, the epoxidation of cyclohexene with oxygen molecules in the pres-

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ence of a reducing agent was examined for high activity and selectivity.

## 2. Experimental

### 2.1. Synthesis of porphyrins

#### 2.1.1. Synthesis of meso-tetrakis(1-methyl-4-pyridino)porphyrinato cobalt complex

Commercially available reagents of special grade were used without any processing. Cobalt meso-tetrakis(1-methyl-4-pyridino)porphyrin (CoTM4PyP) was synthesized following the method of Pasternack et al. [16] and Kuwana and coworkers [17]. Pyrrole (25 ml) and 4-pyridinecarbaldehyde (25 ml) were refluxed in propionic acid (300 ml) for 30 min to produce meso-tetrakis(4-pyridinio)porphyrin (T4PyP). Next, T4PyP (1 g) and cobalt acetate (1 g) were refluxed in dimethylformamide (100 ml) for 3 h under nitrogen stream to form a cobalt complex. To a solution of CoT4PyP (1 g) in dimethylformamide (100 ml) was added methyl *p*-toluenesulfonate (10 ml) under nitrogen stream and the mixture was refluxed for 10 h. The product was purified by recrystallization from water–acetone to yield CoTM4PyP (Fig. 1).

#### 2.1.2. Synthesis of meso-tetrakis(1-alkyl-3-pyridino)porphyrinato cobalt complexes

Meso-tetrakis(1-alkyl-3-pyridino)porphyrinato complexes (alkyl: methyl or ethyl) were synthesized by following the method of Ishii and Koh [18]. Pyrrole (25 ml) and pyridine-3-aldehyde (25 ml) were refluxed in propionic acid (300 ml) for 30 min to produce meso-tetrakis(3-pyridinio)porphyrin (T3PyP). Next, T3PyP (1 g) and cobalt acetate (1 g) were refluxed in dimethylformamide (100 ml) for 3 h under nitrogen stream to form a cobalt complex. To a solution of CoT3PyP (1 g) in dimethylformamide (100 ml) was added alkyl-*p*-toluenesulfonate (alkyl: methyl or ethyl, 10 ml) under nitrogen stream and the mixture was refluxed for 10 h. The products were purified by recrystallization from water–acetone to yield CoTM3PyP and CoTE3PyP, respectively.

### 2.2. Preparation of montmorillonite interlayer-fixed porphyrinato cobalt complex

To 200 ml of 0.1 M nitric acid solution,  $(4.2\text{--}100) \times 10^{-5}$  mol of the porphyrinato cobalt complex was dissolved. To the solution was added a suspension of Na-montmorillonite (Kunipia G

made by Kunimine Industry Co., 2.5 g) in water (200 ml) and the mixture was refluxed for 5 h. The solid was filtered, washed with water, and dried at room temperature to form the montmorillonite interlayer-fixed porphyrinato cobalt complexes. The porphyrin complex concentration of the filtrate was measured, from which the amounts of porphyrin adsorbed into clay were calculated.

### 2.3. Analysis

#### 2.3.1. Powder X-ray analysis

A powder X-ray diffractometer RAD-C made by Rigaku Denki Co. was used. The sample was crushed in an agate mortar, and its basal plane spacing  $d_{001}$  was measured by the peak in the range of  $3\text{--}10^\circ$ . Cu  $K\alpha$  was used as an X-ray source, and slit width of  $1/2^\circ$  and scanning speed of  $1^\circ/\text{min}$  were adopted.

#### 2.3.2. Specific surface area and pore distribution

An automatic specific surface area measurement instrument ASAP2000 made by Micromeritex Co. was used and a nitrogen molecule adsorption method at 77 K was adopted. The sample was heated at  $110^\circ\text{C}$  for 12 h or more under vacuum before measurement.

### 2.4. Oxidation

The interlayer-fixed porphyrinato cobalt complex catalyst (20 mg) was dried at  $120^\circ\text{C}$  for 2 h under nitrogen stream, and swelled with acetonitrile (10 ml). To this suspension was added cyclohexene (0.04 mol) and isobutyraldehyde (0.06 mol) and then the mixture was stirred under 1 atm of oxygen at room temperature. The reaction products were analyzed by gas chromatography (Shimadzu GC-16A) using toluene as an internal standard substance. As a separation column, a TC-FFAP fused silica capillary column ( $30\text{ m} \times 0.25\text{ mm i.d.}$ ) was used.

