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Ti-MCM-36: a new mesoporous epoxidation catalyst

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Ti-containing MCM-36 catalyst was synthesized from a Ti-MCM-22 precursor (P) via surfactant swelling followed by polymeric silica pillaring. Mesoporous region with ca. 2.8 nm pore size was created by expansion between lamellar crystalline sheets in Ti-MCM-22 (P). Characterization of Ti-MCM-36 was conducted using XRD, BET surface area measurement, ICP, and UV-vis spectroscopy. Catalytic performances in 1-hexene and propylene epoxidation reactions using H_2O_2 as an oxidant demonstrated superior performance of Ti-MCM-36 over Ti-MCM-22 or TS-1.

KEY WORDS: Ti-MCM-22; Ti-MCM-36; pillaring; epoxidation; 1-hexene; propylene.

1. Introduction

MCM-22 is a relatively new molecular sieve with MWW topology in which two independent 10-membered ring (MR) sinusoidal channels and 12-membered ring supercages are positioned next to each other independently in a three dimensional arrangement [1,2]. This combination of large and medium pores was reported to be of great advantage in a variety of catalytic applications in petrochemical industry [3]. Recently, several studies have been reported on isomorphous substitution of Al in MCM-22 with trivalent elements, such as B, Fe, and Ga [4–6]. Isomorphous substitution of other transition metal ions to MCM-22 can also produce metallosilicates with redox properties. Among these, we have been particularly interested in Ti-MCM-22, a novel titanosilicate with MWW topology first proposed by Wu *et al.* [7]. Ti-MCM-22 was reported to exhibit superior catalytic performances in selected epoxidation reactions using H_2O_2 as an oxidant to those of the best known commercial catalyst, TS-1 (titanium silicalite-1) [8,9] but has received very little attention from other research groups. As suggested earlier, unique sinusoidal 10 MR channels of the so-called within layers of MWW zeolite seem to serve as more effective reaction spaces than the tunnel type 10 MR channels of TS-1 and the Ti-active sites within the MWW-structure are believed to be characteristically different from those of TS-1 [9,10].

MCM-36, on the other hand, is a pillared molecular sieve prepared from MCM-22 (P) after a combined treatment of surfactant swelling followed by SiO_2 pillaring and is made of both micropores in its crystalline layers and mesopores in the interlayer space, thus demonstrating high specific surface area and good accessibility for relatively large molecules [11,12]. In a similar manner, it will be possible to prepare Ti-MCM-36 in which active isolated tetrahedral Ti sites are located in the framework having both mesopores and micropores starting from Ti-MCM-22(P). Ti-MCM-36 is expected to have many advantages as an active and selective catalyst for partial oxidation reactions using H_2O_2 as an oxidant by allowing bulky organic molecules to easier access to Ti active sites in the framework than that of Ti-MCM-22 or TS-1. Ti-MCM-36 is also expected to provide a more stable Ti species against leaching because they are incorporated inside a robust zeolytic structure, not like amorphous Ti species in Ti-MCM-41.

In this study, synthesis and catalytic performance of Ti-MCM-36 are reported for the first time and its structural evolution from Ti-MCM-22 precursor was investigated in a systematic manner.

2. Experimental

Ti-MCM-22 was prepared using the post synthesis method reported by Wu and Tatsumi [8] which utilizes Ti substitution to vacant T sites created in B-MCM-22 precursor (P) by acid leaching. For this purpose, boron containing MCM-22 precursor was initially prepared following the synthesis method reported by Millini *et al.* [4] and the material was treated with 6 M HNO_3 three times to remove boron completely. Afterwards, it was mixed with H_2O, piperidine (PI), tetrabutyl orthotitanate (TBOT) to the molar composition of 1.0 SiO_2:0.03 TiO_2:1.0 PI:19 H_2O, and the mixture was heated in a Teflon stainless-steel autoclave at 448 K for 7 days. Ti-MCM-22 precursor prepared was again treated with 2 M HNO_3 to remove extra-framework Ti species that is known to be detrimental to catalytic epoxidation

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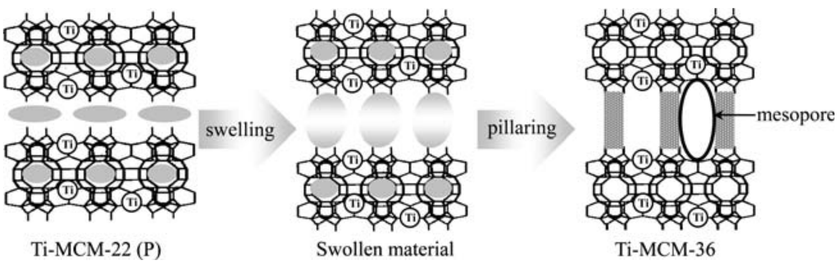

Figure 1. Schematic representation of Ti-MCM-36.

reactions. Finally, calcination was performed at 803 K for 10 h to prepare Ti-MCM-22 catalyst.

