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Effect of Ti-modified mesoporous materials on the direct epoxidation of propylene by molecular oxygen

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Abstract

Ti- and Al-containing MCM-41 (Al-c-MCM-41 and Al–Ti-c-MCM-41) have been synthesized and tested for direct oxidation of propylene with molecular oxygen. The reaction occurred over Al- and Ti-containing MCM-41 like materials. Al–Ti-c-MCM-41 was found to be more effective than Al-c-MCM-41, while no product was formed for MCM-41 alone. The catalyst performances of Al–Ti-c-MCM-41 at 523 K were dependent on the Si/Al_2 and Si/Ti ratios and the highest PO yield was 3% when Si/Al_2 of 150 and Si/Ti ratios of 100 were used. A postulated scheme containing Al and Ti species is proposed.

Keywords: Ti-modified mesoporous materials; Epoxidation; Si/Al_2 ratio

1. Introduction

A direct propylene oxidation by molecular oxygen without H_2 into propylene oxide is a growing interest [1]. In the vapor phase epoxidations, the possibility to form PO was shown using $AgNO_3$, KNO_3 supported on TS-1 and K_2CO_3 or KCl on the same matrix with the PO yield of 0.02% [2]. ARCO Chemical Technology has recently reported improved propene oxide yield in the presence of ethyl chloride [3]. In these cases without hydrogen, acidic compounds such as nitrate and chloride over catalyst surface could be important in propylene and oxygen activation. In fact, we have already reported Ti-modified high silica zeolites (HSZ) where catalytic activity depend on the Si/Al_2 ratio of HSZ supports [4]. These zeolite families are commercially available. Thus our following interest is to examine an effectiveness of porous materials based on MCM-41 and MCM-22 for the epoxidation of propylene with oxygen without hydrogen under vapor phase conditions, because these materials would be expected to have structural and/or chemical properties different from H-ZSM-5 families. So we wish to report on the results about Ti- and Al-containing MCM-41 catalyst as well as MCM-22 catalyst at vapor phase and then, we briefly report on the results from MCM-22.

2. Experimental

Zeolite MCM-41 and MCM-22 as supports were synthesized according to the reported procedures [5,6]. $Si(OEt)_4$ as well as water glass was used for MCM-41 synthesis. Ti- and/or Al-containing MCM-41 (Al-c-MCM-41 and Al–Ti-c-MCM-41) were made in the presence of $Ti(O\text{-}i\text{Pr})_4$ and/or $Al(NO_3)_3$ according to the same procedure as MCM-41 alone. Al-c-MCM-41 was prepared by adding drop-wise a clear solution of $Si(OEt)_4$ (11.6 g) in *i*-PrOH (28.4 g) to a stirring solution of hexadecyltrimethylammonium chloride (HTMAC, 13.4 g), followed by addition of a solution of $Al(i\text{-OPr})_3$ in *i*-PrOH (10 ml) and successive addition of tetramethylammoniurn hydroxide (TMAH, 5.09 g) in water (8.05 g)/*i*-PrOH (36.8 g) mixture. The pH was approximately adjusted to 11.4 with diluted H_2SO_4. Then, H_2O (72.9 g) was added. Allowing the resulting gel to age for 6 days at 373 K afforded the crystalline templated product. After filtration, the obtained samples were air-dried at 373 K and calcined at 813 K in air for 8 h to remove the structurally incorporated template. Al-c-MCM-41 (W) was prepared using water glass in place of $Si(OEt)_4$.

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Al–Ti-c-MCM-41 was prepared according to the same procedure as Al-c-MCM-41 synthesis except that a solution of Ti(*i*-OPr)$_3$ in *i*-PrOH (10 ml) was further added.

MCM-22 was synthesized by reported procedure [6]. 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. After the resulting mixture was stirred for 30 min. at room temperature, it was transferred to 23 ml, Teflon-lined stainless-steel autoclaves, followed by heating at 318 K overnight. The mixture was aged for 7 days at 423 K in an oven designed to rotate the autoclaves, under different rotating conditions between 30 and 100 rpm. Products from the synthesis 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), which were calcined by heating as-synthesized materials for 20 h in air at 811 K to form calcined products (4.61 g). Ti-modified MCM-22 containing 7.5 wt.% Ti was prepared by the impregnation method, accompanied by calcinations at 973 K for 3 h.

