Organic−Inorganic Hybrid Zeolites with Framework Organic Groups

Katsutoshi Yamamoto,[†,‡] Yuki Nohara,[§] Yusuke Domon,[§] Yoko Takahashi,[§]
Yasuyuki Sakata,[||,⊥] Jacques Plévert,[†,#] and Takashi Tatsumi*[,§]

Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan; Division of Materials Science & Engineering, Graduate School of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan; and Yokohama Laboratory, CACs, Inc., 1000 Kamoshida-cho, Aoba-ku, Yokohama 227-0033, Japan

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A novel type of organic−inorganic hybrid zeolite has been successfully synthesized, in which lattice oxygen atoms are partially superseded by methylene groups. Various types of hybrid materials with the LTA, MFI, and *BEA structures are obtained from an organosilane in which a methylene group bridges two silicon atoms under synthesis conditions similar to those for conventional zeolites. The presence of a methylene group in the framework is demonstrated by ^{29}Si and ^{13}C MAS NMR and IR, although the Si−C bonds are partially cleaved during the hydrothermal synthesis to give rise to terminal methyl groups. The organic framework is thermally stable enough to remain after the combustion of the occluded organic structure directing agents (SDAs). The thermal stability of the organic framework is much higher than that in amorphous materials synthesized from the same silicon source and is dependent on the zeolite structures. The SDA-free materials not only show microporosity like ordinary zeolites but also exhibit distinctively high lipophilicity/hydrophobicity in a shape-selective way. These findings clearly indicate that these materials are not physical mixtures of conventional inorganic zeolites and amorphous organic-containing materials but contain true organic−inorganic hybrid zeolites.

Introduction

The realm of zeolites has been extended by the emergence of innovative synthetic materials. Since the first discovery in 1756, zeolites had been generally regarded for a long time as microporous crystalline aluminosilicates having ion-exchangeable cations and reversibly desorbable water molecules, after the characteristics of natural zeolites.[1] In 1978, however, a purely siliceous MFI-type zeolitic material silicalite[2] was synthesized; this aluminum-free material does not have an ion-exchanging ability and shows hydrophobicity, in marked contrast to aluminum-rich zeolites. In 1982, researchers at Union Carbide succeeded in synthesizing microporous phosphate-based materials $AlPO_4$[3,4] by incorporating phosphorus atoms into the framework. This series of materials was also electrostatically neutral, and a lot of new framework types were discovered by taking this approach.[3−5]

Various other heteroatoms can be introduced into the framework of zeolites. Ti-containing zeolites, particularly the MFI-type material TS-1,[6] have achieved a great success as highly active oxidation catalysts. Besides these, B-, Ga-, Fe-, and Ge-containing materials were successfully synthesized and characterized in detail. It is to be noted that a lot of new topologies have been discovered by introducing heteroatoms as tetrahedrally coordinated elements. The International Zeolite Association has approved several tens of framework types which were newly synthesized by introducing heteroatoms such as Co, Mg, Be, or Zn in oxide-based or phosphate-based materials.[7] It has been also proposed that the incorporation of Li into the framework gives other new framework types.[8,9] Furthermore, a new framework type material consisting only of germanium oxide was recently synthesized.[10]

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* Corresponding author. E-mail: ttatsumi@cat.res.titech.ac.jp. Current address: Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan.

[†] The University of Tokyo

[‡] Current address: Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan.

[§] Yokohama National University.

[||] CSCs Inc.

[⊥] Current address: Mitsubishi Chemical Group, Science and Technology Research Center, Inc., Yokkaichi 510-8530, Japan.

[#] Current address: Institute of Environmental Science and Engineering, Nanyang Technological University, Singapore 637723, Singapore.

(1) For example, see: Dyer, A. *An Introduction to Zeolite Molecular Sieves;* John Wiley & Sons: New York, 1988; p 1.

(2) Flanigen, E. M.; Bennett, J. M.; Grose, R. W.; Cohen, J. P.; Patton, R. L.; Kirchner, R. M.; Smith, J. V. *Nature* **1978**, *271*, 512.

(3) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 1146.

(4) Flanigen, E. M.; Lok, B. M.; Patton, R. L.; Wilson, S. T. *New Development in Zeolite Science and Technology, Proceedings of the 7th International Zeolite Conference;* Kodansha: Tokyo 1986; p 103.

(5) Davis, M. E.; Saldarriaga, C.; Montes, C.; Garces, J.; Crowder, C. *Nature* **1988**, *331*, 698.

(6) Tramasso, M.; Perego, G.; Notari, B. U.S. Patent 4,410,501, 1983.

(7) Baerlocher, Ch.; Meier, W. M.; Olson, D. H. *Atlas of Zeolite Framework Types,* 5th revised ed.; Elsevier: Amsterdam, 2001.

(8) Park, S. H.; Daniels, P.; Gies, H. *Microporous Mesoporous Mater.* **2000**, *37*, 129.

(9) Park, S. H.; Parise, J. B.; Gies, H.; Liu, H. M.; Grey, G. P.; Toby, B. H. *J. Am. Chem. Soc.* **2000**, *122*, 11023.

(10) Conradsson, T.; Dadachov, M. S.; Zou, X. D. *Micropor. Mesopor. Mater.* **2000**, *41*, 183.

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In this way, a lot of novel materials, which were beyond the original definition of zeolite, were synthesized by using various tetrahedrally coordinated atoms to be incorporated into the framework. As a result, zeolites are currently defined as "open 4-connected 3D nets which have the general (approximate) composition AB_2, where A is a tetrahedrally connected atom and B is any 2-connected atom, which may or may not be shared, between two neighboring A atoms." [7]

Here we report a new class of materials, ZOL (zeolite with organic groups as lattice), in which a methylene group is incorporated in the framework as a 2-connected species.[11,12] ZOL materials are the first organic−inorganic hybrid composite in which an organic group is incorporated into a crystalline microporous material not as a pendant functional group but as part of the framework. Organic−inorganic hybrid zeolites of this type are synthesized from an organosilane having a bridging methylene group between two silicon atoms to be substituted for a siloxane bridge. The typical bond length of Si−C is 1.88 Å, which is longer than that of Si−O (∼1.6 Å). However, the Si−C−Si angle (∼109°) is usually smaller than the Si−O−Si angles; for example, those in MFI-type zeolite range from 140° to 170°.[13] This smaller bond angle would compensate for the distance of two silicon atoms to enable the crystallization of this new type of hybrid zeolitic material. It is noteworthy that Astala and Auerbach have very recently demonstrated the high structural stability of methylene introduced in the LTA and SOD framework based on a calculation using the density functional theory.[14]

Such organic functionalization can widen not only the realm of zeolites but also the range of their applications.[15] Jones et al. succeeded in synthesizing *BEA-type zeolites functionalized by terminal organic groups that were applied to shape-selective reactions.[16−20] This approach using an organosilane with a pendant organic group succeeded in adding new functions to the inorganic matrix. In the same way, the strategy of methylene-substitution for a lattice oxygen atom would be able to provide zeolites with new functions of organic groups as well as distinctively lipophilic/hydrophobic surface property.

