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Epoxidation of n-Hexene and Cyclohexene over Titanium-Containing Catalysts

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Abstract–TS-1, Ti-beta and Ti-MCM-41 molecular sieves have been prepared by direct hydrothermal synthesis method and applied to the epoxidation of n-hexene and cyclohexene with H_2O_2 under mild conditions. Ti-beta with extremely low Al content was synthesized by using a seed method to suppress the formation of diol produced by Brønsted acid sites present in Ti-beta. It was also found that a large amount of by-products (1-ol and 1-one) formed over hydrophilic Ti-MCM-41. We further modified Ti-MCM-41 by silylation with bis(trimethylsilyl) trifluoroacetamide (BSTFA). Among these catalysts, the Ti-beta with low content of Al enhanced the yield of epoxide and suppressed the formation of diol markedly. The silylated Ti-MCM-41 reduced the formation of by-products and promoted the yields of epoxide significantly. Based on experimental results, a reaction mechanism with two parallel and competitive reactions was proposed.

Key words: TS-1, Ti-beta, Ti-MCM-41, Epoxidation, Silylation, Brønsted Acid, Hydrophobic

INTRODUCTION

Since TS-1 was first synthesized in 1983 [Taramasso et al., 1983], the incorporation of titanium into the framework of high-silica zeolites has expanded the application of these materials in the field of organic synthesis. The Ti-containing molecular sieves can oxyfunctionalize or oxidize a variety of organic compounds such as alkanes, olefins, aromatics, amines, thioethers, etc. [Ramaswamy and Sivasanker, 1993; Ratnasamy and Kumar, 1993].

One of the most important reactions is the catalytic epoxidation of olefins with H_2O_2 over titanium-containing catalysts. Epoxides owe their importance to their high reactivity, which is due to the opening of the highly strained three-membered ring. Obviously, the epoxides turn out to be very important chemical products for synthesis of other materials in the fine chemicals industry, and this subject has led to the synthesis of other medium-pore Ti-zeolites; e.g., TS-2 [Tuel, 1995] and Ti-ZSM-48 [Serrano et al., 1992]. More recently, the large-pore molecular sieve Ti-beta [Camblor et al., 1993; Van der Waal et al., 1996], extra-large-pore zeolite Ti-UTD-1 [Balkus et al., 1996] and mesopore molecular sieve Ti-MCM-41 [Blasco et al., 1995; Koyano and Tatsumi, 1997; Lee et al., 1998; Kang et al., 1999] have been extensively studied.

Despite much progress made during the last decade for developing titanium-containing catalysts, the procedure of catalyst synthesis is somewhat complicated. Moreover, the elementary steps of the selective oxidation, the active sites in titanium-containing catalysts, the surface characteristics, and their effects on the formation of by-products are not well understood.

In this work, it is intended to synthesize TiO_2-free TS-1 and Ti-beta by using of TiF_4. Especially, a seed method is employed to synthesize low Al-containing Ti-beta. Furthermore, the surface modification of Ti-MCM-41 is conducted by silylation to obtain hydrophobic Ti-MCM-41. The epoxidation of n-hexene and cyclohexene with H_2O_2 is carried out over these catalysts. The effects of the Brønsted acidity and hydrophilic nature on the product selectivity are also investigated.

EXPERIMENTAL

1. Synthesis of Catalysts

1-1. TS-1

TiF_4 was used as Ti source and the synthesis procedure was the same as the one proposed by Jorda et al. [1997]. Crystallization was carried out at 175 °C for 4 days. The TS-1 was recovered by centrifugation, washed with distilled water several times, and then dried at 110 °C overnight. Finally, the catalyst was calcined in air at 550 °C for 10 hours.

