

Epoxidation of alkenes catalyzed by heteropolyoxometalate as pillars in layered double hydroxides

Y. Watanabe, K. Yamamoto, T. Tatsumi *

Department of Applied Chemistry, Graduated School of Engineering, The University of Tokyo, Hongo, Tokyo 113, Japan

Received 20 November 1998; accepted 16 December 1998

Abstract

The epoxidation of alkenes with hydrogen peroxide or molecular oxygen, in the presence of aldehyde catalyzed by heteropolyoxometalate (HPOM) salts and layered double hydroxides (LDHs) containing HPOM anions as pillars, has been investigated. In the case of oxidation with hydrogen peroxide, a lacunary Keggin-ion, $\text{SiW}_{11}\text{O}_{39}^{8-}$, was more active than $\text{SiW}_{12}\text{O}_{40}^{4-}$. For this reaction system using hydrogen peroxide, intercalated $\text{SiW}_{11}\text{O}_{39}^{8-}$ showed higher stability in structure and activity than free $\text{K}_8\text{SiW}_{11}\text{O}_{39}$. For the oxidation using molecular oxygen and aldehyde, $\text{SiW}_{12}\text{O}_{40}^{4-}$ showed higher activity than $\text{SiW}_{11}\text{O}_{39}^{8-}$. It was confirmed that $\text{SiW}_{12}\text{O}_{40}^{4-}$ was intercalated between the brucite-type layers of the LDHs without change in structure. Ni-containing LDHs without any interstitial polyoxometalate showed high activity for the oxidation of cyclohexene with the combination of O_2 and aldehyde. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Layered double hydroxides; Heteropolyoxometalate; Alkene epoxidation

1. Introduction

Layered double hydroxides (LDHs) are mirror-image to the smectites insofar as the layers are positively charged and the gallery ions are anions. The general LDHs formula is $[\text{M}_x^{2+}\text{M}^{3+}(\text{OH})_{2x+2}]^+[A^{n-}]_{1/n} \cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} are divalent and trivalent metal cations such as Mg^{2+} or Cu^{2+} and Al^{3+} or Cr^{3+} , respectively, and A^{n-} is a simple or complex organic or inorganic anion [1]. In this paper, LDHs with the above composition are denoted

as $\text{M}_x^{2+}\text{M}^{3+} - A$. There are numerous investigations of LDHs as the generation of solid base catalysts [2] and catalysts for organic halide exchange [3]. Since the gallery anions are exchangeable, it is in principle possible to prepare pillared LDHs derivatives by intercalative ion exchange.

Heteropolyoxometalate (HPOM) is known to act as a versatile oxidation catalyst, and its anion carries a large negative charge [4,5]. Currently, there is a great deal of interest in the pillaring of LDHs by catalytically active polyoxometalate (POM) anions. We have reported that LDHs pillared by POM anions (LDHs–POM) showed significant shape selectivity for the epoxidation of alkenes [6]. For the synthesis of LDHs–POM, various methods have been

* Corresponding author. Present address: Division of Materials Science and Chemical Engineering, Faculty of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan. Fax: +81-45-339-3943

reported [7,8]: (i) aqueous ion exchange of the pillaring ions such as Cl^- , NO_3^- , and terephthalate anion with POM anions [9]; (ii) rehydration of calcined LDHs in the aqueous solution containing POM anions [10]; and (iii) direct synthesis by coprecipitation of M^{2+} and M^{3+} in moderately acidic POM solution [11]. We have communicated that $\text{SiW}_{12}\text{O}_{40}^{4-}$, with the Keggin-type structure, is intercalatively introduced into LDHs (Mg_2Al) as pillar and the resulting intercalates show catalytic activity for the epoxidation of alkenes with H_2O_2 [12]. In contrast, it has been reported that no exchange of LDHs (Zn_2Al) is observed for the Keggin-ion whose negative charge is less than five [13]. In this regard, there is a possibility of partial decomposition of the anion, $\text{SiW}_{12}\text{O}_{40}^{4-}$, into a lacunary Keggin-ion, $\text{SiW}_{11}\text{O}_{39}^{8-}$ or $\text{SiW}_9\text{O}_{34}^{9-}$, whose negative charge is higher than five. In the present work, we report on the difference between LDHs– $\text{SiW}_{12}\text{O}_{40}^{4-}$, – $\text{SiW}_{11}\text{O}_{39}^{8-}$ and – $\text{SiW}_9\text{O}_{34}^{9-}$ and the results of epoxidation of alkenes with H_2O_2 or molecular O_2 in the presence of isobutyraldehyde using LDH–HPOM samples as catalysts.

2. Experimental

2.1. Preparation of LDHs

2.1.1. Preparation of $\text{Zn}_n\text{Al-NO}_3$, $\text{Mg}_2\text{Al-NO}_3$, and $\text{Ni}_2\text{Al-NO}_3$

These compounds were prepared by adaption of the induced hydrolysis method of Taylor [14]. Deionized water, kept under a N_2 purge to remove dissolved CO_2 , was used for the preparation of all solutions. For the preparation of $\text{Zn}_2\text{Al-NO}_3$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (23.8 g, 80 mmol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (15.0 g, 40 mmol) were dissolved in 65 ml deionized water under a N_2 atmosphere (solution A). An aqueous solution of 4 M NaOH was added dropwise to the solution A for 90 min with vigorous stirring, the pH of the reaction mixture being adjusted to

7.0. Following the addition, the mixture was kept at 346 K for 18 h with good mixing. The slurry was then cooled to room temperature, and the solid product was separated by filtration, and washed thoroughly with deionized water. The solid obtained was dried at 393 K overnight. For the preparation of $\text{Zn}_3\text{Al-NO}_3$ and $\text{Zn}_4\text{Al-NO}_3$, a solution A containing $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (90, 96 mmol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (30, 24 mmol) were used, respectively.