Ti-MCM-36 was prepared based on the synthesis protocol for Al-MCM-36 reported by He *et al.* [11] using the Ti-MCM-22 precursor without calcination, designated here as Ti-MCM-22(P). Swelling process was carried out by refluxing a mixture of Ti-MCM-22(P):4 CTMACl (cetyltrimethyl ammonium hydroxide):1.2 TPAOH, followed by mixing the product obtained with TEOS at a weight ratio of 1:5 for pillaring. After filtration and drying, hydrolysis step was carried out in water at 413 K for 6 h. Finally, Ti-MCM-36 was obtained by calcination at 723 K for 3 h in nitrogen and subsequently at 813 K for 6 h in air (heating rate of 2 K/min).

The crystallinity of the samples prepared was measured by X-ray diffraction using Ni-filtered CuKα radiation (Rigaku-miniflex) and the specific surface area and average pore diameters were determined by N_2 adsorption–desorption using a Micromeretics ASAP 2000 automatic analyzer. UV-visible spectrum was measured in air on a Varian cary-3E double beam spectrometer using SiO_2 as a reference. The amounts of Ti and B were determined by inductively coupled plasma emission spectrometry (ICP, JY-138). Catalytic performance was investigated by 1-hexene and propylene epoxidation with H_2O_2 as an oxidant. 1-Hexene epoxidation reaction was carried out under vigorous stirring in a chemistation PPS-250 (EYELA, CCA-1100) fitted with a condenser and a thermometer using 2.02 g of substrate, 150 mg of catalyst, 20 ml acetonitrile as a solvent, and 0.76 g of H_2O_2 (30% aq.). The reaction was performed at 313 K for 2 h and the products were analyzed using a gas chromatograph (HP 5890 series II) equipped with a capillary column (HP-20 M) and a FID detector. Catalytic performance in propylene epoxidation was evaluated using a high pressure semi-batch reactor, and product distribution was monitored by the same gas chromatograph system. The amount of H_2O_2 remained after reaction was measured by titration using 0.1 M cerium sulfate (IV) in H_2SO_4 solution. The standard set of reaction condition were 318 K, 7 atm propylene inlet pressure, 0.2 g catalyst, and 3.4 g H_2O_2 (30wt% aq.) at 1000 rpm stirring and 30 min reaction time in acetonitrile solvent.

3. Results and discussion

Schematic representation of Ti-MCM-36 structural evolution is described in figure 1. Ti-MCM-22(P) has lamellar structure and the three-dimensional MWW framework in Ti-MCM-22 was formed upon calcination as a result of condensation of hydroxyl groups between the layers. Swollen Ti-MCM-22 (P), on the other hand, is shown to have an expansion of interlayer distance and Ti-MCM-36 after further pillaring process has a mesoporous region created by polymeric silica pillars formed by TEOS hydrolysis.

XRD patterns of the related materials evolved in sequence are compared in figure 2. The pattern of B-MCM-22 precursor was characterized by (001) and (002) peaks at $2\theta = 3\sim7°$ due to *c*-axis. Deboronated MCM-22 using 6 M HNO_3 by post treatment created linkages of lamellar structures after removal of organic template species, which is reflected by the disappearance of (001) and (002) peaks at $2\theta = 3\sim7°$. Ti-MCM-22(P) demonstrates the same XRD pattern as B-MCM-22 (P)

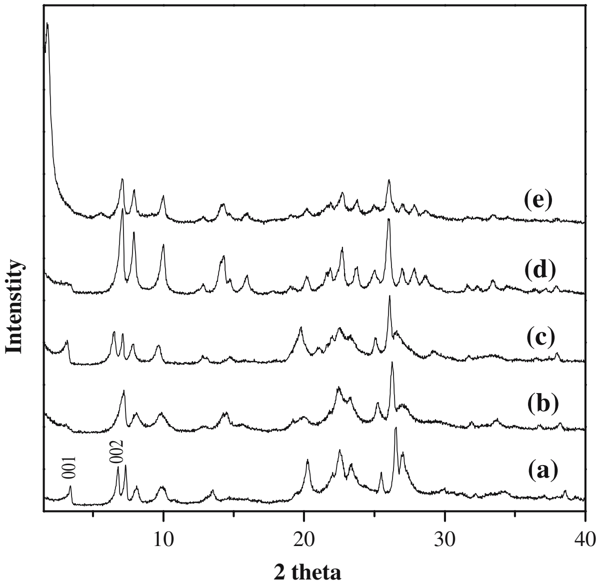

Figure 2. XRD patterns of Ti-MCM-22 and Ti-MCM-36; (a) as-synthesized B-MCM-22(P), (b) acid treated B-MCM-22(P), (c) as-synthesized Ti-MCM-22(P), (d) calcined Ti-MCM-22, and (e) Ti-MCM-36.

