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Selective oxidation of propylene to propylene oxide over Ti–MCM-41 supporting metal nitrate

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Abstract

The direct gas-phase oxidation of propylene with molecular oxygen was carried out over Ti–MCM-41 impregnated with metal nitrates to produce propylene oxide (PO) selectively. The effects of Ti-loading on MCM-41, nitrate additives, acid treatment of the support, and the presence of molecular oxygen were investigated. The PO yield increased with increasing Ti content of Ti–MCM-41 and reached a maximum at an optimum Si/Ti ratio of 100. Calcium nitrate was the most suitable additive among various nitrates of alkali and alkaline earth metals investigated, and the acid treatment of Ti–MCM-41 effectively improved its catalytic performance for the PO formation. The presence of both nitrate and molecular oxygen was essential for the PO formation. A synergetic mechanism between the Ti species and metal nitrate was proposed to be responsible for the selective formation of PO. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Direct gas-phase oxidation; Ti–MCM-41; Metal nitrates

1. Introduction

Propylene oxide (PO), one of the most important organic intermediates, is now commercially produced by the chlorohydrin method or the co-oxidation method. Both the methods have drawbacks, because the former method consumes a large quantity of chlorine to produce the $CaCl_2$ wastes, and the latter inevitably leads to the formation of equimolar styrene or isobutene (or *t*-butanol) as by-products. There could be often imbalance between the demands of PO and those by-products. Therefore, from the environmental and economic viewpoints, it is ideal to develop a catalytic process to produce PO efficiently and cleanly through the oxidation of propylene with the inexpensive oxidant of molecular oxygen.

Extensive researches have been carried out to develop new methods for the PO production. Titanium silicate-1 (TS-1) is reported to be effective for the selective epoxidation of propylene to PO with hydrogen peroxide in the liquid phase [1–3]. A bifunctional catalyst of Pd-containing TS-1 is able to produce PO from propylene, hydrogen and oxygen through the in situ formation of hydrogen peroxide [4]. It is worth noting that it is claimed in a number of patents [5,6] that PO can be produced from the direct oxidation of propylene with oxygen over TS-1 impregnated with metal nitrate. However, none of these methods have reached the level of industrialization despite of the longstanding efforts of many researchers.

With the purpose of finding more effective catalysts for the direct oxidation of propylene with oxygen, we have investigated the catalytic performance of various titanium silicates with both microporous and mesoporous structures, such as Ti–MCM-41, TS-1

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and Ti–MWW. The influence of reaction conditions, Ti content, nitrate additives, and acid treatment on the PO yield have been studied.

2. Experimental

2.1. Catalyst preparation

Ti–MCM-41 samples were hydrothermally synthesized according to the literature method [7] from tetraethyl orthosilicate (TEOS, TCI), tetrabutyl orthotitate (TBOT, Kanto Chemical), dodecyltrimethylammonium chloride (DTMACl, TCI), and tetramethylammonium hydroxide (TMAOH, Aldrich). The molar composition of the gel was as follows: TEOS:TBOT:DTMACl:TMAOH:$H_2O = 1:x:0.6:0.3:60$ ($x = 0$–0.03). The solution was transferred into a Teflon-lined vessel and heated at 373 K for 10 days. All the products were filtered, washed and calcined in air at 813 K for 6 h. The calcined samples were typically treated with 0.5 M HCl/EtOH at 353 K for 16 h. After the acid treatment, all the samples were formed into a 20–40 mesh size and then calcined. Thus the obtained sample was impregnated with a proper amount of additive by the incipient wetness method.

Amorphous TiO_2–SiO_2 was prepared by hydrolysis of TEOS and tetraethyl orthotitanate (TCI) at 423 K. TS-1 was prepared by a method reported in a literature [8] using TEOS, TBOT and tetrapropylammonium hydroxide (25 wt.% aq., TCI). Ti–MWW was prepared as reported previously [9] using fumed silica (Cab-o-sil M7D), TBOT, boric acid (Wako) and piperidine (Wako). These samples were treated by the same methods as for Ti–MCM-41.

