

Deprotection of a Silyl Group with Mesoporous Silica

Akichika ITOH,* Tomohiro KODAMA, and Yukio MASAKI

Gifu Pharmaceutical University; Mitahora-higashi, Gifu 502–8585, Japan.

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The triethylsilyl (TES) group of silyl ethers of several types is selectively and easily removed in the presence of a *t*-butyldimethylsilyl (TBDMS) group with a mesoporous silica MCM-41/MeOH heterogeneous system. Comparison of the efficiency was carried out among several solvents, and among such promoters as common zeolites and ion-exchange resins. Furthermore, FSM-16, another mesoporous silica, was examined for the possibility of recycling by re-calcination at 400 °C after the reaction.

Key words *t*-butyldimethylsilyl; deprotection; FSM-16; MCM-41; mesoporous silica; triethylsilyl

The silyl group has been widely used in organic synthesis as a typical hydroxyl protecting group. Especially, the triethylsilyl (TES) group and *t*-butyldimethylsilyl (TBDMS) group have been used for synthesis of natural products by many researchers since they are comparatively stable against acids and are easy to handle.¹⁾ Although, in general, deprotection of these groups is carried out with acids or fluorine anion, the work-up to remove the acids, especially on a large scale, is tedious and the fluorine anion tends to give rise to side reactions due to its strong basicity. With this background in mind, recently, reaction fields for achieving environmentally benign processes have been designed by many researchers in synthetic organic chemistry.²⁾ Easy work-up is an important factor for achieving an environmentally benign process and the use of heterogeneous catalysts is advantageous. Among them, mesoporous silicas, which possess uniform meso pores, of which pore sizes are 2–50 nm,³⁾ and narrow pore-distribution and high surface area against amorphous mesoporous materials, such as silica gel or alumina, have been paid much attention due to their potential utility as new heterogeneous catalysts and in providing shape selectivity. In the course of our study on the utility of mesoporous silicas in organic synthesis as solid acid, we have found that their use is feasible for deprotection of silyl groups, and, especially, MCM-41,^{4,5)} a typical mesoporous silica enables us to deprotect the TES group selectively from the TBDMS group. Selective deprotection of silyl groups can be performed with a variety of liquid protonic and Lewis acids^{6–9)}; however, the work-up to remove the acids is tedious as mentioned above. On the other hand, the heterogeneous system is facile from the viewpoint of convenience of the work-up in which mesoporous silicas can be removed by only filtration, and, furthermore, mesoporous silicas have the possibility of recycling. In this paper, we report our detailed study on the scope and limitation of using mesoporous silicas for deprotection of silyl groups.

Results and Discussion

Table 1 shows the results for the deprotection of several silyl ethers (**1**) of dodecanol with MCM-41 in MeOH. The trimethylsilyl (TMS) and TES ethers (**1a**, **b**) were completely deprotected to dodecanol (**2**); however, the TBDMS and triisopropylsilyl (TIPS) ethers (**1c**, **d**) were intact during the indicated reaction time. These results show that selective deprotection of the TES group from the TBDMS group is feasi-

ble with the MCM-41/MeOH system.

Table 2 shows the results of selective deprotection of the TES group under several conditions by using a typical solid catalyst and TES and TBDMS ether of 1,4-butanediol (**3a**) as test substrate. In THF, the starting material (**3a**) was almost intact after stirring for 4 h (entry 1). When acetonitrile, acetone, water, and ethanol were used as a solvent, reactions were sluggish (entries 2–5). On the other hand, methanol was the solvent of choice, and mono-TBDMS ether of 1,4-butanediol (**4a**) was obtained in 83% yield with a small

Table 1. Deprotection of Silyl Ethers of 1-Dodecanol with MCM-41 in MeOH

$$\text{n-C}_{12}\text{H}_{25}\text{O}-\text{P} \xrightarrow[\text{MeOH (5 ml), r.t., 2 h}]{\text{MCM-41 (300 mg)}} \text{n-C}_{12}\text{H}_{25}\text{OH}$$