indicating the restored lamellar structure upon Ti incorporation. For Ti-MCM-36, the characteristic (002) plane peak at $2\theta = 6.6°$ in Ti-MCM-22(P) disappeared after swelling and pillaring, and instead a new characteristic peak at $2\theta = 1{\sim}2°$ appeared indicating an increase in *c* parameter and subsequent formation of mesopore region.

Figure 3 shows nitrogen adsorption–desorption isotherms of Ti-MCM-22 and Ti-MCM-36. The isotherm of Ti-MCM-22 is of type I reflecting the microporous nature of the material, whereas the isotherm of Ti-MCM-36 is of type IV with a hysteresis loop beginning at $p/p_o = 0.4$ due to the presence of mesopores. Ti-MCM-36 exhibited enlarged specific surface area and external surface area in comparison to Ti-MCM-22. BET surface areas of Ti-MCM-36 and Ti-MCM-22 were 674 m^2/g and 471 m^2/g, respectively. The external surface areas were also estimated by *t*-plots, and Ti-MCM-36 had 105 m^2/g, which is somewhat higher than 87 m^2/g of Ti-MCM-22. Apparently, swelling and pillaring in MCM-36 resulted in increases in inter-lamellar sheet distance forming mesopores. The total pore volume of Ti-MCM-36 was 0.51 cm^3/g, on the other hand, pore volume of Ti-MCM-22 was 0.37 cm^3/g. Both Ti-MCM-22 and Ti-MCM-36 had shown significant portion of textural porosity [13] as shown by capillary condensation at partial pressures > 0.90. This textural porosity seems to originate from the aggregated platelets crystals as observed by SEM in both samples (not shown).

UV-visible spectra of the samples prepared are shown in figure 4. Those of TS-1 and Ti-MCM-22 are also shown for comparison. Absorption band of Ti-MCM-22 (P) produced both 220 nm peak corresponding to the catalytically active tetrahedral Ti sites as well as 260 nm peak corresponding to inactive octahedral Ti species; surface Ti species may share the same oxygen with a neighboring Ti to have a Ti–O–Ti linkage and maintain its electronic balance by bonding with other coordinated groups such as hydroxyl groups or water [7]. This kind of Ti thus shows an octahedral coordination in Ti-MCM-22(P), which can form anatase phase during swelling/pillaring. Consequently, extra-framework Ti species of Ti-MCM-22(P) should be removed by acid treatment for synthesis of Ti-MCM-36. As shown in figure 4, UV-vis spectra of Ti-MCM-36 sample using Ti-MCM-22(P) without acid treatment showed band at 260 nm and new band at 330 nm due to anatase phase formed. On the other hand, Ti-MCM-36 sample in which the Ti-MCM-22(P) was treated using 2 M HNO_3 showed that most of 260 nm band due to octahedral Ti species were removed. However, part of anatase phase formed during the swelling/pillaring step of Ti-MCM-36 still remained.

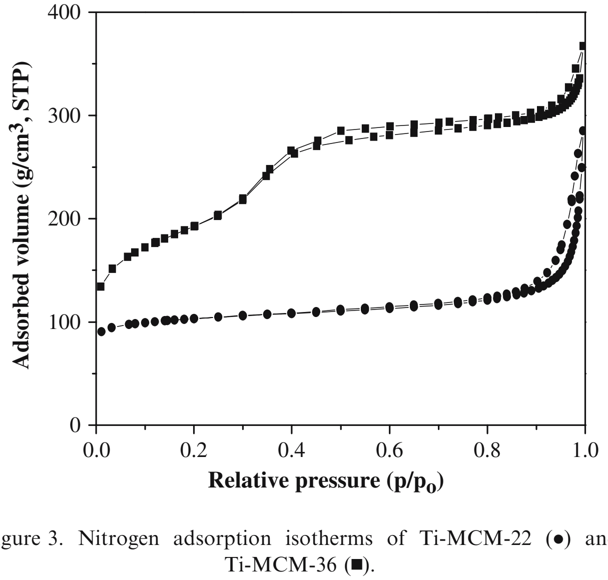

Figure 3. Nitrogen adsorption isotherms of Ti-MCM-22 (●) and Ti-MCM-36 (■).