2.2. Catalyst characterization

X-ray powder diffraction patterns were measured on a MAC Science MX-Labo diffractometer using Cu Kα radiation. Chemical composition of the samples was determined by inductively coupled plasma emission spectrometry on a Shimazu ICPS-8000E. IR spectra were obtained on a Perkin-Elmer 1600 FT-IR spectrometer using the KBr pellet techniques. UV–Vis diffuse reflectance spectra were recorded on Varian DMS 300 spectrometer using $BaSO_4$ as a reference.

2.3. Propylene oxidation

Propylene oxidation experiments were performed in a fixed-bed quartz-tube reactor (i.d. = 13 mm) at 423 K under atmospheric pressure. The reaction temperature was measured by a thermocouple placed within the catalyst bed. The catalyst (0.50 g) was placed into the reactor and pre-treated in N_2 at 423 K for 2 h. Then, a gaseous mixture of propylene and oxygen (flow rate: 12 and 6 ml/min) was fed through the catalyst to start the reaction. The propylene remained unconverted and products were separated on a Porapak QS plus T column, and hydrogenated into methane at 723 K in a methanator containing Ru/Al_2O_3 catalyst. The quantification was then carried out on an FID detector.

3. Results and discussion

3.1. Structural effect of Ti on C_3H_6 oxidation

Propylene oxidation was carried out over four kinds of catalysts having different structures, namely amorphous TiO_2–SiO_2, TS-1, Ti–MWW and Ti–MCM-41 to investigate the structural effect of Ti (Table 1). The samples contained a similar amount of Ti except for TiO_2–SiO_2 and were impregnated with the same amount of cesium nitrate (0.4 mmol/g-cat). The products consisted of propylene oxide (PO), CO and CO_2 (CO_X), acetaldehyde (AA), propanal and acrolein (C_2CHO) and acetone (Ace) together with other minor by-products such as isopropanol (others). $CsNO_3/TiO_2$–SiO_2 catalyst was virtually inactive and the PO was not obtained at all at 423 K, unless when the reaction was carried out at a higher temperature of 473 K. On the other hand, zeolites TS-1 and Ti–MWW and mesoporous material Ti–MCM-41 exhibited appreciable activity at 423 K. TS-1 catalyst was relatively active for the PO formation at the initial reaction stage, but deactivated with time on stream (TOS). Ti–MWW or Ti–MCM-41 showed stable catalytic activity for the PO formation.

Table 1
Structural effect of Ti on C_3H_6 oxidation[a]

Support	Si/Ti	TOS[b] (h)	C_3H_6 Conversion (%)	Selectivity (%)						PO yield (%)
				PO	CO_X	AA	C_2CHO	Ace	Others	
TiO_2–SiO_2	85	2	0.002	0	65	35	0	0	0	0
		5[c]	0.11	16	28	36	15	3	1	0.019
TS-1	55	2	0.14	17	24	28	16	11	4	0.025
		5	0.06	24	28	25	17	6	0	0.013
Ti–MWW	62	2	0.24	10	13	31	26	6	11	0.025
		5	0.12	23	14	28	25	7	3	0.025
Ti–MCM-41	58	2	0.25	15	24	30	17	6	9	0.038
		5	0.12	28	27	27	15	3	1	0.034

[a] Reaction conditions: C_3H_6 12 ml/min + O_2 6 ml/min; temperature, 423 K; catalysts, 0.50 g; $CsNO_3$ loading, 0.4 mmol/g-cat.
[b] Time on stream.
[c] Temperature, 473 K.

3.2. *Influence of titanium loading on catalytic activity*

Fig. 1 shows the dependence of propylene conversion and PO yield on the TOS over $CsNO_3$/Si–MCM-41 and $CsNO_3$/Ti–MCM-41 (Si/Ti = 103). Ti-free catalyst produced a small amount of PO at 1 h of TOS, but was essentially inactive at 5 h of TOS. In contrast, Ti-containing catalyst produced PO in a stable yield, although the conversion decreased with TOS. The amount of AA decreased gradually with TOS, which led to the increase in the selectivity for PO up to 40% at 5 h of TOS. These results indicate that the Ti species are required for the sustainable formation of PO.