X-ray diffraction (XRD) patterns were recorded using a Philips 1850 diffractometer with Cu radiation operated at 40 kV and 40 mA. BET surface areas were measured at 77 K using a Shimadzu Gemini 2375 adsorption instrument.

All chemicals were commercially available. For vapor phase epoxidation, the catalytic reactions were performed under atmospheric pressure at temperatures between 473 and 673 K. A fixed-bed reactor (o.d. = 1.25 cm) was filled with 1.0 g of catalyst powder and quartz sand (6.9 g). A pretreatment was done prior to each reaction at 673 K under air flow 25 ml min^{-1} for 2 h and then the temperature was decreased to 473 K. The reactant feeds were C_3H_6 (7.5 ml min^{-1}) and air (17.5 ml min^{-1}). Product analysis was performed by on-line TCD and FID gas chromatography. Hydrocarbons (C3–C9) and oxygenated compounds were analyzed by two FIDs, one with Porapack Q (2 m) at 473 K, the other with FFAP capillary column (i.d. = 0.25 mm, 60 m, 0.25 μm) at 313 K. Gaseous products such as CO, CO_2, H_2, and C1–C2 hydrocarbons were analyzed by TCD equipped with Porapak Q column (3 m) and molecular sieve 5A column (3 m) kept at 383 K.

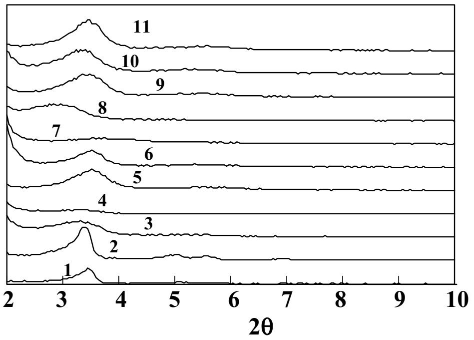

Fig. 1. The XRD patterns of (**1**) MCM-41 (W), (**2**) Al-c-MCM-41 (W) (Si/Al_2 = 150), (**3**) Al-c-MCM-41 (Si/Al_2 = 150), (**4**) Al-c-MCM-41 (Si/Al_2 = 250), (**5**) Al-c-MCM-41 (Si/Al_2 = 500), (**6**) Al-c-MCM-41 (Si/Al_2 = 1000), (**7**) Al-c-MCM-41 (Si/Al_2 = 2000), (**8**) Al–Ti-c-MCM-41 (Si/Al_2 = 150, Si/Ti = 100), (**9**) Al–Ti-c-MCM-41 (Si/Al_2 = 500, Si/Ti = 100), (**10**) Al–Ti-c-MCM-41 (Si/Al_2 = 1000, Si/Ti = 100), and (**11**) Al–Ti-c-MCM-41 (Si/Al_2 = 2000, Si/Ti = 100).

3. Results and discussion

3.1. Physico-chemical features of Al- and/or Ti-modified MCM-41 families

The X-ray diffraction patterns of various samples are shown in Fig. 1. Each sample exhibits a reflection corresponding to the (1 0 0) plane at 2–4° and a broad shoulder near 5–6°. These patterns are typical structures of MCM-41 materials assembled from long alkyl chain quarternary ammonium salts as surfactants [5], although their crystallinities were not satisfactory. The d_{100} spacing and crystallite size (L_c) values, estimated by XRD, are shown in Table 1.

Table 1
Effect of MCM-41 like materials with different Si/Al_2 and Si/Ti ratios on the C_3H_6 oxidation[a]