Experimental Section

Synthesis. ZOL materials were synthesized by using bis(triethoxysilyl)methane (BTESM, Azmax) as a silicon source in which a methylene group bridges two Si atoms. $NaAlO_2$ (Al_2O_3 47.1 wt %, Na_2O 29.7 wt %) as an aluminum source and NaOH as an alkaline source were obtained from Nacalai-tesque and Koso, respectively. Tetrapropylammonium hydroxide (TPAOH, 20 wt % aqueous solution, TCI), triethylmethylammonium bromide (TEMABr, Fluka), and tetraethylammonium hydroxide (TEAOH, 35 wt % aqueous solution, Aldrich) were used as organic structure-directing agents (SDAs). All chemicals were used as received.

(a) ZOL-1 and ZOL-2. ZOL-1, a purely siliceous MFI-type ZOL material, was synthesized in the presence of TPAOH as an organic SDA. In the synthesis of ZOL-1, 6.11 g of BTESM was added to 16.95 g of 20 wt % aqueous solution of TPAOH and the mixture was stirred for 1 h. After the removal of ethanol by heating to 353 K, the mother gel with the molar composition of 1/0.47/21 Si:TPAOH:H_2O was transferred into a Teflon-lined stainless vessel and hydrothermally treated at 443 K for 5 days under tumbling condition to obtain ZOL-1. The mother gel of ZOL-2 was prepared by using TEMABr as an SDA and NaOH as an alkaline source in the same way as ZOL-1. The mother gel had the molar composition of 1/0.25/0.13/1 Si:TEMABr:Na_2O:H_2O. After the hydrothermal synthesis under static conditions at 413 K for 20 days, another purely siliceous MFI-type material ZOL-2 was obtained. The products were filtered, washed with deionized water, and dried under vacuum.

(b) ZOL-5. ZOL-5, an aluminosilicate form of an MFI-type ZOL material, was synthesized in the absence of organic SDA.[21] NaOH (0.093 g) and $NaAlO_2$ (0.195 g) were dissolved in 52.2 g of H_2O. To this solution was added dropwise 8.51 g of BTESM, and the resulting mixture was stirred for 1 h at room temperature. After the mixture became opaque, ethanol was removed by heating the solution to 353 K in a water bath. The resulting gel had the molar composition of 1/0.018/0.042/58 Si:Al_2O_3:Na_2O:H_2O. This mother gel was hydrothermally treated in a Teflon-lined stainless steel vessel at 463 K for 7 days under static condition to crystallize ZOL-5.

(c) ZOL-A. ZOL-A, a ZOL material with the LTA structure crystallized in the absence of organic SDA, was synthesized in a manner similar to its inorganic counterpart, zeolite A.[22] NaOH (2.21 g) was dissolved in 29.9 g of H_2O, and to this solution was added 8.51 g of BTESM. The resulting mixture was stirred overnight at room temperature to remove ethanol formed by the hydrolysis of BTESM. $NaAlO_2$ (5.63 g) and NaOH (2.21 g) were dissolved in 29.9 g of H_2O, and this solution was added to the Si-containing gel. The resulting gel, having the molar composition of 1/0.52/1.64/66.5 Si:Al_2O_3:Na_2O:H_2O was hydrothermally treated in a Teflon bottle at 373 K for 14 days under static conditions.

(d) ZOL-B(F) and ZOL-1(F). ZOL-B(F), a ZOL material with the *BEA structure, was synthesized in a fluoride medium[23] by using a mixture of BTESM and TEOS as a silicon source. In a typical synthesis, 1.70 g of BTESM and 8.34 g of TEOS (BTESM:TEOS 2/8 as Si) were added to 5.02 g of 35 wt % TEAOH aqueous solution at 273 K and stirred for 1 h. To this mixture was added zeolite beta seed crystals (SiO_2/Al_2O_3 = 25) corresponding to 5 mol % of total Si. After being stirred for another 1 h, the gel was heated at 353 K for 4 h to remove ethanol. Aqueous HF was added to this mixture at room temperature, and the resulting viscous gel with the molar composition of 1/0.54/0.54/7.63 Si:TEAOH:HF:H_2O was transferred into a Teflon-lined stainless vessel and hydrothermally treated under tumbling condition at 413

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(11) Yamamoto, K.; Takahashi, Y.; Tatsumi, T. *Stud. Surf. Sci. Catal.* **2001**, *135*, 299.

(12) Yamamoto, K.; Sakata, Y.; Nohara, Y., Takahashi, Y.; Tatsumi, T. *Science* **2003**, *300*, 470.

(13) Petrovic, I.; Navrotsky, A.; Davis, M. E.; Zones, S. I. *Chem. Mater.* **1993**, *5*, 1805.

(14) Astala, R.; Auerbach S. M. *J. Am. Chem. Soc.* **2004**, *126*, 1843.

(15) Wright, A. P.; Davis, M. E. *Chem. Rev.* **2002**, *102*, 3589.

(16) Jones, C. W.; Tsuji, K.; Davis, M. E. *Nature* **1998**, *393*, 52.

(17) Jones, C. W.; Tsuji, K.; Davis, M. E. *Proceedings of the 12th International Zeolite Conference*; Materials Research Society, 1999; p 1479.

(18) Tsuji, K.; Jones, C. W.; Davis, M. E. *Microporous Mesoporous Mater.* **1999**, *29*, 339.

(19) Jones, C. W.; Tsuji, K.; Davis, M. E. *Micropor. Mesopor. Mater.* **1999**, *33*, 223.

(20) Jones, C. W.; Tsapatsis, M.; Okubo, T.; Davis, M. E. *Microporous Mesoporous Mater.* **2001**, *42*, 21.