The influence of Ti content on the PO formation was further investigated, as shown in Fig. 2. The conversion of propylene increased gradually with increasing Ti content of Ti–MCM-41, while the PO yield reached a maximum at an optimum Ti/(Si + Ti) ratio of 0.01

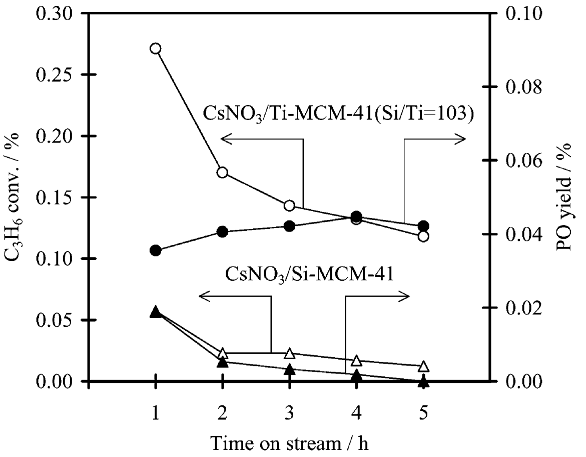


Fig. 1. Propylene oxidation over $CsNO_3$/Si–MCM-41 and $CsNO_3$/Ti–MCM-41 (Si/Ti = 103). For reaction conditions, see Table 1.

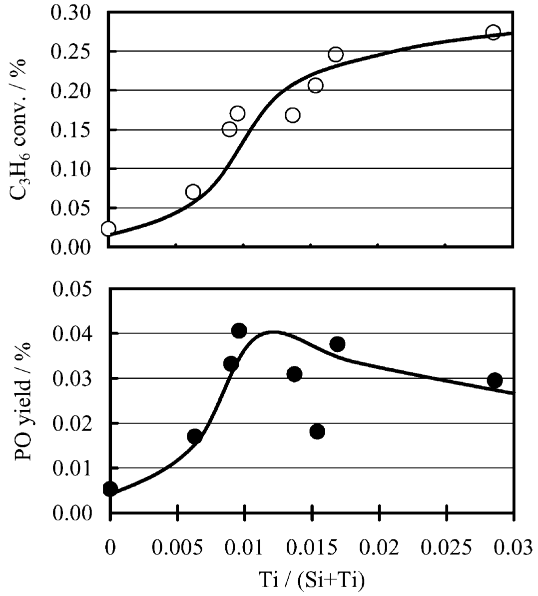


Fig. 2. Influence of Ti content of $CsNO_3$/Ti–MCM-41 on the propylene oxidation. Reaction conditions: TOS, 2 h; for others, see Table 1.

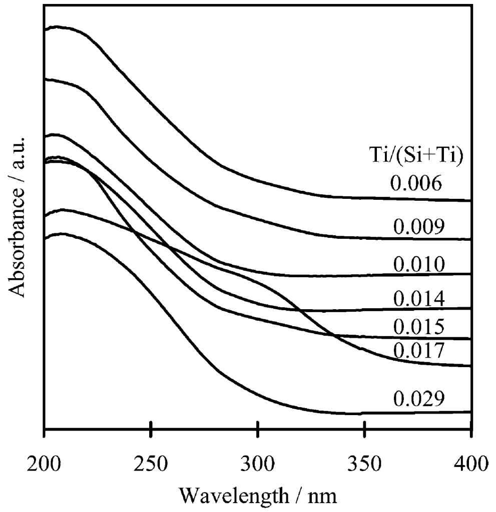


Fig. 3. UV–Vis spectra of $CsNO_3$/Ti–MCM-41 with various Ti contents.

corresponding to a Si/Ti ratio of 100. The decrease in the PO yield at higher Ti levels was caused by the increase in non-selective combustion of propylene to CO_X.