Substrate		2	Recovery
P		(%)	of 1 (%)
1a	TMS	100	0
1b	TES	99	0
1c	TBDMS	0	99
1d	TIPS	0	100

Table 2. Deprotection of TES and TBDMS Ethers of 1,4-Butanediol with MCM-41

$$\text{3a (100 mg)} \xrightarrow[\text{solvent (5 ml), r.t., 4 h}]{\text{additive (300 mg)}} \text{4a + 5a}$$

Entry	Additives	Solvent	Recovery of 3a (%)	Products (%)	
				4a	5a
1	MCM-41	THF	96	0	0
2	MCM-41	MeCN	43	46	2
3	MCM-41	Me ₂ CO	85	12	0
4	MCM-41	H ₂ O	76	8	7
5	MCM-41	EtOH	54	40	<1
6	MCM-41	MeOH	0	83	3
7	FSM-16	MeOH	0	83	6
8	HMS	MeOH	35	54	<1
9	SiO ₂ ^{a)}	MeOH	43	54	<1
10	H-ZSM-5	MeOH	0	68	21
11	H-Y	MeOH	0	0	92
12	Na-Y	MeOH	92	5	0
13	Amberlite IR-120B	MeOH	0	0	90
14	Amberlite IRC-50	MeOH	57	57	0

a) The silica gel was pretreated with HCl aq.

* To whom correspondence should be addressed. e-mail: itoha@gifu-pu.ac.jp

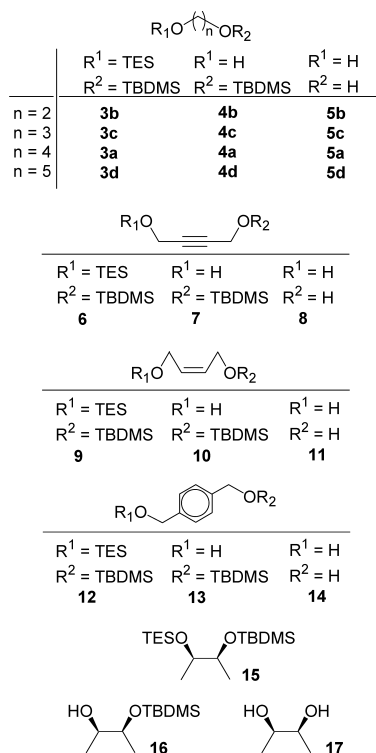


Fig. 1

amount of 1,4-butanediol (**5a**) (entry 6). Among other mesoporous silicas, FSM-16^(10,11) showed similar reactivity as MCM-41 for 4 h; however, HMS,⁽¹²⁾ was not so effective (entries 7, 8). Silica gel,⁽¹³⁾ which was pre-treated with HCl aq. to remove the Na⁺ ion, was not so effective as MCM-41 (entry 9). H-ZSM-5⁽¹⁴⁾ and H-Y,⁽¹⁵⁾ which are typical zeolites, were too strongly acidic to differentiate the TES and TBDMS groups (entries 10, 11). Na-Y zeolite,⁽¹⁵⁾ in which the H⁺ ion was exchanged to the Na⁺ ion, was not effective (entry 12). Amberlite IR-120B, which is a strongly acidic ion exchange resin of sulfonic acid type, afforded only diol **5a**, and Amberlite IRC-50, which is a weakly acidic ion exchange resin of the carboxylic acid type, was not so effective as MCM-41 (entries 13, 14).

Table 3 shows the results of selective deprotection between TBDMS and TES by using several types of mixed silylated diols with MCM-41 under the conditions outlined above. TBDMS and TES ethers of ethylene glycol (**3b**), 1,3-propanediol (**3c**), 1,5-pentanediol (**3d**) afforded the corresponding products **4** in high yields analogous to that from **3a** (entries 1–4). The type of butynediol ether **6** gave the selectively deprotected alcohol **7** in 85% yield in a similar manner as the case of **3** (entry 5). For the substrates **9** and **12**, which are a type of allylic and benzylic ether, respectively, the corresponding products (**10**, **13**) were obtained in over 90% yields, although the deprotection reaction took long time (8 h) (entries 6, 7). On the other hand, the silyl ethers of meso-2,3-butanediol (**15**) resisted the deprotection with MCM-41, and afforded the product **16** in no more than 38% yield even after 24 h due to its steric hindrance (entry 8).

