Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Catalysis 220 (2003) 513–518

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Research Note

Epoxidation of propylene with molecular oxygen/methanol over a catalyst system containing palladium and Ti-modified MCM-22 without hydrogen

Kazuhisa Murata,* Yanyong Liu, Naoki Mimura, and Megumu Inaba

National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba Central 5, 1-1-1, Higashi, Tsukuba, Ibaraki 305-8565, Japan

Received 6 May 2003; revised 4 August 2003; accepted 4 August 2003

Abstract

The catalyst system consisting of Pd, Ti-modified MCM-22, and methanol was found to catalyze the epoxidation of propylene with molecular oxygen without hydrogen and PO was formed with a PO yield above 19.5% and 458 turnovers based on palladium. The catalyst performance of Pd is affected by the properties of Ti-modified MCM-22 such as BET surface area and the amount of NH_3 adsorption. The catalyst material consisting of palladium and Ti-modified MCM-22 can be recovered and used 3 times without reduction in the PO yield. It is assumed that not only palladium but also peroxy intermediates derived from methanol/oxygen play an important role in the oxidation of propylene.

Keywords: Propylene; Epoxidation; Propylene oxide; Oxygen; Palladium; Ti-modified MCM-22; Methanol solvent

1. Introduction

The oxidation of propylene to propylene oxide (PO) has attracted much interest [1]. The benefits deriving from the availability, low cost, and absence of wastes make molecular oxygen a candidate as the oxidant for manufacture of bulk chemicals. However, selectivity due to the severe conditions often required and the short lifetime due to polymerization of oxygenate products on the catalysts are common obstacles to its wider use in the synthetic chemistry. In fact, in our previous reports using $Ti(SO_4)_2$-modified zirconia [2] and Ti-modified high silica zeolites (HSZ) [3], these problems were encounted.

An alternative process is to utilize in situ generated oxidants derived from hydrogen, carbon monoxide, aldehydes, hydrides, and other organic reductants [4]. Of these, the use of hydrogen/oxygen, in which in situ formation of hydrogen peroxide could be expected, is widely investigated, because only water is formed as a by-product [5]. Typical catalyst systems are Pd (alone and with Pt) on TS-1 in the presence of hydrogen, and methanol/water are used as solvents [4,5a,6]. In general it has been concluded that methanol is needed as part of the solvent mixture to perform efficient epoxidation, since it behaves in the reaction as a cocatalyst by promoting the formation of the active species and taking part in the reaction mechanism [4]. Alternatively, Danciu et al. have recently reported the use of CO_2 solvent, but hydrogen was still employed as reductant [7].

Our goal is to confirm the effectiveness of methanol for activation of oxygen without hydrogen and to improve the catalyst performance for PO formation. Mukaiyama et al. have reported the epoxidation of aliphatic olefins with molecular oxygen and primary alcohols such as n-butanol catalyzed by a Ni(II) complex in the presence of molecular sieves 4A [8]. Kuti et al. have reported that photosensitized oxidation of methanol in acetonitrile in the presence of anthraquinone produced formaldehyde, formic acid, hydrogen peroxide and hydroxymethyl-hydroperoxide [9]. Schuchardt and co-workers have reported that, when the catalyst system consisting of palladium acetate, heteropolyacid, and acetic acid was used in the presence of oxygen without hydrogen, oxidative decomposition of acetic acid occurred to form fragmentation products such as CH_3, CH_2CO_2H, and formaldehyde [10]. The formation of peroxy radicals by oxidative degradation of organic materials has been reported by El-Agamey and McGarvey [11]. However, little is known about the participation of these methanol-derived peroxy intermediates for epoxidation of propylene without any other reductants such as hydrogen. Thus, we have investigated the

---

[*] Corresponding author.
E-mail address: kazu-murata@aist.go.jp (K. Murata).

0021-9517/$ – see front matter © 2003 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2003.08.004

use of methanol as the sole solvent for epoxidation from propylene and oxygen in the absence of water/hydrogen, in which a Pd/Ti-modified MCM-22 catalyst was used. We examined the possibility of peroxy intermediates derived from methanol in the absence of hydrogen/water and whether Ti-modified MCM-22 compounds could be effective for the reaction in methanol solvent.