For the preparation of $\text{Mg}_2\text{Al-NO}_3$ and $\text{Ni}_2\text{Al-NO}_3$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was used in place of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The solution mixture of $\text{Ni}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ was added dropwise to 100 ml of aqueous solution of 4 M NaOH. The following procedure was the same as in the case of $\text{Zn}_2\text{Al-NO}_3$.

2.1.2. Preparation of $\text{Ni}_2\text{Al-TA}$ (TA = terephthalate dianion)

$\text{Ni}_2\text{Al-TA}$ were prepared by the method of Drezdron [9].

2.1.3. Preparation of LDHs– $\text{SiW}_{12}\text{O}_{40}$ by ion exchange reaction

A solution of $\text{Na}_4\text{SiW}_{12}\text{O}_{40}$ in 200 ml deionized water was added to the LDHs precursor (not dried) slurry. The HPOM was in 50–100% stoichiometric excess. After the mixture was stirred for 15 min, 4 M HNO_3 was slowly added to the mixture with vigorous stirring, resulting in a pH drop to about 4. After 10 min of additional stirring, the product was separated by filtration, washed, and dried at 393 K overnight.

2.1.4. Preparation of $\text{Zn}_2\text{Al-SiW}_9\text{O}_{34}$

$\text{Na}_9\text{SiW}_9\text{O}_{34}$ were synthesized by the reported method [15]. The procedure above described for $\text{Zn}_2\text{Al-SiW}_{12}\text{O}_{40}$ was followed except that no HNO_3 was added.

2.1.5. Preparation of $\text{Zn}_3\text{Al-SiW}_{11}\text{O}_{39}$

$\text{K}_8\text{SiW}_{11}\text{O}_{39} \cdot 13\text{H}_2\text{O}$ was prepared according to the published method [15], and then $\text{Zn}_3\text{Al-SiW}_{11}\text{O}_{39}$ was prepared directly by the method of Narita et al. [11].

2.2. Physical methods

The LDH compounds were analyzed by X-ray diffractometry (XRD) and Fourier transform infrared spectrometry (FT-IR). X-ray diffractograms were recorded on a Rigaku Denki RINT 2400. FT-IR spectra were obtained on a Perkin Elmer 1600 FTIR spectrometer. Samples were prepared according to the standard KBr pellet technique. Chemical compositions of LDH–HPOM samples were measured with an energy-dispersive spectrometer (EDS/KeveX μ X 7000). The surface area of the catalyst was determined by a N_2 –BET (Brunauer–Emmet–Teller) measurement on a BEL Japan Belsorp 28SA analyzer. Before the N_2 –BET measurement, LDHs compounds were kept in vacuum at 403 K for 5 h.

Table 1 shows chemical compositions of prepared LDH–HPOM samples.

2.3. Catalytic reactions

2.3.1. Oxidation of alkenes with H_2O_2

Oxidation reactions of alkenes were carried out in a 100-ml flask containing catalyst (1 mmol of polymetal), alkene (100 ml) and 10 wt.% H_2O_2 (100 mmol) in tributyl phosphate (TBP), at 343 K for 3 h. A non-aqueous H_2O_2 –TBP solution was prepared by adding 30% H_2O_2 aqueous solution to TBP, followed by evaporation of water under reduced pressure at 323 K [16].

2.3.2. Oxidation of alkenes with molecular O_2 in the presence of isobutyraldehyde

Oxidation reactions of alkenes were carried out in a 50-ml flask containing catalyst (1 mmol of polymetal), alkene (100 mmol), isobutyraldehyde (150 mmol) and dichloromethane (20 ml), at 313 K for 10 h. Molecular O_2 was supplied through a bubbler made of glass filter.

2.3.3. Product analysis

Products were analyzed on a gas chromatograph using a 2-m OV-17 column.

3. Results and discussion

Table 1 summarizes the chemical compositions of the LDHs intercalates synthesized in this study. The X-ray powder diffraction patterns of LDHs (Zn_nAl , n : Zn/Al ratio in the reactant) pillared with silicotungstate anions are shown in Fig. 1. All samples were dried at 393 K before measuring XRD patterns. For Zn_2Al – $SiW_{12}O_{40}$ (Fig. 1b), the characteristic peaks of LDHs containing HPOM anions around $2\theta = 6.1^\circ$, 12° , and 18° were insignificant and prominent peaks due to the precursor Zn_2Al – NO_3 (Fig. 1a) were observed. Thus, the intercalation of $SiW_{12}O_{40}^{4-}$ between layers of Zn_2Al – NO_3 did not proceed smoothly in agreement with the findings reported by Kwon and Pinnavaia [13]. They reported that the Keggin-type HPOM,

Table 1
Chemical compositions and methods of synthesis

Sample	Chemical composition (molar ratio) $M^{2+}:Al^{3+}:metal^a$	Method of synthesis
Zn_2Al – $SiW_{12}O_{40}$	2.0:1.0:0.44	ion exchange of Zn_3Al – NO_3
Zn_3Al – $SiW_{12}O_{40}$	3.0:1.0:0.78	ion exchange of Zn_3Al – NO_3
Zn_4Al – $SiW_{12}O_{40}$	3.3:1.0:0.12	ion exchange of Zn_3Al – NO_3
Zn_3Al – $SiW_{11}O_{39}$	2.9:1.0:1.4	direct synthesis
Zn_2Al – SiW_9O_{34}	2.0:1.0:1.2	ion exchange of Zn_2Al – NO_3
Mg_2Al – $SiW_{12}O_{40}$	2.3:1.0:1.2	ion exchange of Mg_2Al – NO_3
Ni_2Al – $SiW_{12}O_{40}$	1.3:1.0:1.6	ion exchange of Ni_2Al – NO_3
Ni_2Al –TA ^b	2.2:1.0:0	direct synthesis

^aPolymetal in HPOM.

