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Selective oxidation of propylene to propylene oxide by molecular oxygen over Ti-Al-HMS catalysts

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Ti- and Al-containing hexagonal mesoporous silicas (HMS) were synthesized at ambient temperature using dodecylamine as surfactant, and the resultant compounds were used as catalysts for the oxidation of propylene by molecular oxygen. Ti-Al-HMS, which was prepared by reaction of Ti(*iso*-$OC_3H_7)_4$, Al(*iso*-$OC_3H_7)_3$ and $Si(OC_2H_5)_4$ in an alcohol-aqueous solution in the presence of dodecylamine, showed 47.8% of conversion and 30.6% of selectivity for propylene oxide (PO) at 523 K. The yield of PO over Ti-Al-HMS (14.6%) was much higher than those over Ti-HMS (1.3%) and Al-HMS (0.9%) at the same reaction conditions. Ti-Al-HMS was also found to be more effective for PO formation than the supported catalysts (Ti/Al-HMS and Al/Ti-HMS) prepared by impregnation method. These results indicated that the simultaneous existence of Ti and Al in HMS was very important for improving the yield of PO from the oxidation of propylene, and the synthesis method influenced the catalytic activity of the Ti- and Al-containing HMS catalysts.

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

1. Introduction

Propylene oxide (PO) is one of the most important chemical feedstock for producing resins such as polyurethane. The major conventional manufacturing methods of PO are the chlorohydrin process and the Halcon process. Both of them require two-stage processes, and the chlorohydrin process causes serious environmental pollution and the Halcon process stoichiometrically produces the coproducts such as *t*-butyl alcohol and styrene. Molecular oxygen is the best oxidant because of the low cost and significant advantages for the environment. Haruta and coworkers have published work relating to epoxidation of propylene by the mixture of oxygen and hydrogen over Au/titania catalysts. The selectivity for PO is high ($>90\%$), but propylene conversion is $<5\%$ and a large amount of hydrogen is consumed to form water [1]. 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 are unsuccessful for the direct epoxidation of propylene due to the highly active allylic C–H bonds of propylene [2,3]. Recently, we have reported that Ti-modified Al-ZSM-5 is effective for the oxidation of propylene to PO by molecular oxygen [4].

The recent synthesis of silica-based mesoporous materials, such as M41S [5], HMS [6] and FSM-16 [7], by the cooperative assembly of periodic inorganic and surfactant-based structures has attracted great interest because it extends the range of molecular-sieve materials into the very large pore regime. High thermal stability (up to 1073 K), large surface area (above $1000\,m^2\,g^{-1}$), uniform-sized pores and adsorption capacity for aromatic organic molecules render these materials very interesting for catalysis [6] and support [8]. Incorporation of transition metal cations in these mesoporous structures is a very interesting and promising field of research. We are focusing on hexagonal mesoporous silicas (HMS) because it has several advantages among the mesoporous materials: (1) HMS can be easily formed by the sol–gel reaction in the presence of primary alkylamine as template at room temperature [6]; (2) transition metal cations, such as Ti^{4+} [6], Al^{3+} [9], Cu^{2+} [10], Zr^{4+} [11], V^{5+} [12], Cr^{3+} [13] and Mn^{2+} [13], can be incorporated into the HMS framework uniformly with high contents and (3) HMS possesses thicker framework walls, small crystallite size of primary particles and complementary textural porosity [14]. In the present study, we intend to incorporate Ti and Al into the HMS framework simultaneously. The novel catalyst showed a higher yield of PO from the oxidation of propylene by molecular oxygen.

2. Experimental

HMS and Ti-HMS were prepared according to the method of Tanev *et al.* [6]. HMS was prepared by adding a clear solution of $Si(OC_2H_5)_4$ (1.00 mol) in ethanol (6.54 mol) to a stirring solution of dodecylamine

