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Direct epoxidation of propylene by molecular oxygen over a catalyst system containing palladium and a peroxo-heteropoly compound in methanol

Yanyong Liu,* Kazuhisa Murata and Megumu Inaba
Research Institute for Green Technology, National Institute of Advanced Industrial Science and Technology, AIST Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan. E-mail: yy.ryuu@aist.go.jp

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A catalyst system consisting of palladium and a peroxo-heteropoly compound in methanol showed 81.6% selectivity for propylene oxide at 42.7% propylene conversion using molecular oxygen as oxidant in an autoclave reactor at 373 K for 6 h.

Propylene oxide (PO) is one of the most important chemical feedstocks for producing polyurethane, surfactants and other products. The two main conventional manufacturing methods of PO are the chlorohydrin process and the hydroperoxide process. Both of them require two-stage processes; the chlorohydrin process causes serious environmental pollution and the hydroperoxide process stoichiometrically produces co-products such as *tert*-butyl alcohol and styrene. Molecular oxygen is the best oxidant due to its low cost and significant advantages for the environment. Alkenes can be epoxidized by molecular oxygen in the presence of an organic reducing reagent.[1] Because the organic reducing reagents reported in the literature are co-oxidized to organic acids which are difficult to reuse as reducing reagents,[2] this process is complicated and needs heavy capital investment. Although the oxidation of propylene to PO by molecular oxygen without any co-products would be important in industry, the heterogeneous catalytic epoxidation of propylene by molecular oxygen usually gives poor selectivity for PO because of the high activity of allylic C–H bonds of propylene.[3] Recently, we have reported that a catalyst system containing palladium and Ti-Al-MCM-22 in methanol showed about 50% selectivity for PO at a conversion of 30% for the epoxidation of propylene by molecular oxygen at 373 K.[4] Because Al sites in Ti-Al-MCM-22 improve the propylene conversion but decrease the selectivity for PO due to the formation of hydrocarbons, it is difficult to increase the propylene conversion and the selectivity for PO simultaneously in the catalyst system.

Heteropoly acids, such as $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$, are very effective catalysts for the epoxidation of alkenes by hydrogen peroxide. The activity of these oxidant systems is due to the formation *in situ* of metal peroxo species, which are the real oxidants.[5] Some of the metal peroxo species (peroxo-heteropoly compounds) have been isolated and showed excellent epoxidizing ability using hydrogen peroxide as an oxidant.[6] However, they cannot act as catalysts for the epoxidation of alkenes using molecular oxygen as an oxidant. In the present study, we report that a catalyst system consisting of palladium and a peroxo-heteropoly compound in methanol effectively catalyzed the epoxidation of propylene by molecular oxygen.

Peroxo-heteropoly compounds $[(C_6H_{13})_4N]_3\{PO_4[W(O)(O_2)_2]_4\}$ (denoted by THA-PW_4) and $[(C_6H_{13})_4N]_3\{PO_4[Mo(O)(O_2)_2]_4\}$ (denoted by THA-PMo_4) were prepared according to the methods reported in the literature.[6]† The oxidation of propylene was carried out in a 50 ml stainless steel autoclave reactor, which was immersed in an oil-bath with temperature control at the required temperature. In a typical run, 0.2 g THA-PW_4 or THA-PMo_4, 0.01 g $Pd(OAc)_2$ and 10 ml methanol were added into the autoclave. Then, 0.8 MPa propylene, 0.4 MPa molecular oxygen and 0.8 MPa Ar were charged into the autoclave at 298 K. After the mixture reacted with vigorous stirring at 373 K for 6 h, both the gas and the liquid were sampled and analyzed for products by gas chromatography.

