New Peroxo-polyoxometalates Pillared Hydrotalcite Catalyst for Propylene Epoxidation by Molecular Oxygen in Methanol

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Peroxo-polyoxometalates pillared hydrotalcite has been synthesized by decomposing $[PW_{11}O_{39}]^{7-}$ pillared MgPdAl-type hydrotalcite with 30% H_2O_2; the novel heterogeneous catalyst showed 91.5% selectivity for propylene oxide at 47.5% propylene conversion for propylene epoxidation by O_2 in methanol at 353 K for 10 h.

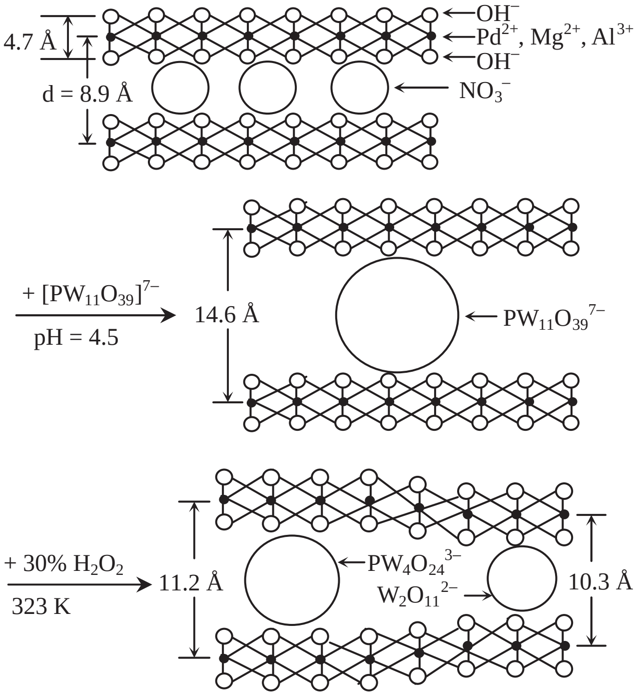
Propylene oxide (PO) is an important chemical feedstock for producing resins such as polyurethane. Two conventional manufacturing methods for PO (chlorohydrin process and hydroperoxide process) cause serious environmental pollution and energy consumption. Molecular oxygen (O_2) is the best oxidant due to low cost and significant advantages for environment. High PO selectivity for PO could be obtained using the mixed gas of O_2 and H_2.[1] Recently, we have reported that a catalyst system consisting of $Pd(OAc)_2$ and THA–PW_4 in methanol effectively catalyzed propylene epoxidation by O_2 without H_2.[2] Since $Pd(OAc)_2$ and THA–PW_4 easily dissolved in methanol, the only possible method for reusing the catalyst is the vacuum distillation of the mixture after reaction. The heterogeneous catalysts are desirable in industry in the point of view of versatility, separation, corrosion, and regenerability.

Hydrotalcite (HT) is a kind of anion clays with the general formula of $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]^{x+}A^{n-}{}_{x/n}\cdot mH_2O$ (M^{2+}, M^{3+} = metal cations, A^{n-} = interlayer anion). Metal cations distributed in the brucite-like layers, and the interlayer anions are fixed between the brucite-like layers by electric charge interaction. The M^{2+} cation is usually Mg^{2+} and the M^{3+} cation is usually Al^{3+}. Pd^{2+} cation can be introduced into the M^{2+} position when $Pd^{2+}/(M^{2+} + M^{3+}) < 5\,\mathrm{mol}\,\%$.[3] The basic MgAl-type HT has been reported to promote the epoxidation of electron-deficient alkenes by H_2O_2.[4]

Heteropolyacid $H_3PW_{12}O_{40}$ is an excellent catalyst for the epoxidation of alkene by 30% H_2O_2.[5] The activity of this system is due to the formation in situ of peroxo-polyoxometalates, such as $\{PO_4[WO(O_2)_2]_4\}^{3-}$ (denoted by PW_4), $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ (denoted by W_2O_{11}), and so on.[6] $H_3PW_{12}O_{40}$ is stable at pH < 2 but decomposes to lacunary $[PW_{11}O_{39}]^{7-}$ at pH value from 3 to 7.[7] $[PW_{11}O_{39}]^{7-}$ anion could be decomposed to PW_4 and W_2O_{11} in 30% H_2O_2 like $[PW_{12}O_{40}]^{3-}$.[5b] Both PW_4 and W_2O_{11} are known as powerful epoxidation catalysts even in the dilute H_2O_2 solution.[6,8]

In this study, we synthesized a novel type of peroxo-polyoxometalate pillared PdMgAl-type HT. The resultant compound is an excellent hetrogeneous catalyst for propylene epoxidation by O_2 in methanol.