^bTA = terephthalate dianion.

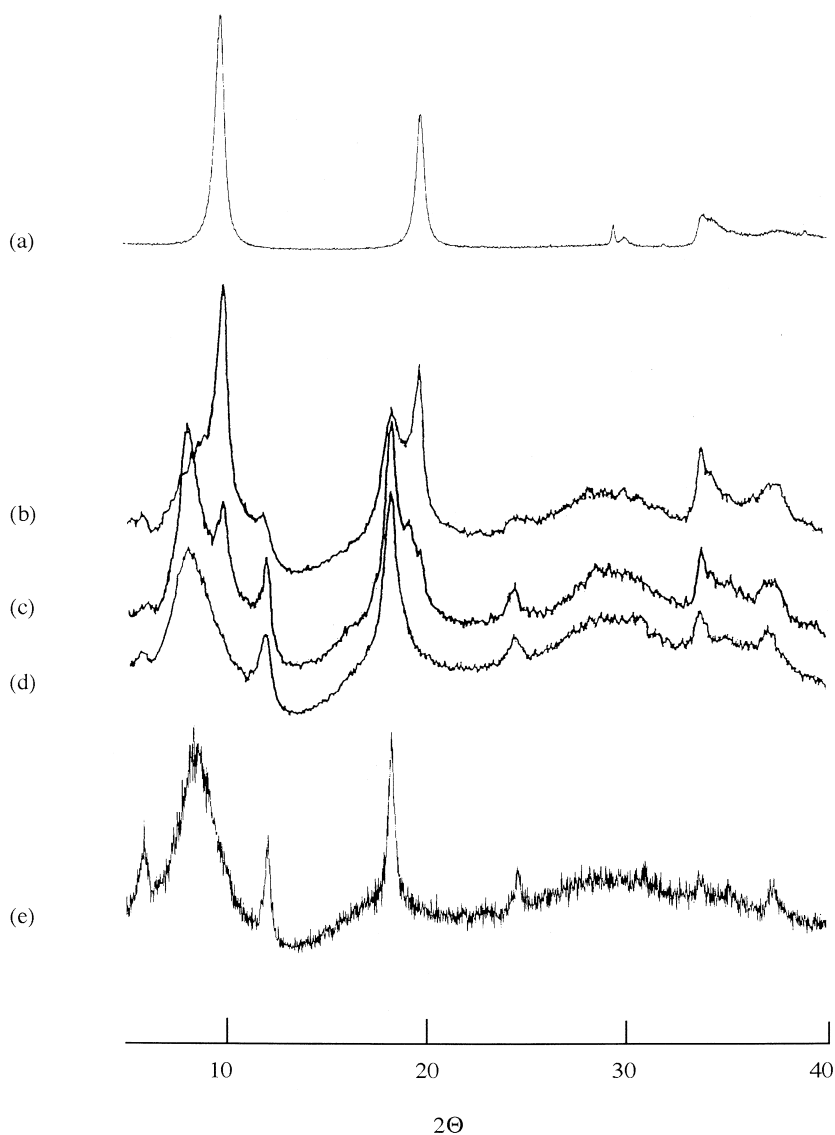


Fig. 1. The XRD patterns of $\text{Zn}_2\text{Al-NO}_3$ (a), $\text{Zn}_2\text{Al-SiW}_{12}\text{O}_{40}$ (b), $\text{Zn}_3\text{Al-SiW}_{12}\text{O}_{40}$ (c), $\text{Zn}_4\text{Al-SiW}_{12}\text{O}_{40}$ (d), and $\text{Zn}_3\text{Al-SiW}_{11}\text{O}_{39}$ (e).

whose negative charge is more than five, could be easily exchanged with NO_3^- in $\text{Zn}_2\text{Al-NO}_3$; for $\text{PCuW}_{11}\text{O}_{39}^{5-}$, however, only partial exchange occurred and for $\text{SiW}_{12}\text{O}_{40}^{4-}$, no exchange occurred at all. The area per unit charge in $\text{Zn}_2\text{Al-NO}_3$ is estimated at ca. 16.6 \AA^2 [17] and the diameter of a Keggin-ion is ca. 9.8 Å. If Keggin-ions are closely packed, the cross-section of each ion is estimated to be 83.1 \AA^2 , occupying the area corresponding to five posi-

tive charges in the brucite-type layer of Zn_2Al . Hence, the Keggin-anion, whose negative charge is 4, could not be incorporated. However, the increase in the Zn/Al ratio (n) should result in an increase in the space/charge ratio in the interstices between LDHs. The $\text{Zn}_3\text{Al-SiW}_{12}\text{O}_{40}$ (Fig. 1c) and $\text{Zn}_4\text{Al-SiW}_{12}\text{O}_{40}$ (Fig. 1d) prepared from $\text{Zn}_3\text{Al-NO}_3$ and $\text{Zn}_4\text{Al-NO}_3$, whose charge densities on the brucite-type layers were lower compared to $\text{Zn}_2\text{Al-NO}_3$, ex-