Fig. 3 shows the UV–Vis spectra of $CsNO_3$/Ti–MCM-41 with various Ti contents. The band at 220 nm is assigned to the isolated framework titanium with tetrahedral coordination, and the band at 310 nm is attributed to the anatase. All the samples contained mainly the tetrahedral Ti species, except for Ti–MCM-41 with the $\mathrm{Ti}/(\mathrm{Si}+\mathrm{Ti})$ ratio of 0.017, which contained a relatively large amount of anatase due to unexpected factors in the synthesis. The anatase phase is known to be inactive for the liquid-phase oxidation using H_2O_2 as an oxidant. However, the sample with the $\mathrm{Ti}/(\mathrm{Si}+\mathrm{Ti})$ ratio of 0.017 was a fairly good catalyst regardless of the presence of anatase, suggesting that anatase shows no negative influence on the catalytic performance.

3.3. Influence of additive salts on C_3H_6 oxidation

Table 2 shows the results of propylene oxidation over Ti–MCM-41 catalysts impregnated with various sodium salts. PO was not produced at all over the catalysts impregnated with sodium carbonate, sulfate or phosphate. When sodium nitrite was supported, PO was not obtained initially, but very small amount of PO started to be formed after 10 h. However, when sodium nitrate was supported, PO was formed at the initial stage and the relatively high PO yield was maintained for a long time; the turnover number reached 4.3 mol/mol-Ti after 20 h. These results indicate that nitrate is a superior additive to the others.

Table 3 shows the catalytic performance of Ti–MCM-41 impregnated with nitrates of various metals. The loading of each nitrate was kept constant at 0.4 mmol-NO_3^-/g-cat. $Ca(NO_3)_2$/Ti–MCM-41 catalyst showed the highest propylene conversion, and higher PO selectivity because of the suppression of the combustion. This could be accounted for by the high stability of $Ca(NO_3)_2$ [10]. Thus, calcium nitrate

Table 2
Oxidation of propylene over Ti–MCM-41(Si/Ti = 114) impregnated with various sodium salts[a]

Additive	TOS (h)	C_3H_6 Conversion (%)	Selectivity (%)						PO yield (%)
			PO	CO_X	AA	C_2CHO	Ace	Others	
Na_2CO_3	1–5	Trace	–	–	–	–	–	–	–
Na_2SO_4	1–5	Trace	–	–	–	–	–	–	–
Na_3PO_4	1–5	Trace	–	–	–	–	–	–	–
$NaNO_2$	2	0.007	0	47	53	0	0	0	0
	5	0.007	0	44	56	0	0	0	0
	10	0.013	44	23	33	0	0	0	0.005
	20	0.011	50	23	27	0	0	0	0.006
$NaNO_3$	2	0.19	35	21	30	10	3	2	0.068
	5	0.14	44	17	26	10	2	1	0.061
	20	0.08	55	16	20	9	0	0	0.046

[a] Reaction conditions: C_3H_6 12 ml/min + O_2 6 ml/min; temperature, 423 K; catalysts, 0.50 g; amount of additive, 0.6 mmol/g-cat.

Table 3
Oxidation of propylene over Ti–MCM-41(Si/Ti = 58) supporting various nitrates[a]

Nitrates	C_3H_6 Conversion (%)	Selectivity (%)						PO yield (%)
		PO	CO_X	AA	C_2CHO	Ace	Others	
$LiNO_3$	0.30	26	20	31	12	4	6	0.077
$NaNO_3$	0.19	37	26	19	12	3	3	0.069
$CsNO_3$	0.19	21	24	28	17	3	8	0.039
$Mg(NO_3)_2$	0.13	27	22	28	13	3	7	0.034
$Ca(NO_3)_2$	0.33	42	12	26	11	4	5	0.136
$La(NO_3)_3$	0.16	32	23	26	12	4	4	0.051

[a] Reaction conditions: C_3H_6 12 ml/min + O_2 6 ml/min; temperature, 423 K; catalysts, 0.50 g; amount of additive, 0.4 mmol-NO_3^-/g-cat.; TOS, 3 h.

was found to be the most suitable additive among the nitrates investigated. $Ca(NO_3)_2$/Si–MCM-41 showed PO formation activity at the initial stage of reaction but the activity was rapidly lost in a shown manner to $CsNO_3$/Si–MCM-41 described in Section 3.2. In contrast, $Ca(NO_3)_2$/Ti–MCM-41 showed durability as will be seen in Fig. 5.

