Cyclic diquaternary ammoniums for nanocrystalline BEA, MTW and MFI zeolites with intercrystalline mesoporosity

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Received 18th May 2009, Accepted 2nd July 2009
First published as an Advance Article on the web 4th August 2009
DOI: 10.1039/b909792a

3,10-Diazoniabicyclo[10.2.2]hexadeca-12,14,15-triene-3,3,10,10-tetramethyl-dichloride is an effective structure-directing agent for BEA zeolite under a high concentration of Na+. The pseudomorphic crystallization process led to nanocrystalline BEA particles possessing a large volume of intercrystalline mesopores. The synthesis of nanocrystalline zeolite has been extended to other cyclic diammonium compounds that can generate BEA, MTW and MFI zeolite structures. Phase diagrams for these nanocrystalline zeolites have been constructed using sodium silicate as a silica source. The nanocrystalline morphologies and intercrystalline mesoporosity have been characterized by electron microscopy and N2 adsorption. The result indicates that the pseudomorphic crystallization process is limited to BEA, and not MTW or MFI despite their nanocrystalline morphologies.

Introduction

Zeolites are a family of crystalline aluminosilicate molecular sieves built with uniform microporous channels and cavities on a molecular scale, and are widely used in heterogeneous catalysis, adsorption, ion exchange, and production of fine chemicals.1–4 Zeolites may be classified into aluminium-rich and high-silica groups according to the Si/Al ratios in their framework.4–6 Aluminium-rich zeolites are suitable as air separating media, ion adsorbents and detergent-builders due to the high concentration of ion exchange sites.2,4 On the other hand, high-silica zeolites are important as heterogeneous catalysts in petrochemical industries, such as oil refineries, and synthesis of value-added chemicals, owing to strong Brönsted acidity, high thermal stability, high affinity with organic compounds, as well as shape selectivity of the pore mouths.9–12 For instance, high-silica zeolites of the BEA and MFI structural types are well known for their excellent catalytic performances on the production of cumene and selective cracking of C5+, olefins, respectively.11,12

In recent years, zeolites with a morphology containing 3-dimensionally interconnected intra- or intercrystalline mesoporosity have attracted much attention, due to improved diffusion, catalytic activity, selectivity and lifetime.13–20 A number of studies have focused on the preparation of hierarchical zeolites, including mesopore generation with a hard template,13–15,19 use of organosilane surfactants as a soft template,17,18 packing of nanosized zeolite crystals,2 and demetallation of zeolites for post-synthetic generation of mesopores.16 In a recent study, Choi et al. synthesized a hierarchically porous BEA zeolite through the pseudomorphic transformation of mesoporous gel in the nanoscale. The mesoporous gel was rapidly generated when 3,10-diaziobicyclo[10.2.2]hexadeca-12,14,15-triene-3,3,10,10-tetra methyl-dichloride was added to a sodium silicate solution as a microporous BEA structure-directing agent (SDA).20 The generation of mesoporosity without the use of additional mesopore-directing agents was attributed to the particularly high affinity of the compound having an organic cyclic diammonium (CDM) structure with silicate species, and its effective structure-directing ability toward the BEA structure.

Here, the work of Choi et al. has been extended to other cyclic diammonium compounds that can generate BEA, MTW and MFI zeolite structures with nanocrystalline morphologies and intercrystalline mesoporosity. The following diammonium compounds were used in the present work: CDM1 was the same CDM compound used by Choi et al. The phenyl group in CDM1 was substituted by biphenyl in CDM2, and hexamethylene in CDM3, respectively. DM363 was an acyclic compound synthesized for comparison. These organic diammonium compounds were tested as zeolite SDAs under hydrothermal synthesis conditions using sodium silicate, similar to the work of Choi et al. The resultant zeolites were characterized by X-ray diffraction, N2 adsorption and electron microscopy. The effects of synthetic variables such as Si/Al molar ratio and the amount of sulfuric acid were investigated. Phase diagrams of the products including BEA, MTW, and MFI zeolites were constructed according to the synthesis result. In addition, particular attention was paid to the formation of hierarchical zeolites, in relation to the CDM structures. The influence of cyclic geometry on the formation of hierarchical structure was investigated through comparison with the synthesis results using an acyclic diammonium molecule (DM363).
Experimental

Syntheses of SDAs

CDM1, CDM2, and CDM3 were synthesized via one-step cyclization reactions. For CDM1 synthesis, 0.01 mol of \(N,N',N'\text{-tetramethyl-1,6-diaminohexane (Aldrich)}\) and 0.01 mol of \(\alpha,\alpha'\text{-dichloro-p-xylene (TCI)}\) were reacted in acetonitrile at 80 °C, with magnetic stirring for 6 h in a 250 mL round-bottomed flask. After cooling to room temperature, the product was filtered, washed with diethyl ether, and dried in a vacuum oven at 50 °C. CDM2 and CDM3 were synthesized in the same manner, except for the substitution of \(\alpha,\alpha'\text{-dichloro-p-xylene} \) by \(4,4'\text{-bis(chloromethyl)}-1,1'\text{-biphenyl (Aldrich)}\) and \(1,6\text{-dibromo-hexane (TCI)}\), respectively. DM363 was synthesized with 0.02 mol of 1-bromopropane (Aldrich) and 0.01 mol of \(N,N',N'\text{-tetramethyl-1,6-diaminohexane, under the same reaction condition used for CDM1.}\)

