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Syntheses of new peroxo-polyoxometalates intercalated layered double hydroxides for propene epoxidation by molecular oxygen in methanol

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Abstract

A new type of layered double hydroxides intercalated by peroxo-polyoxometalates was synthesized by treating PdMAl-$[PW_{11}O_{39}]$ (M = Mg^{2+} or Zn^{2+}) with 30% H_2O_2. XRD, FT-IR, and ^{31}P MAS NMR revealed that the interlayer anion $[PW_{11}O_{39}]^{7-}$ was converted mainly to $\{PO_4[WO(O_2)_2]_4\}^{3-}$ and $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$. ^{27}Al MAS NMR revealed that the brucite-like layers did not collapse during synthesis. PdMgAl-$[PW_4 + W_2]$ showed 91.5% selectivity for propene oxide at 47.5% conversion during propene epoxidation by O_2 in methanol at 353 K for 10 h. The catalytic ability of PdMgAl-$[PW_4 + W_2]$ can be attributed to the presence of highly active Pd particles in the brucite-like layers that generate H_2O_2 in situ, the strong epoxidation ability of interlayer peroxo-polyoxometalates with dilute H_2O_2, and the promotion effect of the basic MgAl-type brucite-like layers toward alkene epoxidation. Moreover, PdMgAl-$[PW_4 + W_2]$ can be separated and reused by filtration without leaching active components into the solvent.

Keywords: Peroxo-polyoxometalate; Layered double hydroxides; Propene epoxidation; Molecular oxygen; Palladium; Methanol; Solid-phase crystallization method

1. Introduction

Propene oxide (PO) is an important chemical feedstock used for producing polyurethane, surfactants, and other products. The two major industrial processes for PO production are the chlorohydrin process and the organic hydroperoxide process. The chlorohydrin process causes serious environmental pollution, and the hydroperoxide process stoichiometrically produces coproducts such as *t*-butyl alcohol and styrene. It is urgent to create a novel clean process for producing PO instead of the current industrial processes. Because the allylic C–H bonds of propene molecules have high activity, PO cannot be manufactured by a heterogeneously catalyzed procedure similar to that applied for manufacturing ethene oxide in industry [1]. Although many scientists have attempted to improve the catalytic gas-phase epoxidation of propene by molecular oxygen [2–7], the selectivity for PO is hardly to be improved up to 50% even at a relatively low propene conversion (about 10%) [2–7]. Haruta and coworkers have studied the catalytic gas-phase epoxidation of propene using a mixture of oxygen and hydrogen over the supported Au catalysts [8,9]. High selectivity for PO (∼90%) could be obtained at a low conversion (<10%), but a large amount of hydrogen was consumed to form water. Moreover, the concentrations of the reactants propene, hydrogen, and oxygen were within the explosion of the mixture during the reaction.

The liquid-phase catalytic epoxidation of propene is attractive because high selectivity for PO can be obtained in a liquid-phase catalytic process. A high selectivity toward PO can be obtained during the epoxidation of propene over TS-1 by using 30% H_2O_2 as an oxidant [10]; however, this oxidant is so expensive that its use cannot ensure an economically viable process. Therefore, a mixture of hydrogen and oxygen has been used instead of 30% H_2O_2 for propene epoxidation over TS-1, in which the mixture of hydrogen and oxygen generates H_2O_2 in situ over a Pt or Pd catalyst [11,12]. However, safety problems also exist in this liquid-phase catalytic process us-

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ing the hydrogen/oxygen mixed gas [11,12]. The epoxidation of propene by oxygen in the absence of hydrogen would be of great significance in industry.

We previously reported a catalyst system containing palladium and Ti–Al-MCM-22 for the epoxidation of propene by molecular oxygen in methanol [13]. The Al sites in Ti–Al-MCM-22 improved the propene conversion but decreased the selectivity for PO (due to the formation of hydrocarbon oligomers). Therefore, it is difficult to simultaneously obtain high propene conversion along with a high selectivity for PO in the catalyst system. Recently, we improved the catalytic system by using peroxo-polyoxometalate instead of Ti–Al-MCM-22 [14,15]. The catalytic system comprising peroxo-polyoxometalate and palladium acetate in methanol showed >80% selectivity for PO at 40% propene conversion for propene epoxidation by molecular oxygen in methanol. This catalytic system is promising due to the high selectivity for PO, the low cost and high safety of oxygen and methanol, and the possibility of recycling coproduct CO_x for synthesizing methanol in industry. A limitation of this catalytic system is that both peroxo-polyoxometalate and palladium acetate readily dissolve in methanol, and thus the only possible method for reusing catalyst is vacuum distillation of the mixture after the reaction. In manufacturing, heterogeneous catalysts are desirable because of their versatility, ease of separation, lack of corrosion, long lifetime, and regenerability [16].

In this study, we synthesized a new type of Pd-containing layered double hydroxide (LDH) compound intercalated by peroxo-polyoxometalates. The novel compound is an excellent heterogeneous catalyst for the epoxidation of propene by molecular oxygen in methanol, and it does not leach active components into the solvent during the reaction.

2. Experimental

2.1. Reagents

All of the reagents used in this study were purchased from Wako Pure Chemical Industries, Ltd. Chemicals with > 99% purity and were used without additional purification. Propene, oxygen, nitrogen, and argon were purchased from Tokyo Gas Chemical Co.; the purity of the gases was >99%.

2.2. Syntheses

$Na_7[PW_{11}O_{39}]$ was prepared from the reaction of $H_3PW_{12}O_{40}$ and an aqueous solution of NaOH. Up to pH 5.0, the aqueous solution of 1 M NaOH was added dropwise to a solution containing 15 g of $H_3PW_{12}O_{40}$ in 50 ml of distilled water at 323 K. The resulting solution was evaporated to 10 ml by stirring at 323 K. Then the solution was refrigerated at 278 K for 24 h. Finally, the deposit was obtained by filtration and was dried at 353 K for 24 h.

$Pd_{0.05}Mg_{0.65}Al_{0.3}(OH)_2(NO_3)_{0.3}$ (designated PdMgAl-NO_3) was prepared by a coprecipitation-aging method. A mixture of $Pd(NO_3)_2$, $Mg(NO_3)_2{\cdot}6H_2O$, and $Al(NO_3)_3{\cdot}9H_2O$ in 100 ml of carbonate-free distilled water and an aqueous solution of 1 M NaOH were simultaneously added dropwise to a large flask containing 100 ml of carbonate-free distilled water with rapid stirring under a nitrogen atmosphere. The relative rates of adding the mixed solution of nitrate salts and the 1 M NaOH solution were adjusted to maintain the pH at 10.0 ± 0.2. Subsequently, the slurry was aged at 343 K for 12 h under a nitrogen atmosphere. Filtration of the suspension produced a wet paste (gel), which was used without drying for the subsequent ion-exchange process.

$Pd_{0.05}Mg_{0.65}Al_{0.3}(OH)_2[PW_{11}O_{39}]_{0.043}$ (designated PdMgAl-PW_{11}) was prepared by an ion-exchange method. A slurry of PdMgAl-NO_3 (2 g of PdMgAl-NO_3 gel in 50 ml of water) and a solution of $Na_7[PW_{11}O_{39}]$ (5 g of $Na_7[PW_{11}O_{39}]$ in 50 ml of water) were simultaneously added dropwise to a flask containing 50 ml of carbonate-free distilled water with rapid stirring under a nitrogen atmosphere at 333 K. While the solution was added, the pH was maintained at 4.5 ± 0.2 by using a dilute HNO_3 solution. After this addition, the slurry was stirred at 333 K for 6 h under a nitrogen atmosphere. Then the solid product was filtered, washed by distilled water, and dried in air at 353 K for 24 h.

PdMgAl-$[PW_4 + W_2]$ was prepared by the reaction of PdMgAl-PW_{11} with 30% H_2O_2. Here, 1.5 g of dried PdMgAl-PW_{11} was stirred in a 30 ml solution of 30% H_2O_2 solution at 323 K for 5 h. Then the solid product was filtered, washed in a large amount of water to remove the absorbed H_2O_2, and dried in air at room temperature.

PdZnAl-$[PW_4 + W_2]$ was prepared following the same method as used for synthesizing PdMgAl-$[PW_4 + W_2]$.

