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Oxidation of propylene to propylene oxide with molecular oxygen by $Pd(OAc)_2$/Ti—Al-HMS/CH_3OH catalyst system

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

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The $Pd(OAc)_2$/Ti—Al-HMS/CH_3OH catalyst system showed 61.2% selectivity for PO at 42.8% propylene conversion for the oxidation of propylene with molecular oxygen in an autoclave reactor at 373 K for 4 h. The catalyst is reusable using the filtration method or the vacuum distillation method after reaction. It is likely that a Ti cyclic peracid-like intermediate was formed in the system made up of a Ti site, an oxygen molecule and a methanol molecule. The Pd species activates the oxygen molecule and the Al site plays a role for stabilizing the Ti cyclic peracid-like intermediate to improve the yield of propylene oxide from the oxidation of propylene with molecular oxygen.

KEY WORDS: propylene; propylene oxide; oxidation; molecular oxygen; Ti—Al-HMS; methanol; palladium.

1. Introduction

Propylene oxide (PO) is used for making polyurethane, unsaturated resins, surfactants and other products. The two main conventional manufacturing methods of PO are the chlorohydrin process and the hydroperoxide process. Both processes require two stages. The chlorohydrin process causes serious environmental pollution and the hydroperoxide process stoichiometrically produces the co-products such as *t*-butyl alcohol and styrene. Although H_2O_2 is a green oxidant and can oxidize propylene to PO at high selectivity [1,2], H_2O_2 is currently too expensive to allow an economically viable process. Molecular oxygen is the best oxidant due to low cost and significant advantages for environment. Haruta and colleagues have published work relating to the epoxidation of propylene by the mixture of oxygen and hydrogen over Au/TiO_2 catalysts. The selectivity for PO is high (>90%), but propylene conversion is <5% and a large amount of hydrogen is consumed to form water [3]. Hoelderich and colleagues have examined the liquid-phase generation of PO from oxygen, hydrogen, and propylene in methanol/water over Pd (alone and with Pt) on TS-1. Inclusion of promoters (such as NaBr) resulted in conversion and selectivity of 40% in batch experiments [4]. Beckman and colleagues have studied the epoxidation of propylene with oxygen and hydrogen in a CO_2 solvent. The selectivity for PO is over 90% at about 8% of propylene conversion [5]. The direct propylene epoxidation by molecular oxygen without hydrogen would be of value in the industry. Although gas phase epoxidation of ethylene by molecular oxygen had been industrialized over silver catalysts, silver catalysts have not been as useful for the direct epoxidation of propylene due to the highly active allylic C—H bonds of propylene [6]. Recently, we have reported that Ti-modified Al-ZSM-5 and Ti—Al-HMS are effective for the epoxidation of propylene with molecular oxygen in a tubular fixed-bed reactor at 523 K [7,8]. In the present study, we wish to report that the $Pd(OAc)_2$/Ti—Al-HMS/CH_3OH catalyst system is effective for the epoxidation of propylene with molecular oxygen in an autoclave reactor at 373 K.

2. Experimental

Ti—Al-HMS was prepared according to the previous report [8]. The mixtures of Al(*iso*-$OC_3H_7)_3$ and Ti(*iso*-$OC_3H_7)_4$ in 35 mL isopropyl alcohol were mixed with 0.2 mol of $Si(OC_2H_5)_4$ in 80 mL ethanol at Si/Al molar ratios in the range 200–20:1 and Si/Ti molar ratios in the range 100–10:1, and then heated with vigorous stirring at 343 K for 4 h to form a clear solution. The resulting solution was added dropwise to a solution containing 0.05 mol dodecylamine, 80 mL water and 120 mL ethanol at room temperature. After complete addition, stirring was maintained for about 30 min. The resulting gel mixture was aged for 20 h at room temperature to obtain a crystalline product. The solid product was separated by filtration, air dried at room temperature and finally calcined in air at 923 K for 4 h. Pd/Ti—Al-HMS (cal) was prepared by the wet impregnation method with a methanol solution of $Pd(OAc)_2$, then dried at 373 K for 24 h and calcined at 923 K for 4 h. Pd/Ti—Al-HMS (red) was obtained by reduction of Pd/Ti—Al-HMS (cal) in flowing H_2 at 573 K for 2 h.