2. Experimental

2.1. Catalyst

Zeolite MCM-22 as support was synthesized by a reported procedure [12]. Sodium hydroxide (0.388 g) and sodium aluminate (0.467 g) were dissolved in deionized water (30 g, Aldrich)). To this solution, silicic acid (5.84 g) and hexamethylene imine (2.97 g) were added, and the resulting mixture was shaken for 30 min at room temperature, followed by heating at 318 K overnight. The mixture was reacted in 23-ml, Teflon-lined stainless-steel autoclaves using a rotating procedure, which involved heating the autoclaves at 423 K for 7 days in an oven designed to rotate the autoclaves under prescribed rotating conditions such as 60 rpm, which is abbreviated as MCM-22(60) (**3′**). Products from the syntheses were washed with deionized water. The wet products were dried overnight in air at 373 K to obtain the as-synthesized products (6.11 g). “Calcined products” were obtained by heating as-synthesized materials for 20 h in air at 811 K (4.61 g). Satisfactory XRD data were obtained for calcined samples, which were used for reaction without any treatment. Ti-modified MCM-22 containing 7.5 wt% Ti was prepared by the impregnation method, where the calcined samples such as MCM-22 were evacuated at 673 K for 3 h in order to eliminate a small amount of water and, then, the sample was impregnated by Ti(O–iPr)$_4$ in i-PrOH, followed by the addition of H$_2$O (25 g) for precipitation of titanium oxide, dried at 373 K for 10 h and finally calcined at 973 K for 3 h. All chemicals were purchased from Soekawarikagaku Co. and Wako Pure Chemicals Co.

2.2. Characterization measurements

X-ray diffraction (XRD) patterns were recorded using a Philips 1850 diffractometer with Cu radiation operated at 40 kV and 40 mA. NH$_3$-temperature-programmed-desorption (TPD) measurements of the supports and Ti-modified supports were also carried out on a NH$_3$-TPD apparatus (Ohkura Riken, Model ATD700A) interfaced to a personal computer. TPD profiles were obtained under vacuum conditions with the temperature varying from 373 to 873 K at 10 K/min in the TPD process. Samples were degassed at 773 K for 1 h under vacuum conditions before measurement. BET measurements were performed by using a Shimazu Gemini 2375.

2.3. Reactions

All reactions were carried out in an 50-ml autoclave, in which 0.25 g of support and 0.0106 g of Pd(OAc)$_2$ (Pd 0.005 g (0.047 mmol)) were introduced with 10 ml MeOH as solvent and stirred with a magnetic stirrer. The vessel was pressurized with propylene (C3′) (0.8 MPa), O$_2$ (0.4 Mpa), and Ar (0.8 Mpa) and the epoxidation reaction was conducted at 373 K. After reaction, gaseous and liquid phases were independently subjected to gas chromatographic analyses.

2.4. Product analyses

Hydrocarbons and oxygenated compounds were detected by TCD and FID gas chromatography, the former with Porapack Q (2 m) at 473 K, the latter with an HR-20M capillary column (i.d. 0.25 mm, 30 m, 0.25 µm) at 323–473 K. Dioxane was used as an internal standard. Products in the gas phase were analyzed by another TCD equipped with a Porapak Q column (3 m) and molecular sieve 5A column (3 m) kept at 383 K. The products were propylene oxide, propionaldehyde (PA), propylene glycol monomethyl ether (PEGM), C$_1$–C$_8$ hydrocarbons (HC), and CO, and CO$_2$ (CO$_x$) and small amounts of other oxygenates (acetaldehyde (AA), acetone (AC)) were also detected. The conversion and the selectivity were estimated on the basis of the number of carbon atoms in compounds: conversion (%) given by $10^2(\sum \alpha_i P_i)/(3C_3^u + \sum \alpha_i P_i)$; selectivity (%) for a product i given by $10^2(\alpha_i P_i)/\sum \alpha_i P_i$. The yield (%) is 10^{-2} (conversion × selectivity). The factors C_3^u, P_i, and α_i are the propylene amount remaining after the reaction, the partial pressure, and the number of carbon in a product i. Space time yields (STY) were calculated as millimole of PO per gram of catalyst per hour.