From these results, the acidity of MCM-41 as solid-acid is assumed to be mild, not so strong as Amberlite IR-120B, H-Y zeolite and H-ZSM-5 zeolite, and not so weak as Amberlite IRC-50 and HMS. The active site and the mechanism

Table 3. Selective Deprotection of TES Group in the Presence of TBDMS Group with MCM-41 in MeOH

Entry	Substrate	Time (h)	Products (%)	
			4b: 80	5b: 0
1	3b	4	4b : 80	5b : 0
2	3c	4	4c : 91	5c : 3
3	3a	4	4a : 83	5a : 3
4	3d	4	4d : 90	5d : 2
5	6	4	7 : 85	8 : 6
6	9	8	10 : 90	11 : 3
7	12	8	13 : 97	14 : <1
8	15	24	16 : 38 ^{a)}	17 : 0

a) 53% of starting silyl ethers (**15**) was recovered.

Table 4. The Ratio of the Framework, BET Surface Area and the Pore Size of the Silicas

Silica	Q^2	Q^3	Q^4	S_{BET} (m ² /g)	Pore size (nm)
HMS	4	27	69	344	2.4
MCM-41	8	9	83	665	2.9
FSM-16	2	28	70	882	2.8

concerning the selectivity in the desilylation are not yet clear; however, catalytic reactivity of mesoporous silicas arises from the silanol moiety on the surface of silica and, especially, the amount and structure of them provide different strengths of reactivity. Table 4 shows the ratios of the framework of MCM-41, HMS and FSM-16, which were analyzed by ²⁹Si-NMR spectra, BET surface area, pore volume and the pore sizes of the silicas, which were measured by the volumetric N₂-gas adsorption method. Although the ratio of the silanol group $((2 \times Q^2 + Q^3)/Q^4)$ for MCM-41 (0.30) is smaller than that of HMS (0.45) by the deconvolution analysis, the total amount of the silanol group of MCM-41 is eventually larger than that of HMS since the BET surface of MCM-41 is about 2 times larger than that of HMS. On the other hand, both the ratio (0.46) and the BET surface of FSM-16 are larger than those of MCM-41. Thus, these were assumed to reflect the different results of desilylation among MCM-41, HMS and FSM-16. Although the solvent effect is not explicable, the polarity of the solvents, the solubility of the substrates are assumed to contribute to the yield of product.⁽¹⁷⁾

As mentioned above, we have found selective deprotection of the TES group with MCM-41, which could not be conducted with other typical solid catalysts. On the other hand, the utility of mesoporous silicas as environmentally benign deprotective reagents will be increased if mesoporous silicas can be recycled. Thus, we studied the possibility of recycling of silica using FSM-16, which showed the similar reactivity as MCM-41 in Table 2 and possesses more rigid structure to withstand the recycling examination than that of MCM-41.⁽¹⁸⁾ Table 5 shows the results, and recovered FSM-16, which was re-calcined at 400 °C for 2 h after the reaction of **1b**, showed high activity after fourth re-use; We measured the BET surface area, pore volume and the pore sizes of the silicas, and found that the BET surface area and pore volume decreased with repetition of the procedure. Thus, new Si–O bonds, which are formed by reaction of the silanol group on the sur-

Table 5. BET Surface Area and the Pore Size of FSM-16

$1b \xrightarrow[\text{MeOH, r.t., 4h}]{\text{FSM-16}} 2$				
Silica	Yield of 2 (%)	S_{BET} (m ² /g)	Pore volume (mm ³ /g)	Pore size (nm)
Control		1046	1404	2.7
1st	93	1111	1389	2.5
2nd	93	983	1217	2.5
3rd	90	983	1172	2.5
4th	72	934	1074	2.5
5th	88	944	1118	2.5

face of mesoporous silica with the silyl group eliminated from the substrate, is thought to reduce all of the values mentioned above. On the other hand, since changes in pore size could not be observed, deprotection of the silyl group is thought to occur in the pore, not on the surface of the mesoporous silicas.