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* To whom correspondence should be addressed.
E-mail: yy.ryuu@aist.go.jp

X-ray diffraction (XRD) patterns were recorded using a MAC Science MX-Labo diffractometer with Cu radiation operated at 40 kV and 50 mA. The oxidation of propylene was carried out in a 50 mL stainless steel autoclave reactor, which was immersed into an oil-bath with temperature-control at the required temperature. In a typical run, 0.3 g Ti—Al-HMS, 0.02 g $Pd(OAc)_2$, 10 mL methanol were added into the autoclave. Then, 0.8 MPa propylene, 0.4 MPa molecular oxygen, 0.8 MPa Ar were charged to the autoclave at 298 K. After the mixture reacted with vigorous stirring at 373 K for 4 h, both the gas and liquid were sampled and analyzed for the products by gas chromatography.

3. Results and discussion

The propylene conversion and product distribution over various catalysts are shown in table 1. $Pd(OAc)_2$ + Ti—Al-HMS showed 42.8% propylene conversion and 61.2% selectivity for PO for the oxidation of propylene at 373 K for 4 h in the methanol medium. The by-products observed were acetone, acrolein, acetaldehyde, propionaldehyde, C_3H_8, C_4—C_6 hydrocarbons and CO_x (CO and CO_2). $Pd(OAc)_2$ showed 1.3% conversion and 16.6% selectivity for PO, and Ti—Al-HMS showed 2.7% conversion and 28.6% selectivity for PO. These results indicate that the simultaneous existence of $Pd(OAc)_2$ and Ti—Al-HMS in the system is very important for improving the yield of PO from the oxidation of propylene. $PdCl_2$ + Ti—Al-HMS showed a lower PO yield than that of $Pd(OAc)_2$ + Ti—Al-HMS because the solubility of $PdCl_2$ is lower than that of $Pd(OAc)_2$ in the methanol medium. As for the supported catalysts, the reduced catalyst Pd/Ti—Al-HMS (red) exhibited a PO yield of 9.6%, which is much higher than that of the unreduced catalyst Pd/Ti—Al-HMS (cal) (3.0%). Methanol is a necessary medium for the system because $Pd(OAc)_2$ + Ti—Al-HMS showed very low activities in some other mediums (such as 1,2-dichloroethane and acetonitrile) for the oxidation of propylene with molecular oxygen.

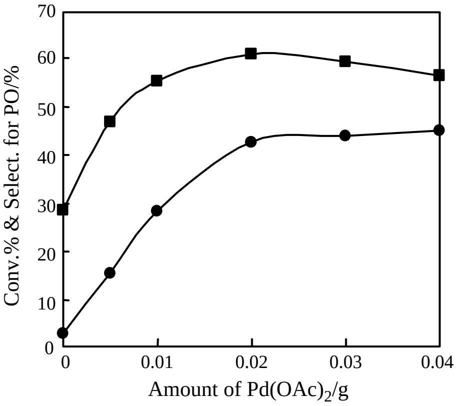


Figure 1. The effect of $Pd(OAc)_2$ amount in the $Pd(OAc)_2$/Ti—Al-HMS/CH_3OH catalyst system for the oxidation of propylene with molecular oxygen at 373 K for 4 h. ●: conversion of propylene, ■: selectivity for PO. Autoclave: 50 mL; methanol: 10 mL; C_3H_6: 0.8 MPa; O_2: 0.4 MPa; Ar: 0.8 MPa; Ti—Al-HMS: 0.3 g; Ti:Al:Si = 1:1:25 (molar ratio).

The effect of the amount of $Pd(OAc)_2$ in the $Pd(OAc)_2$/Ti—Al-HMS/CH_3OH catalyst system for the oxidation of propylene is shown in figure 1. The Ti—Al-HMS amount was kept in a constant value (0.3 g). Both the propylene conversion and the selectivity for PO increased with the increase in the $Pd(OAc)_2$ amount from 0 to 0.02 g. The conversion slightly increased but the selectivity for PO slightly decreased when the $Pd(OAc)_2$ amount was over 0.02 g. The effect of Ti—Al-HMS amount in the $Pd(OAc)_2$/Ti—Al-HMS/CH_3OH catalyst system for the propylene oxidation is

Table 1

Oxidation of propylene with molecular oxygen over various catalysts in methanol at 373 K for 4 h[a]