(21) Dai, F.-Y.; Deguchi, K.; Suzuki, M.; Takahashi, H.; Saito, Y. *Chem. Lett.* **1988**, 869.

(22) Robson, H.; Lillerud, K. P. *Verified Synthesis of Zeolitic Materials*, 2nd ed.; Elsevier: Amsterdam, **2001**, 179.

(23) Blasco, T.; Camblor, M. A.; Corma, A.; Esteve, P.; Guil, J. M.; Martinez, A.; Perdigon-Melon, J. A.; Valencia, S. *J. Phys. Chem. B* **1998**, *102*, 75.

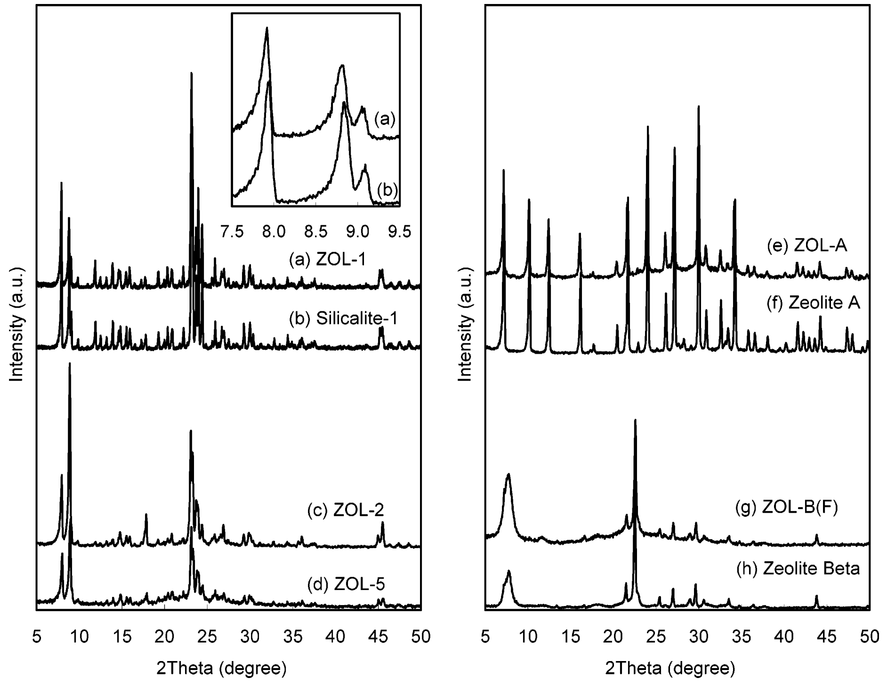

Figure 1. Powder XRD patterns of as-synthesized ZOL materials and their inorganic counterparts: (a) ZOL-1, (b) silicalite-1, (c) ZOL-2, (d) ZOL-5, (e) ZOL-A, (f) zeolite A, (g) ZOL-B(F), and (h) zeolite beta.

K for 14 days to obtain ZOL-B(F). An MFI-type ZOL material also synthesized in a fluoride medium, ZOL-1(F), was crystallized in a similar way, except for the use of silicalite-1 seed crystals and TPAOH.

(e) Methylated Zeolites. For a control, zeolite materials functionalized with methyl groups were synthesized from an equimolar mixture of TEOS and methyltriethoxysilane (MTES, TCI) as silicon sources. Methylated zeolite materials synthesized in the same way as ZOL-1, ZOL-5, and ZOL-A, except for the silicon source, are designated as Me-silicalite-1, Me-ZSM-5, and Me-A, respectively.

Characterization. Powder X-ray diffraction (XRD) patterns were collected with a MAC Science MX Labo diffractometer using Cu Kα irradiation. Scanning electron microscopy (SEM) images were taken with a JEOL VXA8900RL microscope. Induced coupled plasma (ICP) and C, H, N elemental analyses were conducted by a Shimadzu ICPS-8000E spectrometer and a Perkin-Elmer 2400 series II CHNS/O analyzer, respectively. Infrared (IR) spectra were obtained with a Perkin-Elmer 1600 series spectrometer. Thermogravimetric and differential thermal analyses (TG-DTA) were conducted in an air stream with a Rigaku Thermoplus TG 8120 analyzer.

^{13}C and ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) measurements were made at room temperature with JEOL JNM-LA400WB and JNM-ECA400 spectrometers operating at 100.563 and 75.57 MHz for ^{13}C and ^{29}Si, respectively. The ^{13}C cross-polarization (CP)/MAS measurements were made with the contact time of 1 ms. The sample spinning rate was 5 kHz.

Adsorption measurements were conducted with Bel Japan Belsorp 28SA and 18 apparatuses. For the LTA type materials, samples were ion-exchanged with 1 M $CaCl_2$ before adsorption measurements. ICP analyses of ion-exchanged materials proved that more than 96% of Na^+ was exchanged for Ca^{2+}. Nitrogen adsorption isotherms were obtained at 77 K after the pretreatment at 473 K under vacuum. Pore volumes were estimated on the basis of the *t*-plot of isotherms. Benzene and *n*-hexane adsorption isotherms were collected for Ca^{2+}-exchanged LTA-type materials at 298 K. Samples were exposed to moisture over a saturated aqueous solution of NH_4Cl at room temperature for 48 h and pretreated at 323 or 473 K under vacuum for 10 h immediately before adsorption measurements. The adsorption properties for *n*-hexane and benzene were evaluated on the basis of the adsorption capacity at 10 Torr of *n*-hexane or benzene vapor pressure, where the adsorption isotherms were flat and the adsorption capacity did not exceed the pore volume.

Results and Discussion

Figure 1 exhibits the powder XRD patterns of as-synthesized ZOL materials and their inorganic counterparts synthesized from TEOS as a silicon source. Obviously, ZOL materials exhibit diffraction patterns similar to those of corresponding conventional zeolites with the MFI, LTA, and *BEA structures, although low and broad peaks around $2\theta = 30°$ in ZOL-A and 23° in ZOL-B(F) suggest the presence of amorphous products as concomitant phases. The unit cell size of as-synthesized ZOL-1 based on its diffraction pattern is estimated as $a = 20.05$ Å, $b = 19.94$ Å, $c = 13.40$ Å, slightly larger than that of silicalite-1,[24] probably because of the insertion of longer $Si-CH_2-Si$ fragments.