Syntheses of zeolites

Zeolite syntheses using the four organic SDAs described above were performed with a sodium-silicate water glass (29 wt% SiO\(_2\)), Si/Na = 1.75, Shinheung Silicate) as the silica source and \(\text{Al}_2(\text{SO}_4)\text{O}_3\cdot18\text{H}_2\text{O (Aldrich)}\) as the alumina source. The silica source was diluted with a dilute NaOH solution, yielding a sodium silicate solution with a molar ratio of 100 SiO\(_2\) : 30 Na\(_2\)O. The alumina source was dissolved in dilute sulfuric acid, to a molar ratio of \(x\text{Al}_2(\text{SO}_4)\text{O}_3 : y\text{H}_2\text{SO}_4 : 1500 \text{H}_2\text{O, where 0.5} \leq x \leq 5 \text{ and 10} \leq y \leq 25.\) The two solutions were mixed \(\text{via vigorous stirring at room temperature. The the resultant mixture was a clear solution. An organic SDA was added dropwise into this solution, under vigorous (magnetic or mechanical) stirring at room temperature. The mixture was gelated immediately with the addition of the SDA. The gel composition was represented as 30Na\(_2\)O : \(x\text{Al}_2\text{O}_3 : 100\text{SiO}_2 : 10\text{SDA: yH}_2\text{SO}_4 : 6000\text{H}_2\text{O in molar ratio, where the SDA was varied with CDM1, CDM2, CDM3, and DM363.}\)

After aging for 1 h at room temperature, the mixture was transferred to a Teflon-coated stainless-steel autoclave and heated at 170 °C under a tumbling condition (60 rpm). Precipitates were filtered, washed with deionized water, dried at 130 °C, and calcined at 550 °C for 4 h under flowing air. The calcined materials were designated as BEA-CDM1, BEA-CDM2, MTW-CDM1, etc. according to the zeolite structures and SDAs used for the syntheses.

Another set of BEA, MTW and MFI zeolite samples were obtained by following the synthesis procedures for conventional zeolites, as described in ref. 21, 22 and 23. These samples were designated as BEA-conv, MTW-conv and MFI-conv, respectively.

Characterization

The crystallinity and phase purity of precipitated solids were investigated by powder X-ray diffraction (XRD). The XRD patterns were recorded on a Rigaku Multiflex diffractometer equipped with Cu K\(\alpha\) radiation (40 kV, 30 mA) at 1.2 kW. Scanning electron micrograph (Hitachi S-4800) images were taken at a low electron acceleration voltage (2 kV) without metal coating. Transmission electron micrograph (JEOL corp. JEM-210F) images were obtained at an operating voltage of 200 kV from the calcined samples after being supported on a porous carbon grid. N\(_2\) adsorption isotherms were measured with a Micromeritics ASAP2020 volumetric adsorption analyzer at liquid N\(_2\) temperature (77.7 K). Before the measurements, all samples were degassed under vacuum for 12 h at 300 °C. The Brunauer–Emmett–Teller (BET) equation was used to calculate the surface area from adsorption branches obtained at \(P/P_0\) between 0.05 and 0.30. The mesopore size distributions were obtained from analyzing the adsorption branch in the N\(_2\) adsorption isotherms using the Barret–Joyner–Halenda (BJH) algorithm. The mesopore volume was calculated as the difference between the micropore volume calculated by a Saito–Foley analysis and the total pore volume derived at \(P/P_0 = 0.97.\)

Geometrical optimization (Fletcher–Reeves algorithm) and molecular dynamics simulation of CDM molecules were performed using HyperChem (ver. 6.03) software.

Results

The zeolite synthesis conditions used in the present work were strongly basic (pH ≈ 14). Accordingly, the synthesis mixture remained transparent for many days as long as the CDM compound was not added. When the CDM was added, the mixture transformed to an opaque gel immediately. The amorphous gel was converted to a crystalline zeolite phase upon hydrothermal treatment at 170 °C. The product structure and the time required for zeolite crystallization depended on parameters such as hydrothermal temperature, gel composition and CDM structure.