2.3. Instrumentation

Powder X-ray diffraction (XRD) patterns were obtained at room temperature using a MAC Science MXP-18 diffractometer with Cu$K\alpha$ radiation operated at 40 kV and 50 mA. Fourier transform infrared (FTIR) spectra were recorded by a JASCO FT/IR-7000 spectrometer using KBr pellets under atmospheric conditions. Inductively coupled plasma (ICP) analyses were carried out using a Thermo Jarrel Ash IRIS/AP. Thermogravimetric and differential thermal analyses (TG-DTA) were performed using a Shimadzu TGA-50 instrument under a flowing nitrogen atmosphere. ^{31}P magic-angle spinning nuclear magnetic resonance (MAS NMR) and ^{27}Al MAS NMR spectra were recorded in 5-mm-o.d. tubes on a Burker ARX-300 apparatus. The ^{31}P chemical shift was referenced with 85% H_3PO_4; the ^{27}Al chemical shift was referenced with 1 M $[Al(H_2O)_6]^{3+}$. X-ray absorption fine structure (XAFS) measurements were conducted at the beamline 10B of the Photon Factory in the National Laboratory for High-Energy Physics, Tsukuba, Japan. The spectra were acquired at room temperature in a transmission mode for the K-edges of Pd. The EXAFS data were analyzed using the UWXAFS 3.0 package licensed from the University of Washington. The pre-edge background was removed by a sample line fitting. The power-scaled EXAFS function $k^n\chi(k)$ in the momentum k space was converted to that in real space by Fourier transformation (with $k_{\min}$ and $k_{\max}$ selected at

2.0 and 12.0 Å^{-1}, respectively), resulting in a radial structural function of the sample.

2.4. Catalytic reaction

The epoxidation of propene was carried out in a 50-ml Teflon-coated autoclave reactor equipped with a pressure gauge. During the reaction, the autoclave reactor was immersed in an oil bath equipped with a temperature control at the required temperatures. In a typical run, 0.3 g of catalyst and 10 ml of methanol were added to the autoclave reactor. Then 0.8 MPa propene, 0.4 MPa oxygen, and 0.8 MPa argon were charged to the autoclave reactor at 298 K. After reaction with vigorous stirring (>600 rpm), both the gas and the liquid were sampled and analyzed by gas chromatography. Hydrocarbons and oxygenated compounds were detected by two FID gas chromatographs, with a Porapak Q column at 473 K and with 20 wt% FFAP on a Chromosorb W column at 373 K. CO, CO_2, and O_2 were detected using a Shimadzu GC 14B TCD gas chromatograph equipped with Porapak Q and MS-5A columns at 343 K. The factor of each component in the gas phase was confirmed using the corresponding standard gas. The components in the liquid phase after reaction were calculated using 1,4-dioxane as an internal reference.

3. Results and discussion

3.1. Synthesis route

The synthesis route for the novel LDH compounds intercalated by peroxo-polyoxometalates is described in Scheme 1.

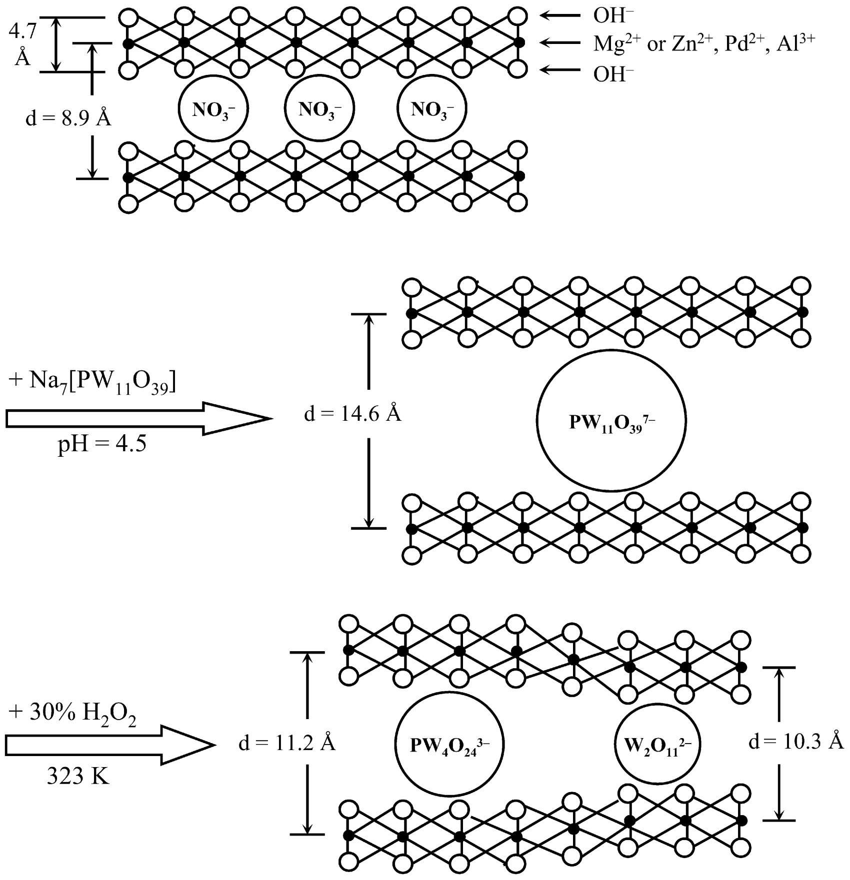
LDH compounds are types of anion clays with the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}A^{n-}_{x/n}\cdot mH_2O$ (M^{2+}, M^{3+} = metal cation, A = interlayer anion) [17]. The metal cations are distributed in the brucite-like layers, and the interlayer anions are fixed between the brucite-like layers by electrical charge interactions. The divalent metal cation is usually Mg^{2+} or Zn^{2+}, and the trivalent metal cation is usually Al^{3+}. Pd^{2+} cation can be introduced into the M^{2+} position of the brucite-like layers in the LDH compounds when the molar ratio of $Pd^{2+}/(M^{2+} + M^{3+})$ is <5 mol% [18]. On the other hand, although the interlayer anions are usually small anions (e.g., CO_3^{2-}, NOs_3^-, OH^-), polyoxometalate anions with large Keggin structures can be intercalated into the interlayer region of the LDH compounds by the ion-exchange method [19–21]. Basic MgAl-type LDH materials have been reported to promote the epoxidation of electron-deficient olefins with 30% H_2O_2 [22]. Polyoxometalate anion-intercalated LDH compounds are very attractive in both synthesis and catalysis [23–25].

The Keggin structure $H_3PW_{12}O_{40}$ is the most popular polyoxometalate for alkene epoxidation by 30% H_2O_2 (the Ishii–Venturello epoxidation) [26,27]. The activity of this epoxidation system is due to the formation of peroxo-polyoxometalates in situ, such as $\{PO_4[WO(O_2)_2]_4\}^{3-}$ (designated PW_4), $\{HPO_4[W(O)(O_2)_2]_2\}^{2-}$ (designated PW_2), and $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ (designated W_2O_{11}), which constitute the real oxidants [28,29]. All of these peroxo-polyoxometalates are powerful catalysts for the olefin epoxidation with 30 wt% H_2O_2 [28–32]; in particular, PW_4 has the ability to carry out olefin epoxidation even with a dilute H_2O_2 solution formed in situ [30]. If the pH of the solution containing the Keggin structure is unstable, then the Keggin structure is hydrolyzed, with progressive loss of one or more MO entities. $[PW_{12}O_{40}]^{3-}$ is rapidly converted to its deficit derivative $[PW_{11}O_{39}]^{7-}$ (lacunary Keggin structure) at pH above 1.5–2 and to $[PW_9O_{32}]^{5-}$ species at pH above 7 [33,34]. Only $[PW_{12}O_{40}]^{3-}$ and $[PW_{11}O_{39}]^{7-}$ can decompose into the smaller active peroxo-polyoxometalates in a 30% H_2O_2 solution [28].