No.	Catalyst	Si/Al_2	Si/Ti	BET surface area/m^2 g^{-1}	d_{100}/nm[b]	Lc/nm[b]	C3′ conv./%	PO yield/%	Selectivity/%			
									PO	Oxy[c]	HC[d]	COx
1	MCM-41 (W)	–	–	1150	3.74	17.4	0	0	–	–	–	–
2	Al-c-MCM-41 (W)	150	–	–	2.60	24.9	0.075	0	0	0	99.99	0.01
3	Al-c-MCM-41	150	–	906	2.65	11.9	1.09	0.75	68.8	7.75	23.4	0.0002
4	Al-c-MCM-41	250	–	939	2.65	9.54	3.00	0.95	31.9	3.63	64.7	0
5	Al-c-MCM-41	500	–	957	2.50	11.1	2.79	1.30	46.5	1.04	52.4	0
6	Al-c-MCM-41	1000	–	1167	2.51	13.6	1.21	0.36	29.3	0	70.7	0.0002
7	Al-c-MCM-41	2000	–	1091	2.37	8.23	0.07	0	0	0	100	0.0029
8	Al-Ti-c-MCM-41	150	100	595	2.98	9.54	8.45	2.99	35.3	3.68	61.0	0
9	Al-Ti-c-MCM-41	500	100	1076	2.55	11.4	5.81	0.49	8.41	10.65	69.8	11.1
10	Al-Ti-c-MCM-41	1000	100	1036	2.60	12.2	2.75	0.35	12.7	23.8	63.5	0
11	Al-Ti-c-MCM-41	2000	100	1139	2.60	12.5	0.097	0	0	0	100	0.0026

[a] Reaction conditions: Catalyst 1 g, temperature 523 K, Gas composition, $C_3H_6/O_2/He = 30/14/56$ (vol.%), W/F = 31.4 g cat h mol^{-1}.
[b] The d and Lc stand for lattice constant and crystallite size, estimated by XRD.
[c] Oxy = sum of acetaldehyde + propionaldehyde + acrolein + acetone + alcohols (MeOH + EtOH + PrOH).
[d] Hydrocarbons (HC, (C1 + C2 + C3 + C4 + C5 + C6 + C7 + C8)), CO and CO_2 (COx).

The d_{100} spacing value of MCM-41 without Al and Ti (no. **1**) was 3.74 nm, which was higher than Al-c-MCM-41 materials (nos. **2**–**7**). The d_{100} values of Al–Ti-c-MCM-41 (Table 1, nos. **8**–**11**) were close to those of Al-c-MCM-41. The crystallite sizes (L_c) of materials synthesized from water glass, estimated by Scherrer equation, were 17.4 nm (no. **1**) and 24.9 nm (no. **2**); These L_c values were higher than those of Al-c-MCM-l41 families obtained from $Si(OEt)_4$ (nos. **3**–**7**). The L_c values of Al–Ti-c-MCM-41 were similar to those of Al-c-MCM-41. However, these values slightly increased with the increase in Si/Al_2 ratio (nos. **8**–**11**). MCM-41 alone showed a large BET surface area of $1150\,m^2\,g^{-1}$. Although the surface areas slightly decreased with the addition of Al and Ti, almost all catalysts prepared in this study possess large BET surface areas above $900\,m^2\,g^{-1}$, except for no. **8**. Satisfactory XRD data were obtained for calcined MCM-22 samples, but after Ti modification, the XRD patterns were approximately amorphous.

The N_2 adsorption/desorption isotherms for the materials nos. **3**, **4**, **7** and **8** are shown in Fig. 2. Capillary condensation steps were observed for nos. **3**, **7** and **8** at relative pressures of $P/P_0 = 0.4$, suggesting that the pore distribution was narrow, characteristic of mesoporous materials with uniform size. However, these isotherms also showed hysteresis loops at high pressure, indicating that the regularity of samples were not high [5]. For sample no. **4**, no distinct step was observed. This could be consistent with weak XRD pattern (Fig. 1). Thus likely, these materials synthesized here, at least in part, really have the MCM-41 structure, except for sample 4, but their regularities were not high.

3.2. Effect of Al- and/or Ti-modified MCM-41 for vapor phase oxidation with oxygen

Ti-MCM-41 impregnated with metal nitrates has been active for the direct gas-phase oxidation of propylene with molecular oxygen to produce propylene oxide (PO) in 0.13% yield [5b]. The Al- and/or Ti-containing MCM-41 like materials, however, were found to be active for the reaction even without calcium nitrate. The propylene conversion and PO selectivity over various MCM-41 catalysts are shown in Table 1 and Fig. 3. No reaction occurred at 523 K over MCM-41 alone, as indicated in Table 1, no. **1**. When Al was added at Si/Al_2 ratio of 150, products were detected. Al-c-MCM-41 (W), prepared from water glass as Si source, showed a low propylene conversion of 0.075% and did not form any oxygenated products (no. **2**). Al-c-MCM-41, obtained from $Si(OEt)_4$ showed a 1.09% conversion with PO selectivity of 68.8% (no. **3**).[1] Besides PO, the products observed were acrolein, acetone, acetaldehyde, propi-