## 3. Results and discussion

### 3.1. Characterization of interlayer-fixed porphyrinato cobalt complexes

The powder X-ray diffraction chart and basal spacing  $d_{001}$  of the synthesized montmorillonite (MT) interlayer compounds are shown in Fig. 2. Compared with the basal spacing of Na–montmorillonite (Na/MT), that of the montmorillonite treated with CoTM4PyP (CoTM4PyP/MT) increased to 1.38 nm, which indicates that CoTM4PyP was fixed into the interlayer of montmorillonite. Ukrainczyk et al. have reported

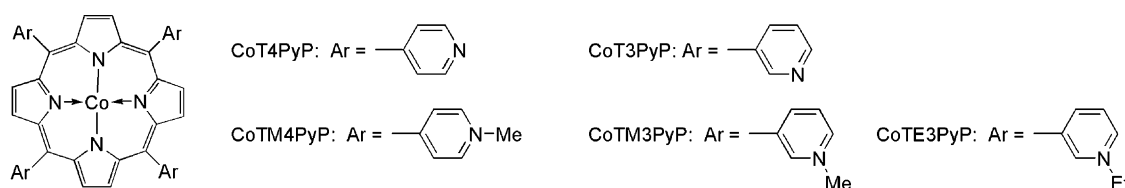


Fig. 1. Structure of cobalt porphyrin complexes.

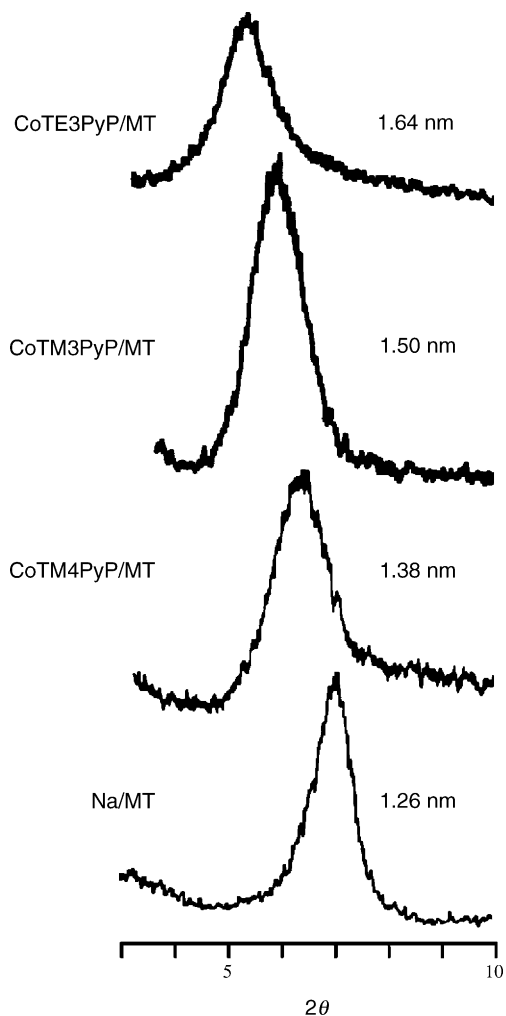


Fig. 2. Powder X-ray diffraction patterns of the montmorillonite interlayer compounds.

that hectorite intercalated with CoTM4PyP has basal spacing of 1.40 nm and the porphyrin plane orients parallel to lamella in this clay [19]. Because the basal spacing of CoTM4PyP/MT in our study agrees well with that of CoTM4PyP/hectorite, the porphyrin in montmorillonite is estimated to orient parallel to the layer. Since the thickness of a montmorillonite crystal layer is about 0.96 nm, the thickness of the intercalated CoTM4PyP is estimated at 0.42 nm. The size of CoTM4PyP in the axial direction changes depending on the angle of the pyridinium groups existing at the meso-position. The pyridine rings generally meet the ring plane of porphyrin at right angles; therefore, the size of CoTM4PyP is estimated at about 0.67 nm. The fact that CoTM4PyP is inserted into the clearance space of 0.42 nm indicates that the pyridine rings incline to an angle of about 30° against the porphyrin plane [20]. In the case of CoTM3PyP/MT and CoTE3PyP/MT, the clearance would increase due to the substituents bonding to nitrogen. Actually, compared with the interlayer spacing of CoTM4PyP/MT, that of CoTM3PyP/MT and CoTE3PyP/MT expands to 0.54 and 0.68 nm, respectively. The porphyrinato cobalt complex intercalated between the montmorillonite layers functions as a pillaring agent and increases the