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(0.27 mol) and HCl (0.02 mol) in water (36.3 mol). Allowing the resulting gel to age for 18 h at ambient temperature afforded the crystalline templated product. Ti-HMS was prepared by an analogous procedure except that a 6.5 : 1.0 molar mixture of $C_2H_5OH : (CH_3)_2CHOH$ was used in place of ethanol. The molar ratio of Ti(*iso*-$OC_3H_7)_4$ and $Si(OC_2H_5)_4$ ranges from 1 : 100 to 1 : 10 in Ti-HMS. Al-HMS was prepared according to the method of Mokaya and Jones [9]. The mixtures of Al(*iso*-$OC_3H_7)_3$ in 35 mL isopropyl alcohol and 0.2 mol of $Si(OC_2H_5)_4$ in 80 mL ethanol at (Si : Al) molar ratios in the range 200–30 : 1 were heated with vigorous stirring at 343 K for 4 h and added to 0.05 mol dodecylamine (in a mixture of 80-mL water and 120 mL ethanol at room temperature). The pH of the reaction mixture was close to 9.5. The resulting gel mixture was allowed to react at room temperature for 20 h, following which the solid product was obtained by filtration. All of the samples were air dried at room temperature and calcined in air at 923 K for 4 h to remove the structurally incorporated template.

Ti-Al-HMS was prepared as follows: 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 200–30 : 1 and Si/Ti molar ratios in the 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. Ti/Al-HMS and Al/Ti-HMS were prepared by the impregnation method. The calcined Al-HMS and calcined Ti-HMS were evacuated at 673 K for 3 h to eliminate small amounts of water. Then, Al-HMS was impregnated with Ti(*iso*-$OC_3H_7)_4$ in isopropyl alcohol and Ti-HMS was impregnated with Al(*iso*-$OC_3H_7)_3$ in isopropyl alcohol, followed by addition of H_2O (25 g) leading to precipitation of titanium oxide and aluminum oxide, respectively. The samples were filtrated, air dried at room temperature and calcined at 923 K for 4 h.

X-ray diffraction (XRD) patterns were recorded using a MAC Science MX-Labo diffractometer with Cu radiation operated at 40 kV and 50 mA. BET surface areas were measured at 77 K using a Shimadzu Gemini 2375 automatic adsorption instrument.

The catalytic reaction was performed at 523 K under atmospheric pressure. A tubular fixed-bed reactor (o.d. = 1.0 cm, length = 40 cm) was filled with 1.0 g of catalyst powder and 2.0 g of quartz sand. A pretreatment was done prior to each reaction at 673 K in the airflow (25 mL min^{-1}) for 2 h. The feed gas consisted of 16.7% (v/v) C_3H_6, 8.3% (v/v) O_2 and 75% (v/v) Ar. The total flow rate was ca. 20 mL min^{-1}. Hydrocarbons and oxygenated compounds were detected by FID gas chromatography (GC), the former with Porapak Q (1 m) at 473 K and the latter with 20 wt% FFAP on Chromosorb W (3 m) at 373 K. CO_x and O_2 were detected by TCD, using a Shimadzu GC 8A equipped with Porapak Q (3 m) and molecular sieve MS-5A (3 m) columns kept at 343 K. The conversion and selectivity were determined after 5 min on stream.

3. Results and discussion

3.1. Characterization of various samples

The X-ray diffraction patterns of various samples are shown in figure 1. Each sample exhibits an intense reflection corresponding to the (100) plane at 2–3° and a broad shoulder near 5°. These patterns are typical wormhole structures of HMS materials assembled from long alkyl chain neutral amines as surfactants [14,15]. The intensity of reflection corresponding to the (100)