The propylene conversion and the selectivity for PO over various catalysts are shown in Table 1. Pd + THA-PW_4 showed 42.7% propylene conversion and 81.6% selectivity for PO in the oxidation of propylene at 373 K for 6 h in methanol. The by-products observed were acetone, acrolein, propionaldehyde and ring-opened products. $Pd(OAc)_2$ showed 2.6% propylene conversion and 5.3% selectivity for PO at 373 K for 6 h in methanol. THA-PW_4 showed a high selectivity for PO of 84.6% but the propylene conversion was only 3.2%. These results indicate that the simultaneous existence of $Pd(OAc)_2$ and THA-PW_4 in the system is very important for improving the yield of PO from the oxidation of propylene. Pd + THA-PMo_4 also catalyzed the epoxidation of propylene in methanol and showed 9.7% propylene conversion and 70.3% selectivity for PO, but the yield of PO was much lower than that over Pd + THA-PW_4. Methanol is a necessary medium for the system because Pd + THA-PW_4 showed low activity in ethanol for the oxidation of propylene by molecular oxygen. The propylene conversion increased with the reaction time and the selectivity for PO remained almost constant over Pd + THA-PW_4. On the other hand, the propylene conversion increased in the first hour but hardly increased after the first hour over THA-PW_4, which indicates that the formed PO over THA-PW_4 was due to the stoichiometric oxidation of propylene with the peroxo oxygen of THA-PW_4. THA-PW_4 did not act as a catalyst for the oxidation of propylene without palladium in methanol. The used catalysts were obtained by vacuum distillation of the mixture after reaction. When the epoxidation of propylene was repeated five times with the reused catalyst, the propylene conversion and the selectivity for PO were obtained at almost the same values as those in the first run over Pd + THA-PW_4 in methanol. This result indicates that the catalyst system is reusable for the oxidation of propylene by molecular oxygen.

The catalyst system containing THA-$PW_{12}O_{40}$ and $Pd(OAc)_2$ in methanol showed a much lower PO yield than that of the catalyst system containing THA-PW_4 and $Pd(OAc)_2$, which indicates that THA-PW_4 could not be formed *in situ* from THA-$PW_{12}O_{40}$ in this catalyst system. The fresh catalyst, which was obtained by vacuum distillation of the mixture before reaction, showed no peak assigned to any Pd species because the $Pd(OAc)_2$ particles on the THA-PW_4 surface are too small to show a peak in the XRD pattern. As for the used catalysts after reaction at 373 K for 6 h, the peak of metallic Pd particles could be observed in the XRD patterns at 40.1°. These results indicate that the active species is Pd^0 species, not Pd^{2+} species, in the catalyst system. $Pd(OAc)_2$ is the best Pd source

Table 1 Oxidation of propylene with molecular oxygen over various catalysts in methanol at 373 K for 6 h[a]

Catalyst	Conv. of propylene (%)	Select. for PO (%)	Conv. of O_2 (%)
Pd + THA-PW_4[b]	42.7	81.6	63.2
$Pd(OAc)_2$[b]	2.6	5.3	8.8
THA-PW_4[b]	3.2	84.6	3.4
Pd + THA-PMo_4[b]	9.7	70.3	20.9
Pd + THA-PW_4[c]	8.5	52.4	22.6
Pd + THA-PW_4[d]	3.1	86.8	3.3

[a] Autoclave: 50 ml; C_3H_6: 0.8 MPa; O_2: 0.4 MPa; Ar: 0.8 MPa. [b] Methanol: 10 ml; $Pd(OAc)_2$: 0.01 g; THA-PW_4 or THA-PMo_4: 0.2 g. [c] Ethanol: 10 ml; $Pd(OAc)_2$: 0.01 g; THA-PW_4: 0.2 g. [d] Acetonitrile: 10 ml; $Pd(OAc)_2$: 0.01 g; THA-PW_4: 0.2 g.

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tested in this study because it easily dissolves in methanol and does not introduce harmful anions (such as Cl^-, Br^-, CN^-, and NH_3). The catalyst system containing commercial metallic Pd powder and THA-PW_4 was also effective for propylene epoxidation, but the yield of PO was lower than that of the catalyst system containing $Pd(OAc)_2$ and THA-PW_4.

The FT-IR spectra of THA-PW_4 before reaction and after reaction in methanol and in acetonitrile have been investigated (Fig. 1). After filtering off the solid Pd material from the mixture after reaction, the filtrate was vacuum distilled to obtain THA-PW_4 after reaction. The peaks assigned to stretching vibration of peroxo O–O bonds were observed at about 840 cm^{-1} in the FT-IR spectra of THA-PW_4 before reaction and after reaction in methanol. These results indicate that the peroxo O–O bonds could be regenerated in the catalyst system containing $Pd(OAc)_2$ and THA-PW_4 in methanol. On the other hand, the peak of stretching vibration of peroxo O–O bonds was not found in the FT-IR spectrum of THA-PW_4 after reaction in acetonitrile, which indicates that the peroxo O–O bonds of THA-PW_4 could not be regenerated in acetonitrile. Thus whether the peroxo O–O bonds could be regenerated or not is a key for which the peroxo-heteropoly compound possess catalytic activity or not in the epoxidation of propylene. The IR spectrum and the XRD pattern of THA-PW_4 are unchanged after reaction in methanol at 373 K for 6 h even after being reused five times, which indicates that THA-PW_4 is stable in the catalyst system.