Catalyst	Conversion (%)	PO yield (%)	Selectivity (%)[b]						
			PO	AC	AL	AA	PA	HC	CO_x
$Pd(OAc)_2$ + Ti—Al-HMS[c]	42.8	26.2	61.2	12.4	5.9	3.6	0.7	11.2	4.9
$Pd(OAc)_2$[d]	1.3	0.2	16.6	22.6	4.8	18.5	0	10.6	26.9
Ti—Al-HMS[e]	2.7	0.8	28.6	6.4	16.8	5.6	0	35.3	7.2
$PdCl_2$ + Ti—Al-HMS[f]	34.4	20.1	58.3	11.1	8.7	6.2	1.6	8.5	5.6
Pd/Ti—Al-HMS (cal)[g]	8.6	3.0	35.3	14.3	4.6	10.8	5.1	15.3	14.6
Pd/Ti—Al-HMS (red)[h]	20.3	9.6	47.1	11.2	10.1	4.7	2.1	13.6	11.3

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

[b] Products: propylene oxide (PO), acetone (AC), acrolein (AL), acetaldehyde (AA), propionaldehyde (PA), hydrocarbons ($HC = C_3H_8 + C_4 + C_5 + C_6$), CO and CO_2 ($CO_x = CO + CO_2$).

[c] $Pd(OAc)_2$: 0.02 g; Ti—Al-HMS: 0.3 g; Ti:Al:Si = 1:1:25 (molar ratio).

[d] $Pd(OAc)_2$: 0.02 g.

[e] Ti—Al-HMS: 0.3 g; Ti:Al:Si = 1:1:25 (molar ratio).

[f] $PdCl_2$: 0.02 g; Ti—Al-HMS: 0.3 g; Ti:Al:Si = 1:1:25 molar ratio).

[g] Pd/Ti—Al-HMS (cal): 0.3 g; Pd: 3.2 wt%; calcined at 923 K for 4 h.

[h] Pd/Ti—Al-HMS (red): 0.3 g; Pd: 3.2 wt%; calcined at 923 K for 4 h and reduced at 573 K for 2 h.

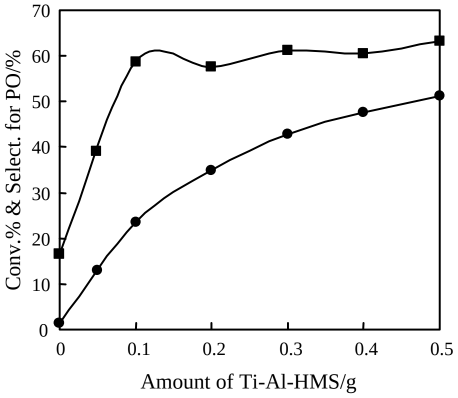


Figure 2. The effect of Ti—Al-HMS amount in the $Pd(OAc)_2$/Ti—Al-HMS/CH_3OH catalyst system for the oxidation of propylene with molecular oxygen at 373 K for 4 h. ●: conversion of propylene, ■: selectivity for PO. Autoclave: 50 mL; methanol: 10 mL; C_3H_6: 0.8 MPa; O_2: 0.4 MPa; Ar: 0.8 MPa; $Pd(OAc)_2$: 0.02 g; Ti:Al:Si = 1:1:25 (molar ratio).

shown in figure 2. The $Pd(OAc)_2$ amount was kept in a constant value (0.02 g). The propylene conversion increased with the increasing amount of Ti—Al-HMS. The selectivity for PO increased with the increase in the Ti—Al-HMS amount when the Ti—Al-HMS amount was less than 0.1 g and almost became constant when the Ti—Al-HMS amount was over 0.1 g.

The reusability of $Pd(OAc)_2$ + Ti—Al-HMS catalyst for the oxidation of propylene in methanol is shown in table 2. The used catalysts were recovered by two methods: one was filtration of the mixture after reaction (denoted by Used-I) and another was vacuum distillation of the mixture after reaction (denoted by Used-II). The conversion and the selectivity for PO did not decrease using either Used-I or Used-II after two cycles (table 2). These results indicate that the $Pd(OAc)_2$/Ti—Al-HMS/CH_3OH catalyst system is reusable for the oxidation of propylene by molecular oxygen. Moreover, the activity of Used-I is similar to the activity of Used-II for the oxidation of propylene, which indicates that there is no active homogeneous catalyst after reaction in the $Pd(OAc)_2$/Ti—Al-HMS/CH_3OH catalyst system.