3. Results and discussion

The X-ray diffraction patterns of various samples before and after Ti modification are shown in Fig. 1. Each sample before Ti modification ((**1′**)–(**5′**)) exhibits a reflection corresponding to the d spacings for MCM-22 structure, which, for example, shows (200) and (201) planes at 14–15° and a (310) plane at ca. 26° [12,13]. On the contrary, each sample after Ti modification ((**1**)–(**5**)) exhibits weak (310) planes, but mostly amorphous.

For (**1′**)–(**5′**) samples, these three spacing values, estimated by XRD, are shown in Table 1. The three d spacings of (**3′**), prepared under rotating conditions of 60 rpm, are 0.616, 0.599, and 0.343 nm, in accordance with 0.617, 0.600, and 0.342 nm for MCM-22 previously reported [12]. The three d values of (**1′**) and (**2′**) are close to those of (**3′**). However, the d spacing values, in particular d_{201} and d_{310}, of (**4′**) and (**5′**) are a little different from those of (**3′**). The intensity of reflection corresponding to the (200) plane for

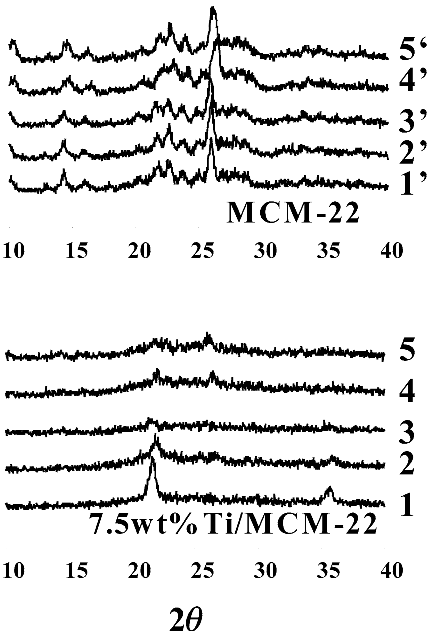

Fig. 1. X-ray diffraction patterns of Ti-unmodified and modified MCM-22 after calcinations. Calcination conditions: see Section 2. Nos. (**1**)–(**5**) and (**1′**)–(**5′**): see Table 1.

each sample is in the order of (**1′**) > (**2′**) > (**5′**) > (**3′**) > (**4′**) and to the (201) plane is (**5′**) > (**4′**) > (**1′**) > (**2′**) = (**3′**) and also to the (310) plane is (**2′**) > (**1′**) > (**5′**) > (**4′**) > (**3′**). Thus, fine structures of MCM-22 seem to be dependent on the rotating rates. Under our synthesis conditions, where synthesis mixtures with $Si/Al_2 = 30$ and $Na/Si = 0.18$ were used, MCM-49 could not be formed, because (1) mixture compositions are different (typical mixtures are $Si/Al_2 = 15–20$ and $Na/Si = 0.3$) [12] and (2) a distinct (004) plane, typical for MCM-49 [13], was not detected for our samples.

Their BET surface areas were between 170 and 300 $m^2\ g^{-1}$, as shown in Table 1. After Ti modification, however, the XRD data obtained from Ti-modified MCM-22 exhibited approximately amorphous patterns, as described in Fig. 1, and their BET surface areas were markedly decreased, as shown in Table 1, (**1**)–(**5**). The degree of decrease was found to be dependent on the rotating rates in MCM-22 syntheses and the order of decrease in the area was in good agreement with the amounts of NH_3 adsorption. It seems likely that these differences come from pore volume and NH_3 adsorption sites inside the pore. In fact, the pore volume of (**5**) was 1.6 times larger than that of (**1**), as estimated by the Dolimore–Heal method. The catalyst system consisting of Pd metal powder commercially available, additives ((**1**)–(**5**)), and methanol was active for the propylene epoxidation with O_2 and the conversion was found to increase with an increase in rotating rate from 30 to 100 rpm, as shown in Table 1. The PO selectivity was kept constant at ca. 60% from 30 rpm (**1**) to 70 rpm (**4**) and dropped to 53% at 100 rpm (**5**). These findings are consistent with a previous report that rotating conditions in MCM-22 synthesis result in a slightly broader crystallization field than static conditions [12] and the effect of Ti/MCM-22 as additive could be associated with NH_3 adsorption sites inside the pore.