Conclusion

In conclusion, we have studied application of mesoporous silicas to deprotection of silyl groups, and we successfully found selective deprotection of the TES group in the presence of a TBDMS group of mixed silyl ether of diols with reusable MCM-41/MeOH. Since this method requires only filtration to work-up, it is very attractive in viewpoint of synthetic organic chemistry and is environmentally benign.

Experimental

General THF was freshly distilled from Na metal/benzophenone ketyl. All other dry solvents were obtained from Kanto Kagaku Co., Ltd. Other chemicals used were of reagent grade and were obtained from Aldrich Chemical Co., Tokyo Kasei Kogyo Co., Ltd. and Wako Pure Chemical Industries, Ltd. H-ZSM-5 (Si/Al=150) was provided by N. E. Chemcat. Co., Tokyo, Japan. H-Y, Na-Y were purchased from TOSOH Co. SiO₂ (230–400 mesh) was purchased from Merck Co. Amberlite IR-120B and IRC-50 were purchased from Organo Co. All reactions were carried out under aerobic conditions. Compounds **4a**, **4c**, **4d** are commercially available, and **4b**,¹⁹⁾ **7**,²⁰⁾ **10**,²¹⁾ **13**,²²⁾ **16**²³⁾ are known compounds. ²⁹Si MAS NMR spectra were measured at 59.6 MHz on a JNM-CMX 300 (JEOL) solid state NMR spectrometer equipped with a magic angle spin probe. The quantitative determination of Q^2 , Q^3 and Q^4 sites was accomplished by deconvolution of the spectra. BET surface area, the pore size and the pore volume were measured by volumetric N₂-gas adsorption method with BELSORP-mini (BEL Japan, Inc.).

Synthesis of MCM-41 Tetraethylorthosilicate (20.8 g, 0.1 mol) was added by pipette to a solution of hexadecyltrimethylammonium bromide (7.3 g, 0.02 mol) and conc. HCl (8.3 ml, 0.1 mol) in H₂O (270 ml), and stirred for 48 h at r.t. The white precipitate was filtered and washed with dist. H₂O. The solid was dried at 120 °C for 12 h, and calcined at 650 °C for 4 h.

Synthesis of HMS A ethanol solution of tetraethylorthosilicate (20.8 g, 0.1 mol) was added to a suspension of dodecylamine (5.0 g, 0.027 mol) in H₂O (38 ml) under vigorous stirring for 1 h, and aged for 18 h at r.t. The white precipitate was washed with ethanol and H₂O, and calcined at 650 °C for 4 h.

Synthesis of FSM-16 Kanemite was prepared as paste by filtration of a suspension of sodium silicate (50 g) and dist. H₂O (500 ml), which was stirred for 3 h at r.t. Kanemite (as paste) was added to an aqueous solution (1 l) of hexadecyltrimethylammonium chloride (32 g, 0.1 mol), and stirred for 3 h at 70 °C. After adjusting the pH at 8.5 with 2 N dil. HCl, the suspension was further stirred for 3 h at 70 °C. The white precipitate was filtered, washed with dist. H₂O, dried at 60 °C for 12 h, and calcined at 550 °C for 5 h.

Synthesis of Disilylether To a solution of *tert*-butyldimethylsilylmoethoxy, triethylsilylchloride (1.1 eq) and imidazole (2.2 eq) in anhydrous dimethylformamide was added and stirred at r.t. for over night. The residue was dissolved in ether and the ether solution was washed with H₂O, brine

and dried with Na₂SO₄. The solution was concentrated under reduced pressure, and the residue was chromatographed on silica gel. The product was further purified by distillation under reduced pressure.