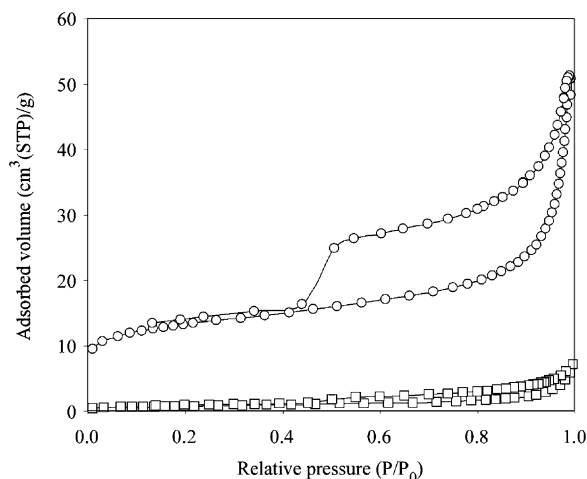


Fig. 3. The nitrogen adsorption of CoTM4PyP/MT (○) and MT (□).

clay basal spacing in proportion to the molecule size of meso-substitutes, which would give rise to the formation of new pores and the increase in specific surface area (vide infra).

An example of the nitrogen adsorption isotherms of CoTM4PyP/MT ([CoTM4PyP]:  $1.6 \times 10^{-5}$  mol/g) is shown in Fig. 3. The adsorption isotherms are type I in the IUPAC classification. The hysteresis loop (H4 type in the IUPAC classification) indicates the presence of mesoporosity [21,22]. The Barrett–Joyner–Halenda method was used for characterizing this mesoporosity. The specific surface areas and the pore volumes of CoTM4PyP/MT samples are summarized in Table 1. The specific external surface areas ( $S_{\text{ext}}$ ) and the specific micropore volumes ( $V_{\mu\text{p}}$ ) were obtained from the  $t$ -plots method. Specific mesopore volumes ( $V_{\text{mp}}$ ) were calculated by subtracting the specific micropore volumes from the specific total pore volumes ( $V_{\text{p}}$ ). The behavior of the specific pore volumes ( $V_{\text{p}}$ ,  $V_{\mu\text{p}}$ ,  $V_{\text{mp}}$ ) of the samples was similar to that of the specific surface area. Nevertheless, the average pore diameters ( $R$ ) and the basal spacings ( $d_{001}$ ) remained almost constant when the amount of the intercalated porphyrin was changed. Fig. 4 shows the relationship between the specific surface area ( $S_{\text{BET}}$ ) and the intercalation quantity of CoTM4PyP/MT and CoTE3PyP/MT. The specific

Table 1  
Specific surface areas, specific pore volumes and basal spacings for CoTM4PyP/MT samples

CoTM4PyP/MT <sup>a</sup>	$S_{\text{BET}}^{\text{b}}$	$S_{\text{ext}}^{\text{c}}$	$V_{\text{p}}^{\text{d}}$	$V_{\mu\text{p}}^{\text{e}}$	$V_{\text{mp}}^{\text{f}}$	$R^{\text{g}}$	$d_{001}^{\text{h}}$
$1.6 \times 10^{-5}$	46	25	0.064	0.010	0.054	12.2	14.0
$2.4 \times 10^{-5}$	72	28	0.065	0.018	0.047	12.4	14.1
$3.2 \times 10^{-5}$	89	34	0.082	0.022	0.060	12.5	13.9
$1.2 \times 10^{-4}$	120	54	0.125	0.027	0.098	13.8	13.7
$1.6 \times 10^{-4}$	115	60	0.126	0.006	0.120	12.4	13.8

<sup>a</sup> Molar quantities of CoTM4PyP intercalated into montmorillonite.