3.4. *Influence of amount of $Ca(NO_3)_2$ supported*

Fig. 4 shows the dependence of propylene conversion and PO yield on the amount of $Ca(NO_3)_2$ supported on Ti–MCM-41. Non-supported $Ca(NO_3)_2$ was almost inactive, indicating that the presence of nitrate was essential for the PO formation. Both the conversion and the PO yield increased gradually with increasing amount of $Ca(NO_3)_2$, and reached the maximum at an optimum loading of 1.2 mmol-NO_3^-/g-cat. This result indicates that a suitable amount of metal nitrate is effective for the formation of PO. No further increase in the PO yield at higher loading level of $Ca(NO_3)_2$ is probably due to a change in the rate-determining step into the elementary reaction solely promoted by Ti species.

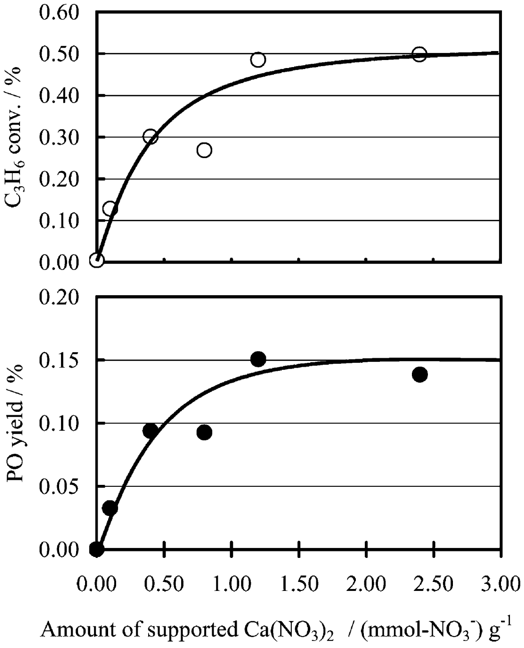


Fig. 4. Influence of additive amount on propylene oxidation. Reaction conditions: TOS, 2 h; for others, see Table 3.

3.5. *Effect of reaction temperature*

The propylene oxidation was carried out at 393, 423 and 453 K to investigate the effect of reaction temperature. At a higher temperature of 453 K, higher propylene conversion and PO yield were achieved, but the catalyst deactivated quickly with TOS, as shown in Fig. 5. Furthermore, non-selective combustion to CO_X increased to lower the PO selectivity. In contrast, PO was formed constantly and in a higher yield at a temperature of 423 K. At 393 K, the catalyst was almost inactive and PO was not obtained at all for 6 h. Therefore, 423 K is the proper temperature for PO formation in this reaction.

3.6. *Effect of acid treatment*

All the catalysts described above were treated with the acid solution (0.5 M HCl/EtOH) before the

