Synthesis and Catalysis of Ti-MCM-41 Materials with Organic–Inorganic Hybrid Network

Katsutoshi Yamamoto, Yuki Nohara,[†] and Takashi Tatsumi*[†]
*Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656*
[†]*Division of Materials Science & Chemical Engineering, Faculty of Engineering, Yokohama National University,
79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501*

Ti-Containing MCM-41 materials were organically modified by employing an organosilane with a bridging organic group between two Si, and employed as catalysts for olefin oxidation using H_2O_2 as oxidant. The incorporation of a bridging organic group resulted in an increase in *d* spacing, in contrast to the modification with organosilane having terminal alkyl group, which provides decreased *d* spacing. High hydrophobicity of organically bridged Ti-MCM-41 materials led to high selectivity to epoxide by depressing allylic oxidation.

Organic modification of mesoporous silica materials such as MCM-41[1,2] has been attracting much attention[3–7] since it can provide silica matrix with a new function of an organic group as well as hydrophobicity. Mesoporous silica materials are known to have generally higher hydrophilicity than crystalline zeolitic materials so as to show less hydrothermal stability[8] and lower catalytic activities[9] in reactions conducted in the presence of water. However, it has been reported that these drawbacks can be overcome by the improvement of hydrophobicity through introducing organic groups in their pore wall by direct methods[10–13] or post-synthesis methods.[14,15] Recently several groups reported the synthesis of a new kind of organically modified mesoporous materials by using organoalkoxysilanes in which organic groups bridge two Si species.[16–19] To date, however, studies on their hydrophobicity or on their applications to catalysts have not yet been reported. Here we reports the synthesis of Ti-containing MCM-41 type mesoporous materials with this kind of bridging organic group and their physical and catalytic properties in comparison with those unmodified or modified with terminal alkyl groups.

Ti-containing MCM-41 materials with a bridging organic group (Ti-BTESE-M41) were synthesized by using bis(triethoxysilyl)ethane (BTESE) as a part of Si source. A mixture of BTESE and TEOS was added to an aqueous solution of octadecyltrimethylammonium chloride (OTMACl) and tetramethyl-ammonium hydroxide (TMAOH). After tetrabutyl orthotitanate was added, the resulting mixture was heated to 70–80 °C to remove the alcohols. The mother gel with the composition of Si : 0.02 Ti : 0.6 OTMACl : 0.5 TMAOH : 100 H_2O was hydrothermally treated in a Teflon bottle for 3 days at 100 °C under static conditions. Templating surfactant was removed by extraction with 1 M HCl in EtOH at room temperature. A mixture of TEOS and methyltriethoxysilane (MTES) was used to synthesize the methyl-modified material (Ti-MTES-M41) as a control. Thus obtained materials and Ti-MCM-41, synthesized only from TEOS as Si source, were characterized by XRD, ^{29}Si MAS NMR, and N_2 and H_2O adsorption

measurements. Their catalytic activity was evaluated by the catalytic oxidation of cyclohexene with 30% H_2O_2 conducted at 50 °C for 3 h.
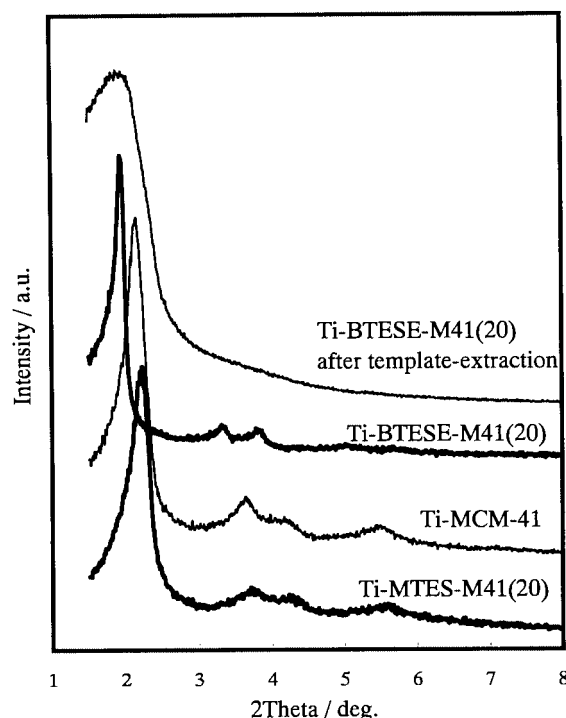

Figure 1. XRD patterns of as-synthesized Ti-containing MCM-41 materials with/without organic modifications.