hibited 001 harmonic characteristic peak of LDHs pillared by HPOM anions with a basal spacing of 14.7 Å. Especially, the peaks of precursor containing NO_3^- as pillar were not observed for $\text{Zn}_4\text{Al-SiW}_{12}\text{O}_{40}$, where the cross-section of Keggin ion occupies the area corresponding to 3.5 charge in the brucite-type layer (Zn/Al ratio in the product was 3.3). In this case, the area corresponding to the four anionic charges is larger than the cross-section. Thus, the intercalation of $\text{SiW}_{12}\text{O}_{40}^{4-}$ between layers of $\text{Zn}_n\text{Al-NO}_3$ was facilitated with increasing number of n , probably because of the increase in the space accommodating the quadrivalent anion. Further increase in n , however, should lead to difficulty in ion exchange owing to charge deficiency of the brucite-type layer. The broad reflection at $2\theta = 6.5^\circ - 10^\circ$ should be due to the formation of a by-product; Narita et al. [11] ascribed this reflection to a $\text{Zn}^{2+}/\text{Al}^{3+}/\text{HPOM}$ salt.

The BET surface area of $\text{Zn}_3\text{Al-NO}_3$ measured by N_2 was $11 \text{ m}^2/\text{g}$, which might be due to only the outer surface because the gallery height of $\text{Zn}_3\text{Al-NO}_3$ was estimated at 3.0 Å, which is too small for molecular N_2 to enter. The BET surface area of $\text{Zn}_3\text{Al-SiW}_{12}\text{O}_{40}$ increased to $46 \text{ m}^2/\text{g}$. This increased BET surface area, as well as XRD patterns, indicated that the layered structure of $\text{Zn}_3\text{Al-SiW}_{12}\text{O}_{40}$ was pillared with the large HPOM anions.

The IR spectra of $\text{K}_4\text{SiW}_{12}\text{O}_{40}$, $\text{K}_8\text{SiW}_{11}\text{O}_{39}$, $\text{Zn}_3\text{Al-SiW}_{12}\text{O}_{40}$, and $\text{Zn}_3\text{Al-SiW}_{11}\text{O}_{39}$ are shown in Fig. 2. Although $\text{K}_4\text{SiW}_{12}\text{O}_{40}$ and $\text{K}_8\text{SiW}_{11}\text{O}_{39}$ were quite different in the IR spectra, $\text{Zn}_3\text{Al-SiW}_{12}\text{O}_{40}$ and $\text{Zn}_3\text{Al-SiW}_{11}\text{O}_{39}$ were similar to the IR spectra because of strong absorption of the brucite-layer. Therefore, it is difficult to clarify the structure of gallery anions by XRD patterns and IR spectra only.

Table 2 shows the results of oxidation of cyclohexene with H_2O_2 catalyzed by LDH-

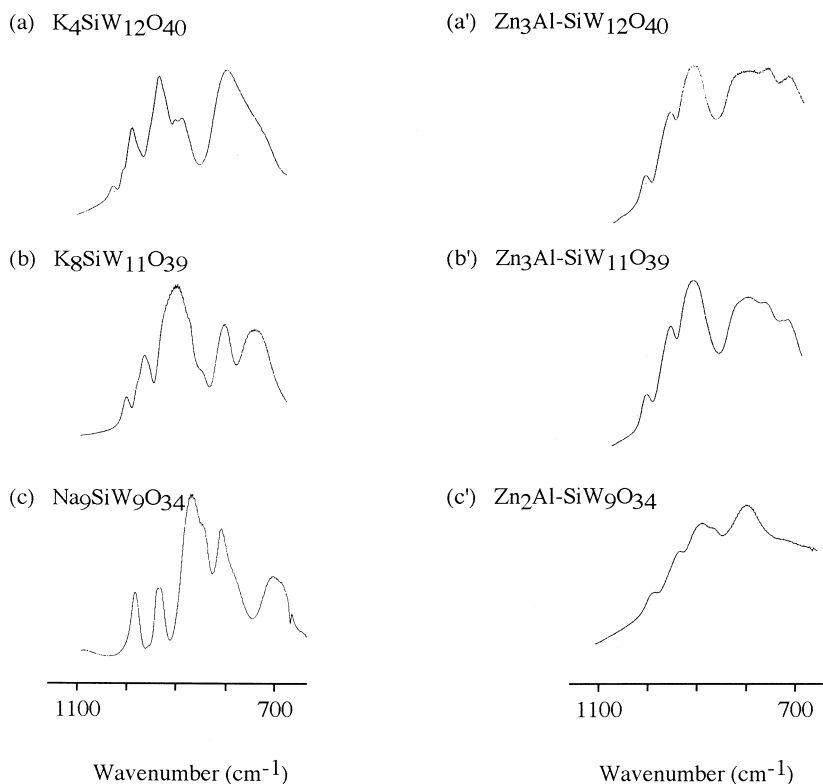


Fig. 2. The IR spectra of free HPOM salts and LDH-HPOM samples.

Table 2
Oxidation of cyclohexene with H_2O_2^a

Catalyst	Turnover number (mol/mol-W)			
	Epoxide	diol + dione	Others	Total
$\text{K}_8\text{SiW}_{11}\text{O}_{39}$	6.5	39	1.7	47
$\text{Zn}_3\text{Al-SiW}_{11}\text{O}_{39}$	8.1	5.6	trace	14
$\text{K}_4\text{SiW}_{12}\text{O}_{40}$	0.19	1.8	1.1	3.1
$\text{Zn}_3\text{Al-SiW}_{12}\text{O}_{40}$	0.89	0.050	0.95	1.9

^aReaction conditions: 1 mmol catalyst (as W), 100 mmol cyclohexene, 30.3 g TBP containing 100 mmol H_2O_2 , 343 K, 3 h.