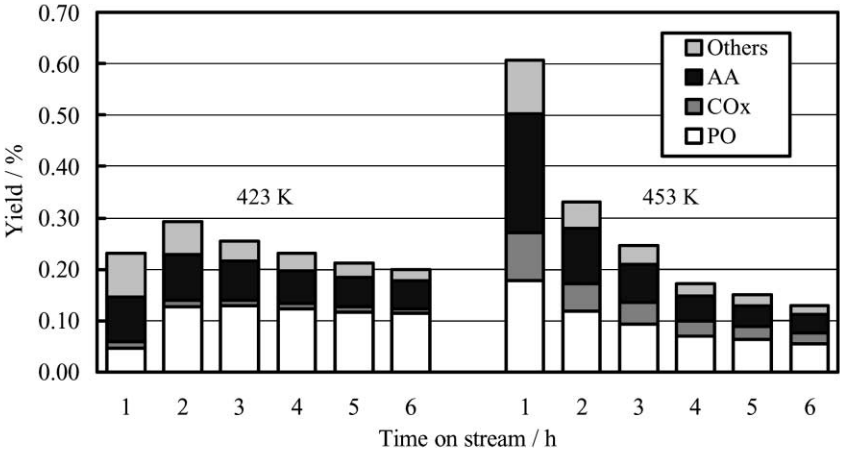


Fig. 5. Propylene oxidation over $Ca(NO_3)_2$/Ti–MCM-41(Si/Ti = 147) at different temperatures. Reaction conditions: C_3H_6 12 ml/min + O_2 6 ml/min; catalysts, 0.50 g; amount of additive, 1.2 mmol-NO_3^-/g-cat.

impregnation with metal salts. Table 4 shows the effect of acid treatment on the oxidation of propylene. Although the Si/Ti ratio of Ti–MCM-41 increased from 67 to 103 by acid treatment, i.e., Ti content of the catalyst decreased, and both the propylene conversion and the PO yield increased. The PO yield was also improved by treating Ti–MCM-41 with H_2SO_4 or HNO_3. In addition, the catalyst treated with HCl/EtOH for three times contains lower amount of Ti, but showed slightly higher PO selectivity and yield.

It is known that acid treatment improves the catalytic performance of TS-1 in the liquid-phase epoxidation with H_2O_2 as an oxidant [11,12]. This is due to removal of the alkali cations such as potassium derived from the contaminants in the structure-directing agent, because the alkali cations poison the Ti active sites. To make this issue clear, the ion-exchange with 0.1 M KOAc /EtOH solution at room temperature for 3 h was performed on the calcined Ti–MCM-41 (Si/K = 2500). The ICP analysis indicated that K was incorporated into Ti–MCM-41 (Si/K = 165). This K-type Ti–MCM-41 impregnated with calcium nitrate showed a comparable PO yield to the untreated Ti–MCM-41 (Table 4), which suggests that the presence of alkali cations dose not affect the performance of the Ti species in the vapor-phase oxidation reaction with molecular oxygen, and that the enhancement by the acid treatment may result from removing the non-selective active Ti sites.

Table 4
Effect of acid treatment on the oxidation of propylene[a]

Treatment	Si/Ti	C_3H_6 Conversion (%)	Selectivity (%)						PO yield (%)
			PO	CO_X	AA	C_2CHO	Ace	Others	
Untreated	67	0.20	35	10	33	14	5	4	0.070
HCl/EtOH	103	0.33	35	10	32	13	4	5	0.116
H_2SO_4/EtOH	101	0.28	37	10	32	14	4	4	0.103
HNO_3/EtOH	72	0.26	38	8	34	14	4	2	0.098
HCl/EtOH × 3	194	0.32	43	8	30	10	4	4	0.135
KOAc/EtOH[b]	84	0.16	40	9	31	15	4	1	0.065

[a] Reaction conditions: C_3H_6 12 ml/min + O_2 6 ml/min; temperature, 423 K; catalysts, 0.50 g; amount of $Ca(NO_3)_2$, 1.2 mmol-NO_3^-/g-cat.; TOS, 3 h.

[b] Si/K ratio of 165.

Table 5
Oxidation of propylene over $Ca(NO_3)_2$/Ti–MCM-41(Si/Ti = 72)[a]

Feed gas	TOS (h)	C_3H_6 Conversion (%)	Selectivity (%)						PO yield (%)
			PO	CO_X	AA	C_2CHO	Ace	Others	
$C_3H_6 + N_2$	3	0.002	0	31	69	0	0	0	0
	5[b]	0.007	0	21	79	0	0	0	0
$C_3H_6 + O_2$	6	0.30	9	14	51	11	12	2	0.028
	7	0.40	23	13	45	10	7	2	0.091
	8	0.36	31	14	38	9	5	2	0.114

[a] Reaction conditions: C_3H_6 12 ml/min + N_2 or O_2 6 ml/min; catalysts, 1.0 g; temperature, 423 K; $Ca(NO_3)_2$ loading, 1.2 mmol-NO_3^-/g-cat.