Figure 2 shows the SEM images of ZOL materials. MFI-type ZOL materials, ZOL-1, ZOL-2, and ZOL-5, exhibit a coffin-like crystal shape, which is a morphology typical of conventional MFI-type zeolites. The cubic crystal shape of ZOL-A is also typical of LTA-type materials, although ZOL-A has a somewhat rounded crystal shape.

Figure 3 shows the ^{13}C CP/MAS NMR spectra of as-synthesized ZOL materials. In the spectrum of ZOL-1, together with three peaks attributable to carbon species in occluded SDA (tetrapropylammonium cation), a peak is clearly observed around 0 ppm. This peak is assignable to carbon species directly bonded to Si, indicating the incor-

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[24] Treacy, M. M. J.; Higgins, J. B. *Collection of Simulated XRD Powder Patterns of Zeolites,* 4th ed., Elsevier: Amsterdam, 2001; p 234.

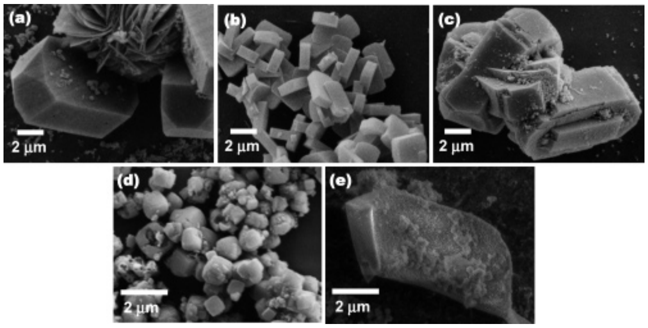


Figure 2. SEM images of (a) ZOL-1, (b) ZOL-2, (c) ZOL-5, (d) ZOL-A, and (e) ZOL-B(F).

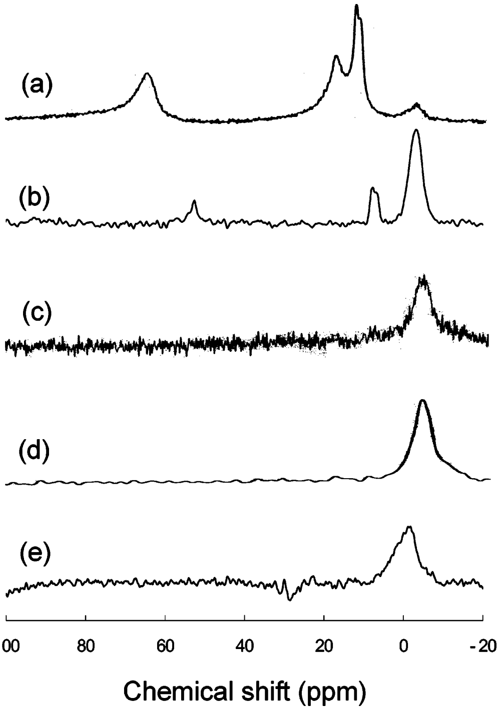


Figure 3. ^{13}C CP/MAS NMR spectra of (a) ZOL-1, (b) ZOL-B(F), (c) ZOL-5, (d) ZOL-2, and (e) ZOL-A. Chemical shifts are given in ppm from TMS.

poration of Si-bonded carbon species derived from the silicon source. Such a resonance peak is also observed for other ZOL materials synthesized in the presence or absence of SDAs to prove the presence of organic−inorganic hybrid structure. It is to be noted that ZOL-2 exhibits no peaks attributable to SDAs, which suggests that this pure silica MFI-type zeolite is crystallized without occluding SDA molecules.

The ^{29}Si dipolar decoupling (DD)/MAS NMR spectrum of as-synthesized ZOL-A (Figure 4a) exhibits a group of resonance peaks around −60 ppm that are not observed for zeolite A (Figure 4c). These peaks are assigned to T-type silicon species, namely silicon species having a Si−C bond, certifying the presence of organically modified silicon species in this material. Other ZOL materials also show such peaks assignable to T-type silicon species (^{29}Si DD/MAS NMR spectra of other ZOL materials are shown below).

The ^{29}Si DD/MAS NMR spectrum of ZOL-A also displays large resonance peaks attributable to inorganic silicon species such as Si(4Al) and Si(3Al). Considering that ZOL-A is synthesized only from BTESM that does not contain such inorganic species, these peaks indicate the formation of inorganic silicon species through the cleavage of the Si−CH_2−Si linkage derived from BTESM during the hydrothermal treatment. This inorganic silicon species would be introduced into ZOL materials through the cocrystallization with organically functionalized silicon species. In accordance with the finding in the NMR spectrum, the C, H, N analysis estimated the carbon content of ZOL-A at 2.2 wt %, which is lower than the calculated value for a product ideally synthesized from BTESM alone (4.3 wt % for $NaSiAlO_{3.5}(CH_2)_{0.5}$). Nevertheless, the ^{29}Si MAS NMR estimated the percentage of organically modified silicon species in ZOL-A at 30 atom % of total silicon, which is much higher than that of the formerly reported organically functionalized *BEA zeolite.[16,19]

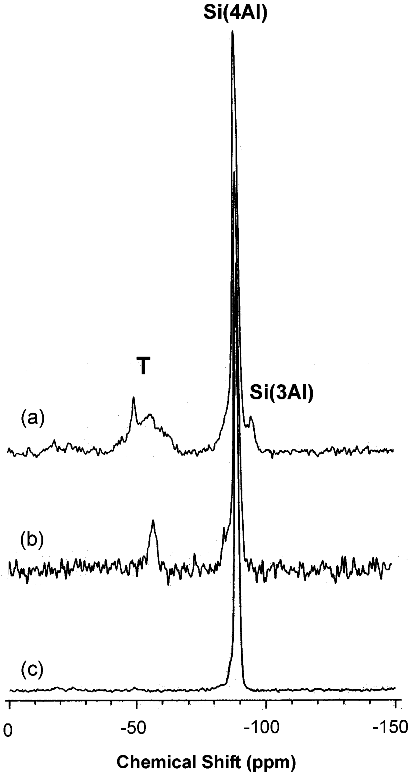


Figure 4. ^{29}Si DD/MAS NMR spectra of (a) ZOL-A, (b) Me-A, and (c) zeolite A. Chemical shifts are given in ppm from TMS.