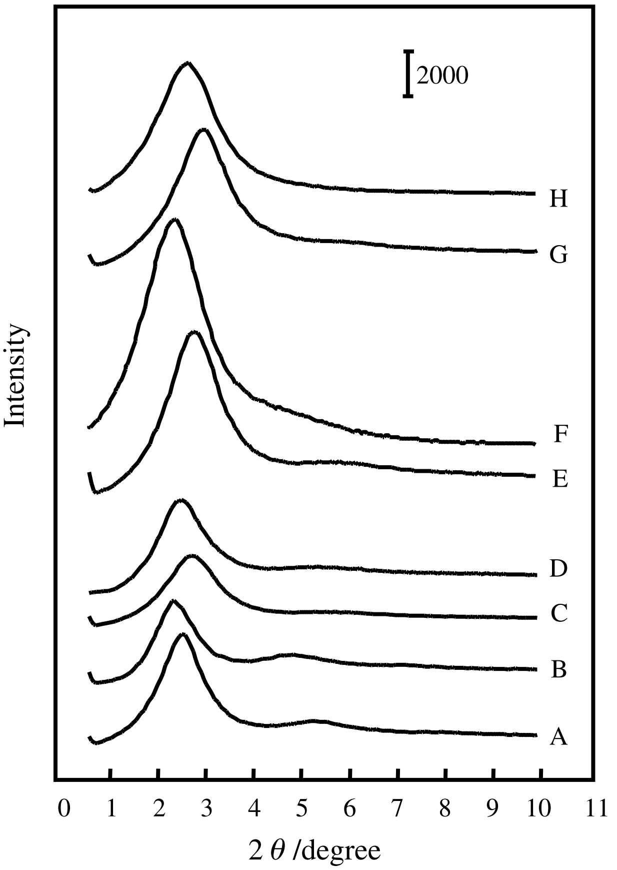


Figure 1. The XRD patterns of (A) HMS (before calcination), (B) Ti-HMS (before calcination, Ti/Si = 4 : 100 (molar ratio)), (C) Al-HMS (before calcination, Al/Si = 1 : 100 (molar ratio)), (D) Ti-Al-HMS (before calcination, Ti/Al/Si = 4 : 1 : 100 (molar ratio)), (E) HMS (after calcination), (F) Ti-HMS (after calcination, Ti/Si = 4 : 100 (molar ratio)), (G) Al-HMS (after calcination, Al/Si = 1 : 100 (molar ratio)), (H) Ti-Al-HMS (after calcination, Ti/Al/Si = 4 : 1 : 100 (molar ratio)).

Table 1
Properties of various samples calcined at 923 K

Sample	Si : Ti : Al (molar ratio)	d_{100}/ (nm)	BET surface area/ ($m^2 g^{-1}$)
HMS	100 : 0 : 0	3.53	1048
Ti-HMS	100 : 4 : 0	3.98	843
Al-HMS	100 : 0 : 1	3.41	984
Ti-Al-HMS	100 : 4 : 1	3.77	817
Ti/Al-HMS	100 : 4 : 1	3.43	895
Al/Ti-HMS	100 : 4 : 1	3.96	852

plane for each sample is in the order of HMS > Ti-Al-HMS > Ti-HMS > Al-HMS before calcination and is in the order of Ti-HMS > HMS > Al-HMS > Ti-Al-HMS after calcination. Physical properties of various samples are shown in table 1. The d_{100} spacing of HMS was 3.53 nm, and the value increased by incorporating Ti in the HMS framework and decreased by incorporating Al in the HMS framework. These results agree with the results reported in the literatures [15,16]. The d_{100} spacing of Ti-Al-HMS was lower than that of Ti-HMS and higher than that of Al-HMS, which is the evidence that Ti and Al were incorporated into the HMS framework. As for the supported catalysts, Ti/Al-HMS showed a value of d_{100} spacing similar to that of Al-HMS and Al/Ti-HMS showed a value of d_{100} spacing similar to that of Ti-HMS. HMS showed a large BET surface area of 1048 $m^2 g^{-1}$. Although the surface areas decreased with the incorporation of Ti and Al into HMS, all catalysts prepared in this study possess large BET surface areas above 800 $m^2 g^{-1}$.

3.2. *Catalytic activity for oxidation of propylene by molecular oxygen*

The propylene conversion and product distribution over various catalysts are shown in table 2. No product was formed through the reactor in the absence of a catalyst. HMS showed a low propylene conversion of 0.5% and did not form any oxygenated products. Ti-Al-HMS showed a 47.8% propylene conversion at 523 K, which was much higher than those over Ti-HMS (3.7%) and Al-HMS (13.5%) at the same reaction conditions. The products observed were PO, acrolein, acetone, acetaldehyde, propionaldehyde, C_4–C_8 hydrocarbons, CO_x (CO and CO_2) and small amounts of other oxygenated compounds (2-propanol, formaldehyde, methanol and ethanol). The selectivities for PO were 30.6, 34.5 and 6.6% over Ti-Al-HMS, Ti-HMS and Al-HMS. Hydrocarbons were the main products over Al-HMS because the oligomerization-cracking of propylene occurred on the acid sites of Al-HMS. Ti-Al-HMS showed the highest yield of PO, which indicated that the simultaneous existence of Ti and Al in HMS was important for improving the yield of PO. As for the supported catalysts, Ti/Al-HMS showed 30.9% of conversion and 24.7% of selectivity for PO, and Al/Ti-HMS showed 22.7% of conversion and 21.8% of selectivity for PO. These results indicated that the sol–gel method was more effective than the impregnation method for the synthesis of Ti- and Al-containing HMS catalysts for the oxidation of propylene by molecular oxygen.