The catalyst performance at 373 K is summarized in Table 2, where $Pd(OAc)_2$ was used instead of Pd powder. No product was formed in the absence of both $Pd(OAc)_2$ and (**3**) (Run 1). Also, in the presence of (**3**) alone, no product was detected (Run 2), whereas in the presence of $Pd(OAc)_2$ alone, the reaction occurred and PO was formed, but PA and AA were major products with hydrocarbons (Run 3). In the presence of both $Pd(OAc)_2$ and (**3**), the catalyst performance was found to be dramatically improved and PO was formed with selectivity of 49.9% and a yield of 15.2% (Run 4). Major by-products were hydrocarbons (HC) with small amounts of other oxygenates. As shown in Fig. 2, the propylene conversion increased with an increase in additive (**3**) and leveled off above 25 $g\,L^{-1}$, while the PO selectivity monotonously increased from 8.3 to 53.4% and it leveled off at 50 $g\,L^{-1}$. Thus, the addition of **3** was found to be ef-

Table 1
Properties and reaction results of MCM-22-like compounds before and after Ti-modification

Additive	BET surface area ($m^2\ g^{-1}$)	d_{200} (nm)	d_{201} (nm)	d_{310} (nm)	NH_3 ads.[b] (μmol) (g_{add})	C3′ conv. (%)[c]	PO sel. (%)
(**1**) (30)[a]	5.93	–			5.00	7.44	60.0
(**1′**) (30)	169	0.616	0.599	0.342	–	–	–
(**2**) (50)	11.3	–			11.3	8.01	60.01
(**2′**) (50)	295	0.613	0.599	0.342	–	–	–
(**3**) (60)	17.1	–			17.1	8.41	61.7
(**3′**) (60)	255	0.616	0.599	0.343	–	–	–
(**4**) (70)	24.5	–			23.7	10.9	65.8
(**4′**) (70)	291	0.616	0.599	0.334	–	–	–
(**5**) (100)	45.4				53.0	25.0	52.4
(**5′**) (100)	258	0.616	0.603	0.339	–	–	–

[a] Additive (**1**)–(**5**), 7.5 wt% Ti/MCM-22, (**1′**)–(**5′**), MCM-22. The number in parentheses stand for the rotating rate (rpm) during synthesis.

[b] The amounts of NH_3 adsorption were estimated by NH_3-TPD method.

[c] Conditions: 373 K for 3 h, catalyst, Pd metal powder (0.5 $g\,L^{-1}$); additive, (**1**)–(**5**) (25 $g\,L^{-1}$); solvent, MeOH 10 ml; gas composition, $C_{3'}/O_2/Ar = 2/2/1$ (total 2 MPa).

Table 2
Epoxidation of propylene with molecular oxygen catalyzed by Pd/additive (**3**) system at 373 K[a]

Run	Catalyst/additive	$C_{3'}$ conv. (%)	STY[g]	Selectivity (%)[h] PO	PA	AA	PM	CO_x	HC
1	–/–	0	0 (0)	0	0	0	0	0	0
2	–/(**3**)	0	0 (0)	0	0	0	0	0	0
3	$Pd(OAc)_2$/–	12.6	8.05 (17.5)	8.27	39.0	20.5[i]	0	0.67	21.1
4	$Pd(OAc)_2$/(**3**)	30.4	4.77 (294)	49.9	7.90	0.97	2.16	1.15	37.9
5[b]	$Pd(OAc)_2$/(**3′**)	22.4	3.86 (209)	54.7	20.8	0	3.72	1.78	19.0
6[c]	Pd metal/(**3**)	12.1	3.05 (25.4)	80.3	3.66	0	4.65	3.37	8.05
7[d]	5% Pd on (**3**)	40.1	6.40 (458)	48.7	5.25	0	1.10	2.65	42.3
8	$[Pt(NH_3)_4](NO_3)_2$/(**3**)	0.0	0 (0)	0	0	0	0	0	0
9	$HAuCl_4$/(**3**)	0.0	0 (0)	0	0	0	0	0	0
10	$Rh(NO_3)_3$/(**3**)	12.5	0.081 (4.9)	2.10	69.7	3.08	0	0.22	24.9
11	$[Ru(NO_3)_3(NO)]$/(**3**)	3.27	0.00672 (2.16)	6.71	63.4	9.39	0	1.68	18.8
12[e]	$Pd(OAc)_2$/(**3**)	3.63	0.00845 (3.04)	7.42	88.1	0	0	4.44	0
13[f]	$Pd(OAc)_2$/phen	47.5	0 (0)	0	64.0	7.16	0.84	0.57	27.4