Typical Procedure A substrate (100 mg) and MCM-41 (300 mg) in MeOH (5 ml) was stirred for the indicated period of time at r.t. The reaction mixture was filtered through glass filter, and the pure products were obtained by preparative T.L.C.

Typical Procedure of Re-use of FSM-16 A suspension of *substrate* (50 mg) and FSM-16 (100 mg) in MeOH (5 ml) was stirred for 4 h at r.t. FSM-16 was then filtered off and washed with acetonitrile. The used FSM-16 was collected and re-calcined at 400 °C for 2 h by an electric furnace before being recycled.

1-*tert*-Butyldimethylsilyloxy-2-triethylsilyloxyethane (3b**):** ¹H-NMR (CDCl₃) δ : 0.06 (s, 6H, –Si–(CH₃)₂), 0.61 (q, J =7.8 Hz, 6H, –Si–(CH₂–CH₃)₃), 0.90 (s, 9H, –Si–*t*-Bu), 0.96 (t, J =7.8 Hz, 9H, –Si–(CH₂–CH₃)₃), 3.66 (t, J =5.4 Hz, 2H, CH₂–OSi–), 3.68 (t, J =5.4 Hz, 2H, CH₂–OSi–). IR (neat): 1255, 1145, 1099, 1006 cm^{–1}. Anal. Calcd for C₁₄H₃₄O₂Si₂: C, 57.87; H, 11.79. Found: C, 57.82; H, 11.94.

1-*tert*-Butyldimethylsilyloxy-3-triethylsilyloxypropane (3c**):** ¹H-NMR (CDCl₃) δ : 0.04 (s, 6H, –Si–(CH₃)₂), 0.59 (q, J =7.8 Hz, 6H, –Si–(CH₂–CH₃)₃), 0.89 (s, 9H, –Si–*t*-Bu), 0.95 (t, J =7.8 Hz, 9H, –Si–(CH₂–CH₃)₃), 1.73 (quint, J =6.4 Hz, 2H, –CH₂–CH₂–CH₂–), 3.69 (t, J =6.4 Hz, 4H, –O–CH₂–CH₂–CH₂–O–). IR (neat): 1255, 1095, 1047, 1006 cm^{–1}. Anal. Calcd for C₁₅H₃₆O₂Si₂: C, 59.14; H, 11.91. Found: C, 58.64; H, 12.08. HR-MS (EI). Calcd for C₁₅H₃₁O₂Si₂ (M⁺–Et): 275.1877. Found: 275.1857.

1-*tert*-Butyldimethylsilyloxy-4-triethylsilyloxybutane (3a**):** ¹H-NMR (CDCl₃) δ : 0.04 (s, 6H, –Si–(CH₃)₂), 0.59 (q, J =7.8 Hz, 6H, –Si–(CH₂–CH₃)₃), 0.89 (s, 9H, –Si–*t*-Bu), 0.96 (t, J =7.8 Hz, 9H, –Si–(CH₂–CH₃)₃), 1.56 (4H, –O–CH₂–(CH₂)₂–CH₂–O–), 3.62 (4H, –O–CH₂–(CH₂)₂–CH₂–O–). IR (neat): 1255, 1201, 1097, 1008 cm^{–1}. HR-MS (FAB⁺). Calcd for C₁₆H₃₈O₂Si₂ (M⁺+1): 319.2527. Found: 319.2471.

1-*tert*-Butyldimethylsilyloxy-3-triethylsilyloxy-pentane (3d**):** ¹H-NMR (CDCl₃) δ : 0.04 (s, 6H, –Si–(CH₃)₂), 0.59 (q, J =7.8 Hz, 6H, –Si–(CH₂–CH₃)₃), 0.89 (s, 9H, –Si–*t*-Bu), 0.95 (t, J =7.8 Hz, 9H, –Si–(CH₂–CH₃)₃), 1.38 (quint, J =8.3 Hz, 2H, –(CH₂)₂–CH₂–(CH₂)₂–), 1.53 (4H, –O–CH₂–CH₂–CH₂–CH₂–O–), 3.60 (t, J =6.3 Hz, 4H, –O–CH₂–(CH₂)₃–CH₂–O–). IR (neat): 1255, 1100, 1049, 1006 cm^{–1}. Anal. Calcd for C₁₇H₄₀O₂Si₂: C, 61.38; H, 12.12. Found: C, 61.20; H, 12.07.