We propose a plausible reaction pathway for the propylene oxidation by molecular oxygen in the Pd + THA-PW_4 catalyst system in methanol as described in Scheme 1. At first, Pd^{2+} species were reduced by methanol to form Pd^0 species and the formed Pd^0 species activated the oxygen molecules dissolved in methanol. The equilibrium of $Pd^0(O_2)^0 \Leftrightarrow Pd^{2+}(O_2)^{2-}$ probably exists, as reported in the Pd/heteropolyacid/O_2 and $Pd(OAc)_2/O_2$/DMSO systems.[7] The activated molecular oxygen oxidized CH_3OH to HCHO, and hydrated HCHO to form $HCH(OH)_2$. Then the peroxy intermediate $HOCH_2COOH$ formed like in other methanol/O_2 systems reported in the literature.[8] We think the peroxy intermediate $HOCH_2COOH$ played a role in regenerating the peroxy O–O bonds of THA-PW_4.

The conversions of molecular oxygen were higher than the conversions of propylene in methanol over various catalysts (Table 1). This result indicates that methanol has been co-oxidized to CO_x during propylene epoxidation in the catalyst system. Methanol has been manufactured from CO_x in very high yields over Cu/ZnO catalysts in industry. Catalyst systems consisting of palladium and peroxo-heteropoly compounds in methanol are promising for industrial manufacture of PO from propylene because the catalyst system manufactures PO in high selectivity and the co-product CO_x can be recycled for the synthesis of methanol.

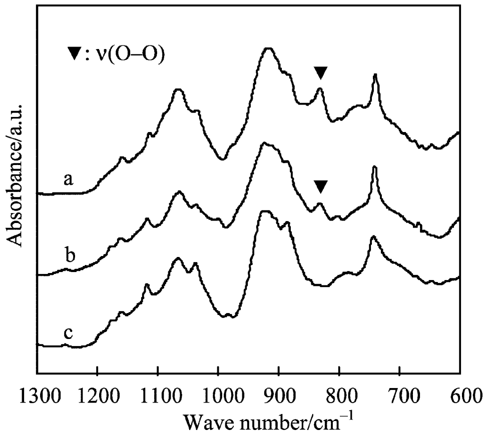
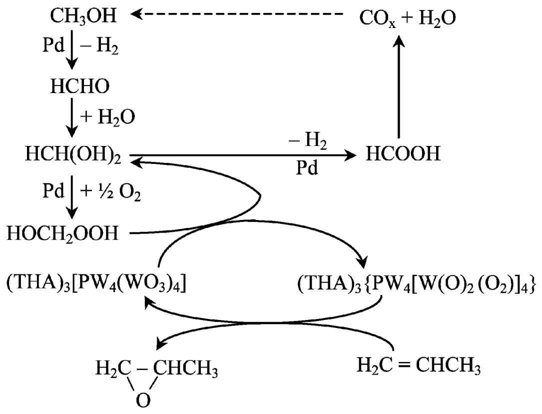


Fig. 1 FT-IR spectra of THA-PW_4 catalyst: a) before reaction, b) after reaction in methanol, c) after reaction in acetonitrile.



Scheme 1 Plausible reaction pathway.

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Notes and references

† Na_2HPO_4 (0.36 g, 2.5 mmol) dissolved in water (5 cm^3) was added to a solution of 10 mmol hydrated WO_3 or MoO_3 in water (15 cm^3) and 30% H_2O_2 (7 cm^3) at 333 K, then a solution of $N(C_6H_{13})_4Cl$ (1.56 g, 4.0 mmol) in benzene (20 cm^3) was added dropwise to the above solution over 2 min. The biphasic mixture was stirred vigorously at room temp. for 2 h, then the solid product was filtered, washed with a small amount of water, benzene and diethyl ether and air dried.

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