[a] Reaction conditions: catalyst, $Pd(OAc)_2$ (0.0472 mmol; Pd 0.5 $g\,L^{-1}$); additive, (**3**) (0.25 g, 25 $g\,L^{-1}$); solvent, MeOH 10 ml; gas composition: propylene/O_2/Ar = 2/1/2, total pressure 2 MPa; reaction time, 2 h.

[b] MCM-22 alone without Ti-modification (**3′**) was used instead of (**3**).

[c] Reaction time, 15 h.

[d] The 5% Pd on (**3**) catalyst was prepared by impregnation of $Pd(NH_3)_2(NO_2)_2$ with (**3**), followed by dryness at 373 K and subsequent calcinations at 973 K for 3 h. The hydrogenation of obtained catalyst was carried out at 773 K for 3 h prior to use.

[e] CH_3CN(10 ml) was used as solvent.

[f] $Pd(OAc)_2$/1,10-phenanthroline (Pd/phen = 1/10 molar ratio) was used as catalyst.

[g] $mmol_{PO}\,g_{cat}^{-1}\,h^{-1}$. The values in parentheses stand for the STY based on $mmol_{PO}\,g_{Pd}^{-1}\,h^{-1}$.

[h] Calculations of $C_{3'}$ conversion and selectivity; see Section 2.

[i] Acetone (2.45%) and ethanol (8.19%) were also detected.

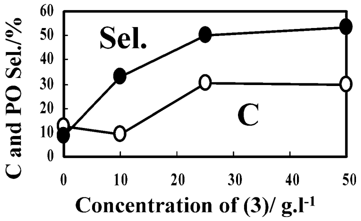

Fig. 2. Effect of concentration of additive (**3**) on the activity of propylene oxidation with molecular oxygen catalyzed by Pd at 373 K for 2 h. Catalyst precursor, $Pd(OAc)_2$ (Pd:0.5 $g\,L^{-1}$); additive, (**3**); solvent, MeOH 10 ml; gas composition, $C_{3'}/O_2/Ar = 2/1/2$ (total 2 MPa). C, conversion.

fective for raising PO yield. When MCM-22 (**3′**) without Ti was used instead of (**3**), propylene conversion was decreased from 30.4 to 22.4%, but PO selectivity was slightly increased (Run 5). The use of metallic Pd power, which is commercially available, resulted in a high PO selectivity of 80.3% (Run 6), while propylene conversion was lower than that of $Pd(OAc)_2$. The 5% Pd supported on (**3**) catalyst was more active than the $Pd(OAc)_2$/(**3**) system, but the PO selectivity was not improved. The PO yield was 19.5% (Run 7), which is 458 turnovers based on Pd, although the STY value is approximately close to those so far reported for the epoxidation of propylene with O_2 alone [14]. The use of other metals instead of Pd resulted in a decrease in the activity. No products were detected in Pt (Run 8) and Au (Run 9) catalysts. Rh (Run 10) and Ru (Run 11) catalysts were active for the reaction, but propylene conversion was not high and PO selectivity was extremely low, while PA was a major product. When CH_3CN was used instead of MeOH, the activity was markedly decreased (Run 12).

The use of 1,10-phenanthroline as additive instead of (**3**) [15] led to high propylene conversion and high PA selectivity, but no PO formation (Run 13). Thus, catalyst derived from Pd and (**3**) was effective for propylene epoxidation with O_2/methanol, even at temperatures as low as 373 K.