3.3. *Effects of Ti amount and Al amount in Ti-Al-HMS*

The effect of Ti amount in Ti-Al-HMS for the propylene oxidation is shown in figure 2. The Al amount in Ti-Al-HMS was kept at a constant value (Al/Si = 1 : 100). Both the propylene conversion and the selectivity for PO increased with the increase in the Ti amount when the (Ti/Si) molar ratios were from 0–4:100, but slightly decreased when the (Ti/Si) molar ratio was over 4 : 100. Gontier and Tuel reported that Ti could incorporate into the framework of HMS when

Table 2
Oxidation of propylene by molecular oxygen over various catalysts at 523 K[a]

Catalyst	Conversion %	PO yield (%) %	Selectivity (%)[e]								
			PO	AL	AC	AA	PA	HC	CO_x	Others	C[f]
HMS	0.5	0	0	0	0	0	0	13.6	86.4	0	0
Ti-Al-HMS[b]	47.8	14.6	30.6	13.3	6.3	14.2	11.0	16.7	2.1	5.1	0.7
Ti-HMS[c]	3.7	1.3	34.5	6.8	8.9	17.3	6.7	5.3	16.2	3.8	0.3
Al-HMS[d]	13.5	0.9	6.6	9.2	8.4	5.3	3.7	58.7	2.3	1.1	4.8
Ti/Al-HMS[b]	30.9	7.6	24.7	14.1	4.6	13.7	3.6	15.3	14.9	6.8	2.3
Al/Ti-HMS[b]	22.7	4.9	21.8	11.4	10.1	7.6	8.1	27.5	4.2	7.7	1.6

[a] Catalyst amount: 1 g, quartz sand: 2 g, C_3H_6: 3.3 mL min^{-1}, 10% O_2/Ar: 16.7 mL min^{-1}.[b] Ti : Al : Si = 4 : 1 : 100 (molar ratio).

[c] Ti : Si = 4 : 100 (molar ratio).

[d] Al : Si = 1 : 100 (molar ratio).

[e] Products: propylene oxide (PO), acrolein (AL), acetone (AC), acetaldehyde (AA), propionaldehyde (PA), hydrocarbons (HC = $C_4 + C_5 + C_6 + C_7 + C_8$), CO and CO_2 (CO_x = CO + CO_2), 2-propanol, formaldehyde, methanol and ethanol (others).

[f] Lost carbon as deposits: shortfall of C (outlet of the reactor) compared to C atoms in the feed.

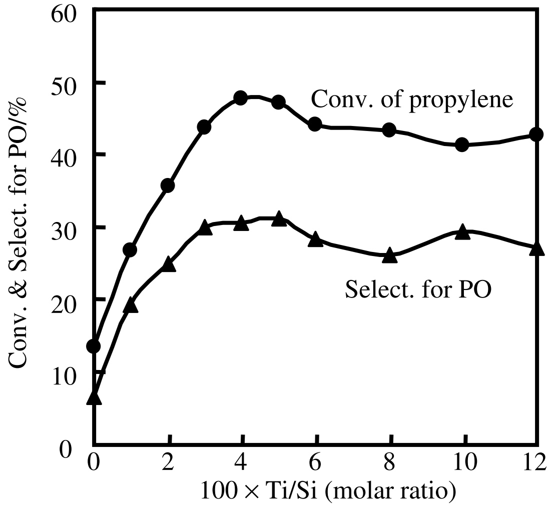


Figure 2. Effect of Ti amount over the Ti-Al-HMS catalyst ($Al/Si = 1 : 100$ (molar ratio)) for the oxidation of propylene at 523 K. ●: Conversion of propylene, ▲: selectivity for PO. Catalyst amount: 1 g, quartz sand: 2 g, C_3H_6: 3.3 mL min^{-1}, 10% O_2/Ar: 16.7 mL min^{-1}.