HPOM samples and free HPOM salts, where HPOM is $\text{SiW}_{12}\text{O}_{40}^{4-}$ or $\text{SiW}_{11}\text{O}_{39}^{8-}$. The main products were cyclohexene oxide, 1,2-cyclohexanediol, and 1,2-cyclohexanedione. The minor products shown as others in tables were 2-cyclohexene-1-ol and 2-cyclohexene-1-one. Although it was recently reported that $\text{Mg}_x\text{Al-CO}_3$ was active in oxidation of alkenes with H_2O_2 [18], $\text{Zn}_3\text{Al-NO}_3$ containing no HPOM showed negligible activity in our reaction conditions. Whether HPOM existed between brucite-layers or not, obviously $\text{SiW}_{11}\text{O}_{39}^{8-}$ had a higher activity than $\text{SiW}_{12}\text{O}_{40}^{4-}$. Each free HPOM salt was more active than the corresponding intercalate. It is noteworthy that the hydrolysis of epoxide was retarded for the intercalates. Recently, Gardner and Pinnavaia [19] reported that $\text{Zn}_2\text{Al-H}_2\text{W}_{12}\text{O}_{40}$ showed high selectivity for diol and that the surface acid–base properties of the LDHs may promote ring opening of the epoxide to the diol. However, the conversion of epoxide to diol by $\text{Zn}_3\text{Al-NO}_3$ was very low in the reaction of cyclohexene oxide and 30 wt.% H_2O_2 (aq.) at 343 K for 3 h. It was considered that the hydrolysis of epoxide mainly occurred on HPOM as shown later. Table 3 shows the results of oxidation of cyclohexene with O_2 in the presence of isobutyraldehyde [20]. With this oxidant system, $\text{SiW}_{12}\text{O}_{40}^{4-}$ was superior to $\text{SiW}_{11}\text{O}_{39}^{8-}$. This was also the case for the LDHs containing these two HPOMs. The similarity in effectiveness of oxidant between free HPOM salts and supported ones strongly suggests that each HPOM anion was intercalated between LDHs layers with keeping its structure.

Table 3
Oxidation of cyclohexene with O_2 in the presence of isobutyraldehyde^a

Catalyst	Turnover number (mol/mol-W)			
	Epoxide	diol + dione	Others	Total
$\text{K}_8\text{SiW}_{11}\text{O}_{39}$	0.21	0.12	0.38	0.71
$\text{Zn}_3\text{Al-SiW}_{11}\text{O}_{39}$	0.36	0.26	0.16	0.78
$\text{K}_4\text{SiW}_{12}\text{O}_{40}$	19	4.1	0.27	23
$\text{Zn}_3\text{Al-SiW}_{12}\text{O}_{40}$	5.8	0.80	0.34	6.9

^aReaction conditions: 1 mmol catalyst (as W), 100 mmol cyclohexene, isobutyraldehyde 150 mmol, 20 ml dichloromethane, 313 K, 10 h.

It is conceivable that $\text{SiW}_{12}\text{O}_{40}^{4-}$ was decomposed into $\text{SiW}_9\text{O}_{34}^{9-}$ during intercalation. However, the spectrum of $\text{Zn}_2\text{Al-SiW}_9\text{O}_{34}$, shown in Fig. 2c', was quite different from the spectra of $\text{Zn}_3\text{Al-SiW}_{11}\text{O}_{39}$ and $\text{Zn}_3\text{Al-SiW}_{12}\text{O}_{40}$. These findings indicated that neither $\text{SiW}_{12}\text{O}_{40}^{4-}$ nor $\text{SiW}_{11}\text{O}_{39}^{8-}$ were changed into $\text{SiW}_9\text{O}_{34}^{9-}$ through the synthesis of LDH-HPOM.

In order to investigate the catalytic performance of $\text{SiW}_{12}\text{O}_{40}^{4-}$ and $\text{SiW}_{11}\text{O}_{39}^{8-}$, a few more experiments were conducted. It was thought that low activity of $\text{SiW}_{12}\text{O}_{40}^{4-}$ with H_2O_2 is due to decomposition of H_2O_2 by $\text{SiW}_{12}\text{O}_{40}^{4-}$. Table 4 shows the results of oxidation catalyzed by $\text{SiW}_{11}\text{O}_{39}^{8-}$. Oxidant A was fresh H_2O_2 in TBP. Oxidant B was H_2O_2 , in TBP, pretreated with $\text{K}_4\text{SiW}_{12}\text{O}_{40}$ at 343 K for 3 h. Oxidant B gave rise to lower epoxidation yield than oxidant A. One might wonder that H_2O_2 might have been thermally decomposed. Oxidant C, which was preheated at 343 K for 3 h without catalyst,

Table 4
Oxidation of cyclohexene over $\text{K}_8\text{SiW}_{11}\text{O}_{39}$ with fresh and pretreated H_2O_2

Oxidant	Turnover number (mol/mol-W)			
	Epoxide	diol + dione	Others	Total
A ^a	6.5	39	1.7	47
B ^b	0.52	22	2.1	25
C ^c	4.2	35	0.75	40

^aThe reaction conditions were the same as in Table 2.

^bTBP containing H_2O_2 were treated with $\text{K}_4\text{SiW}_{12}\text{O}_{40}$ at 343 K for 3 h before cyclohexene addition.

^cTBP containing H_2O_2 were heated at 343 K for 3 h before cyclohexene addition.