Peroxo-isopolyanion W_2O_{11}-intercalated LDH compounds have been synthesized by the reaction of WO_4^{2-}-intercalated LDH with 30% H_2O_2 [35]. Moreover, organ-peroxotungstate-intercalated LDH compounds have been synthesized by the reaction of organic-phosphorous-intercalated LDH with W_2O_{11} [36]. All of these compounds are excellent catalysts for olefin epoxidation by 30% H_2O_2 [35,36]. However, to the best of our knowledge, peroxo-heteropolyanion PW_4—the most active peroxo-polyoxometalate that can be used with a dilute H_2O_2 solution formed in situ—has not yet been successfully intercalated into the interlayer region of LDH compounds.

As shown in Scheme 1, NO_3^--type LDH compounds (designated PdMgAl-NO_3 and PdZnAl-NO_3) were selected as host LDH compounds in this study, because the interlayer NO_3^- anions have low charges; as a result, they are easily exchanged by polyoxometalate anions. The molar ratio of $Pd^{2+}/(M^{2+} + M^{3+})$ of 5 mol% was chosen, because this is the maximum limitation for introducing a large Pd^{2+} cation into the M^{2+} position of the brucite-like layers in the LDH compounds [18]. A pH value of 4.5 was chosen for the ion exchange of NO_3^- by polyoxometalate anions, because the weak acid condition is appropriate for the ion exchange of the interlayer anion in the LDH compounds [19–21]. The $[PW_{11}O_{39}]^{7-}$ anion was selected because it is stable at pH 4.5 and forms active peroxo-polyoxometalates in the 30% H_2O_2 solution (similar to the performance of $[PW_{12}O_{40}]^{3-}$) [28]. Moreover, $[PW_{11}O_{39}]^{7-}$ anions can be introduced relatively easily into the interlayer region of LDH compounds by ion-exchange due to their high charges. An excess amount of 30% H_2O_2 was used for treating PdMgAl-PW_{11} and PdZnAl-PW_{11} to ensure the complete decomposition of the interlayer $[PW_{11}O_{39}]^{7-}$ anion. As soon as the active peroxo-polyoxometalates (such as PW_4 and W_2O_{11}) were formed, they were fixed in the interlayer region between the brucite-like layers by electrical charge interactions and hydrogen bonds. The absorbed H_2O_2 on the solid product was removed by washing several times with a large amount of water. The peroxo-polyoxometalate-intercalated LDH compounds thus formed are designated PdMgAl-$[PW_4 + W_2]$ and PdZnAl-$[PW_4 + W_2]$.

Therefore, Scheme 1 (for preparing the novel compounds) is based on three facts. First, a small amount of Pd^{2+} cations can be introduced into the M^{2+} position of the brucite-like layers in the LDH compounds. Second, LDH compounds have ion-exchange capability, and the large $[PW_{11}O_{39}]^{7-}$ can be intercalated into the LDH compounds because $[PW_{11}O_{39}]^{7-}$



Scheme 1. Synthesis route of layered double hydroxides intercalated by peroxo-polyoxometalates.

has a much higher negative electric charge than NO_3^-. Third, $[PW_{11}O_{39}]^{7-}$ anion decomposes to small active peroxo-polyoxometalates in the 30% H_2O_2 solution. Evidence supporting Scheme 1 is presented in the next section. As shown in Scheme 1, peroxo-polyoxometalates are synthesized in the interlayer region, and Pd^{2+} ions are distributed in the brucite-like layers in the novel compounds. Thus, the novel compounds are expected to act as effective heterogeneous catalysts for the epoxidation of propene by molecular oxygen in methanol compared with the homogeneous catalytic system comprising peroxo-polyoxometalate and palladium acetate in methanol [14,15].

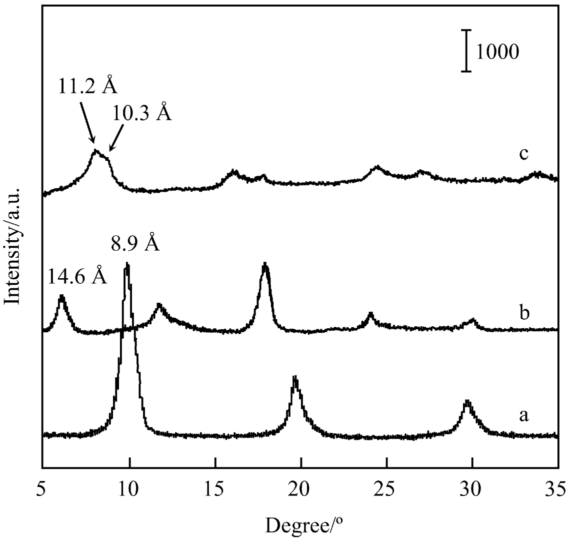


Fig. 1. XRD patterns of various samples: (a) PdMgAl-NO_3; (b) PdMgAl-PW_{11}; (c) PdMgAl-$[PW_4 + W_2]$.

3.2. Sample characterization

XRD pattern provides the most common method for determining the gallery heights of the layered structure compounds. The XRD patterns of various samples are shown in Fig. 1. The XRD pattern of PdMgAl-NO_3 indicates the presence of only a well-crystallized LDH phase in the sample. LDH compounds crystallize with the $3R$ symmetry; the parameters of the unit cell are designated "c" and "a." The basal d_{003} spacing at the lowest angle is 8.9 Å for PdMgAl-NO_3, indicating that the value of the parameter c is 26.7 Å in PdMgAl-NO_3 because $c = 3 \times d_{003}$ in the LDH compounds [17]. As shown in the model of the LDH compounds in Scheme 1, the value of the d_{003} spacing in the XRD pattern includes the thickness of the host layer and the height of the interlayer region [37]. Thus, both d_{003} spacing and parameter c certainly change if there is an alteration of the anions in the interlayer region. On the other hand, the value of parameter a is not affected by the size of the interlayer anions. The (110) reflection for PdMgAl-NO_3 appears at around 61° in the XRD pattern (not shown in Fig. 1), corresponding to a d_{110}

value of 1.52 Å. Thus, the value of the parameter a is 3.04 Å in PdMgAl-NO_3, because $a = 2 \times d_{110}$ in the LDH compounds [17]. The thickness of the host layer of MgAl-type LDH compounds is usually assumed to be about 4.7 Å [19–21,37]. Subtracting the thickness of the host layer (4.7 Å) from the value of the d_{003} spacing (8.9 Å) of PdMgAl-NO_3 gives a gallery height of the NO_3^- anion in PdMgAl-NO_3 of 4.2 Å. On the other hand, in the XRD pattern of PdMgAl-PW_{11}, all of the reflections of the NO^{3-}-type LDH compounds disappear and the basal d_{003} spacing shifts to 14.6 Å, indicating a PdMgAl-PW_{11} gallery height of 9.9 Å. This gallery height is in agreement with the sphere diameter of Keggin structure polyoxometalate anions (approximately 10 Å) [33]. Because the reflections of PdMgAl-NO_3 and $Na_7[PW_{11}O_{39}]$ cannot be observed in the XRD pattern of PdMgAl-PW_{11}, the mixture of PdMgAl-NO_3 and $Na_7[PW_{11}O_{39}]$ does not exist in the PdMgAl-PW_{11} sample. There results indicate that $[PW_{11}O_{39}]^{7-}$ has been successfully introduced into the interlayer region of LDH by the ion exchange of PdMgAl-NO_3 with $Na_7[PW_{11}O_{39}]$ [19–21]. The reflection intensity of PdMgAl-PW_{11} is much lower than that of PdMgAl-NO_3 in the XRD pattern, indicating that the intercalation of large Keggin structure polyoxometalate anions into the interlayer region instead of small NO_3^- anions greatly decreases the crystallinity of the LDH materials [19–21]. After treating PdMgAl-PW_{11} with 30% H_2O_2 at 323 K for 5 h, the reflection for a d spacing of 14.6 Å disappeared, and a broad reflection appeared in the XRD pattern with two main peaks at 11.2 and 10.3 Å (Fig. 1).

These results suggest that after treatment with 30% H_2O, $[PW_{11}O_{39}]^{7-}$ anions decompose mainly into two types of anions with sizes of 6.5 and 5.6 Å in the interlayer region of the LDH. According to the molecule sizes of PW_4 and W_2O_{11} [38,39], PW_4 likely lies down and W_2O_{11} likely stands up in the interlayer region in PdMgAl-$[PW_4 + W_2]$.