The synthesis route for the novel peroxo-polyoxometalates pillared HT is described in Scheme 1.



Scheme 1. Synthesis route of peroxo-polyoxomatalates pillared hydrotalcite.

$Pd_{0.05}Mg_{0.65}Al_{0.3}(OH)_2(NO_3)_{0.3}\cdot mH_2O$ (PdMgAl–NO_3) was prepared using a coprecipitation-aging method at pH = 10.0 under N_2 atmosphere. $Na_7[PW_{11}O_{39}]$ was prepared from the decomposition of $H_3PW_{12}O_{40}$ by adding NaOH solution till pH = 5.0. $Pd_{0.05}Mg_{0.65}Al_{0.3}(OH)_2[PW_{11}O_{39}]_{0.04}\cdot mH_2O$ (PdMgAl–PW_{11}) was prepared from PdMgAl–NO_3 and $Na_7[PW_{11}O_{39}]$ using an ion-exchange method at pH = 4.5 under N_2 atmosphere. PdMgAl–$[PW_4 + W_2]$ was prepared from the treatment of PdMgAl–PW_{11} by 30% H_2O_2 at 323 K for 5 h.

The epoxidation of propylene was carried out in a 50 mL teflon-lined autoclave reactor, which was immersed into an oil-bath with temperature-control. A portion of 0.3 g of catalyst and 10-mL methanol were added into the autoclave. Then, 0.8 MPa propylene, 0.4 MPa O_2, and 0.8 MPa Ar were charged to the autoclave. After reacted with vigorous stirring, both the gas and the liquid were analyzed by gas chromatographys.

As shown in Figure 1, the XRD pattern of PdMgAl–NO_3 showed the presence of only well crystallized HT phase and the basal *d* spacing at the lowest angle was 8.9 Å. When the thickness of the MgAl–HT layer (4.7 Å) was subtracted from the basal *d* spacing (8.9 Å), the gallery height of NO^{3-} anion was 4.2 Å. As for PdMgAl–PW_{11}, the reflection at the lowest angle shifted to 14.6 Å, which indicates that the gallery height

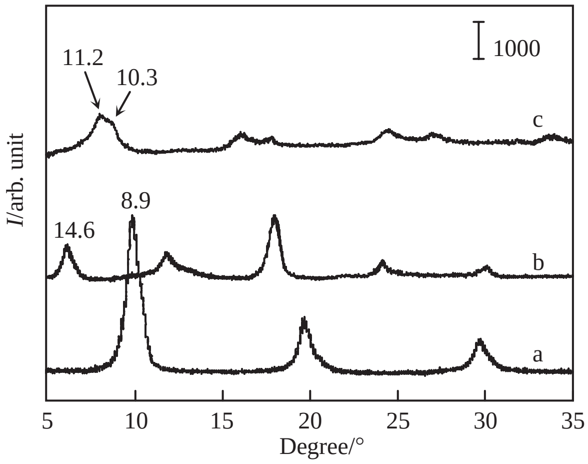


Figure 1. XRD patterns of (a) PdMgAl–NO_3; (b) PdMgAl–PW_{11}; (c) PdMgAl–[$PW_4 + W_2$].

of PdMgAl–PW_{11} was 9.9 Å, in agreement with the sphere diameter of Keggin structure polyoxometalate anion.[9] After PdMgAl–PW_{11} was treated by 30% H_2O_2, the reflection at 14.6 Å disappeared and a broad reflection with two main peaks at 11.2 and 10.3 Å appeared. This suggests that $PW_{11}O_{39}{}^{7-}$ anion decomposed to two sort of anions whose sizes are 6.5 and 5.6 Å in the interlayer region of HT after treated by 30% H_2O_2. Considering the molecular sizes of PW_4 and W_2O_{11},[6a,10] PW_4 probably lies down in the interlayer and W_2O_{11} probably stands in the interlayer in PdMgAl–[$PW_4 + W_2$]. The characteristic peaks of PW_4 and W_2O_{11} could be observed in the FT-IR spectrum of PdMgAl–[$PW_4 + W_2$], especially the vibration of peroxo-oxygen bond at about 850 cm^{-1} was quite strong. The formula and chemical composition of various samples are available in Supporting Information.