<sup>b</sup> Specific surface areas in  $\text{m}^2/\text{g}$ .

<sup>c</sup> Specific external surface areas in  $\text{m}^2/\text{g}$ .

<sup>d</sup> Specific total pore volumes in  $\text{ml}/\text{g}$ .

<sup>e</sup> Specific micropore volumes in  $\text{ml}/\text{g}$ .

<sup>f</sup> Specific mesopore volumes in  $\text{ml}/\text{g}$ .

<sup>g</sup> Average pore diameters in nm.

<sup>h</sup> Basal spacings in nm.

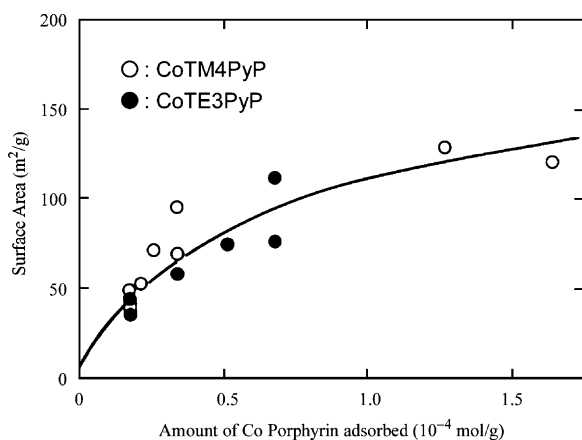


Fig. 4. Relationship between the specific surface area and intercalation quantity of interlayer compounds.

surface area of the samples increased with the increase in amount of the complex although it is not affected by the species of intercalated porphyrin. When the amount of porphyrin intercalated into montmorillonite was  $1.2 \times 10^{-4}$  mol/g, the specific surface area of the synthesized CoTM4PyP/MT reached  $120 \text{ m}^2/\text{g}$ , but a further increase in porphyrin produced almost no change of specific surface areas. This result seems to accord well with the fact that the adsorption quantity of CoTM4PyP in montmorillonite reached a point of saturation as shown in Fig. 5. Since the cation exchange capacity of montmorillonite is 115 mequiv./100 g and the electric charge of the porphyrinato cobalt complex used in this experiment is +4, the intercalation of  $2.9 \times 10^{-4}$  mol/g of the complex is theoretically possible. However, the maximum adsorption quantity of CoTM4PyP was  $1.6 \times 10^{-4}$  mol/g, which is a half of the cation exchange capacity of montmorillonite. According to the report of Fripiat and coworkers, the adsorption quantity of the meso-tetrakis(4-pyridinio)porphyrinato complex (T4PyP) into montmorillonite was  $1.9 \times 10^{-4}$  mol/g [23]. The value obtained in this experiment can be considered small compared with that in the literature even if the molecular size of TM4PyP is taken into account. The decrease in cation exchange capacity due to ion exchange under 0.1 M nitric acid acidic condition is considered to have brought about the decrease in porphyrin adsorption quantity [24].

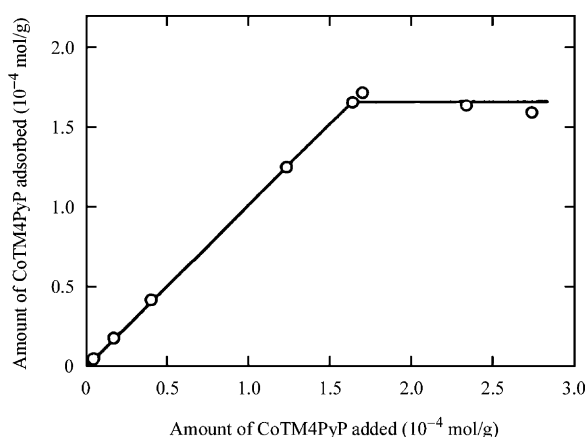


Fig. 5. Adsorption quantity of CoTM4PyP onto montmorillonite.