The mechanism of oxidation of propene over Pd/Ti-modified MCM-22 catalysts is not clear. However, it is likely that peroxy intermediates derived from methanol/oxygen [9] play an important role in the reaction of propylene with oxygen. A postulated scheme is illustrated in Fig. 3. A peroxide-like species might be formed by collaboration among Pd, Ti, and Al acid sites when oxygen molecules are absorbed on the MCM-22 surface. The Pd–oxygen species possibly exists as in the $Pd(OAc)_2/O_2$/DMSO system [16]. Then, methanol undergoes oxidation with the peroxide-like species to form hydroxymethylhydroperoxide, which was allowed to react with propylene coordinated to titanium to give propylene oxide with formaldehyde and H_2O. In fact, a small amount of formaldehyde was detected by GC analysis. The use of CH_3CN instead of methanol resulted in a decrease in the propylene conversion and PO selectivity (Table 2, run 12). The catalyst performances is improved by the addition of Ti-modified MCM-22, the effect of which could arise from the surface acid sites for NH_3 adsorption, as described above. For comparison, when other additives

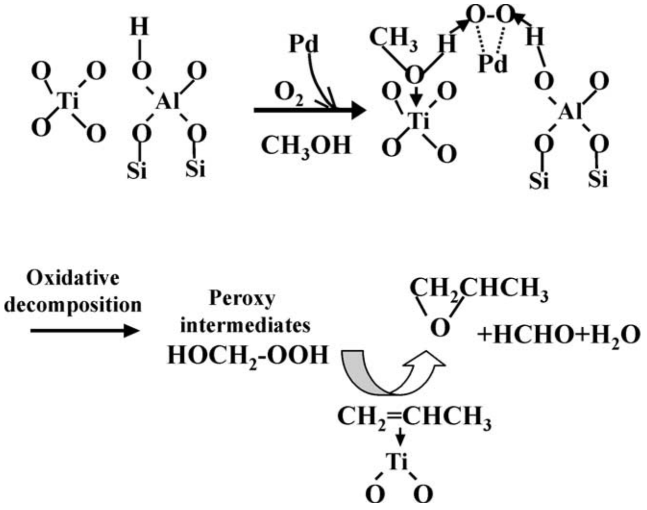

Fig. 3. A postulated scheme.

modified by 7.5 wt% Ti were tested at 373 K in the presence of metallic Pd catalyst, the order of PO yield was as follows: MCM-22 > Al_2O_3 > SiO_2 > none > HSZ(1900) > HSZ(68) > HSZ(190), where high silica zeolite is abbreviated as HSZ and the number in parentheses stands for Si/Al_2 ratio. Schuchardt and co-workers have reported that oxidative decomposition of acetic acid occurred to form fragmentation products such as CH_3, CH_2CO_2H, and formaldehyde, when the catalyst system consisting of palladium acetate, heteropolyacid, and acetic acid was used in the presence of oxygen and H_2O without hydrogen [10]. These results as well as previous reports are consistent with the scheme shown in Fig. 3, which is a little different from previous schemes containing methanol, oxygen, and hydrogen, in which in situ generation of H_2O_2 over Pd sites could be assumed from hydrogen and oxygen, as already noted by Clerici et al. [4] and Holderich and co-workers and Haruta and Date [5].

Of our catalyst components, the major species active for the reaction is likely metallic Pd, being consistent with the results of XRD observations, where the used sample exhibits weak (311), (331), and (420) planes of metallic Pd. In fact, no reaction occurred on (**3**) alone without Pd (Table 2, Run 2). Also, the use of metallic Pd instead of $Pd(OAc)_2$ resulted in PO formation with high selectivity (Table 2, Run 6). Catalyst solution obtained after reaction in Run 4 (Table 2) was not homogeneous and turbid.

When the used catalyst was separated by filtration and subjected to a further two runs by adding methanol under the same conditions, the PO yields were almost the same as those in the first run, as shown in Fig. 4. These findings would be useful for establishing an industrial epoxidation process. The solution obtained from a $Pd(OAc)_2$/1,10-phenanthroline (phen) system was homogeneous, but the system gave no PO formation (Table 2, Run 13). Taking all these data into account, it can be presumed that heterogeneous Pd species such as metal would play an important role in this reaction.