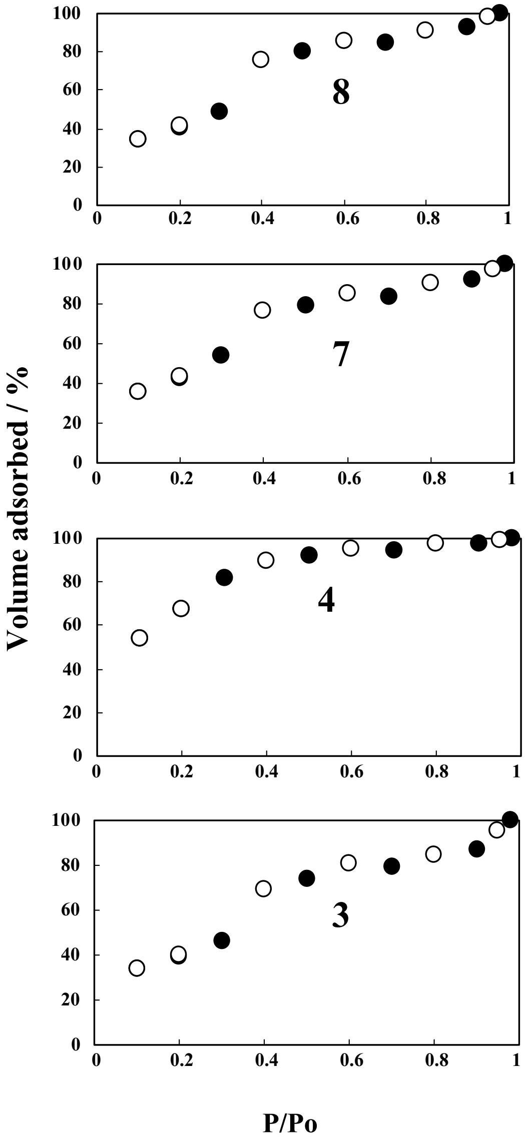

Fig. 2. Adsorption isotherm of nitrogen at 77 K on **3**, **4**, **7**, and **8**. Solid symbol denotes adsorption; open symbol denotes desorption.

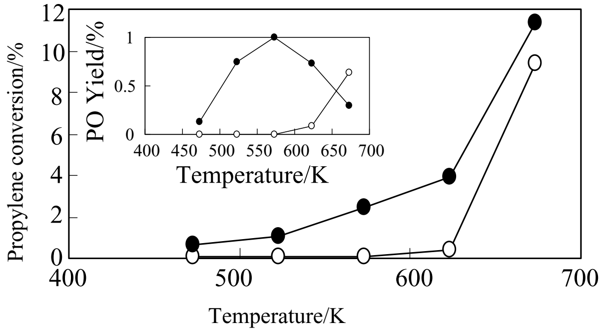

Fig. 3. Temperature dependence on the activity of propylene oxidation with molecular oxygen catalyzed by Al-c-MCM-41 (W) (no. **2**) and Al-c-MCM-41 (no. **3**). Inset: PO yield. $W/F = 25.9\,g\,h\,mol^{-1}$. Gas composition, $C3'/O_2/He = 33/13.2/53.8$ vol.%.

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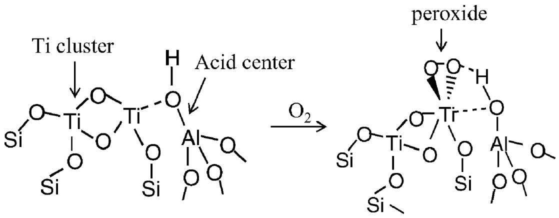
[1] A possibility of the presence of homogeneous reaction was checked in the absence of catalyst. At 523 K, no products were detected. So, in our conditions, a homogeneous reaction would not be a predominant pathway. However, the probability that the reaction was initiated by the catalyst, followed by homogeneous pathway, could not be ruled out [7].