### 3.2. Catalytic oxidation of cyclohexene with molecular oxygen

When the oxidation of cyclohexene by molecular oxygen was carried out by using CoTE3PyP/MT catalyst in the presence of various aliphatic aldehydes, 1,2-epoxycyclohexane was preferentially obtained, and aliphatic carboxylic acids corresponding to the used aliphatic aldehydes were obtained. This reaction did not proceed in the absence of aliphatic aldehyde. Aliphatic aldehyde plays a role of a reducing agent, having an important effect on the yield of epoxide. Among  $C_4$ – $C_6$  aliphatic aldehydes examined in this experiment, the epoxide yield was the highest when isobutyraldehyde was used in the reaction.

Furthermore, the effect of isobutyraldehyde concentration on this reaction was explored. When the ratio of the reducing agent and substrate was 1.5 mol/mol, the highest value of epoxide yield was obtained, and the more increase in the isobutyraldehyde concentration brought about rather decreased epoxide yield. When isobutyraldehyde/cyclohexene was 4 mol/mol, the dimer of isobutyric acid was detected by GC–MS. The diffusion of the substrate to porphyrin active sites in the montmorillonite interlayer seems to be impeded by the large excess of the reducing agent. A polar solvent acetonitrile was the most suitable solvent and a non-polar solvent benzene and a coordinate solvent pyridine remarkably retarded this reaction. Thus, hereafter, all oxidations of cyclohexene were carried out in acetonitrile in the presence of 1.5 mol equivalent isobutyraldehyde under 1 atm of oxygen at room temperature.

Fig. 6 shows the relationship between the yield of epoxide and reaction time in the oxygen oxidation of cyclohexene in the presence of isobutyraldehyde using the CoTE3PyP/MT catalyst, in comparison with the cases of the reaction in a homogeneous system using the CoTE3PyP complex and the reaction of pure montmorillonite. Although the homogeneous complex catalyst contained about 20 times as much CoTE3PyP as the

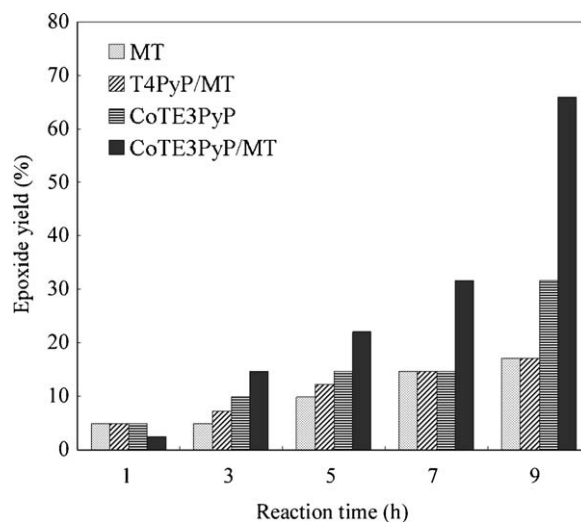


Fig. 6. Relationship between the yield of 1,2-epoxycyclohexane and reaction time. Conditions: cat., 20 mg (in case of T4PyP/MT and CoTE3PyP/MT, [porphyrin]:  $6.4 \times 10^{-5}$  mol/g); cyclohexene, 0.04 mol; isobutyraldehyde, 0.06 mol; acetonitrile, 10 ml.

interlayer-fixed catalyst, its activity for the oxidation was very low. Although a slight quantity of epoxide was generated in the presence of pure MT or T4PyP/MT free of a metal, the reaction stopped in about 5 h; the yield of 1,2-epoxycyclohexane was quite similar to that in the oxidation without catalyst. Therefore, it is suggested that peroxides contained in the substrate or reducing agent were involved in the reaction, and that neither MT nor T4PyP/MT was active for the oxygen oxidation. In the reaction using CoTE3PyP/MT as a catalyst, there was an induction period in the initial stage of the reaction and the yield of epoxide remarkably increased after 5 h. This result is attributed to the interlayer expansion by the swelling of montmorillonite to enhance the degree of freedom of catalytic sites and diffusion of reactants.