FTIR spectra of the various samples are shown in Fig. 2. PdMgAl-NO_3 exhibits a very strong peak at 1380 cm^{-1} due to the vibration of the NO_3^- anion in the interlayer region. In the FTIR spectrum of $Na_7[PW_{11}O_{39}]$, five characteristic peaks of $[PW_{11}O_{39}]^{7-}$ can be seen in the range of 600–1200 cm^{-1}. The peaks at approximately 1100 and 1050 cm^{-1} are attributed to the vibration of P–O_a, and the peak at approximately 950 cm^{-1} is attributed to that of W–O_d. Furthermore, the peak at approximately 890 cm^{-1} is attributed to the vibration of W–O_b–W, and the peaks at approximately 810 and 740 cm^{-1} are attributed to that of W–O_c–W [30]. The peak of NO_3^- at 1380 cm^{-1} becomes very small in the FTIR spectrum of PdMgAl-PW_{11}. This indicates that NO_3^- anion rarely exists in the PdMgAl-PW_{11} sample. Thus the PdMgAl-PW_{11} sample is not a physical mixture of PdMgAl-NO_3 and $Na_7[PW_{11}O_{39}]$. Moreover, all five characteristic peaks of $[PW_{11}O_{39}]^{7-}$ can be clearly observed in the FTIR spectrum of PdMgAl-PW_{11}. These results indicate that $[PW_{11}O_{39}]^{7-}$ anions are successfully intercalated into the interlayer region without collapsing after the ion-exchange process of PdMgAl-NO_3 with $Na_7[PW_{11}O_{39}]$. In the FTIR spectrum of TBA-PW_4, the peaks at 1075 and 1045 cm^{-1} are attributed to the stretching vibration of P–O. The peaks at 940 and 840 cm^{-1} are attributed to the stretching vibrations of W–O and the peroxo-oxygen bond O–O, respectively; in addition, the peaks in the range 1350–1500 cm^{-1} are assigned to the stretching vibration of the ammonium group in TBA. On the other hand, in accordance with data reported in the literature [27–31], $K_2[W_2O_3(O_2)_4(H_2O)_2]$, obtained by adding KCl to a $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ solution, shows peaks at approximately 980, 960, 850, 835, 775, and 615 cm^{-1} in the IR spectrum. After treatment of PdMgAl-PW_{11} with 30 wt% H_2O_2, all of the characteristic peaks of $[PW_{11}O_{39}]^{7-}$ disappear and those of PW_4 and W_2O_{11} appear; in particular, the vibration of the peroxo-oxygen bond O–O at approximately 840 cm^{-1} is very strong in the FTIR spectrum. These results indicate that after treatment with 30 wt% H_2O_2, the $[PW_{11}O_{39}]^{7-}$ anions in PdMgAl-PW_{11} are converted into several peroxopolyoxometalates with the peroxo-oxygen bond O–O in the interlayer region of LDH compounds.

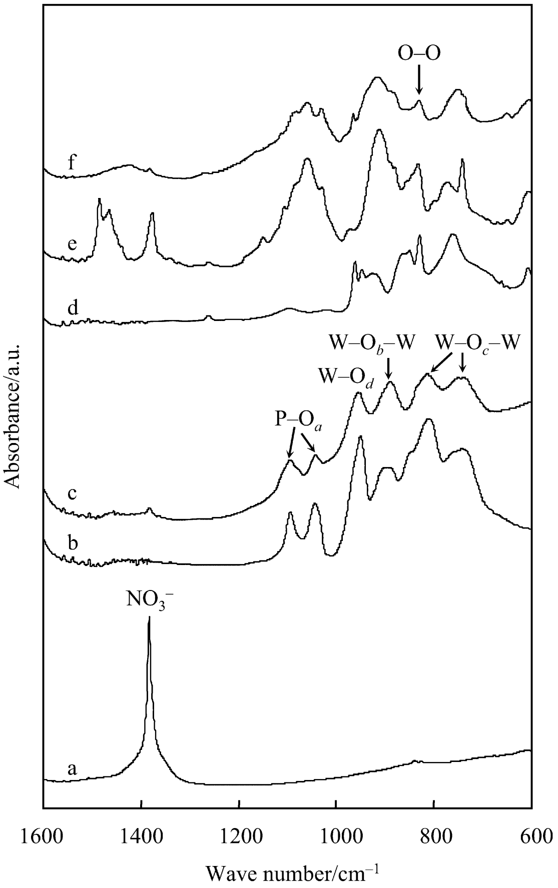


Fig. 2. FT-IR spectra of various samples: (a) PdMgAl-NO_3; (b) Na_7-$[PW_{11}O_{39}]$; (c) PdMgAl-PW_{11}; (d) $K_2[W_2O_3(O_2)_4(H_2O)_2]$; (e) TBA-$PO_4[W(O)(O_2)_2]_4$; (f) PdMgAl-$[PW_4 + W_2]$.

The ^{31}P MAS NMR spectra of various samples are shown in Fig. 3. $Na_7[PW_{11}O_{39}]$ exhibits a signal at $\delta = -10.4$ ppm in the ^{31}P MAS NMR spectrum, coinciding with the position of the $[PW_{11}O_{39}]^{7-}$ anion reported in the literature [33]. PdMgAl-PW_{11} shows a signal with the same shape at the same position as that of $Na_7[PW_{11}O_{39}]$ in the ^{31}P MAS NMR spectrum, verifying that the $[PW_{11}O_{39}]^{7-}$ anions did not decompose during the intercalation process. After treatment of PdMgAl-PW_{11} with 30 wt% H_2O_2 at 323 K for 5 h, the signal at

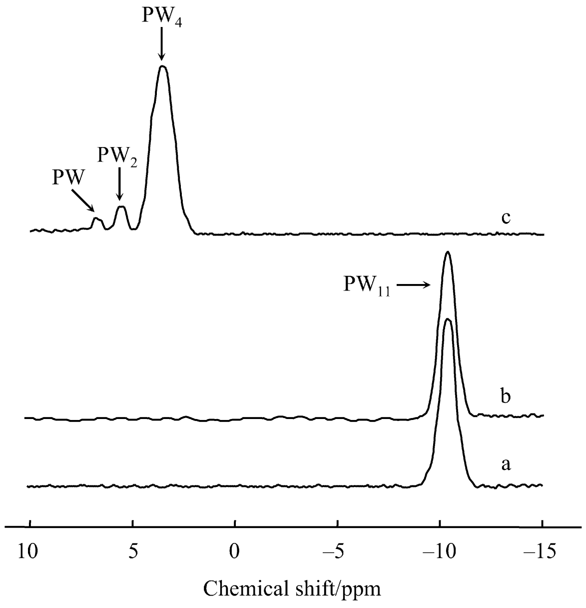


Fig. 3. ^{31}P MAS NMR spectra of various samples: (a) $Na_7[PW_{11}O_{39}]$; (b) PdMgAl-PW_{11}; (c) PdMgAl-[PW_4 + W_2].

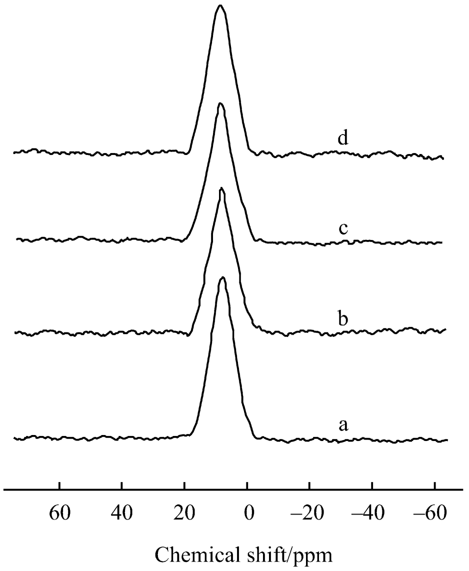


Fig. 4. ^{27}Al MAS NMR spectra of various samples: (a) MgAl-NO_3; (b) PdMgAl-NO_3; (c) PdMgAl-PW_{11}; (d) PdMgAl-[PW_4 + W_2].