Table 1. Physical properties of Ti-containing MCM-41 materials with/without organic modifications

	$T/(Q+T)^a$ / %	d_{100}^b / Å	A_{BET}^c / $m^2 \cdot g^{-1}$	$Vm_{H_2O}^d$ / nm^{-2}
Ti-MCM41	–	40.7	711	4.1
Ti-BTESE-M41(20)	28	45.3	1020	2.5
Ti-BTESE-M41(40)	49	47.7	931	2.2
Ti-MTES-M41(20)	15	39.4	845	3.0
Ti-MTES-M41(40)	39	35.9	1103	1.2

Values in parentheses are the ratios of Si having Si–C bond in corresponding mother gels. [a]The ratio of organically modified Si against total Si evaluated by ^{29}Si MAS NMR measurements. [b]*d* spacings for corresponding as-synthesized materials. [c]BET surface area estimated from N_2 adsorption at −196 °C. [d]Number of adsorbed H_2O molecules per nm^2 of surface area calculated from H_2O monolayer adsorption capacity at 25 °C and BET surface area.

Table 2. Catalytic activities of Ti-containing MCM-41 materials in cyclohexene oxidation

| | Si/Ti | Conv.[a] / mol% | T.O.N.[b] | Selectivity / mol% | | | H2O2 | |
				Epoxide[c]	Diol[d]	allylic-oxidation[e]	Conv. / %	Eff.[f] / %
Ti-MCM-41	49	5.1	9	4	56	40	25	24
Ti-BTESE-M41(20)	58	5.5	15	3	73	24	52	12
Ti-BTESE-M41(40)	37	7.9	15	4	81	15	51	17
Ti-MTES-M41(20)	38	7.4	14	3	70	27	45	18
Ti-MTES-M41(40)	25	27.1	30	1	69	30	69	45

Reaction conditions: cyclohexene 25 mmol, H_2O_2 5 mmol, catalyst 50 mg, 50 °C, 3 h. Values in parentheses are the ratios of Si having Si−C bond in corresponding mother gels. [a]Conversion multiplied by cyclohexene/H_2O_2 ratio. [b](Epoxide + Diol)-mol per Ti-mol. [c]Cyclohexene oxide. [d]1,2-Cyclohexanediol. [e]2-Cyclohexen-1-ol and 2-cyclohexenone. [f]Percentage of effectively used H_2O_2 based on consumed H_2O_2.

Figure 1 shows the X-ray diffraction (XRD) patterns of as-synthesized Ti-containing mesoporous materials, indicating that these materials have the 2d-hexagonal symmetry. As reported previously,[4] the use of MTES as a part of Si source gives mesoporous materials with smaller d spacing compared with that of purely inorganic MCM-41. In contrast, Ti-BTESE-M41 exhibits larger d spacing than Ti-MCM-41. The substitution of two methylene units for an oxygen atom might be responsible for this expansion. As shown in Table 1, the d spacing of Ti-BTESE-M41 increases with increasing content of bridging organic group. After the template removal, their ordered structures seem to be damaged because their XRD patterns show only the (100) peak. However, these materials have large BET surface areas, indicating the retention of porous structures. The hydrophobicity is slightly increased by the incorporation of bridging organic group, as is shown by H_2O monolayer adsorption capacities per nm^2, although the hydrophobicity of Ti-BTESE-M41 cannot be improved greatly by the increase in organic content in contrast to that of Ti-MTES-M41.