1-*tert*-Butyldimethylsilyloxy-4-triethylsilyloxy-2-butyne (6**):** ¹H-NMR (CDCl₃) δ : 0.11 (s, 6H, –Si–(CH₃)₂), 0.65 (q, J =7.8 Hz, 6H, –Si–(CH₂–CH₃)₃), 0.90 (s, 9H, –Si–*t*-Bu), 0.97 (t, J =7.8 Hz, 9H, –Si–(CH₂–CH₃)₃), 4.34 (s, 4H, –O–CH₂–C≡C–CH₂–O–). IR (neat): 1255, 1135, 1097, 1071, 1006 cm^{–1}. Anal. Calcd for C₁₆H₃₄O₂Si₂: C, 61.08; H, 10.89. Found: C, 60.51; H, 11.05. HR-MS (EI). Calcd for C₁₄H₂₉O₂Si₂ (M⁺–Et): 285.1718. Found: 285.1702.

1-*tert*-Butyldimethylsilyloxy-4-triethylsilyloxy-2-butene (9**):** ¹H-NMR (CDCl₃) δ : 0.07 (s, 6H, –Si–(CH₃)₂), 0.61 (q, J =7.8 Hz, 6H, –Si–(CH₂–CH₃)₃), 0.90 (s, 9H, –Si–*t*-Bu), 0.96 (t, J =7.8 Hz, 9H, –Si–(CH₂–CH₃)₃), 4.22 (d, J =2.0 Hz, 2H, –CH₂–O–Si–), 4.23 (d, J =2.0 Hz, 2H, –CH₂–O–Si–), 5.55–5.57 (2H, –H–C=C–H–). IR (neat): 1255, 1085, 1006, 745 cm^{–1}. Anal. Calcd for C₁₆H₃₆O₂Si₂: C, 60.49; H, 11.46. Found: C, 60.43; H, 11.54.

1-(*tert*-Butyldimethylsilyloxymethyl)-4-triethylsilyloxymethylbenzene (12**):** ¹H-NMR (CDCl₃) δ : 0.09 (s, 6H, –Si–(CH₃)₂), 0.64 (q, J =7.8 Hz, 6H, –Si–(CH₂–CH₃)₃), 0.93 (s, 9H, –Si–*t*-Bu), 0.97 (t, J =7.8 Hz, 9H, –Si–(CH₂–CH₃)₃), 4.72 (s, 2H, Ph–CH₂–O–Si–), 4.73 (s, 2H, Ph–CH₂–O–Si–), 7.29–7.31 (4H, ArH). IR (neat): 1253, 1213, 1087, 1017, 1006, 742, 668 cm^{–1}. Anal. Calcd for C₂₀H₃₈O₂Si₂: C, 65.51; H, 10.44. Found: C, 65.22; H, 10.31.

2-*tert*-Butyldimethylsilyloxy-3-triethylsilyloxybutane (15**):** ¹H-NMR (CDCl₃) δ : 0.05 (s, 6H, –Si–(CH₃)₂), 0.60 (q, J =7.8 Hz, 6H, –Si–(CH₂–CH₃)₃), 0.88 (s, 9H, –Si–*t*-Bu), 0.96 (t, J =7.8 Hz, 9H, –Si–(CH₂–CH₃)₃), 1.11 (d, J =2.4 Hz, 3H, CH₃), 1.13 (d, J =2.4 Hz, 3H, CH₃), 3.50–3.55 (2H, –O–CH–CH–O–). IR (neat): 1253, 1170, 1114, 1084, 1036, 1006 cm^{–1}. Anal. Calcd for C₁₆H₃₈O₂Si₂: C, 60.31; H, 12.02. Found: C, 59.94; H, 12.09. HR-MS (EI). Calcd for C₁₄H₃₃O₂Si₂ (M⁺–Et): 289.2054. Found: 289.2027.