$\delta = -10.4$ ppm disappeared and a strong signal at $\delta = 3.6$ ppm and two weak signals at $\delta = 5.6$ and 6.8 ppm appeared in the ^{31}P MAS NMR spectrum. These results indicate that the $[PW_{11}O_{39}]^{7-}$ anion in PdMgAl-PW_{11} is decomposed into several compounds by treatment with 30% H_2O_2 for 5 h. According to the chemical shift of the signals in the ^{31}P MAS NMR spectrum of PdMgAl-[PW_4 + W_2], the strong signal at $\delta = 3.6$ ppm can be attributed to PW_4, whereas the two weak signals at $\delta = 5.6$ and 6.8 ppm can be assigned to PW_2 and a peroxo-polyoxometalate with P/W = 1 (molar ratio), respectively [28,29].

The ^{27}Al MAS NMR spectra of the various samples are shown in Fig. 4. The ^{27}Al MAS NMR spectrum was used to evaluate the changes in the brucite-like layers during synthesis. In the LDH compounds, Al ions in the host brucite-like layers lie in the surrounding octahedral with 6-coordination [17]. As shown in Fig. 4, MgAl-NO_3 exhibits a strong single signal at approximately 8 ppm, indicating the presence of octahedral Al only in the brucite-like layers [20,21,38]. PdMgAl-NO_3, PdMgAl-PW_{11}, and PdMgAl-[PW_4 + W_2] exhibit ^{27}Al MAS NMR signals at almost the same position as that of the signal of MgAl-NO_3 without the appearance of the signal of tetrahedral Al. These results indicate that the MgAl-type brucite-like layers did not collapse during the three syntheses considered in this study: the introduction of Pd^{2+} cations into Mg^{2+} sites in the brucite-like layers, ion exchange of interlayer NO_3^- anions by $[PW_{11}O_{39}]^{7-}$ anions, and treatment of PdMgAl-PW_{11} with 30% H_2O_2 to obtain PdMgAl-[PW_4 + W_2].

The chemical compositions and the formulas of the various samples are given in Table 1. The actual amounts of the various elements in the samples were measured by ICP analysis, and the amount of water in each sample was calculated from the TG-DTA curve. The formulas of the various samples could be determined using the data from elemental and thermogravimetric analyses according to the general formula of the LDH compounds: $([M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}A^{n-}_{x/n}\cdot mH_2O)$ [17]. The actual amounts of metals (Pd, Mg, and Al) measured by the ICP analysis are consistent with the initially anticipated amounts for the samples. As shown in Table 1, the molar ratio of W/P was found to be 11 for PdMgAl-PW_{11}, indicating that the $[PW_{11}O_{39}]^{7-}$ anions did not collapse during the ion-exchange process. The molar ratio of W/P changed to 8.2 in PdMgAl-[PW_4 + W_2], implying that about 25% of the W ions were dissolved in the aqueous solution after treating PdMgAl-PW_{11} with 30 wt% H_2O_2. On the other hand, by analyzing the aqueous solution that after treating PdMgAl-PW_{11}, the P ions were barely dissolved in the solution during the process of treating PdMgAl-PW_{11} with 30 wt% H_2O_2 to obtain PdMgAl-[PW_4 + W_2].

Because no chemical bond is formed between the brucite-like layers and the interlayer anions in the LDH compounds, the interlayer region of the LDH compounds provides a reactive environment for the interlayer anions without changing their nature. Thus, it is comprehensible that $[PW_{11}O_{39}]^{7-}$ anions between the brucite-like layers in PdMgAl-PW_{11} decompose to form PW_4 and W_2O_{11} peroxo-polyoxometalates by treating with 30% H_2O_2 in a manner similar to the treatment of $Na_7[PW_{11}O_{39}]$ in the aqueous solution [28]. The brucite-like layers of the LDH compounds have positive charges, which are balanced by the interlayer anions. It is possible that one LDH compound contains two types of interlayer anions with different sizes to balance the positive charges of the brucite-like layers; for example, [WO_4^{2-}, Cl^-]-LDH, [WO_4^{2-}, SO_4^{2-}]-LDH, and [WO_4^{2-}, *p*-toluenesulphonate$^-$]-LDH exhibit excellent activity for alkene epoxidation with 30% H_2O_2 [41]. In this study, the negative charge of the formed $\{PO_4[W(O)(O_2)]\}^{3-}$ anion is lower than that of $[PW_{11}O_{39}]^{7-}$ during the process of treating PdMgAl-PW_{11} with 30 wt% H_2O_2; this causes the brucite-like layers to have excess positive charges and to capture sufficient amounts of $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ anions to balance these

Table 1
Chemical compositions and formulas of various samples

Compounds	Chemical composition (wt%)[a]					Formula[b]
	Pd	Mg	Al	P	W	
PdMgAl-NO_3	5.9	17.4	8.9	–	–	$[Pd_{0.05}Mg_{0.65}Al_{0.30}(OH)_2](NO_3)_{0.30}\cdot0.5H_2O$
PdMgAl-PW_{11}	2.8	8.4	4.3	0.70	46.0	$[Pd_{0.05}M_{0.65}Al_{0.30}(OH)_2](PW_{11}O_{39})_{0.043}\cdot0.6H_2O$
PdMgAl-$[PW_4 + W_2]$	3.1	9.3	4.8	0.76	37.0	$[Pd_{0.05}Mg_{0.65}Al_{0.30}(OH)_2](PW_4O_{24})_{0.042}(W_2O_{11})_{0.088}\cdot0.6H_2O$
PdZnAl-$[PW_4 + W_2]$	2.7	21.8[c]	4.2	0.67	31.8	$[Pd_{0.05}Zn_{0.65}Al_{0.30}(OH)_2](PW_4O_{24})_{0.042}(W_2O_{11})_{0.085}\cdot0.6H_2O$

[a] Obtained by ICP elemental analysis.

[b] Calculated using the results of elemental analysis and the general formula of LDHs; the amount of water was obtained from the TG curve.

[c] Amount of Zn.

positive charges. Once the positive charges of the brucite-like layers are balanced, the excess $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ anions are released into the liquid phase.

3.3. Catalytic propene epoxidation by molecular oxygen in methanol

Table 2 gives the propene conversions and selectivities for PO over various catalysts for the epoxidation of propene by molecular oxygen in methanol at 353 K for 10 h. PdMgAl-$[PW_4 + W_2]$ showed 91.5% selectivity for PO at 47.5% propene conversion during the epoxidation of propene by molecular oxygen in methanol at 353 K for 10 h, with acetone, acrolein, propionaldehyde, propane, and ring-opened products as byproducts. PdMgAl-$[PW_4 + W_2]$ exhibited higher activity and selectivity for PO than PdZnAl-$[PW_4 + W_2]$ due to the promotion effect of the basic MgAl type brucite-like layers for the epoxidation of electron-deficient olefins [22]. MgAl-$[PW_4 + W_2]$, a catalyst without Pd, exhibited a high selectivity for PO (94.7%), but the propene conversion was only 2.2% during propene epoxidation. This indicates that the MgAl-$[PW_4 + W_2]$ epoxidized the propene molecules using the peroxy-oxygen bonds of the peroxo-polyoxometalates in the interlayer region, but the peroxy-oxygen bonds could not be regenerated by molecular oxygen without Pd in the catalytic system. PdMgAl-NO_3, a catalyst without peroxo-polyoxometalate, exhibited low propene conversion (4.3%) and selectivity toward PO (8.9%) during propene epoxidation. These results indicate that a catalyst containing both peroxo-polyoxometalate and Pd is indispensable for propene epoxidation by molecular oxygen in methanol. Moreover, when acetonitrile instead of methanol was used as a solvent in the catalytic system, PdMgAl-$[PW_4 + W_2]$ demonstrated low conversion (2.3%) although the selectivity for PO was high (95.1%) during the reaction. These results indicate that the peroxy-oxygen bonds of the peroxo-polyoxometalates in PdMgAl-$[PW_4 + W_2]$ could not be regenerated in acetonitrile solvent; in other words, the catalytic turnover for the propene epoxidation could not be achieved in acetonitrile solvent over PdMgAl-$[PW_4 + W_2]$. On the other hand, PdMgAl-PW_{11} exhibited low propene conversion (5.9%) during the epoxidation of propene at 353 K for 10 h, indicating that PdMgAl-$[PW_4 + W_2]$ could not be formed in situ from PdMgAl-PW_{11} by molecular oxygen in methanol. These results demonstrate that the simultaneous existence of Pd, peroxo-polyoxometalate, and methanol in the catalytic system is very important for promoting the yield of PO in the epoxidation of propene by molecular oxygen.