Table 2

Recycling of catalyst in $Pd(OAc)_2$/Ti—Al-HMS/CH_3OH catalyst system for the oxidation of propylene with molecular oxygen at 373 K for 4 h[a]

Catalyst	Cycle no.	Conv. (%)	Select. for PO (%)
Fresh	1	42.8	61.2
Used-I[b]	2	41.9	62.4
	3	42.3	61.8
Used-II[c]	2	43.2	61.7
	3	42.6	62.1

[a] Autoclave: 50 mL; methanol: 10 mL; C_3H_6: 0.8 MPa; O_2: 0.4 MPa; Ar: 0.8 MPa; $Pd(OAc)_2$: 0.02 g; Ti—Al-HMS: 0.3 g; Ti:Al:Si = 1:1:25 (molar ratio).

[b] Separated by filtration of the mixture after reaction.

[c] Separated by vacuum distillation of the mixture after reaction.

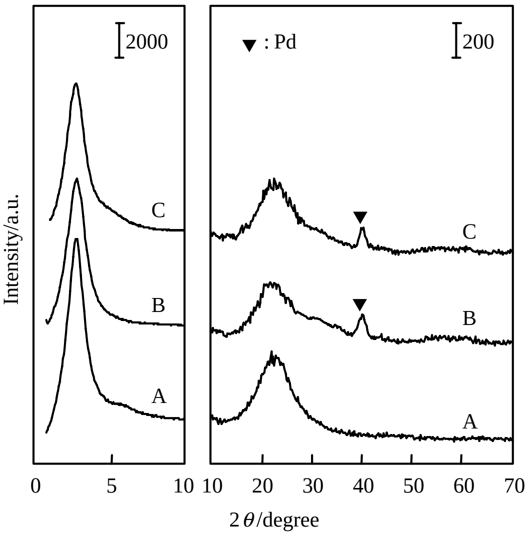
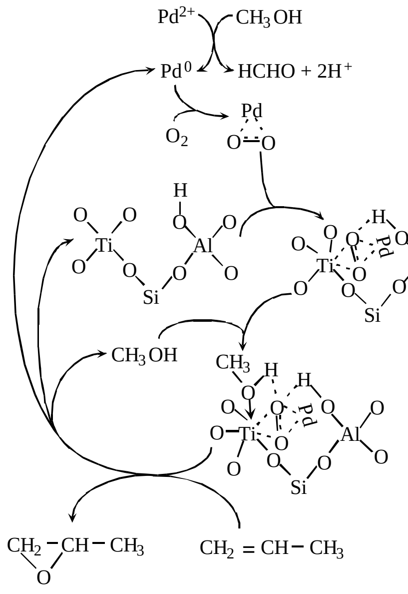


Figure 3. The XRD patterns of (A) fresh catalyst, obtained by vacuum distillation of the mixture before reaction, (B) Used-I, separated by filtration of the mixture after reaction, (C) Used-II, separated by vacuum distillation of the mixture after reaction. $Pd(OAc)_2$: 0.02 g; Ti—Al-HMS: 0.3 g; Ti:Al:Si = 1:1:25 (molar ratio).

The XRD patterns of fresh catalyst and used catalysts for the oxidation of propylene with molecular oxygen in methanol are shown in figure 3. Each sample exhibited an intense reflection corresponding to the (100) plane at 2–3°, which indicates that the mesoporous structure of HMS had been preserved after reaction. 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 Ti—Al-HMS surface are too small to show a peak in the XRD pattern. As for the used catalysts after reaction at 373 K for 4 h, Pd particle peaks could be observed in the XRD patterns at 40.1°. The propylene conversions of both Used-I and Used-II were similar to the propylene conversions of the fresh catalyst (table 2); both Used-I and Used-II showed Pd particle peaks in the XRD patterns (figure 3); Pd/Ti—Al-HMS (red) showed much higher yield of PO than that of Pd/Ti—Al-HMS (cal). These results indicate that the active species is Pd^0 species, not a Pd^{2+} species in the $Pd(OAc)_2$/Ti—Al-HMS/CH_3OH catalyst system for the oxidation of propylene.