References and Notes

- Greene T. W., Wuts P. G. M., "Protective Groups in Organic Synthesis," 2nd ed., Wiley, N. Y., 1991, p. 68.
- Sheldon R. A., *Chemtech*, **24**, 38–47 (1994).
- IUPAC recommends classification of pores to micropore ($D < 2$ nm; D , pore diameter) and mesopore ($2 \text{ nm} < D < 50 \text{ nm}$), see: Everett D. H., *Pure Appl. Chem.*, **31**, 579–638 (1972).
- Kresge C. T., Leonowicz M. E., Roth W. J., Vartul J. C., Beck J. S., *Nature* (London), **359**, 710–712 (1992).

- 5) MCM-41 was prepared according to the literature: Zhang W., Froba M., Wang J., Tanev P. T., Wong J., Pinnavaia T. J., *J. Am. Chem. Soc.*, **118**, 9164—9171 (1996).
- 6) Toshima K., Mukaiyama S., Kinoshita M., Tatsuta K., *Tetrahedron Lett.*, **30**, 6413—6416 (1989).
- 7) Boschelli D., Takemasa T., Nishitani Y., Masamune S., *Tetrahedron Lett.*, **26**, 5239—5242 (1985).
- 8) Collington E. W., Finch H., Smith I. J., *Tetrahedron Lett.*, **26**, 681—684 (1985).
- 9) Hart T. W., Metcalfe D. A., Scheinmann F., *J. Chem. Soc., Chem. Commun.*, **1979**, 156—157 (1979).
- 10) Inagaki S., Koiwai A., Suzuki N., Fukushima Y., Kuroda K., *Bull. Chem. Soc. Jpn.*, **69**, 1449—1457 (1996).
- 11) Inagaki S., Fukushima Y., Kuroda K., *J. Chem. Soc., Chem. Commun.*, **1993**, 680—682 (1993).
- 12) Tanev P. J., Pinnavaia T. J., *Science*, **267**, 865—867 (1995).
- 13) The silica gel (Merck Silica gel 60, 9385, 230—400 mesh ASTM), which was pretreated with 1 N HCl aq., washed with water, and dried at 80 °C under reduced pressure, was used in this study.
- 14) H-ZSM-5 zeolite (Si/Al=150) was provided by N. E. Chemcat Co., Tokyo, Japan.
- 15) H-Y and Na-Y zeolite were purchased from Tosoh Co., Tokyo, Japan.
- 16) Silica consists of the unit of the composition shown with $\text{Si}(\text{OSi})_n(\text{OH})_{4-n}$, and, in general, shows this by Q^n , see: Thomas J. M., Klinowski J., *Adv. Catal.*, **33**, 199—374 (1985).
- 17) Halpaap H., “Einführung in die HPDC,” ed. by Kaiser R. E., Verlag/Bad, Dürkheim, 1976.
- 18) Inaki Y., Yoshida H., Kimura K., Inagaki S., Fukushima Y., Hattori T., *Phys. Chem. Chem. Phys.*, **2**, 5293—5297 (2000).
- 19) McDougal P. G., Rico J. G., Oh Y.-I., Condon B. D., *J. Org. Chem.*, **51**, 3388—3390 (1986).
- 20) Irie H., Matsumoto K., Kitagawa T., Zhang Y., *Chem. Pharm. Bull.*, **38**, 1451—1461 (1990).
- 21) Hull H. M., Knight D. W., *J. Chem. Soc., Perkin Trans. 1*, **1997**, 857—863 (1997).
- 22) Pilcher A. S., Hill D. K., Shimshock S. J., Waltermire R. E., DeShong P., *J. Org. Chem.*, **57**, 2492—2495 (1992).
- 23) Cainelli G., Giacomini D., Perciaccante F., Trere A., *Tetrahedron: Asymmetry*, **5**, 1913—1916 (1994).