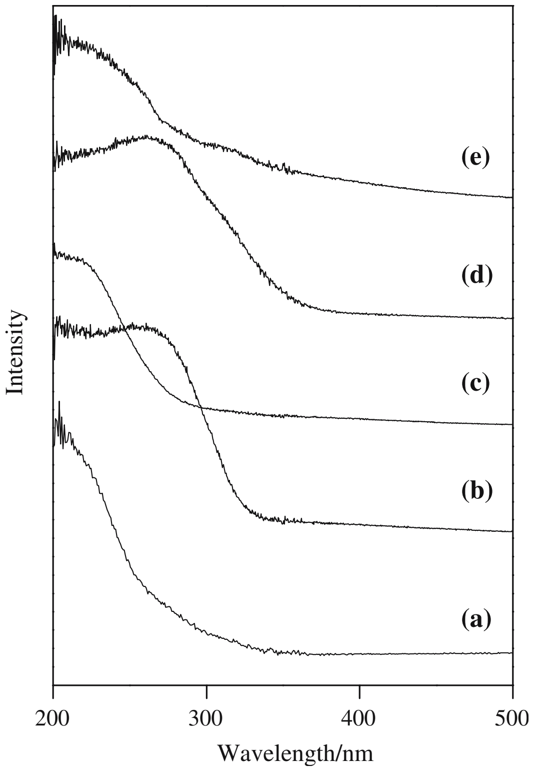

Figure 4. UV-vis spectra: (a) TS-1, (b) Ti-MCM-22 (P), (c) calcined Ti-MCM-22, (d) calcined Ti-MCM-36 without acid treatment, and (e) Ti-MCM-36 acid treated with 2 M HNO_3 followed by calcination.

Finally, catalytic properties of Ti-MCM-36 were compared with those of other titanosilicates in liquid phase epoxidation using H_2O_2 as an oxidant. Firstly, catalytic performance data for 1-hexene epoxidation are shown in Table 1. We have chosen 1-hexene epoxidation as a probe reaction since it is known to be strongly affected by substrate pore diffusion in TS-1 [14], and the reaction reflects the catalytic activities of Ti species in crystalline zeolytic environment. Cyclohexene molecule, on the other hand, is also activated by Ti species in

Table 1
Catalytic performances of Ti-containing catalysts in 1-hexene epoxidation[a]

Catalyst	Si/Ti[b]	TON[c]	1-hexene		H_2O_2	
			Conversion (mol%)	Selectivity (mol%)	Conversion (mol%)	Selectivity (mol%)
TS-1	46	81	18	99 >	66	96
Ti-MCM-22	49	125	26	99 >	94	97
Ti-MCM-36	88	257	30	99 >	99 >	99 >

[a] Reaction conditions: Cat., 0.15 g; 1-hexene, 0.024 mol; H_2O_2 (30% aqueous solution), 0.0067 mol; acetonitrile (Ti-MCM-22 and Ti-MCM-36) or methanol (TS-1), 20 ml; temp., 45°C; time, 2 h.
[b] By ICP analysis.
[c] mol product per mol Ti.

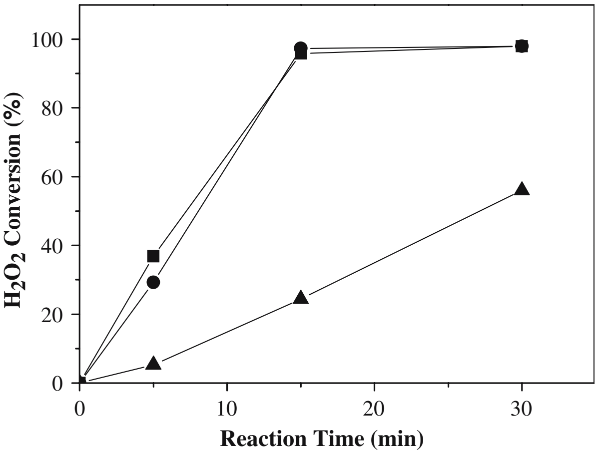

Figure 5. H_2O_2 conversion profiles in C_3H_6 epoxidation; Ti-MCM-22 (■), Ti-MCM-36 (●), and TS-1 (▲). Reaction conditions: 45°C, 7 atm, 2.5wt% H_2O_2 (30% aqueous solution), 0.2 g catalyst, 45 ml acetonitrile (Ti-MCM-22 and Ti-MCM-36) and methanol (TS-1), 1,000 rpm stirring.