In the previous work [8], Ti—Al-HMS effectively catalyzed the oxidation of propylene to PO with molecular oxygen at 523 K because an epoxide-like species which is similar to the Ti(η_2-OOH) species in the titanosilicate-H_2O_2 oxidation system [9] was formed between Ti—Al-HMS and the absorbed oxygen molecule. In the present study, Ti—Al-HMS showed low activity for the propylene oxidation due to low reaction temperature (373 K). However, the activity and the



Scheme 1. Plausible reaction pathway.

selectivity for PO greatly improved by adding $Pd(OAc)_2$ to the system,. We propose a plausible reaction pathway for the propylene oxidation by molecular oxygen in the $Pd(OAc)_2$/Ti—Al-HMS/CH_3OH catalyst system as described in scheme 1. At first, Pd^{2+} species was reduced by methanol to form Pd^0 species and the formed Pd^0 species activated the oxygen molecule resolved in the methanol medium. The equilibrium of $Pd^0(O_2)^0 \Leftrightarrow Pd^{2+}(O_2)^{2-}$ probably exists in the $Pd(OAc)_2$/Ti—Al-HMS/CH_3OH catalyst system like in the Pd/heteropolyacid/O_2 system [10] and $Pd(OAc)_2/O_2$/DMSO system [11]. Then, the activated oxygen molecule was added to the Ti site in Ti—Al-HMS to form an epoxide-like species. Methanol is not only a preferable solvent, but also contributes to form a Ti cyclic peracid-like intermediate like in the titanosilicate-H_2O_2 oxidation system [12] for the propylene oxidation. The Al site in Ti—Al-HMS stabilized the Ti cyclic peracid-like intermediate as reported in the previous work [8]. Further work is focusing on improving the yield of PO and designing experiments to explain the reaction mechanism in more detail.

4. Conclusions

The $Pd(OAc)_2$/Ti—Al-HMS/CH_3OH catalyst system effectively catalyzed the oxidation of propylene to PO with molecular oxygen in the methanol medium at 373 K. The system is reusable using both the filtration method and the vacuum distillation method. Pd^{2+} species was reduced by methanol to form Pd^0 species and the formed Pd^0 species activated the oxygen molecules resolved in the methanol medium. A Ti cyclic peracid-like intermediate is suggested to be formed among the Ti site in HMS, the oxygen molecule and the CH_3OH molecule like in the titanosilicate-H_2O_2 oxidation system for the oxidation of propylene. Activated by Pd^0 species gave molecular oxygen a possibility of substituting for peroxide compounds to form the Ti cyclic peracid-like intermediate in the oxidation of propylene.

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References

[1] M.G. Clerici, G. Bellussi and U. Romano, J. Catal. 129 (1991) 159.
[2] Z. Xi, N. Zhou, Y. Sun and K. Li, Science 292 (2001) 1139.
[3] T. Hayashi, K. Tanaka and M. Haruta, J. Catal. 178 (1998) 566.
[4] W. Laufer and W.F. Hoelderich, Appl. Catal. A: Gen. 213 (2001) 163.
[5] T. Danciu, E.J. Beckman, D. Hancu, R.N. Cochran, R. Grey, D.M. Hajnik and J. Jewson, Angew. Chem. Int. Ed. 42 (2003) 1140.
[6] A. Palermo, A. Husain, M.S. Tikhov and R.M. Lambert, J. Catal. 207 (2002) 331.
[7] K. Murata and Y. Kiyozumi, Chem. Commun. (2001) 1356.
[8] Y. Liu, K. Murata, M. Inaba and N. Mimura, Catal. Lett. 89 (2003) 49.
[9] P.E. Sinclair and C.R.A. Catlow, J. Phys. Chem. B 103 (1999) 1084.
[10] N.I. Kuznetsova, L.G. Detusheva, L.I. Kuznetsova, M.A. Fedotov and V.A. Likholobov, J. Mol. Catal. A: Chem. 114 (1996) 31.
[11] B.A. Steinhoff, S.R. Fix and S.S Stahl, J. Am. Chem. Soc. 124 (2002) 766.
[12] M.G. Clerici and P. Ingallina, J. Catal. 140 (1993) 71.