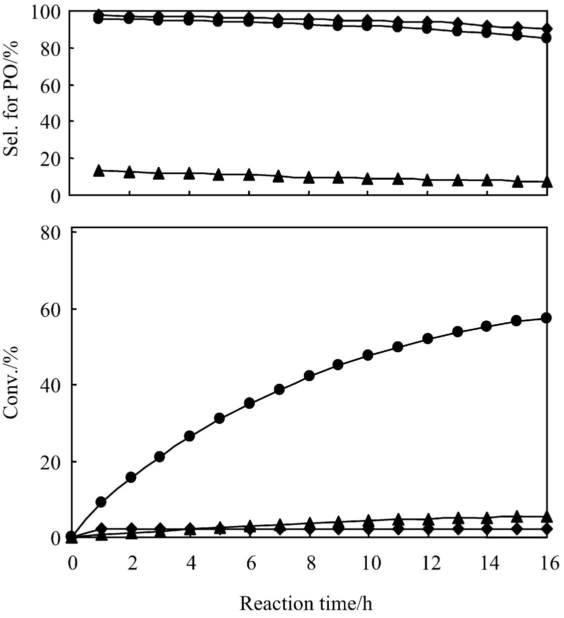


Fig. 5. Effect of reaction time on the epoxidation of propene by molecular oxygen in methanol over various catalysts at 353 K. (●) PdMgAl-$[PW_4 + W_2]$; (◆) MgAl-$[PW_4 + W_2]$; (▲) PdMgAl-NO_3. Autoclave 50 ml; C_3H_6 0.8 MPa; O_2 0.4 MPa; Ar 0.8 MPa; catalyst amount 0.3 g; methanol 10 ml.

The effect of reaction time on the epoxidation of propene over various catalysts by molecular oxygen in methanol at 353 K is shown in Fig. 5. PdMgAl-NO_3 showed a low conversion (<7%) even after a 16-h reaction, and the selectivity for PO was very low throughout the reaction. The propene conversion over MgAl-$[PW_4 + W_2]$ increased during the first hour of the reaction but increased only negligibly thereafter, suggesting that the formation of PO over MgAl-$[PW_4 + W_2]$ was due to the stoichiometric epoxidation of propene by the peroxo-oxygen bonds of the peroxo-polyoxometalates in the interlayer region. On the other hand, propene conversion over PdMgAl-$[PW_4 + W_2]$ increased to approximately 60% (with >85% selectivity for PO) with increasing reaction time, indicating that PdMgAl-$[PW_4 + W_2]$ is an active catalyst for achieving catalytic turnover for the epoxidation of propene in methanol by molecular oxygen. However, the selectivity for PO over PdMgAl-$[PW_4 + W_2]$ gradually decreased with increas-

Table 2
Epoxidation of propene by molecular oxygen in methanol over various catalysts at 353 K for 10 h[a]

Catalyst	Conversion (%)		Selectivity to PO (%)	Consumption (mmol)			Formation (mmol)		
	C_3H_6	O_2		C_3H_6	O_2	CH_3OH	PO	By-products[b]	Co-products[c]
PdMgAl-[$PW_4 + W_2$]	47.5	68.8	91.5	6.22	4.50	1.63	5.69	0.53	1.62
PdZnAl-[$PW_4 + W_2$]	40.2	60.5	88.7	5.26	3.99	1.55	4.67	0.59	1.55
MgAl-[$PW_4 + W_2$]	2.2	2.2	94.7	0.29	0.15	0	0.27	0.02	0
PdMgAl-NO_3	4.3	17.2	8.9	0.56	1.12	1.18	0.05	0.51	1.18
PdMgAl-[$PW_4 + W_2$][d]	2.3	2.3	95.1	0.30	0.15	0	0.28	0.02	0
PdMgAl-PW_{11}	5.9	20.5	32.2	0.77	1.27	1.24	0.25	0.52	1.23

[a] Autoclave 50 ml; C_3H_6 0.8 MPa; O_2 0.4 MPa; Ar 0.8 MPa; catalyst amount 0.3 g; methanol 10 ml.

[b] Byproducts from propylene epoxidation: acetone, acrolein, propionaldehyde, propane, and ring-opened compounds.

[c] Coproducts from methanol co-oxidation: CO_x ($CO + CO_2$) with small amounts of HCHO, HCOOH, and $HCH(OH)_2$.

[d] Using 10 ml of acetonitrile as a solvent instead of methanol.

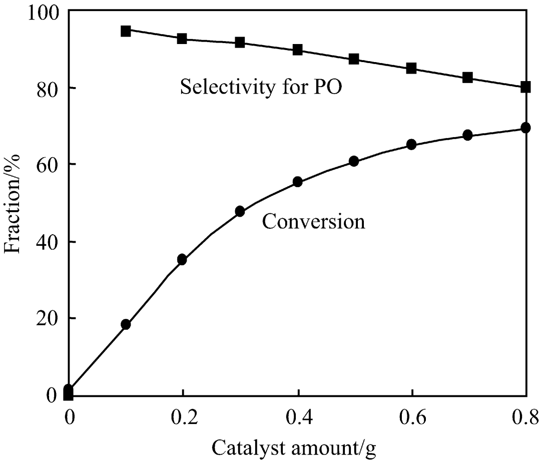


Fig. 6. Effect of the catalyst amount on the propene epoxidation by molecular oxygen in methanol over PdMgAl-[$PW_4 + W_2$] at 353 K for 10 h. Autoclave 50 ml; C_3H_6 0.8 MPa; O_2 0.4 MPa; Ar 0.8 MPa; methanol 10 ml.

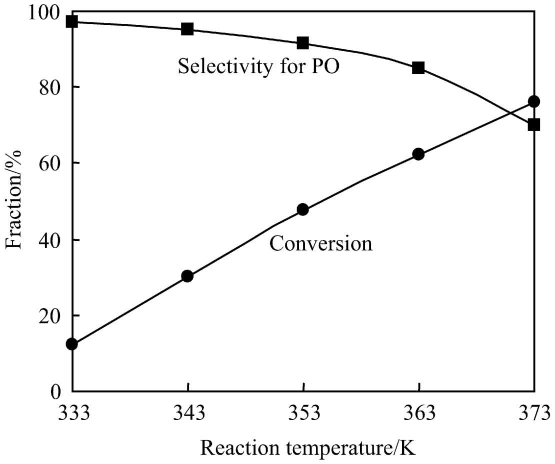


Fig. 7. Effect of the reaction temperature on the propene epoxidation by molecular oxygen in methanol over PdMgAl-[$PW_4 + W_2$] for 10 h. Autoclave 50 ml; C_3H_6 0.8 MPa; O_2 0.4 MPa; Ar 0.8 MPa; catalyst amount 0.3 g; methanol 10 ml.

ing reaction time, because a prolonged reaction time results in the formation of ring-opened byproducts.

The effect of the amount of catalyst on the epoxidation of propene by molecular oxygen in methanol over PdMgAl-[$PW_4 + W_2$] at 353 K for 10 h is shown in Fig. 6. As the amount of PdMgAl-[$PW_4 + W_2$] increased, the propene conversion increased, but the selectivity for PO decreased. A large amount of PdMgAl-[$PW_4 + W_2$] indicates the existence of a large amount of Pd in the catalytic system, which increases the amount of propane during the reaction. The selectivity for PO decreased to $<90\%$ when the amount of PdMgAl-[$PW_4 + W_2$] exceeded 0.4 g during the epoxidation of propene by molecular oxygen in methanol at 353 K for 10 h.

The effect of reaction temperature on the epoxidation of propene over PdMgAl-[$PW_4 + W_2$] by molecular oxygen in methanol for 10 h is shown in Fig. 7. As the reaction temperature increased, propene conversion increased, but the selectivity for PO decreased considerably. The amounts of acrolein and acetone increased significantly at high reaction temperatures. Because the allylic C–H bonds of propene molecules are very active, a low reaction temperature is desirable for increasing the selectivity for PO.