It generally takes a long time for the crystallization of ZOL materials, compared with that of their inorganic counterparts. The crystallization of ZOL-A, for example, requires 14 days, while zeolite A synthesized from TEOS is crystallized in only 1 day under the same synthesis conditions. Presumably, a slightly longer Si−CH_2−Si fragment cannot be easily introduced into the crystalline zeolitic framework. Therefore, crystallized materials cannot be obtained until a certain amount of inorganic silicon source is formed through the decomposition of BTESM (Figure 5). In fact, ZOL-A can be obtained in 3 days when the mixture of TEOS and BTESM (TEOS:BTESM 4/1) is used as a silicon source, although naturally the carbon content becomes low (0.91 wt %). This could be also the reason neither ZOL-B(F) nor ZOL-1(F) can be obtained when BTESM alone is used as a silicon source, because the Si−CH_2−Si linkage is not cleaved in the nearly neutral fluoride media.

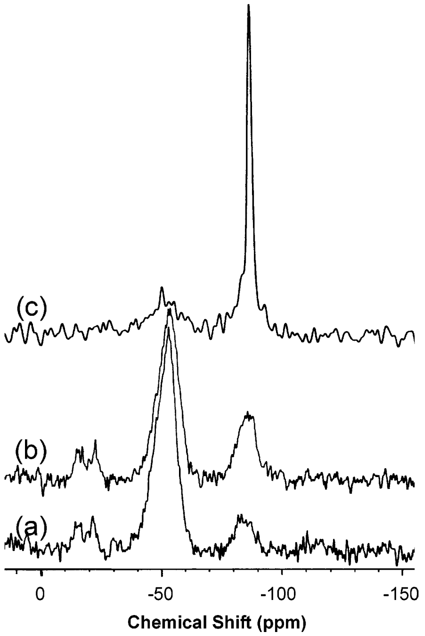


Figure 5. ^{29}Si DD/MAS NMR spectra of the products synthesized from BTESM after the hydrothermal treatment for (a) 3 days and (b) 7 days with an amorphous phase and (c) 14 days with the LTA phase (ZOL-A). Chemical shifts are given in ppm from TMS.

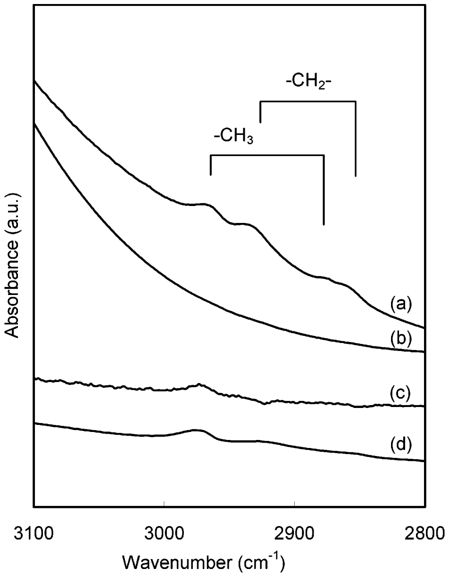


Figure 6. IR spectra of (a) ZOL-A, (b) zeolite A, (c) ZOL-2, and (d) ZOL-5.

Figure 6 shows the IR spectra of as-synthesized ZOL materials that contain no organic SDAs. In the spectra of ZOL-A (Figure 6a), peaks appear at 2938 and 2862 cm^{-1}, which are not observed in the spectrum of inorganic zeolite A (Figure 6b). These peaks are assigned to the asymmetric and symmetric C−H stretching vibration of $-CH_2-$ fragments, respectively. They clearly demonstrate the preservation of the $Si-CH_2-Si$ linkage, although the presence of $-CH_3$ groups is also suggested by the other two peaks at 2970 and 2880 cm^{-1}. Also in the IR spectra of ZOL-2 and ZOL-5, peaks attributable to both methylene and methyl groups are observed, although the peaks of the methylene groups around 2940 cm^{-1} are much smaller than those of the methyl group.

Table 1. Physical Properties of SDA-Free ZOL Materials

material	phase	Al/(Si + Al)	C content[a] (wt %)	V_p[b] (cm^3/g)
ZOL-2	MFI	0	1.9	0.092
ZOL-5	MFI	0.034	3.2	0.091
ZOL-A	LTA	0.45	2.2	0.20

[a] Carbon content estimated by C, H, N analyses. [b] Micropore volume based on the *t*-plot of the N_2 adsorption isotherm at 77 K.

Table 2. Adsorption Properties of ZOL-A and Zeolite A

material[a]	H_2O adsorbed at pretreatment temperature[b] (g of H_2O/g of zeolite)	adsorption capacity (mL of liquid/g of zeolite)[c] *n*-hexane	benzene
	pretreated at 473 K		
ZOL-A (0.20)	0.023	0.059	0.0043
zeolite A (0.25)	0.042	0.078	0.0010
	pretreated at 323 K		
ZOL-A (0.20)	0.191	0.028	0.0019
zeolite A (0.25)	0.241	0.0069	0.0016

[a] Values in parentheses indicate the micropore volume estimated on the basis of the *t*-plot of the N_2 adsorption isotherm at 77 K. [b] Values are estimated by the TG analyses for water adsorbed materials treated in saturated water vapor at room temperature. [c] Adsorption capacity for *n*-hexane or benzene at 298 K at 10 Torr.

These SDA-free ZOL materials exhibit microporosity like conventional zeolites, as exhibited in Figure 7 and Table 1. The N_2 adsorption/desorption isotherms of as-synthesized ZOL-A and ZOL-5 prepared in the absence of SDAs show a large adsorption step around $P/P_0 = 0$, clearly indicating the presence of micropores. The micropore volumes estimated on the basis of the *t*-plot seem smaller than those of conventional zeolites, which would be due to concomitant amorphous phases and/or the larger size of the CH_2 group versus that of the bridging oxygen. ZOL-2 also shows microporosity without any template removal procedures, in accordance with its ^{13}C CP/MAS NMR spectrum.