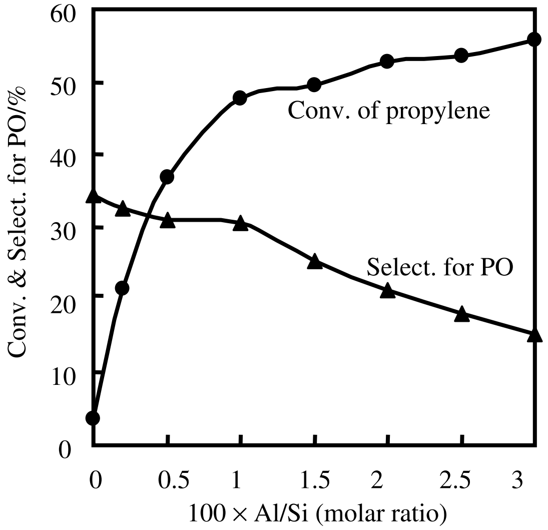


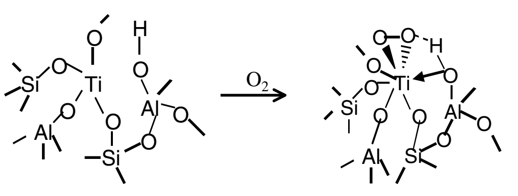
Figure 3. Effect of Al amount over the Ti-Al-HMS catalyst ($Ti/Si = 4 : 100$ (molar ratio)) for the oxidation of propylene at 523 K. ●: Conversion of propylene, ▲: selectivity for PO. Catalyst amount: 1 g, quartz sand: 2 g, C_3H_6: 3.3 mL min^{-1}, 10% O_2/Ar: 16.7 mL min^{-1}.

$Si/Ti < 25$ (molar ratio) in the gel and formed highly dispersed oxide species after calcination, and polymerized Ti species appeared when $Si/Al > 25$ (molar ratio) [17]. We think this is the reason the optimum ratio of Ti to Si is 4 : 100 for the oxidation of propylene over Ti-Al-HMS at 523 K.

The effect of Al amount in Ti-Al-HMS for the propylene oxidation is shown in figure 3. The Ti amount in Ti-Al-HMS was kept at a constant value ($Ti/Si = 4 : 100$). The propylene conversion increased with the increase in the Al amount, but the selectivity for PO decreased with the increase in the Al amount because large amounts of hydrocarbons were formed over Ti-Al-HMS with high aluminum contents. The yield of PO showed a maximum value at $Al : Si = 1 : 100$ (molar ratio). Therefore, the optimum molar ratio of Si/Ti/Al is 100 : 4 : 1 in Ti-Al-HMS for the oxidation of propylene by molecular oxygen.

3.4. *Presumable active sites in Ti-Al-HMS*

In the previous work, Ti/Al-ZSM-5 showed a high yield of PO from the oxidation of propylene by molecular oxygen [3]. The present study has shown that PO effectively formed over Ti-Al-HMS but formed in low yields over Ti-HMS and Al-HMS. 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 Ti-Al-HMS for the propylene oxidation by molecular oxygen as described in scheme 1. An epoxide-like species might be formed between Ti cluster and Al acid site when oxygen molecules are absorbed on the HMS surface. This epoxide-like species is similar to the Ti(η_2-OOH) species formed in the titanosilicate-H_2O_2 oxidation system [18] and catalyzed the oxidation of propylene to PO.



Scheme 1.

Ti-Al-HMS showed an initial conversion of 47.8% (table 1) at 523 K, but it decreased to 28.9% after 1 h on-stream. The deactivated catalyst could be regenerated by calcination in air at 923 K for 4 h. These results indicated that carbonaceous deposits formed on the catalyst surface caused the catalyst deactivation. The addition of a small amount of hydrogen in the feed gas obviously decreased the speed of deactivation. Further works are focusing on improving the yield of PO and suppressing the deactivation of the catalyst for the oxidation of propylene by molecular oxygen.

4. Conclusions

Ti- and Al-containing mesoporous silicas (Ti-Al-HMS) have been synthesized in the presence of dodecylamine as template molecules at ambient temperature. Ti-Al-HMS ($Si/Ti/Al = 100 : 4 : 1$ (molar ratio)) is more effective than Ti-HMS and Al-HMS for the epoxidation of propylene by molecular oxygen. The coexistence of Ti and Al is essential, which suggests that a synergetic mechanism between Ti cluster and Al acid site may be responsible for the selective formation of PO on the present catalyst system. The sol–gel method is more effective than the impregnation method for preparing the Ti- and Al-containing HMS catalysts.

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