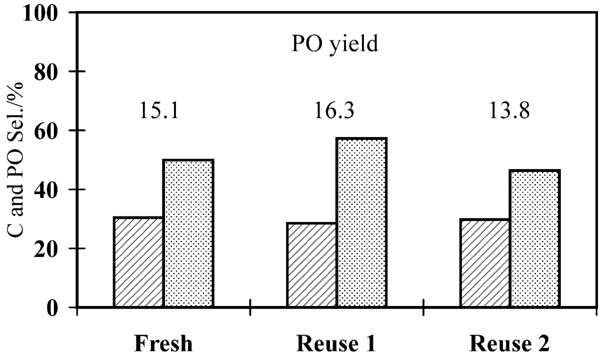

Fig. 4. Effect of catalyst reuse on the catalyst performances. Conditions: see Fig. 1. At the second and the third run, another MeOH (10 ml) was added after filtration, followed by repressurization. C, conversion. C, ▨; Sel., ▩.

In conclusion, systems consisting of Pd, Ti-modified MCM-22, and methanol were found to catalyze the epoxidation of propylene with molecular oxygen without hydrogen and PO was formed with a PO yield of above 19.5% and 458 turnovers based on palladium. In the absence of hydrogen, methanol could act not only as solvent but also as origin of peroxy intermediates, which would play an important role in Pd-catalyzed propylene oxidation. That the catalyst performance of Pd is affected by the properties of Ti-modified MCM-22 such as BET surface area and the amount of NH_3 adsorption is consistent with the presence of peroxy intermediates. Palladium and Ti-modified MCM-22 can be recovered and used 3 times without reduction in the PO yield. These findings would be useful for establishing an industrial epoxidation process. Detailed investigations on the reaction mechanism containing methanol-derived peroxy intermediates are in progress.

References

[1] B. Notari, Catal. Today 18 (1993) 163.
[2] K. Murata, K.E. Bere, T. Hayakawa, S. Hamakawa, K. Suzuki, K. Matano, React. Kinet. Catal. Lett. 72 (2001) 57.
[3] K. Murata, Y. Kiyozumi, Chem. Commun. (2001) 1356.
[4] M.G. Clerici , P. Ingallina, Catal. Today 41 (1998) 351;
M.G. Clerici, G. Bellusi, U. Romano, J. Catal. 129 (1991) 159;
M.G. Clerici, P. Ingallina, J. Catal. 140 (1993) 71.
[5] (a) R. Meiers, W.F. Holderich, Catal. Lett. 59 (1999) 161;
W. Laufer, W.F. Holderich, Appl. Catal. A 213 (2001) 163;
(b) M. Haruta, M. Date, Appl. Catal. A 222 (2001) 427.
[6] G. Jenzer, T. Mallat, M. Maciejewski, F. Eigenmann, A. Baiker, Appl. Catal. A 208 (2001) 125.
[7] T. Danciu, E.J. Beckman, D. Hancu, R.N. Cochran, R. Grey, D.M. Hajnik, J. Jewson, Angew. Chem., Int. Ed. Engl. 42 (2003) 1140.
[8] T. Mukaiyama, T. Takai, T. Yamada, O. Rhode, Chem. Lett. (1990) 1661.
[9] Z. Kuti, D. Gal, Ber. Bunsen-Ges. Phys. Chem. 96 (1992) 1843.
[10] L.C. Passoni, A.T. Cruz, R. Buffon, U. Schuchardt, J. Mol. Catal. A 120 (1997) 117;
W. Partenheimer, J. Mol. Catal. A 67 (1991) 35.

[11] A. El-Agamey, D.J. McGarvey, Phys. Chem. Chem. Phys. 4 (2002) 1611–1617.

[12] I. Güray, J. Warzywoda, N. Baç, A. Sacco Jr., Micropor. Mesopor. Mater. 31 (1999) 241.

[13] S.L. Lawton, A.S. Fung, G.J. Kennedy, L.B. Alemany, C.D. Chang, G.H. Hatzikos, D.N. Nissy, M.K. Rubin, H.-K.C. Timken, S. Steuernagel, D.E. Woessner, J. Phys. Chem. 100 (1996) 3788.

[14] G. Lu, X. Zuo, Catal. Lett. 58 (1999) 67;
J. Lu, M. Luo, H. Lei, C. Li, Appl. Catal. A 237 (2002) 11.

[15] P.I. Pasichnyk, M.K. Starchevsky, Y.A. Pazdersky, V.P. Zagorodnikov, M.N. Vargaftik, I.I. Moiseev, Mendeleev Commun. 1 (1994) 1.

[16] B.A. Steinhoff, S.R. Fix, S.S. Stahl, J. Am. Chem. Soc. 124 (2002) 766.