1-2. Ti-beta

Aerosil 200 (Degussa), TiF_4, TEAOH (Aldrich, 35 wt%), and aluminum nitrate nonahydrate were used as reagents. At first, the TEAOH was mixed with TiF_4 under stirring to obtain clear solution containing Ti^{4+} ion. The Aerosil and water were then added slowly, and finally the Al source was added. The approximate composition of homogeneous solution was $SiO_2 : 0.025\ TiO_2 : 0.005\ Al_2O_3 : 0.552$ TEAOH : 15 H_2O, and the ratios of Si/Ti and Si/Al could be adjusted as needed. Crystallization was carried out at 150 °C for 7 days. After cooling, the sample was centrifuged at 10,000 rpm. The recovered solid was washed until pH became equal to 9 and then dried in air at 80 °C. The as-synthesized catalyst was calcined in air at 580 °C for 5 hours.

To obtain Ti-beta with low Al-content, the synthesized Al-containing Ti-beta was used as seed. The gel solution containing

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Table 1. Summary of the synthesized Ti-containing catalysts

Structure	Catalyst	Si/Ti	Si/Al	BET surface area (m^2/g)	Pore diameter (Å)	Adsorption of H_2O (g/g·cat.)
MFI	TS-1	53.2	-	-	-	-
BETA	TB-1	76.5	39.1	-	-	-
	TB-2[a]	57.1	400	-	-	0.192
MCM-41	TM-1	60.3	-	1405	26.1	0.301
	TM-2[b]	66.7	-	1213	23.1	0.157

[a] Using TB-1 as seeds.

[b] Silylation of TM-1 with bis(trimethylsilyl) trifluoroacetamide (BSTFA).

Si and Ti sources was first prepared by the procedure mentioned above, and then the synthesized Ti-beta seed was added under stirring. The ratio of seed to SiO_2 in the gel solution was 4/100 (g/g). Crystallization was carried out at 140 °C for 10 days. The ratios of Si/Ti and Si/Al are listed in Table 1.

1-3. Ti-MCM-41

CTMA-Br ([$C_{16}H_{33}N(CH_3)_3$]Br, TCI) was used as surfactant. At first, the TBOT was added to the TEAOH solution and stirred for 30 minutes, and then the TEOS and water were added. Finally, the surfactant was added and the mixture was stirred for 1 hour. After the gel was prepared in an autoclave at 135 °C under static conditions for 24 hours, the autoclave was cooled down to room temperature, and the pH value of the mixture was adjusted to 11 approximately by dropwise addition of acetic acid with vigorous stirring. The mixture was synthesized in the autoclave at 135 °C for 24 h again. The solid was washed, dried in air at 80 °C overnight and calcined at 540 °C in dry air for 6 hours.

The procedure for the silylation of catalyst with bis(trimethylsilyl) trifluoroacetamide (BSTFA) is the same as the one proposed by D'Amore [D'Amore and Schwarz, 1999].

2. Characterization

The structure and crystallinity of the catalysts were confirmed by X-ray power diffraction analysis. The XRD spectra were obtained by using CuKα radiation (λ=1.5406 Å). Infrared spectra were recorded on a Nicolet Impact 410 FT-IR instrument (in the range of 400-4,000 cm^{-1}) by using the KBr pellet technique. UV-vis spectroscopic measurements were taken on a Varian CARY 3E double beams spectrometer using dehydrated MgO as a reference in the range of 190-820 nm. The ratios of Si/Ti and Si/Al were obtained by XRF.

3. Reaction Experiment

Epoxidation of n-hexene and cyclohexene with H_2O_2 was conducted in a magnetically stirred three-necked flask at 70 °C. In practice, 0.05 g of catalyst was dispersed in the solution containing 0.02 mol of alkene and 20 ml of solvent. In the case of TS-1, methanol was used as solvent, while for Ti-beta and Ti-MCM-41, acetonitrile was used. The mixtures were then heated to 70 °C under stirring and 0.01 mol of H_2O_2 (35 wt% aqueous solution) was introduced in one lot. The sample was periodically collected and analyzed by gas chromatography (HP 5890 Series II) equipped with FID and HP-1 capillary column.