As shown in Table 1, PdMgAl–[$PW_4 + W_2$] showed 47.5% conversion and 91.5% selectivity for PO for the epoxidation of propylene by O_2 at 353 K for 10 h in methanol. The by-products observed were acetone, acrolein, propionaldehyde, propane, and ring-opened products. MgAl–[$PW_4 + W_2$] showed a high selectivity for PO of 94.7% but the propylene conversion was only 2.2%, which suggests that MgAl–[$PW_4 + W_2$] epoxidized propylene using the peroxy oxygen bonds of peroxo-polyoxometalates between the brucite-like layers but the peroxy-oxygen bonds could not be regenerated by O_2 in methanol without Pd. PdMgAl–PW_{11} showed a low propylene conversion of 6.9% at 353 K for 10 h, which indicates that PdMgAl–[$PW_4 + W_2$] could not be formed from PdMgAl–PW_{11} in situ during the reaction. PdMgAl–NO_3 showed low conversion and low selectivity for PO. The simultaneous existence of Pd and peroxo-polyoxometalate in the catalyst system is indispensable for improving PO yield.

Table 1. Reaction results of propylene epoxidation by O_2 over various catalysts in methanol at 353 K for 10 h[a]

Catalyst	Conv. of Propylene/%	Select. for PO/%	Conv. of O_2/%
PdMgAl–[$PW_4 + W_2$]	47.5	91.5	68.8
MgAl–[$PW_4 + W_2$]	2.2	94.7	2.2
PdMgAl–PW_{11}	6.9	52.2	12.8
PdMgAl–NO_3	4.3	37.7	10.5

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

O_2 is consumed both for oxidizing propylene and for oxidizing methanol medium. The O_2 conversion (68.8%) was higher than the propylene conversion (47.5%) over PdMgAl–[$PW_4 + W_2$], suggesting that a part of methanol (about half of the amount of reacted propylene) was co-oxidized during the propylene epoxidation. CO_x was the main co-product because other co-products were not stable in the catalyst system and finally discomposed to CO_x and H_2O. The co-product CO_x formed from the co-oxidation of methanol can be recycled for synthesizing methanol over Cu/ZnO catalyst in industry.

There are several possible routes for generating H_2O_2 in situ in the catalyst system. Firstly, Pd-hydride species could be generated by reacting Pd^{2+} with co-product CO and H_2O or by reacting Pd^0 with proton.[11] The formed Pd-hydride species reacts with O_2 to form H_2O_2.[12] Secondly, co-product CO reacts with co-product H_2O to form CO_2 and H_2, and then the formed H_2 reacts with O_2 to form H_2O_2 catalyzed by Pd.[13] Thirdly, a part of $HOCH_2OOH$ intermediate formed from the co-oxidation of methanol with O_2 over Pd decomposes to HCHO and H_2O_2.[14] Peroxo-polyoxometalates possess high active for alkene epoxidation even in the dilute H_2O_2 solution.[6c]

The used PdMgAl–[$PW_4 + W_2$] catalyst was obtained by filtrating the mixture after reaction. The conversion and the selectivity for PO did not decrease after reused for five times. On the other hand, the solution that filtered out the solid catalyst showed no activity for propylene epoxidation. These results indicate that PdMgAl–[$PW_4 + W_2$] catalyst could be reused by the filtration method and the active components did not leach to the methanol medium during the reaction.

In summary, the novel peroxo-polyoxometalates pillared PdMgAl-type HT synthesized in this study is very effective for propylene epoxidation by O_2 in methanol because of the highly epoxidizing ability of the interlayer peroxo-polyoxometalates with dilute H_2O_2, the uniformly distributed Pd in the brucite-like layers for generating H_2O_2 in situ, and the promoted effect of basic MgAl-type HT for alkene epoxidation.

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