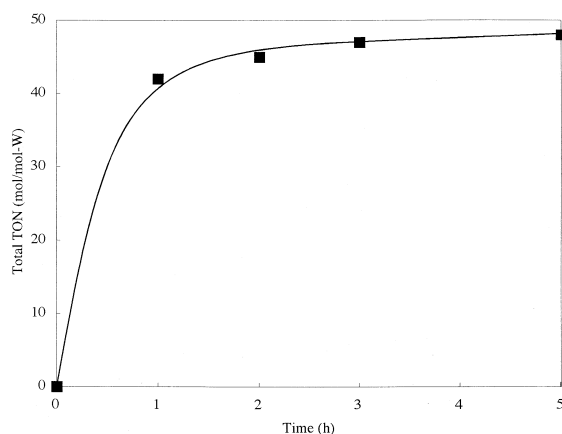


Fig. 3. The time course of cyclohexene oxidation with H_2O_2 on $\text{K}_8\text{SiW}_{11}\text{O}_{39}$. Reaction conditions: except for reaction time, the reaction conditions were the same as in Table 2.

showed no significant difference in the total yield from oxidant A. These results indicate that H_2O_2 was decomposed non-productively by $\text{K}_4\text{SiW}_{12}\text{O}_{40}$, which would be one of the reasons $\text{K}_4\text{SiW}_{12}\text{O}_{40}$ showed low catalytic activity for the epoxidation with H_2O_2 as an oxidant.

Fig. 3 shows the time course of oxidation of cyclohexene with H_2O_2 using $\text{K}_8\text{SiW}_{11}\text{O}_{39}$. This oxidation reaction proceeded smoothly up to 1 h after the start of the reaction. However, the TON then levelled off. Fig. 4(a0) and (a1) show IR spectra of $\text{K}_8\text{SiW}_{11}\text{O}_{39}$ before and after the reaction for 2 h, respectively. The catalyst used for 2 h showed no catalytic activity. The spectrum of the catalyst used for 2 h was significantly different from that of $\text{K}_8\text{SiW}_{11}\text{O}_{39}$. Although decomposition of $\text{K}_8\text{SiW}_{11}\text{O}_{39}$ might have occurred during cyclohexene oxidation with H_2O_2 , both $\text{Na}_9\text{SiW}_9\text{O}_{34}$ and Na_2WO_4 showed quite different spectra from the used catalyst; no clear assignment of the IR spectrum of the used catalyst could be done. Fig. 4(b0) and (b1) show IR spectra of $\text{Zn}_3\text{Al-SiW}_{11}\text{O}_{39}$ before and after oxidation reaction for 3 h with H_2O_2 , respectively. The peak at 1030 cm^{-1} is due to the $\text{P}=\text{O}$ stretching frequency of solvent TBP. Although there was no significant change between fresh and used $\text{Zn}_3\text{Al-SiW}_{11}\text{O}_{39}$, this

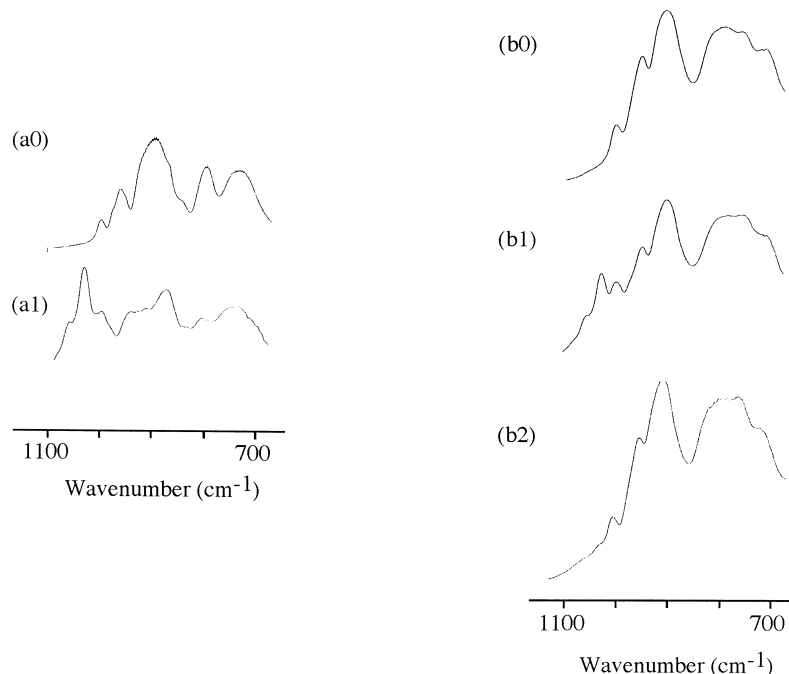


Fig. 4. The IR spectra of HPOM salts and LDH-HPOM sample before and after cyclohexene oxidation. (a0) $\text{K}_8\text{SiW}_{11}\text{O}_{39}$ before reaction and (a1) $\text{K}_8\text{SiW}_{11}\text{O}_{39}$ after 2 h reaction using H_2O_2 as oxidant. (b0) $\text{Zn}_3\text{-Al-SiW}_{11}\text{O}_{39}$ before reaction. (b1) $\text{Zn}_3\text{-Al-SiW}_{11}\text{O}_{39}$ after 3 h reaction using H_2O_2 as oxidant. (b2) $\text{Zn}_3\text{-Al-SiW}_{11}\text{O}_{39}$ used five times (total 15 h) in reactions using H_2O_2 as oxidant.