RESULTS AND DISCUSSION

1. Characterization

The XRD patterns of synthesized TS-1, Ti-beta and Ti-MCM-41 match well with those reported in the literature [Taramasso et al., 1983; Van der Waal et al., 1996; Koyano and Tatsumi, 1997]. The absence of a band at about 340 nm in the UV-vis spectra indicates the absence of titanium oxide impurities in all synthesized samples. As described by Jorda [Jorda et al., 1997], TiF_4 is stable in air, in water, and even in basic TPAOH compared to $Ti(OR)_4$. It was also found that TiF_4 was soluble in TEAOH solution (a template for synthesis of beta) and no anatase phase was formed during preparation of the gel. Thus the synthesis of TS-1 or Ti-beta was considerably simplified.

Table 1 shows the physical and chemical properties of titanium-containing molecular sieves. The Si/Al ratio of TB-2, synthesized by seed method, is significantly increased, and this indicates that Ti-beta can grow over the Ti(Al)-beta seed and the Al content of the seed determines the total Al content in the mixture of gel. Thus the Al content can be reduced to an extremely low level. This method is similar to that reported by Camblor [Camblor et al., 1996].

Fig. 1 presents the FT-IR spectra of samples dispersed in KBr. All the samples display a visible band at 960 cm^{-1}. For pure silicate or aluminosilicates this band has been assigned to the Si-O stretching vibrations of $Si\text{-}O^-R^+$ groups. The strong intensity of this band in the siliceous MCM-41 is due to the large amount of silanol groups present in the calcined material. For Ti-containing molecular sieves, a band at 960 cm^{-1} is attributed to the stretching vibration of SiO_4 tetrahedral bound to the Ti atoms, that is, Si-O-Ti [Deo et al., 1993; Camblor et al., 1993;

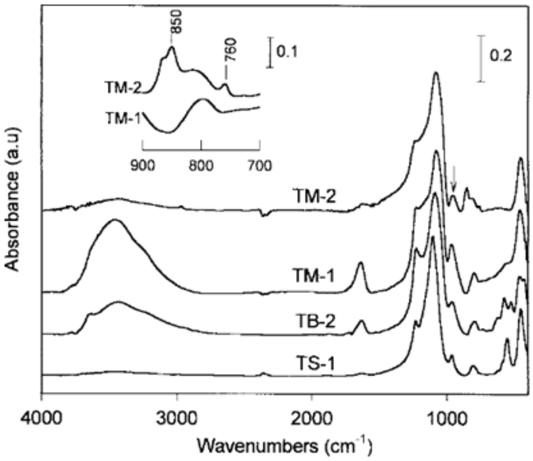


Fig. 1. IR spectra of Ti-containing catalysts.

De Man and Sauer, 1996]. The systematic increase in the intensity of this band with the Ti content is usually taken as the evidence of incorporation of titanium into the framework [Boccuti et al., 1989].

The silylation added bands to the IR spectra can be taken as important evidence for alkylsilyl group ($SiMe_3$) replacing the hydrogen in silanol. As depicted in Fig. 1, several new bands appeared after silylation of TM-1 with BSTFA. The band at 2,962 cm^{-1} is assigned to C-H oscillation band of the methyl group [Grorge and Mcintyre, 1987]. This band is also observed in the IR spectrum of the hydrophobic silica (AEROSIL R812), which was obtained from Degussa. The $SiMe_3$ group is also easily recognized by one or more bands in the 870 to 750 cm^{-1} region from the $-CH_3$ rocking and the Si-C stretching vibrations [Anderson, 1974]. The bands at 850 and 760 cm^{-1} can be observed in the silylated sample. These observations strongly suggest that the $SiMe_3$ groups were bonded on the surface of BSTFA silylated catalyst (TM-2). It agrees with the amount of H_2O adsorbed in Ti-MCM-41 as presented in Table 1. In other words, silylation improves the hydrophobicity of catalyst and results in the decrease of H_2O adsorbed.