The visible light absorption spectrum of porphyrinato cobalt complexes during the reaction process is shown in Fig. 7. Fig. 7(A) shows the change in the absorption spectrum in the interlayer-fixed catalyst, which was measured at intervals of 1 h for 20 h. Profound change was not observed in two absorption bands B ( $4a_{2u} \rightarrow 5_{eq}$ ) and Q ( $2b_{2u} \rightarrow 5_{eq}$ ) based on the excitation of  $\pi$  electrons of the porphyrin ring under the reaction conditions. However, in Fig. 7(B), which is the spectra of the sole porphyrinato cobalt complex measured at intervals of 20 min for 5 h, the above-mentioned specific absorption bands have completely disappeared. This result can be attributed to the fact that the resonance structure of 18- $\pi$  electron system was destroyed by the direct oxidation of the porphyrin ring [25,26].

Next, the time course of the reaction is shown in Fig. 8. Since the isobutyric acid were generated as much as the epoxide in the initial stage of reaction, this reaction can be expressed by the following stoichiometric formula:

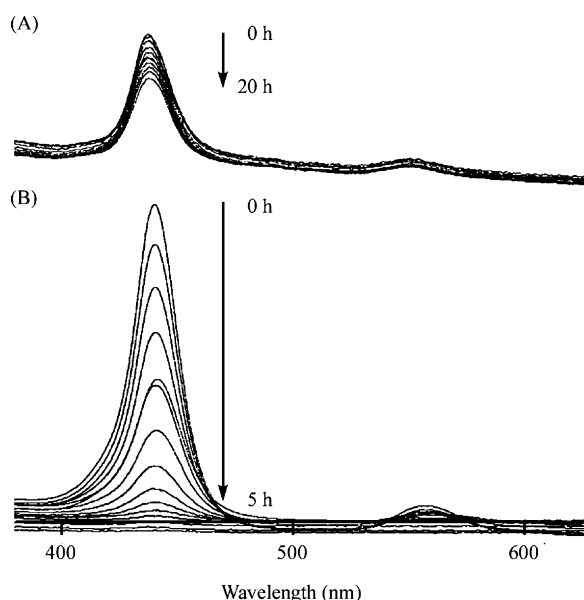
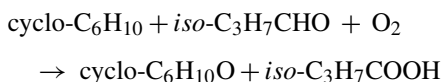


Fig. 7. Visible light absorption spectra of CoTE3PyP/MT (A) and CoTE3PyP (B) during reaction process.

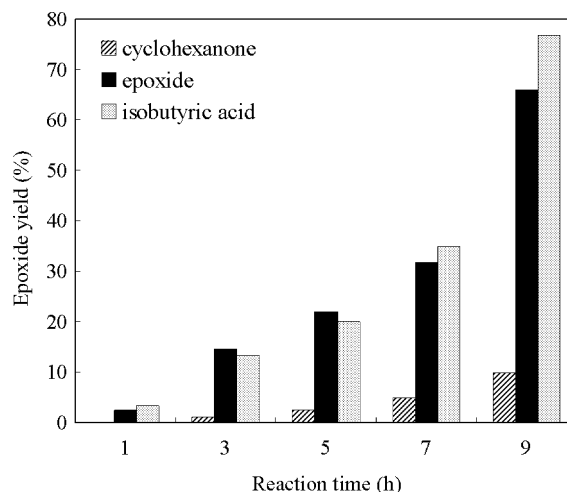


Fig. 8. Time-course of reaction. Conditions: CoTE3PyP/MT, 20 mg ([CoTE3PyP]:  $6.4 \times 10^{-5}$  mol/g); cyclohexene, 0.04 mol; isobutyraldehyde, 0.06 mol; acetonitrile, 10 ml.

In addition, since the generated epoxide changed to cyclohexanone through acid catalyst cleavage reaction, cyclohexanone gradually increased.