Table 2 compares the adsorption properties of Ca^{2+}-exchanged ZOL-A and zeolite A. For these materials, *n*-hexane and benzene adsorption are measured after the water adsorption followed by the thermal pretreatment under vacuum. When pretreated at 473 K, both ZOL-A and zeolite A desorb most of the water molecules adsorbed, so they can show large adsorption capacities for *n*-hexane in proportion to their pore volumes, indicating that *n*-hexane is mainly adsorbed inside the pores. After the pretreatment at 323 K, however, the amount of water on ZOL-A would be much smaller than that on zeolite A, presumably owing to the higher hydrophobicity caused by the presence of an organic framework. As a result, ZOL-A adsorbs much larger amounts of *n*-hexane than zeolite A. In contrast, ZOL-A can adsorb quite a small amount of benzene, because bulky benzene molecules cannot adsorb on the inner surface of ZOL-A. In this way, ZOL-A exhibits the high lipophilicity/hydrophobicity in a shape-selective way. This shape-selective lipophilicity/hydrophobicity suggests that organic moieties in ZOL-A exist not outside of the pore as a separate phase but inside the pore as a framework.

It is of interest that the thermal stability of the organic framework is much improved when it is incorporated into ZOL materials. Figure 8 shows the DTA profiles of ZOL-A materials synthesized from the mixture of BTESM and TEOS (BTESM:TEOS 1/4) together with their XRD patterns. When

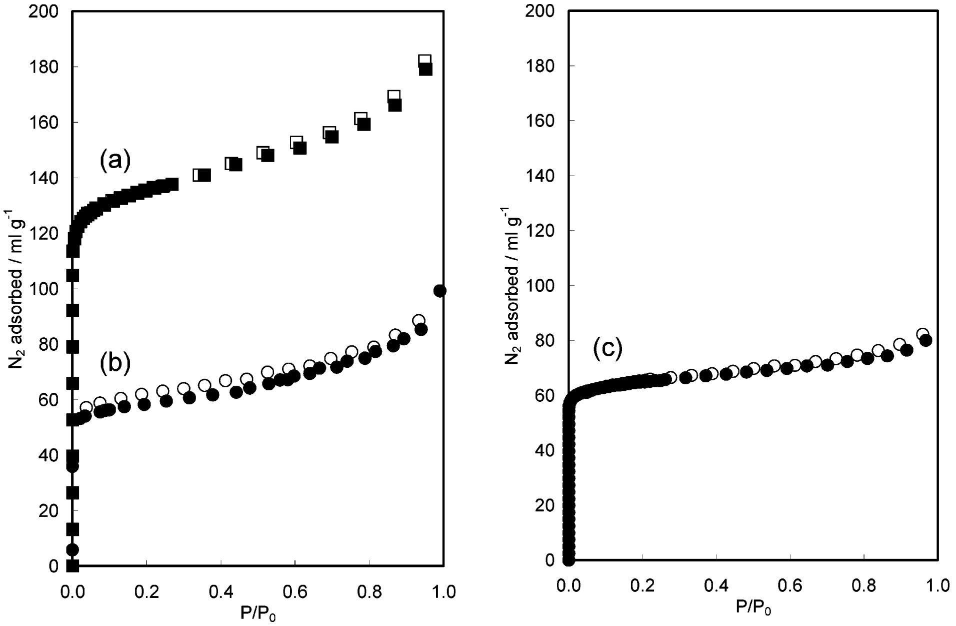


Figure 7. N_2 adsorption/desorption isotherms of as-synthesized ZOL materials at 77 K: (a) ZOL-A, (b) ZOL-5, and (c) ZOL-2.

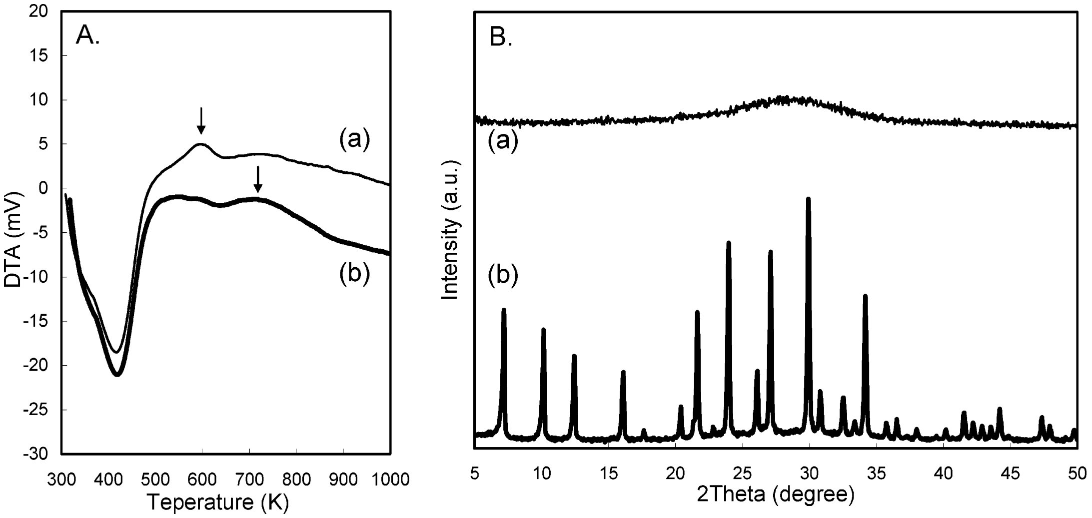


Figure 8. (A) DTA curves of ZOL-A synthesized from the mixtuire of BTESM and TEOS (BTESM:TEOS 1/4) for (a) 1 day and (b) 3 days and (B) XRD patterns of the corresponding materials.

Table 3. Thermal Stability of the Organic Framework

material	phase	occluded organic SDA	exothermic peak[a] (K)
ZOL-1	MFI	TPA	920
ZOL-1(F)	MFI	TPA	909
ZOL-2	MFI		825
ZOL-5	MFI		811
ZOL-A	LTA		725
ZOL-B(F)	*BEA	TEA	929

[a] Peak top temperature of the DTA exothermic peak attributable to the combustion of the organic framework.

the synthesis time is 1 day, the obtained material is amorphous, and the exothermic DTA peak is observed at 600 K. After 3 days the LTA-type material is crystallized, and the exothermic peak attributable to the combustion of organic moieties appears at higher temperature, indicating the higher thermal stability of organic moieties in crystalline ZOL-A. Table 3 exhibits the exothermic peak temperature assignable to the combustion of organic framework in as-synthesized ZOL materials, suggesting that framework organic groups in ZOL materials have proved generally thermally stable. It is also to be noted that the combustion resistance of the framework organic group is explicitly dependent on the structure of the material. These findings demonstrate that organic moieties are mainly involved not in a concomitant amorphous material but in a zeolite framework.