2. Epoxidation of n-Hexene and Cyclohexene

As shown in Table 2, in the case of n-hexene epoxidation, Ti-beta shows the highest selectivity to epoxide, TS-1 gives the highest conversion, and Ti-MCM-41 produces the largest amount of by-products. In regard to the epoxidation of cyclohexene, only epoxide is produced over TS-1, which may due to the diffusion limitation in the medium-pore structure of TS-1. Over Ti-beta and Ti-MCM-41, the formation of diol can be observed. Compared to Ti-MCM-41, Ti-beta gives higher selectivities to epoxide and diol. However, Ti-MCM-41 prefers to form more amounts of by-products in both of n-hexene and cyclohexene epoxidation.

Fig. 2 gives the variation of each product formed over TB-1 for cyclohexene epoxidation. In the beginning of the reaction, the primary products, epoxide and 2-cyclohexene-1-ol (1-ol), appear and tend to decrease with reaction time. Subsequently, the secondary products, diol and 2-cyclohexene-1-one (1-one), are observed and tend to increase. We also note that the sum selectivity of epoxide and diol stays at a high value (80%) and shows constant during the reaction. These results indicate that Ti(Al)-beta favor to attack the C=C in cyclohexene. Fig. 3 presents the results of the same reaction over Ti-MCM-41. It gives the same products and shows similar variation for each product. However, the selectivities of products are very different from those observed over the Ti-beta. The sum selectivity of 1-ol and 1-one arrives up to 70%. We could conclude that the Ti-MCM-41 is more preferable to the formation of by-products than to the producing of epoxide.

Table 2. Epoxidation of alkenes with H_2O_2 over Ti-containing catalysts

Catalyst	Alkene	Conversion (mol%)	Selectivity (mol%)		
			Epoxide	Diol	By-product
TS-1	n-hexene	48.6	62.3	0	37.7
	cyclohexene	15.3	100.0	0	0
TB-1	n-hexene	22.8	89.8	0	10.2
	cyclohexene	33.2	45.4	33.6	21.0
TB-2	cyclohexene	39.3	65.6	8.6	25.8
TM-1	n-hexene	19.1	12.2	0	87.8
	cyclohexene	21.2	13.7	18.0	68.3
TM-2	cyclohexene	39.1	26.1	15.9	58.0

Conversion is based on alkene. Reaction conditions: 0.05 g of catalyst, 0.02 mol of alkene, 0.01 mol of H_2O_2 (35 wt% in water), and 20 ml of solvent. Temperature=70 °C, time=5 h.

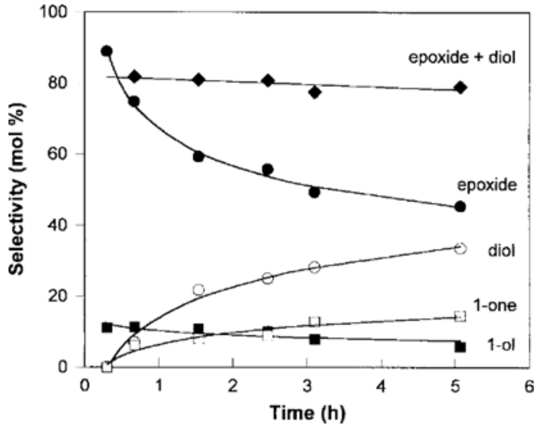


Fig. 2. Epoxidation of cyclohexene with H_2O_2 over Ti(Al)-beta (TB-1).