Because molecular oxygen is difficult to dissolve in methanol or water, the catalytic liquid-phase epoxidation of olefin by molecule oxygen always gives a lower reaction rate than that in a vapor-phase process. The merit of a liquid-phase catalytic process is its high selectivity for product. To make good use of this merit, a low reaction rate is usually chosen for increasing selectivity by decreasing reaction temperature and/or using a small amount of catalyst [42]. The liquid catalytic system Pt–Pd/TS-1/H_2/O_2 showed about 25% conversion and 46% selectivity for PO after a 2-h reaction for the propene epoxidation [11]. Using CO_2 as a solvent, Pd/TS-1/H_2/O_2 system could obtain 91.2% selectivity for PO at 6.5% conversion after a 4.5-h reaction for the propene epoxidation [12]. In this study, we obtained 91.5% selectivity for PO at 47.5% conversion after a 10-h reaction for propene epoxidation (Table 2). Although the catalytic system reported in this study has a relatively low reaction rate, this catalytic system is promising for producing PO from propene due to the high selectivity for PO and the cost-effectiveness and safety of the oxygen oxidant and methanol reagent.

In this catalytic system, molecular oxygen is consumed for oxidizing both propene and methanol. As shown in Table 2, the conversion of oxygen (68.8%) was higher than that of propene (47.5%) over PdMgAl-[$PW_4 + W_2$], indicating that a fraction of methanol was co-oxidized during propene epoxidation.

In the case of the co-oxidation of methanol, CO_x (CO and CO_2) was the main coproduct, because the other coproducts (HCHO, HCOOH, and $HCH(OH)_2$) were unstable in the catalytic system and eventually decomposed into CO_x and H_2O. The charged amounts of the reactants propene and molecular oxygen in the autoclave reactor before reaction were 13.09 and 6.55 mmol. After reaction at 353 K for 10 h, PdMgAl-[PW_4 + W_2] converted 6.22 mmol of propene to 5.69 mmol of PO and 0.53 mmol of byproducts and simultaneously consumed 1.63 mmol of methanol to form coproducts during the reaction (Table 2). Therefore, methanol can serve not only as a solvent, but also as an organic reducing reagent for oxygen molecules in the epoxidation of propene. One advantage of the catalytic system reported in this study is that the coproduct CO_x obtained from the co-oxidation of methanol can be easily recycled for synthesizing methanol over Cu/ZnO catalyst in industry. On the other hand, the organic reducing reagents reported in the literature (e.g., 1-butanol, isobutyraldehyde, benzaldehyde) used for olefin epoxidation by molecular oxygen are co-oxidized to form the corresponding organic acids. It is difficult to reuse these organic acids as reducing reagents for olefin epoxidation by molecular oxygen [39–41].

Because catalytic turnover could not be achieved in the inert acetonitrile solvent (Table 2), the reaction mechanism in this study is not the dioxygen addition mechanism with an intermediate metal–oxygen species [42]. Moreover, because a small amount of methanol solvent was co-oxidized to CO_x during the reaction, it seems that the reaction mechanism of the catalytic system (containing peroxo-polyoxometalates, palladium, and methanol) is similar to that of catalytic liquid-phase olefin epoxidation by molecular oxygen in the presence of hydrogen or organic acids [11,12,43–45]. In these catalytic systems, H_2O_2 or organic peroxy intermediates that formed in situ during the reaction are the real oxidants for the olefin epoxidation. The active intermediate is relatively complicated in this study because several peroxy intermediates may be formed in situ in the catalytic system. We propose that both the organic peroxy compound $HOCH_2OOH$ and H_2O_2 are formed in situ during the reaction and play important roles in regenerating the peroxy-oxygen bonds of peroxo-polyoxometalates for the epoxidation of propene [14,15]. $HOCH_2OOH$ can be formed from the methanol co-oxidation by O_2 over Pd catalyst but is unstable [46,47]. Because $HOCH_2OOH$ formed from methanol co-oxidation eventually decomposes to CO_x and H_2O, methanol is consumed during propene epoxidation. On the other hand, H_2O_2 formed in situ is a relatively stable active intermediate for propene epoxidation.

H_2O_2 can be generated in situ in the catalytic system through several possible routes. First, a Pd-hydride species can be generated in this system either by the reaction of Pd^{2+} with coproducts CO and H_2O or by the reaction of Pd^0 with a proton [48]. The Pd-hydride species thus formed readily reacts with O_2 to form H_2O_2 [49]. Second, coproduct CO can react with H_2O to form CO_2 and H_2, then the formed H_2 can react with O_2 to form H_2O_2 in a reaction catalyzed by palladium [50,51]. Third, the peroxy intermediate $HOCH_2OOH$ can be decomposed to HCHO and H_2O_2 as well as to HCOOH and H_2O [52]. In addition, the HCOOH thus formed also acts as a promoter for propene epoxidation in the presence of Pd, as mentioned in the literature [53,54]. The concentrations of the peroxy intermediates formed in situ in the catalytic system are low; as a result, it is not possible to convert PdMgAl-PW_{11} to PdMgAl-[PW_4 + W_2] in situ during the reaction, and thus PdMgAl-PW_{11} exhibits low activity during propene epoxidation (Table 2).

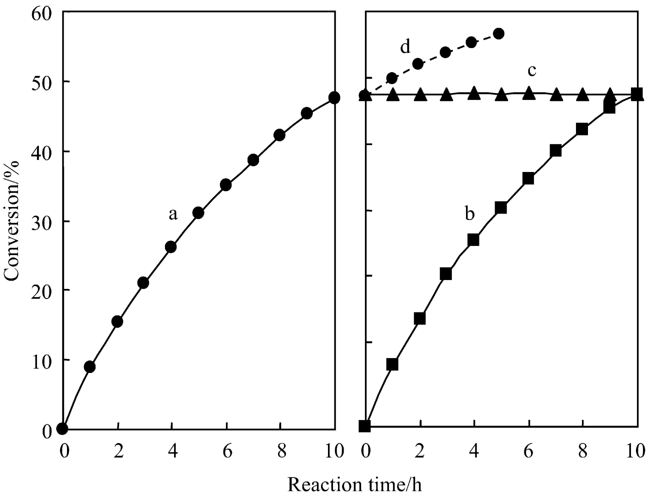


Fig. 8. Stability of the solid catalyst PdMgAl-[PW_4 + W_2] for the propene epoxidation by molecular oxygen in methanol at 353 K. (a) Catalyst used for the first run, (b) filtered catalyst used for the second run, (c) reaction of filtered solution after the first run without the solid catalyst, (d) reaction of filtered solution after the first run with the addition of the solid catalyst. Autoclave 50 ml; C_3H_6 0.8 MPa; O_2 0.4 MPa; Ar 0.8 MPa; catalyst amount 0.3 g; methanol 10 ml.

The stability of the solid catalyst PdMgAl-[PW_4 + W_2] was confirmed using a method reported previously [55] in which 0.3 g of PdMgAl-[PW_4 + W_2] was used to catalyze propene epoxidation at 353 K for 10 h, after which the solid catalyst was filtered. The filtered solid catalyst was placed in a new autoclave filled with reactants and solvents, charged with the reaction gases, and allowed to react for another 10 h at 353 K. Meanwhile, the filtered solution without the solid catalyst was also charged with the reaction gases and allowed to react for another 10 h at 353 K. As shown in Fig. 8, the solid catalyst PdMgAl-[PW_4 + W_2] exhibited no decrease in catalytic activity when used for the second run, in contrast to the situation in the first run. On the other hand, the filtered solution from which the solid catalyst was removed did not react further at 353 K. These results indicate that the solid catalyst PdMgAl-[PW_4 + W_2] is stable during the epoxidation of propene by molecular oxygen at 353 K for 10 h in methanol.