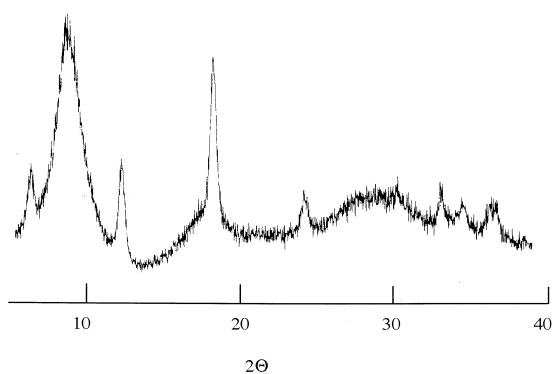


Fig. 5. The XRD pattern of $\text{Zn}_3\text{Al-SiW}_{11}\text{O}_{39}$ used five times in reactions.

gives no substantial evidence for the stability of intercalated $\text{SiW}_{11}\text{O}_{39}^{8-}$ because the activity of $\text{Zn}_3\text{Al-SiW}_{11}\text{O}_{39}$ was much lower than that of $\text{K}_8\text{SiW}_{11}\text{O}_{39}$, as shown in Table 2. In order to investigate the stability of intercalated $\text{SiW}_{11}\text{O}_{39}^{8-}$, this catalyst was five times reused for the oxidation of cyclohexene with H_2O_2 . The TON for the second reaction decreased by 30% as compared with the first reaction. The decrease in activity might be due to the decomposition of by-product $\text{SiW}_{11}\text{O}_{39}^{8-}$ salts which were not intercalated between the layers. For the following reactions, the reused catalyst showed stabilized (ca. 70% of the first run) activity; thus, the combined TON exceeded the TON obtained with $\text{K}_8\text{SiW}_{11}\text{O}_{39}$. Furthermore, there was no significant difference in IR spectra (Fig. 4(b0) and (b2)) and XRD patterns (Figs. 1e and 5) between fresh $\text{Zn}_3\text{Al-SiW}_{11}\text{O}_{39}$ and that used for five times. Therefore, it is considered that intercalated $\text{SiW}_{11}\text{O}_{39}^{8-}$ is much more stable than free $\text{SiW}_{11}\text{O}_{39}^{8-}$, whereas it was re-

ported that intercalated isopolyoxometalate anions such as $\text{Mo}_7\text{O}_{24}^{6-}$ and $\text{W}_7\text{O}_{24}^{6-}$ were decomposed during reaction [19]. The ratio of epoxide to diol + dione in the first reaction by $\text{Zn}_3\text{Al-SiW}_{11}\text{O}_{39}$ was much higher than that in the others. It was considered that the hydrolysis of epoxide mainly occurred on $\text{SiW}_{11}\text{O}_{39}^{8-}$ salts existing outside interlayers as by-product.

Table 5 shows the results of oxidation of various cyclic alkenes with H_2O_2 with free $\text{K}_8\text{SiW}_{11}\text{O}_{39}$ and $\text{Zn}_3\text{Al-SiW}_{11}\text{O}_{39}$ as catalysts. The reactivity of cyclic alkenes on $\text{Zn}_3\text{Al-SiW}_{11}\text{O}_{39}$ decreased with increasing carbon number of ring. The relative rates $r(\text{Zn}_3\text{Al-SiW}_{11}\text{O}_{39})/r(\text{free K}_8\text{SiW}_{11}\text{O}_{39})$ of cyclohexene, cyclooctene and cyclododecene were 0.30, 0.15 and 0.10, respectively. This indicates noticeable shape selectivity of the LDHs intercalates. It is considered that the diffusivity of cyclic alkenes into the pores between layers decreases with increasing number of carbon ring and that the low relative rates for bulky molecules might be due to the restriction of oxidation on the internal surface of $\text{Zn}_3\text{Al-SiW}_{11}\text{O}_{39}$.

The results of oxidation of cyclohexene by various LDH-HPOM samples using molecular O_2 in the presence of isobutyraldehyde are shown in Table 6. The difference between the brucite-type layers containing Zn^{2+} and Mg^{2+} was of little consequence; the activities of $\text{Mg}_2\text{Al-SiW}_{12}\text{O}_{40}$ and $\text{Zn}_3\text{Al-SiW}_{12}\text{O}_{40}$ showed no marked difference. The activity of $\text{Ni}_2\text{Al-SiW}_{12}\text{O}_{40}$ proved to be much higher than those of $\text{Mg}_2\text{Al-SiW}_{12}\text{O}_{40}$ and $\text{Zn}_3\text{Al-SiW}_{12}\text{O}_{40}$. We found that $\text{Ni}_2\text{Al-NO}_3$ containing no HPOM between layers showed activity

Table 5

Oxidation of various cyclic alkenes with H_2O_2 over $\text{K}_8\text{SiW}_{11}\text{O}_{39}$ and $\text{Zn}_3\text{Al-SiW}_{11}\text{O}_{39}$

Catalyst substrate	Turnover number (mol/mol-W)								Relative rate [$r(\text{Zn}_3\text{Al-SiW}_{11}\text{O}_{39})/$ $r(\text{K}_8\text{SiW}_{11}\text{O}_{39})$]
	$\text{K}_8\text{SiW}_{11}\text{O}_{39}$				$\text{Zn}_3\text{Al-SiW}_{11}\text{O}_{39}$				
	Epoxide	diol	Others	Total	Epoxide	diol	Others	Total	
Cyclohexene	6.5	39	1.7	47	8.1	5.6	trace	14	0.30
Cyclooctene	58	1.7	2.7	62	5.9	0.36	3.6	9.9	0.15
Cyclododecene	45	3.3	3.3	52	1.2	2.4	1.5	5.1	0.10

^aReaction conditions: 1 mmol catalyst (as W), 100 mmol substrate, 30.3 g TBP containing 100 mmol H_2O_2 , 343 K, 3 h.