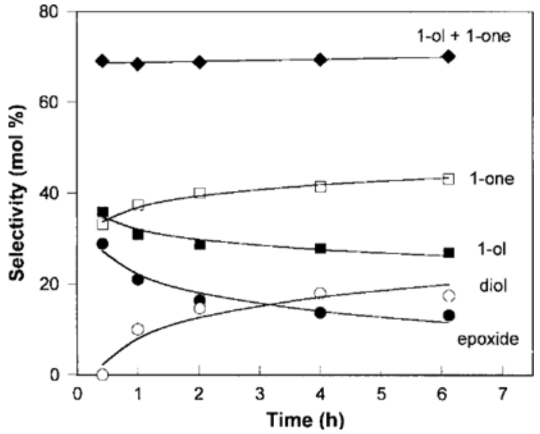


Fig. 3. Epoxidation of cyclohexene with H_2O_2 over Ti-MCM-41 (TM-1).

3. Influence of Brønsted Acid and Hydrophobicity on Epoxidation

Fig. 4 presents the experimental results over TB-1 and TB-2. The low Al-containing TB-2 gives higher selectivity to epoxide than TB-1 does. It also suppresses the formation of diol. However, the formation of by-products (1-ol and 1-one) and the conversion are not unaffected by the Al contents in Ti-beta. Thus, one may conclude that the epoxide is hydrolyzed to the diol mostly on Brønsted acid sites originating from the Al^{3+} in Ti-beta. Nevertheless, the effect of Al contents in Ti-beta on the formation of 1-ol and 1-one is insignificant. Fig. 5 shows the comparison results of cyclohexene epoxidation over TM-1 and

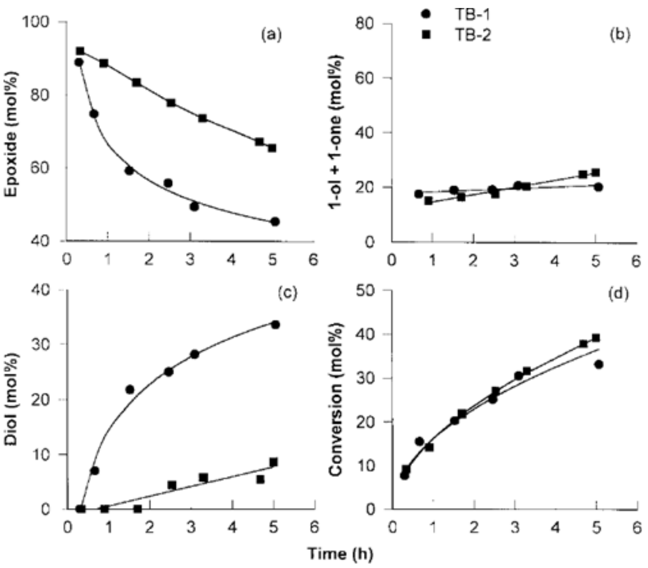


Fig. 4. Effects of Brønsted acid on the product selectivity for cyclohexene epoxidation over Ti(Al)-beta catalysts.

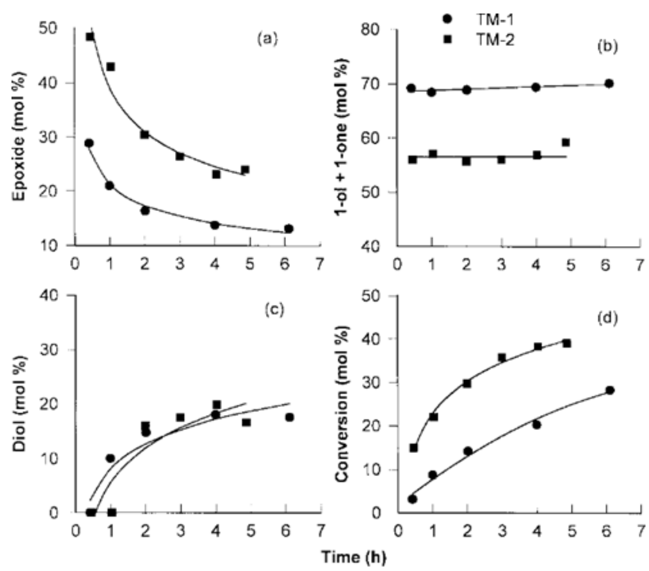
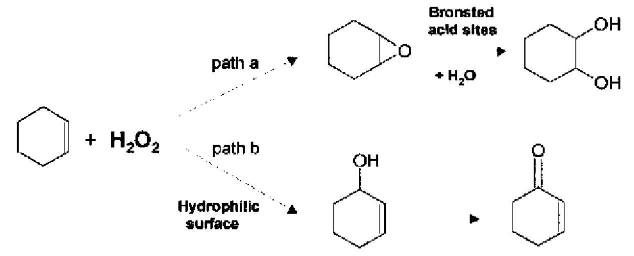