The reusability of the solid catalyst PdMgAl-[PW_4 + W_2] for the epoxidation of propene in methanol by molecular oxygen is shown in Table 3. The used solid catalysts were obtained by filtering the mixture after the reaction at 353 K for 10 h. The propene conversion and selectivity for PO did not decrease even after five runs. These results indicate that the PdMgAl-[PW_4 + W_2] catalyst can be reused by the simple filtration method, and that the active components did not leach into the methanol medium after five runs. As shown in Scheme 1, in the novel compound PdMgAl-[PW_4 + W_2], the Pd^{2+} ions entered

Table 3
Reusability of PdMgAl-[$PW_4 + W_2$] for the epoxidation of propene by molecular oxygen in methanol at 353 K for 10 h[a]

Catalyst	Cycle No.[b]	Conversion (%)	Selectivity for PO (%)
Fresh	1	47.5	91.5
Used[b]	2	48.2	90.7
	3	47.3	91.1
	4	47.6	90.8
	5	47.1	91.2

[a] Autoclave 50 ml; C_3H_6 0.8 MPa; O_2 0.4 MPa; Ar 0.8 MPa; catalyst amount 0.3 g; methanol 10 ml.

[b] Catalyst was separated by filtering the mixture after the reaction.

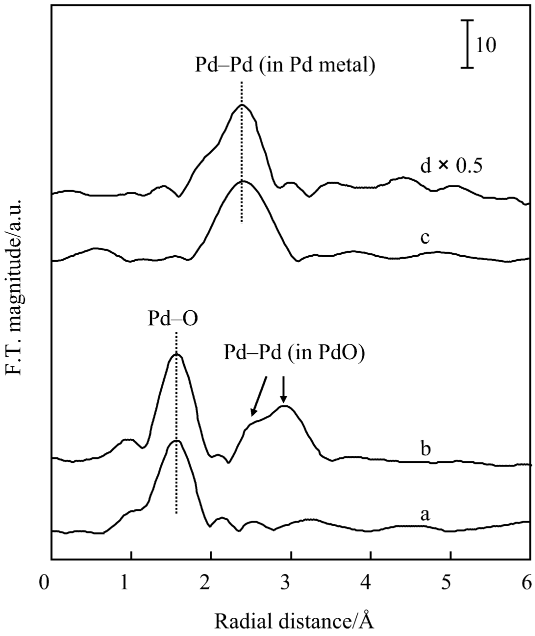


Fig. 9. Pd *K*-edge EXAFS Fourier transforms of various samples. (a) PdMgAl-[$PW_4 + W_2$] before reaction; (b) PdO; (c) PdMgAl-[$PW_4 + W_2$] after reaction; (d) Pd foil.

the position of the Mg^{2+} in the brucite-like layers, and peroxo-polyoxometalate anions were fixed in the interlayer region by electrical charge interactions; as a result, the active components in PdMgAl-[$PW_4 + W_2$] did not leach into the methanol solvent during the epoxidation of propene by molecular oxygen.

The Pd K-edge EXAFS Fourier transforms of the various samples are shown in Fig. 9. The PdO reference [obtained by precipitating $Pd(NO_3)_2$ with NaOH at pH 10 and then drying at 353 K] showed a Pd–O interaction at 1.6 Å and first and second Pd–Pd shell interactions in PdO at 2.5 and 2.9 Å, respectively. In the spectrum of PdMgAl-[$PW_4 + W_2$] before the reaction, the intensity of the first Pd–Pd shell interaction in PdO became very weak, and the second Pd–Pd shell interaction in PdO could not be observed. If Pd^{2+} cations in PdMgAl-[$PW_4 + W_2$] did not enter into the Mg^{2+} positions in the brucite-like layers, then PdO particles would be formed on the surface, and the Pd–Pd shell interactions in PdO would appear in the EXAFS spectrum. Therefore, Pd species in PdMgAl-[$PW_4 + W_2$] have the same charge number as PdO (due to the same Pd–O shell interaction in EXAFS), but PdO particles are not formed in PdMgAl-[$PW_4 + W_2$] (due to absence of Pd–Pd shell interaction in EXAFS). These results imply that Pd^{2+} cations entered into the Mg^{2+} positions in the brucite-like layers in PdMgAl-[$PW_4 + W_2$] before the reaction. After the reaction, the Pd–O interaction disappeared, whereas an interaction attributed to the Pd–Pd bond in Pd metal appeared at 2.3 Å in the spectrum of PdMgAl-[$PW_4 + W_2$]. These results indicate that the Pd^{2+} cations in PdMgAl-[$PW_4 + W_2$] were reduced to metallic Pd particles (Pd^0 species) during the reaction.

The results of EXAFS spectra confirm that metallic Pd^0 species was formed during the reaction. The used PdMgAl-[$PW_4 + W_2$] catalyst containing Pd^0 species exhibited almost the same activity as that over the fresh catalyst for propylene epoxidation in methanol (Fig. 8; Table 3). Thus, Pd^0 species is considered the active species for propene epoxidation by molecular oxygen in methanol [14,15]. Pd^{2+} cations in PdMgAl-[$PW_4 + W_2$] could be rapidly reduced to Pd^0 species by methanol solvent at 353 K. Therefore, to be precise, the novel compound PdMgAl-[$PW_4 + W_2$] is a catalyst precursor; the real catalyst is the reduction state of PdMgAl-[$PW_4 + W_2$] formed by methanol reduction in situ during the reaction. In general, the transition metal ions (e.g., Ni^{2+}, Pd^{2+}, Ru^{3+}, Pt^{2+}) that entered into the Mg^{2+} or Al^{3+} positions in the brucite-like layers are not catalytically active unless they separate out from the structure of LDH compounds to form metallic species [18,56]. The layered structure of the LDH compounds may partially or totally collapse during this separation process, which does affect the activity of the catalysts. In this study, because PdMgAl-[$PW_4 + W_2$] contains a small amount of Pd^{2+} in the brucite-like layers ($Pd^{2+}/(M^{2+} + M^{3+}) = 5$ mol%) and there is no calcination step for PdMgAl-[$PW_4 + W_2$] before reaction, PdMgAl-[$PW_4 + W_2$] remains the layer structure after reaction.

The use of multicomponent precursors may yield well-dispersed metal particles on the surface of supports after calcination and reduction; this property, known as solid-phase crystallization (SPC), is important in the preparation of highly active metal-supported catalysts [57–60]. We used the concept of SPC when designing the catalysts used in this study. Pd^{2+}, which entered the Mg^{2+} position of the LDH layers in PdMgAl-[$PW_4 + W_2$], was reduced by methanol to form highly active Pd^0 species during the reaction. These highly active Pd^0 species effectively catalyzed the formation of peroxy intermediates (e.g., $HOCH_2OOH$, H_2O_2) in situ from oxygen and methanol molecules. The peroxo-polyoxometalates that intercalated in the interlayer region of PdMgAl-[$PW_4 + W_2$] catalyzed the epoxidation of propene using these peroxy intermediates formed in situ.

4. Conclusion

A new type of Pd^{2+}-containing layered double hydroxides intercalated by peroxo-polyoxometalates was synthesized by treating the layered double hydroxide intercalated by the lacunary Keggin-type polyoxometalate anion $[PW_{11}O_{39}]^{7-}$ with 30% H_2O_2. The main peroxo-polyoxometalates anions formed in the interlayer region were $\{PO_4[WO(O_2)_2]_4\}^{3-}$ and $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ in the novel compounds. The novel solid catalyst exhibited high propene conversion and high selectivity for propene oxide during the epoxidation of propene by molecular oxygen in methanol. Peroxo-polyoxometalate, palladium, and methanol are indispensable for improving the yield of propene oxide in the catalytic system. PdMgAl-$[PW_4 + W_2]$ was found to be the most effective solid catalyst for propene epoxidation by molecular oxygen in methanol. The high catalytic ability of PdMgAl-$[PW_4 + W_2]$ stems from the highly active Pd particles formed by the solid-phase crystallization method on the brucite-like layers for effectively generating peroxy intermediates in situ, the good epoxidation capability of the peroxo-polyoxometalates in the interlayer region with dilute H_2O_2, and the promoting effect of the basic MgAl-type brucite-like layers for olefin epoxidation. Moreover, because Pd^{2+} ions are introduced into the Mg^{2+} position in the brucite-like layers and the peroxo-polyoxometalate anions are fixed in the interlayer region before the reaction, PdMgAl-$[PW_4 + W_2]$ is a real heterogeneous catalyst that can be reused through a simple filtration method without leaching active components into the solvent during the reaction.

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