The use of seed crystals promotes the crystallization of ZOL materials. In the absence of seed crystals, ZOL-B(F) is not crystallized until 2 months under the same hydrothermal conditions. When seed crystals are used in the synthesis of ZOL-1, the organic content, calculated by reducing the contributions from SDAs, is increased from 1.0 to 3.3 wt %. Simultaneously, the XRD peak positions shift to a lower angle (Figure 9), implying a further unit cell expansion resulting from the insertion of larger amounts of organic framework.

Ti atoms can be introduced into the framework of ZOL materials. Figure 10 shows the UV−vis spectrum of Ti-

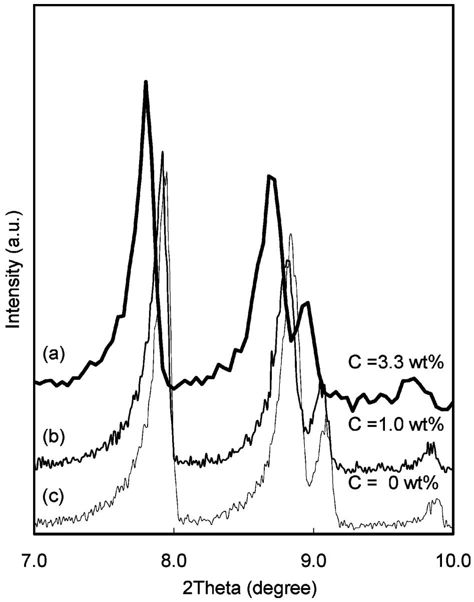


Figure 9. Low-angle XRD patterns of as-synthesized ZOL-1 prepared in the (a) presence and (b) absence of seed crystals and (c) silicalite-1.

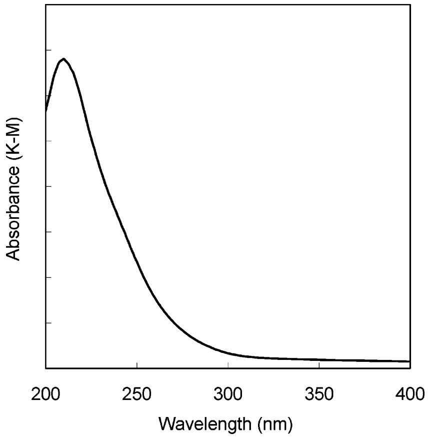


Figure 10. UV−vis spectrum of Ti-containing ZOL-1(F). TEOS:BTESM in mother gel is 4/1 (as Si).

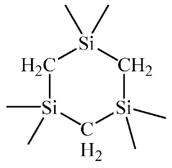
containing ZOL-1(F) synthesized from a mother gel with tetrabutyl orthotitanate as a Ti source (Si/Ti = 50). A peak at 210 nm clearly indicates the successful incorporation of Ti into the framework of ZOL-1(F). Ti can be introduced also into ZOL-1 synthesized in alkaline medium and ZOL-B materials to show the potential for their catalytic applications.

A possible scheme for the crystallization of ZOL materials is illustrated in Figure 11. First, Si−CH_2−Si linkage in BTESM would be cleaved under the alkaline hydrothermal synthesis conditions. Si−C bonds are usually stable enough to be resistant to hydrolysis. Only in the case of Si−CH_2−Si, however, a vacant d orbital of a silicon atom can stabilize the neighboring carbanion, CH_2^-−Si, which is a possible intermediate species formed through the nucleophilic substitution by a hydroxyl anion. Then, the thus formed inorganic silicon species and organically functionalized species (Si−CH_2−Si or CH_3−Si) would cocrystallize to form ZOL materials. In contrast, in the fluoride medium fluoride anions can attack silicon atoms to form five-coordinated silicon species[25] without cleaving the Si−C bond. Accordingly, an inorganic silicon source such as TEOS must be added for the crystallization of ZOL materials.

Figure 12 compares the ^{29}Si DD/MAS NMR spectra of zeolite materials synthesized from methylene- or methyl-functionalized silicon sources. In contrast to ZOL-5, Me-ZSM-5, synthesized from an equimolar mixture of TEOS and MTES, does not exhibit T-type peaks. This finding means that organically functionalized silicon species incorporated into the framework of ZOL-5 are derived only from Si−CH_2−Si species. It is conceivable that Si−CH_2−Si fragments would be cleaved to form CH_3−Si species after its incorporation. On the other hand, T-type peaks are observed in the spectrum of Me-silicalite-1, which implies that both methylene- and methyl-functionalized silicon sources could be incorporated into the framework of ZOL-1 (Figure 12), as is the case of Me-A (Figure 4).

In this regard, it is noteworthy that the ^{29}Si NMR spectrum of ZOL-A has a peak at −94.5 ppm assignable to Si(3Al) (Figure 4). Since neither zeolite A nor Me-A shows this peak, the emergence of Si(3Al) species are caused by the incorporation of the Si−CH_2−Si fragment. When the Si−CH_2−Si fragment is introduced into the LTA framework, Si(3Al) species ($^{\#}$Si in Figure 11) would be formed by substituting the organically bonded Si for Al. The Si/Al ratio of ZOL-A is estimated at 1.2 by the ICP measurement, in accordance with this explanation. The absence of Si(3Al) species in Me-A suggests that the incorporated methylene linkage could be cleaved to form methyl groups after crystallization.

To date, we have not yet obtained a zeolitic material from other organically bridged organosilanes that have been used in the synthesis of inorganic−organic hybrid amorphous silica materials.[26−41] Presumably, long bridging organic groups cannot be incorporated into crystalline materials to be substituted for oxygen atoms. However, methylene-bridged three-membered ring (**1**)[42,43] or other similar subunits could be introduced into the framework.