[b] Temperature, 453 K.

3.7. Effect of molecular oxygen

To investigate the effect of molecular oxygen on the propylene oxidation, the reaction was performed by feeding propylene and nitrogen instead of oxygen (Table 5). The amount of catalyst used here was twice as much as that used under the normal conditions. In this case, propylene was negligibly converted and the PO was not formed even by raising the reaction temperature to 453 K. However, by replacing nitrogen with oxygen after 5 h, PO was formed and increased gradually with TOS. This result suggests that the presence of molecular oxygen is indispensable for the PO formation.

Fig. 6 shows the IR spectra of the catalyst at various stages. The peak at 1384 cm^{-1} assigned to nitrate was observed throughout the reaction. When the used catalyst was calcined at 843 K in air, it showed no peak at 1384 cm^{-1} and was inactive for the oxidation of propylene by oxygen. Therefore, the formation of PO would be due to the presence of both nitrate on Ti–MCM-41 (see Section 3.4) and molecular oxygen.

3.8. Presumable epoxidation mechanism

The present study has shown that PO is formed negligibly over Ti-free catalysts under stabilized conditions but very effectively over Ti-containing ones, and the PO formation is enhanced by the impregnation of nitrate additives. This allows us to propose an epoxidation mechanism as described in Scheme 1. A synergy between the nitrate species and the Ti site would make

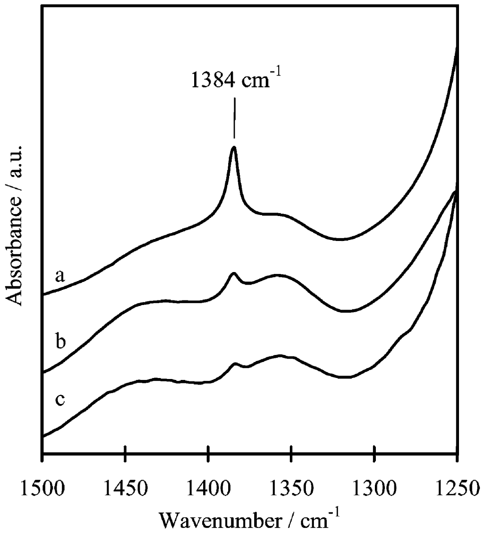
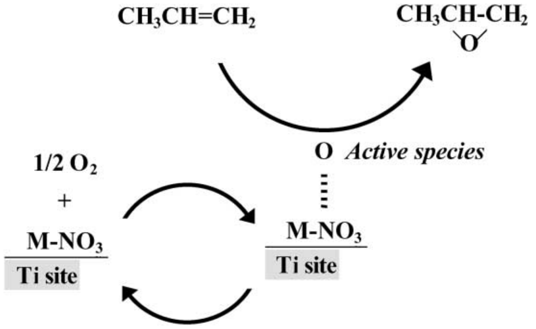


Fig. 6. IR spectra of $Ca(NO_3)_2$/Ti–MCM-41: (a) before the reaction; (b) after the reaction in N_2 for 5 h; (c) after the reaction in O_2 for 8 h.



Scheme 1.

O_2 dissociate into active O species (electronic character not clear) which oxidizes propylene molecules adsorbed on the catalyst surface into PO. The Ti–NO_3 species go further into catalytic cycles by interacting with O_2.

4. Conclusions

When impregnated with nitrates, Ti–MCM-41 and Ti–MWW were suitable as a catalyst than TS-1 for the propylene oxidation with oxygen. The presence of an appropriate amount of titanium within a catalyst is necessary for stable PO formation. Calcium nitrate is a superior additive to the others investigated. The PO yield depends more considerably on the amount of supported nitrate than on that of loaded titanium. The acid treatment of Ti–MCM-41 greatly enhances the PO yield. The coexistence of nitrate and molecular oxygen is essential, which suggests that a synergetic mechanism between the Ti species and the nitrate additive may be responsible for the selective formation of PO on the present catalyst system.

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