This research has clarified that the interlayer crosslinking clay catalyst, in which porphyrinato cobalt complex is intercalated between the layers, remarkably accelerates the epoxidation of cyclohexene by oxygen molecule in the presence of isobutyraldehyde. Montmorillonite seems to contribute to the stabilization of the porphyrinato cobalt complex, and also plays a role in accelerating oxidation by activating oxygen molecules by way of constructing a reaction field that is regulated three-dimensionally. The clay basal spacing of the synthesized interlayer compound was 1.4–1.6 nm, which depended on the molecular structure of guest molecules. The results of the oxidation of cyclohexene by using various interlayer-fixed porphyrinato cobalt complexes, that is, the catalysts having the different clay basal spacing are shown in Table 2. CoTE3PyP/MT, which has the largest interlayer spacing, gave the highest epoxide yield. Moreover, the oxygen oxidation of cyclohexene was carried out using CoTE3PyP/MT catalysts containing intercalated CoTE3PyP in the range of  $(1.6\text{--}6.4) \times 10^{-5}$  mol/g. The epoxide yield improved with the quantity of CoTE3PyP and by using CoTE3PyP/MT catalyst with a content of  $6.4 \times 10^{-5}$  mol/g the epoxide yield reached 65.9% in a reaction time of 9 h. On the other hand, the use of CoTM4PyP/MT and CoTM3PyP/MT, of which the interlayer spacing are 0.42 and 0.54 nm, respectively, as catalyst gave the low yield of epoxide. Their space on the central metal for the oxidation to occur must be restricted because of the thickness of the porphyrin molecule. Thus, it is difficult for cyclohexene of which the size is about 0.45 nm to pull in this space. By contrast, CoTE3PyP/MT having the interlayer spacing of 0.68 nm seems to provide sufficient space so that cyclohexene approaches the central metal of porphyrin. These results indicate that the formation of a reaction field can be controlled by a kind of meso-substituent of the porphyrinato cobalt complex intercalated between montmorillonite layers and the oxidation

Table 2

Oxidations of cyclohexene by using various interlayer-fixed porphyrinato cobalt complexes as catalyst<sup>a</sup>

Catalysts	Time (h)	Yield (%)		Turn over number
		1,2-Epoxy cyclohexane	Cyclohexanone	
CoTM4PyP/MT	9	17.6	2.6	25250
	24	36.6	7.7	55375
CoTM3PyP/MT	9	23.8	2.8	33250
	24	31.1	5.1	45250
CoTE3PyP/MT	9	41.5	4.9	58000
	24	56.1	9.8	82375
CoTE3PyP/MT <sup>b</sup>	9	48.8	7.3	23375
	24	56.1	12.2	28458
CoTE3PyP/MT <sup>c</sup>	9	65.9	9.8	23656
	24	61.0	12.2	22875
CoTE3PyP	9	31.7	4.9	580
	24	34.1	4.9	618
MT	9	17.1	2.4	–
	24	22.0	4.9	–

<sup>a</sup> Conditions: cat., 20 mg ([porphyrin]:  $1.6 \times 10^{-5}$  mol/g); cyclohexene, 0.04 mol; isobutyraldehyde, 0.06 mol; acetonitrile, 10 ml.

<sup>b</sup> Conditions: cat., 20 mg ([porphyrin]:  $4.8 \times 10^{-5}$  mol/g); cyclohexene, 0.04 mol; isobutyraldehyde, 0.06 mol; acetonitrile, 10 ml.

<sup>c</sup> Conditions: cat., 20 mg ([porphyrin]:  $6.4 \times 10^{-5}$  mol/g); cyclohexene, 0.04 mol; isobutyraldehyde, 0.06 mol; acetonitrile, 10 ml.

can proceed selectively in the molecule size of the substrate by means of this reaction field.

#### 4. Conclusion

Various cationic porphyrinato cobalt complexes with the substituents of the quaternary ammonium salt of heterocyclic amine were intercalated into montmorillonite layers to give the composite materials. The clay basal spacing of montmorillonite increased by about 1.4–1.6 nm depending on the meso-substituents of the intercalated porphyrinato cobalt complex. The specific surface area of intercalated compound increases in proportion to the intercalation quantity of the porphyrin complex without being affected by the chemical structure of porphyrin complex.

The catalytic activity of these composite materials was remarkably high in the oxidation of cyclohexene by oxygen molecules in the presence of isobutyraldehyde, compared with the homogeneous complex catalyst. Especially, the tetrakis(1-ethyl-3-pyridinio)porphyrinato cobalt complex fixed between montmorillonite layers, which had the largest interlayer spacing, showed the highest catalytic activity. Montmorillonite seems to contribute to the stabilization of porphyrinato cobalt complex and also plays a role in accelerating epoxidation by the construction of a reaction field based on the spatial interaction with guest molecules.

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