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This leads to an expectation that the zeolite framework can be designed by building the structure with already-built favorable subunits, which could formulate a new strategy

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(25) Koller, H.; Wölker, A.; Villaescusa, L. A.; Díaz-Cabañas, M. J.; Valencia, S.; Camblor, M. A.; *J. Am. Chem. Soc.* **1999**, *121*, 3368.
(26) Shea, K. J.; Loy, D. A.; Webster, O. W. *Chem. Mater.* **1989**, *1*, 572.
(27) Corriu, R. J. P.; Moreau, J. J. E.; Thepot, P.; Man, M. W. C. *Chem. Mater.* **1992**, *4*, 1217.
(28) Loy, D. A.; Shea, K. J. *Chem. Rev.* **1995**, *95*, 1431.
(29) Shea, K. J.; Loy, D. A. *Chem. Mater.* **2001**, *13*, 3306.
(30) Inagaki, S.; Guan, S.; Fukushima, Y.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **1999**, *121*, 9611.
(31) Melde, B. J.; Holland, B. T.; Blanford, C. F.; Stein, A. *Chem. Mater.* **1999**, *11*, 3302.
(32) Asefa, T.; MacLachlan, M. J.; Coombs, N.; Ozin G. A. *Nature* **1999**, *402*, 867.
(33) Ishii, C. Y.; Asefa, T.; Coombs, N.; MacLachlan, M. J.; Ozin, G. A. *Chem. Commun.* **1999**, 2539.
(34) Lu, Y. et al. *J. Am. Chem. Soc.* **2000**, *122*, 5258.
(35) Guan, S.; Inagaki, S.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **2000**, *122*, 5660.

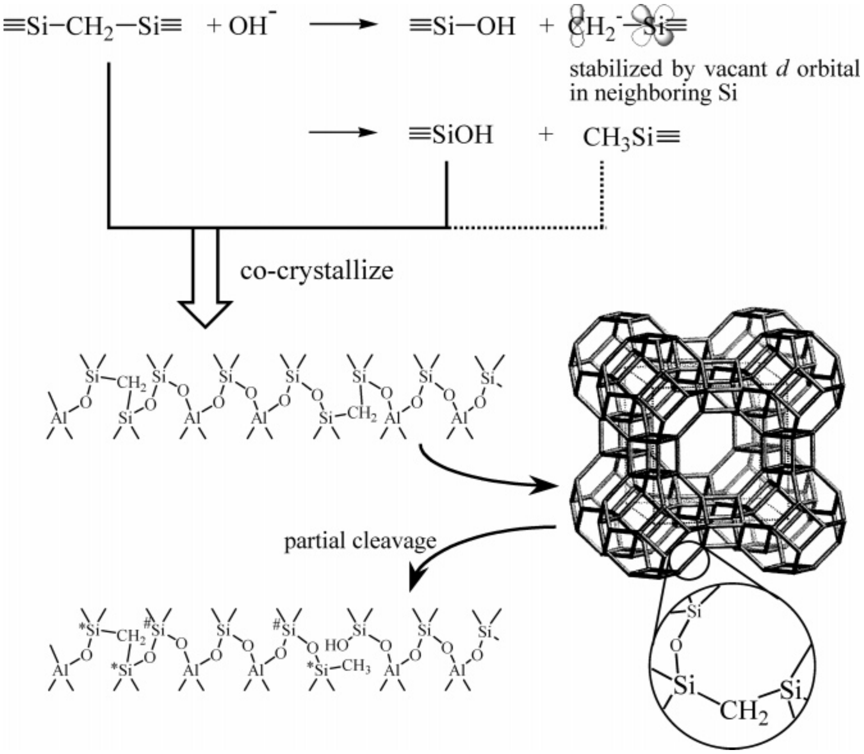

Figure 11. Possible crystallization scheme of ZOL materials. *Si: T^3 silicon species.

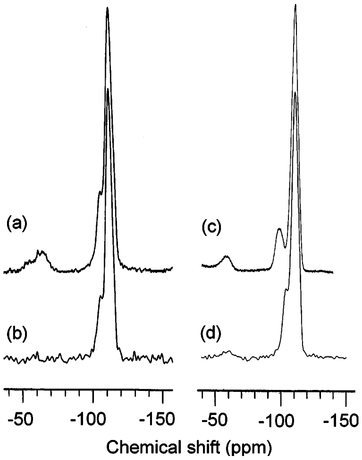

Figure 12. ^{29}Si DD/MAS NMR spectra of (a) ZOL-5, (b) Me-ZSM-5, (c) ZOL-1, and (d) Me-silicalite-1. Chemical shifts are given in ppm from TMS.

for synthesizing zeolites. Moreover, the incorporation of such organic−inorganic hybrid subunits could further extend the definition of zeolite by creating a new porous material that is not currently recognized as a “zeolite”.

Ongoing studies on the synthesis of a new type of organic−inorganic hybrid zeolite as well as those on the detailed analyses of the NMR and adsorption measurements will be published elsewhere.

Conclusion

Organic−inorganic hybrid zeolite materials were successfully synthesized by using a methylene-bridged organosilane as a silicon source and proved to possess methylene groups in the zeolitic lattice. Their surprisingly high thermal stability and shape-selective lipophilicity/hydrophobicity indicate that ZOL material is not a physical mixture of conventional zeolite and carbon-containing amorphous material but a genuine organic−inorganic hybrid crystalline zeolitic material. We believe that this method would be a general and highly promising way to synthesize organic−inorganic hybrid zeolites to be applied to new types of catalysts, adsorbents, and nanodevices.

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(36) Asefa, T.; MacLachlan, M. J.; Grondey, H.; Coombs, N.; Ozin G. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 1808.

(37) Asefa, T.; Ishii, C. Y.; MacLachlan, M. J.; Ozin, G. A. *J. Mater. Chem.* **2000**, *10*, 1751.

(38) Inagaki, S.; Guan, S.; Ohsuna, T., Terasaki, O. *Nature* **2002**, 416, 304.

(39) Yang, Q. H.; Kapoor, M. P.; Inagaki, S. *J. Am. Chem. Soc.* **2002**, *124*, 9694.

(40) Goto, Y.; Inagaki, S. *Chem. Commun.* **2002**, 2410.

(41) Kuroki, M.; Asefa, T.; Whitnal, W.; Kruk, M.; Yoshina-Ishii, C.; Jaroniec, M.; Ozin, G. A. *J. Am. Chem. Soc.* **2002**, *124*, 13886.

(42) Brondani, D. J.; Corriu, R. J. P.; Ayoubi, S. El; Moreau, J. E.; Man, M. W. C. *Tetrahedron Lett.* **1993**, *34*, 2111.

(43) Landskron, K.; Hatton, B. D.; Perovic, D. D.; Ozin G. A. *Science* **2003**, *302*, 266.