Table 6
Oxidation of cyclohexene with O₂ in the presence of isobutyraldehyde^a

Catalyst	Turnover number (mol/mol-W or Ni)			
	Epoxide	diol + dione	Others	Total
Zn ₃ Al–SiW ₁₁ O ₃₉	0.36	0.26	0.16	0.88
Zn ₃ Al–SiW ₁₂ O ₄₀	5.8	0.80	0.34	6.7
Mg ₂ Al–SiW ₁₂ O ₄₀	3.9	n.d.	0.17	4.1
Ni ₂ Al–SiW ₁₂ O ₄₀	24	n.d.	1.0	25
Ni ₂ Al–SiW ₁₂ O ₄₀ ^b	30	n.d.	1.2	31
Ni ₂ Al–NO ₃ ^b	7.3	n.d.	0.67	8.0
Ni ₂ Al–TA ^b	32	0.80	3.8	37
Ni (5%)/SiO ₂ ^{b,c}	22	1.1	1.6	25

^aThe reaction conditions were as shown in Table 3.

^bTurnover numbers were based on Ni.

^cPrepared by impregnating SiO₂ with aqueous Ni(NO₃)₂ solution.

for epoxidation of cyclohexene. It is considered that the oxidation of cyclohexene was catalyzed by Ni in the brucite-type layers. Actually, Ni-supported silica prepared by the impregnation method was found to be active in the oxidation of cyclohexene in the presence of molecular O₂ and isobutyraldehyde, as shown in Table 6. For Ni₂Al–NO₃, this reaction might proceed on the outer surface because the size of cyclohexene is much larger than the gallery height (ca. 3.0 Å) between the brucite-like layers. In agreement with this hypothesis, Ni₂Al–TA, whose gallery height (ca. 9.8 Å) is much higher than that of Ni₂Al–NO₃, was about four times as active as Ni₂Al–NO₃. The improvement of activity is attributed to the reaction occurring between layers.

4. Conclusions

Zn₃Al–SiW₁₂O₄₀ and Zn₃Al–SiW₁₁O₃₉ reflect the property of the corresponding free HPOM in terms of epoxidation of alkenes; molecular O₂ in the presence of isobutyraldehyde is an effective oxidant in the SiW₁₂O₄₀⁴⁻-catalyzed reaction, whereas H₂O₂ is effective in

the SiW₁₁O₃₉⁸⁻-catalyzed reaction. It seems that SiW₁₂O₄₀⁴⁻ was introduced into the interstices between the LDHs layers without change in structure. The ineffectiveness of H₂O₂ in the SiW₁₂O₄₀⁴⁻-catalyzed reaction is partly due to decomposition of H₂O₂ by SiW₁₂O₄₀⁴⁻. SiW₁₁O₃₉⁸⁻ intercalated between the LDHs layers are more stabilized than free SiW₁₁O₃₉⁸⁻ and exhibited noticeable shape selectivity for the oxidation of cyclohexene with H₂O₂. Both Ni in brucite-like layers of LDHs and Ni supported on silica showed activity for the oxidation of cyclohexene with O₂ and isobutyraldehyde.

References

- [1] W.T. Reichle, *Chemtech.* (1986) 58.
- [2] F. Cavani, F. Trifiro, A. Voccaro, *Catal. Today* 11 (1991) 173.
- [3] E. Suzuki, M. Okamoto, Y. Ono, *J. Mol. Catal.* 61 (1990) 283.
- [4] I.V. Kozhevnikov, *Chem. Rev.* 98 (1998) 171.
- [5] N. Mizuno, M. Misono, *Chem. Rev.* 98 (1998) 199.
- [6] T. Tatsumi, K. Yamamoto, H. Tajima, H. Tominaga, *Chem. Lett.* 5 (1992) 815.
- [7] S.K. Yun, T.J. Pinnavaia, *Inorg. Chem.* 35 (1996) 6853.
- [8] J. Evans, M. Pillinger, J. Zhang, *J. Chem. Soc., Dalton Trans.* (1996) 2963.
- [9] M.A. Drezdson, *Inorg. Chem.* 27 (1988) 4628.
- [10] K. Chibwe, W. Hohnes, *Chem. Mater.* 1 (1989) 489.
- [11] E. Narita, P.D. Kaviratna, T.J. Pinnavaia, *J. Chem. Soc. Chem. Commun.* (1993) 60.
- [12] T. Tatsumi, K. Yamamoto, *Advanced Materials '93: IIA. Biomaterials, Organic, Intelligent Materials, Vol. 15A, 1994*, p. 141.
- [13] T. Kwon, T.J. Pinnavaia, *J. Mol. Catal.* 74 (1992) 23.
- [14] R.M. Taylor, *Clay Minerals* 19 (1984) 591.
- [15] W.G. Klemperer, *Inorg. Synth.* 27 (1990) 87.
- [16] H. Fukuhara, T. Nakamura, H. Inagaki, E. Nishikawa, C. Imai, M. Misono, *Chem. Lett.* (1988) 877.
- [17] T.J. Pinnavaia, in: M.L. Occelli, H. Robson (Eds.), *Expanded Catalyst and Other Microporous Solids*, Van Nostrand-Reinhold, New York, 1992, p. 1.
- [18] S. Ueno, K. Yamaguchi, K. Yoshida, K. Ebitani, K. Kaneda, *Chem. Commun.* (1998) 295.
- [19] E. Gardner, T.J. Pinnavaia, *Appl. Catal.* 167 (1998) 65.
- [20] T. Yamada, T. Takai, O. Rhode, T. Mukaiyama, *Chem. Lett.* (1991) 1.