Table 2 exhibits the catalytic activity of these materials in the oxidation of cyclohexene using H_2O_2 as oxidant. Ti-BTESE-M41, as well as Ti-MTES-M41,[11–13] shows higher catalytic activity in terms of T.O.N. than unmodified Ti-MCM-41 presumably because of its higher hydrophobicity. However, the catalytic activity of Ti-BTESE-M41 is not improved by raising its carbon content in contrast to that of Ti-MTES-M41; the degree of activity improvement is in good agreement with that of hydrophobicity improvement (Table 1). It is conceivable that the terminal methyl group can sit just around Ti to improve the hydrophobicity around Ti site, resulting in the enhancement of the epoxidation, in contrast to the bridging ethylene group bonded between Si. It is also to be noted that organically modified materials, Ti-BTESE-M41 in particular, have higher selectivity to epoxidation products, the sum of cyclohexene oxide and 1,2-cyclohexanediol produced by the hydrolysis of cyclohexene oxide, than Ti-MCM-41. The higher hydrophobicity causes the concentration of H_2O_2 near the surface of the catalysts to decrease, resulting in low H_2O_2/olefin ratio in microscopic point of view, would promote the epoxidation in preference to the allylic oxidation.[20]

References
1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, *Nature*, **359**, 710 (1992).
2 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, and J. L. Schlenkwe, *J. Am. Chem. Soc.*, **114**, 10834 (1992).
3 S. L. Burkett, S. D. Sims, and S. Mann, *Chem. Commun.*, **1996**, 1367.
4 D. J. Macquarrie, *Chem. Commun.*, **1996**, 1961.
5 X. Feng, G. E. Fryxell, L.-Q. Wang, A. Y. Kim, J. Liu, and K. M. Kemner, *Science*, **276**, 923 (1997).
6 M. H. Lim, C. F. Blanford, and A. Stein, *J. Am. Chem. Soc.*, **119**, 4090 (1997).
7 W. M. Rhijn, D. E. De Vos, B. F. Sels, W. D. Bossaert, and P. A. Jacobs, *Chem. Commun.*, **1998**, 317.
8 T. Tatsumi, K. A. Koyano, Y. Tanaka, and S. Nakata, *Chem. Lett.*, **1997**, 469.
9 T. Blasco, A. Corma, M. T. Navarro, and J. P. Pariente, *J. Catal.*, **156**, 65 (1995).
10 N. Igarashi, Y. Tanaka, S. Nakata, and T. Tatsumi, *Chem. Lett.*, **1999**, 1.
11 A. Corma, J. L. Jorda, M. T. Navarro, and F. Rey, *Chem. Commun.*, **1998**, 1899.
12 N. Igarashi, S. Kidani, Rizwan-Ahemaito, and T. Tatsumi, *Stud. Surf. Sci. Catal.*, **129**, 163 (2000).
13 N. Igarashi, S. Kidani, Rizwan-Ahemaito, and T. Tatsumi, *Zeolitic Mater.*, **1**, 15 (2000).
14 K. A. Koyano, T. Tatsumi, Y. Tanaka, and S. Nakata, *J. Phys. Chem. B*, **101**, 9436 (1997).
15 T. Tatsumi, K. A. Koyano, and N. Igarashi, *Chem. Commun.*, **1998**, 325.
16 S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna, and O. Terasaki, *J. Am. Chem. Soc.*, **121**, 9611 (1999).
17 B. J. Melde, B. T. Holland, C. F. Blanford, and A. Stein, *Chem. Mater.*, **11**, 3302 (1999).
18 T. Asefa, M. J. MacLachlan, N. Coombs, and G. A. Ozin, *Nature*, **402**, 867 (1999).
19 Y. Lu, H. Fan, N. Doke, D. A. Loy, R. A. Assink, D. A. LaVan, and C. J. Brinker, *J. Am. Chem. Soc.*, **122**, 5258 (2000).
20 J. M. Fraile, J. I. Garcia, J. A. Mayoral, and E. Vispe, *J. Catal.*, **189**, 40 (2000).