amorphous environment such as in Ti-MCM-41 [15] and is not adequate for this work. For meaningful comparison, reactions were carried out in the most suitable solvent for each catalyst system; acetonitrile for Ti-MCM-22 and Ti-MCM-36, and in methanol for TS-1. This solvent effect can be related to the different hydrophobic/hydrophilic characteristics of the different catalysts and well explained in [16]. Swelling/pillaring step is expected to produce a large number of silanol groups, which may confer Ti-MCM-36 some hydrophilic character. Although Ti content varied somewhat among the titanosilicates, Ti-MCM-36 clearly exhibited the highest specific activity with high turnover number (TON) for the conversion of 1-hexene with high H_2O_2 efficiency. The high activity of Ti-MCM-36 should come from the contribution of more open and accessible reaction space produced by swelling/pillaring and enhanced diffusion of substrates and products in the channels due to expansion of interlayer sheets.

Commercially more relevant epoxidation of propylene was also performed to supplement the potential of Ti-MCM-36 as an effective epoxidation catalyst, and the corresponding reaction profile is compared in figure 5. At the standard reaction condition in the propylene epoxidation selected, ca. 98% conversion of H_2O_2 (limiting reactant) was obtained over both Ti-MCM-22 and Ti-MCM-36 catalyst. It is worth mentioning that no by-products were observed in these catalysts, which is very desirable compare with the result with TS-1 that produced ring-opened side products in methanol solvent system. In terms of TON, Ti-MCM-36 is apparently better than Ti-MCM-22 due to lower Ti/Si ratio in the pillared structure; the TON turned out to be 782 and 440 mol (mol of Ti)$^{-1}$ for Ti-MCM-36 and Ti-MCM-22, respectively.

4. Conclusions

Ti-MCM-36 was successfully synthesized from a Ti-MCM-22 precursor by surfactant swelling followed by silica pillaring and the structural evolution was confirmed by various characterization tools. Improved textural properties of substantially enhanced surface area accompanied by mesopores were obtained, which are desirable for handling sterically-demanding organic molecules. Catalytic activity and selectivity in 1-hexene and propylene epoxidation using H_2O_2 (30%, aqueous) as an oxidant, exhibited superior performances of Ti-MCM-36 to those of either Ti-MCM-22 or TS-1.

Acknowledgment

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References

[1] G. Kennedy, S. Lawton and M. Rubin, J. Am. Chem. Soc. 116 (1994) 11000.
[2] A. Corma, C. Corell and J. Pérez-Pariente, Zeolites 15 (1995) 2.
[3] A. Corma, V. Martínez-Soria and E. Schnoeveld, J. Catal. 192 (2000) 163.

[4] R. Millini, G. Perego, W. Parker, G. Bellussi and L. Carluccio, Micropor. Mater. 4 (1995) 221.

[5] F. Testa, F. Crea, G. Diodati, L. Pasqua, R. Aiello, G. Terwagne, P. Lentz and J. Nagy, Micropor. Mesopor. Mater. 30 (1999) 187.

[6] R. Morrison and M. Rubin, U.S. Patent 5,382,742 (1995).

[7] P. Wu, T. Tatsumi, T. Komatsu and T. Yashima, J. Phys. Chem. B 105 (2001) 2897.

[8] P. Wu and T. Tatsumi, Chem. Commun. 10 (2002) 1026.

[9] P. Wu and T. Tatsumi, Catal. Surv. Asia 8 (2004) 137.

[10] P. Wu and T. Tatsumi, J. Catal. 214 (2003) 317.

[11] Y. He, G. Nivarthy, F. Eder, K. Seshan and J. Lercher, Micropor. Mesopor. Mater. 25 (1998) 207.

[12] S. Laforge, P. Ayrault, D. Martin and M. Guisnet, Appl. Catal. A Gen. 279 (2005) 79.

[13] T.R. Pauly, Y. Liu, T.J. Pinnavaia, S.J.L. Billinge and T.P. Rieker, J. Am. Chem. Soc. 121 (1999) 8835.

[14] W.J. Kim, T.J. Kim, W.S. Ahn, Y.J. Lee and K.B. Yoon, Catal. Lett. 91 (2003) 123.

[15] W.S. Ahn, N.K. Kim and S.Y. Jeong, Catal. Today 68 (2001) 83.

[16] H. Wu, L. Wang, H. Zhang, Y. Liu, P. Wu and M. He, Green. Chem. 8 (2006) 78.