onaldehyde, C1–C8 hydrocarbons, CO_x (CO and CO_2) and small amounts of other oxygenated compounds (2-propanol, methanol and ethanol). The temperature dependence on catalyst performances are shown in Fig. 3. The propylene conversion increased with increasing temperature, but the selectivity for PO increased with temperature and reached maximum values at 523 K for Al-c-MCM-41 and at 623 K for Al-c-MCM-41 (W), and then, decreased thereafter. The yield of PO showed maximum values at 573 K for Al-c-MCM-41 and at 673 K for Al-c-MCM-41 (W) (Fig. 3, inset). Thus, catalyst performances for Al-c-MCM-41 families were examined at 523 K, because the highest value of PO selectivity was obtained at 523 K.

The effect of Si/A1$_2$ ratio on Al-c-MCM-41 conversion is shown in Table 1, nos. **3–7**. The conversion of propylene increased with the increase in Si/Al$_2$ ratio of 150–250 and a highest value of 3.0% was achieved at $Si/Al_2 = 250$, and then, decreased with increasing Si/Al$_2$. The selectivity for PO decreased with the increase in Si/Al$_2$ ratio, while hydrocarbons increased. Thus, the yield of PO showed a maximum value of 1.3% at $Si/Al_2 = 500$ with PO selectivity of 46.5% (no. **5**).

The effect of Si/Al$_2$ ratio in Al–Ti-c-MCM-41 is shown in Table 1, nos. **8–11**, where the Si/Ti ratio in Al–Ti-MCM-41 was kept at a constant value of 100. In the presence of Ti, the propylene conversion was higher than that without Ti, while the PO selectivity was a little lower than that in the absence of Ti. The conversion decreased with the increase in the Si/Al$_2$ ratio and as a result, a maximum PO yield at $Si/Al_2 = 150$ was 2.99%, being 2.5 times that without Ti. T. Miyaji et al. reported that Ti-MCM-41 impregnated with calcium nitrates was active for the gas-phase oxidation of propylene with molecular oxygen to produce PO in 0.13% yield [5]. The PO yield for Al- and/or Ti-containing MCM-41, reported here, were higher than that of $Ca(NO_3)_2$/Ti-MCM-41. Thus, these indicated that Al- and Ti-containing MCM-41 systems were promising candidates of catalysts active for direct oxidation of propylene by molecular oxygen.

In the previous work, Ti/Al-ZSM-5 showed a high yield of PO from the oxidation of propylene by molecular oxygen [4]. The present study has shown that PO could form over Al-c-MCM-41 and the addition of Ti improved PO yield. These results indicate that the simultaneous existence of Ti and Al in silica-based materials is very important for improving the yield of PO from the propylene oxidation by molecular oxygen. We propose a model of active site in Al–Ti-c-MCM-41 for the propylene oxidation by molecular oxygen as described in Scheme 1. A peroxide-like species might be formed between Ti cluster and Al acid site when oxygen molecule was absorbed on the MCM-41 surface. This peroxide-like species is similar to the $Ti(\eta_2\text{-OOH})$ species formed in the titanosilicate-H_2O_2 oxidation system [7] and catalyzed the oxidation of propylene to PO.



Scheme 1. A postulated mechanism of propylene oxidation with molecular oxygen over Al–Ti-c-MCM-41.

4. Conclusion

Ti- and Al-containing MCM-41 (Al-c-MCM-41 and Al–Ti-c-MCM-41) have been synthesized in the presence of hexadecyltrimethylammonium chloride as structure-directing agent at 373 K and the effects of Ti-modified mesoporous materials on the C_3H_6 oxidation with O_2 were examined under vapor phase conditions. The reaction occurred over Al- and Ti-containing MCM-41 like materials. Al–Ti-c-MCM-41 was found to be more effective than Al-c-MCM-41. The catalyst performances of Al–Ti-c-MCM-41 at 523 K were dependent on the Si/Al$_2$ and Si/Ti ratios and the highest PO yield was 3%, when Si/Al$_2$ of 150 and Si/Ti ratios of 100 were used. These findings could be consistent with the assumption that a synergistic mechanism between Ti species and the acid sites may be responsible for the formation of PO, as previously reported.

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