Fig. 5. Effects of hydrophobicity on the product selectivity for cyclohexene epoxidation over Ti-MCM-41 catalysts.

TM-2. The silylated Ti-MCM-41 improves the activity of cyclohexene epoxidation, enhances the production of epoxide and reduces the formation of 1-ol and 1-one. It gives no effect on the selectivity of diol. We can further conclude that the hydrophilic nature of catalysts leads to the formation of 1-ol. In addition, the sum selectivities of 1-ol and 1-one remain unchanged (Fig. 2, Fig. 3); this indicates that the 1-ol, a primary product, can be further oxidized to 1-one. Based on the experimental results and the form of Ti active site Ti-OOH [Tozzola et al., 1998], a reaction mechanism for epoxidation of alkenes can be proposed (Scheme 1).

This reaction scheme may give a reasonable explanation for the significant difference in the product selectivity of Ti-beta and Ti-MCM-41. The oxidations proceed via two parallel pathways. The path (a) can yield epoxide and diol, herein the selectivity of diol is mainly determined by the Brønsted acid sites in catalysts, which accords with the experimental results over TB-1 and TB-2 samples. On the other hand, over the hydrophilic catalyst, the reactions appear preferable to following the path (b) and producing a larger amount of 1-ol and 1-one, which is confirmed by the epoxidations over TM-1 and TM-2. Obviously, because the Ti-MCM-41 shows more hydrophilic than Ti-beta, it gives higher selectivity of 1-ol and 1-one than Ti-beta does.



Scheme 1. Postulated mechanism.

In addition, Tatsumi [Bhaumik and Tatsumi, 1998] proposed that the titanium hydroperoxo species (TiOO-H) generated in TS-1/H_2O_2/H_2O system has a labile Brønsted proton, which activates the oxirane oxygen toward hydrolysis. We also noted that a small amount of diol formed over Ti-MCM-41 catalysts. The Ti-MCM-41/H_2O_2/H_2O system may give rise to the generation of the titanium hydroperoxo species, which results in the formation of diol. Further studies on the Brønsted proton in Ti-MCM-41/H_2O_2/H_2O system are in progress.

CONCLUSIONS

For epoxidation of n-hexene and cyclohexene, TS-1 and Ti-beta gave higher selectivity to epoxide, whereas Ti-MCM-41 favored the formation of by-products. The Al^{3+} ions in Ti-beta form Brønsted acid sites, on which the epoxide is converted to diol. For this reason, the seed method was employed to synthesize Ti-beta with extremely low content of Al. Over this Ti-beta catalyst, the production of epoxide is enhanced while the formation of diol is significantly suppressed. On the other hand, the hydrophilic Ti-MCM-41 was found to result in the formation of by-product, 1-ol, which can be further oxidized to 1-one. When Ti-MCM-41 was modified by silylation with BSTFA, it became hydrophobic. The silylated catalyst improves the activity of cyclohexene epoxidation, gives high selectivity to epoxide and reduces the formation of 1-ol and 1-one. Based on the experimental results, a presumable mechanism with two parallel and competitive reaction paths is proposed for cyclohexene epoxidation.

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