![Fig. 1](image-url) Phase diagrams constructed with organic SDAs (a) CDM1, (b) CDM2, and (c) CDM3.)
Fig. 1 show three phase diagrams for zeolite products, which were synthesized at 170 °C using CDM1, CDM2, and CDM3, respectively. The gel compositions in mole ratio were 30Na2O : xAl2O3 : 100SiO2 : yH2SO4 : 6000H2O, where x and y were varied over 0.5 ≤ x ≤ 5 and 10 ≤ y ≤ 25. As shown in Fig. 1(a) and (b), the phase diagrams corresponding to CDM1 and CDM2 are very similar to each other. BEA and MTW zeolites were obtained in pure phases over wide ranges of gel composition (Si/Al = 10–80 and 40–∞, respectively). The BEA phase domain in Fig. 1(a) includes the gel composition of 30Na2O : 2.5Al2O3 : 100SiO2 : 10SDA : 15H2SO4 : 6000H2O, at which Choi et al. discovered the BEA synthesis using CDM1.20 As compared with the BEA domain, Fig. 1(a) shows that the MTW zeolite was obtained at low Al and high H2SO4 contents. Both the BEA and MTW zeolites were rapidly crystallized in less than 1 d at 170 °C. Approximately 2–3 d of synthesis time was necessary for their complete crystallization at 130 °C. All the CDM compounds used in these works were not decomposed even at 170 °C. As shown in Fig. 1(c), BEA was not obtained at all when CDM3 was used as an SDA. Instead, MFI zeolite was obtained. MTW was also obtained as a mixture with MFI at high sulfuric acid concentrations and high Si/Al ratios. An amorphous gel was preserved without crystallization at high Al and high H2SO4 contents.

In previous works on BEA zeolite, syntheses were generally performed at low concentrations of Na+, the reason being that the zeolite with mesoporous texture is attributed to pseudomorphic conversion of the initial zeolite-synthesis gel to the zeolite phase. Since CDM1 can cause a highly mesoporous gel structure, the hydrothermal crystallization leads to the formation of BEA and MTW zeolites having secondary mesoporosity. According to our results, the highly mesoporous zeolites were rapidly generated within 12 h at 170 °C. The mesoporous texture did not change even when the products were collected after waiting for 3 d. That is, there was no indication of crystal ripening processes that could lead to a significant increase of crystal thickness during 3 d.

Fig. 2 shows representative SEM and TEM images of MFI-DM363 and MFI-CDM3 zeolites, in comparison with conventional MFI zeolites. As shown in Fig. 5(a) and 5(b), MFI-CDM3 is composed of an aggregation of needle-like nanocrystals less than 20 nm thick, whereas MFI-DM363 is composed of spherical agglomeration of tiny nanocrystals whose average diameters are about 30 nm. The diameters increase in the following order: MFI-CDM3 < MFI-DM363 < MFI-conv, which is in good agreement with the increasing XRD line widths (MFI-CDM3 > MFI-DM363 > MFI-conv) presented in Fig. 2(c). All the zeolites synthesized using diammonium compounds had high BET surface areas with large mesopore volumes, compared with conventional zeolites. The mesoporous zeolites exhibited type IV N2 adsorption isotherms with a hysteresis loop corresponding to capillary condensation in mesopores. As shown in the insets of Fig. 6, the zeolites exhibited a broad distribution of mesopore diameters, which is consistent with the random aggregation of nanosized crystals. The MFI zeolites synthesized with CDM3 and DM363 possessed relatively low mesopore volumes, compared with the BEA zeolites synthesized with CDM1 or CDM2. Thus, the mesoporosity of the zeolites decreased in the following order: BEA-CDM1 ≈ BEA-CDM2 > MFI-CDM3 >> MFI-DM363 >> MFI-conv. Detailed properties of the mesoporous texture are summarized in Table 1.

Discussion

In previous works on BEA zeolite, syntheses were generally performed at low concentrations of Na+, the reason being that

![Fig. 2](image-url) Powder X-ray diffraction patterns of (a) BEA, (b) MTW, and (c) MFI zeolites synthesized using organic SDAs. These zeolites were synthesized at the following gel compositions: 1.25Al2O3/15H2SO4 for BEA-CDM1 (or CDM2), 0.625Al2O3/20H2SO4 for MTW-CDM1 (or CDM2), and 0.625Al2O3/15H2SO4 for MFI-CDM3 (or DM363). Conventional zeolites are given for comparison.
Na+ ions dominantly generated other zeolite phases. At high concentrations of Na+, MFI and MOR were the major zeolite phases. With CDM1 in the present work, however, BEA was exclusively generated even at very high Na+ concentrations, as presented in Fig. 1(a) and (b) (Na+/SiO2 = 0.6). High purity and highly mesoporous BEA zeolites were readily generated in the range 0 < Na+/SiO2 < 0.6, including the use of water glass. The

<table>
<thead>
<tr>
<th>Zeolites</th>
<th>Average crystal size (nm)a</th>
<th>S BET (m²/g)b</th>
<th>V micro (mL/g)c</th>
<th>V meso (mL/g)d</th>
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<tbody>
<tr>
<td>BEA-conv</td>
<td>25–30</td>
<td>490</td>
<td>0.17</td>
<td>0.22</td>
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<tr>
<td>BEA-CDM1</td>
<td>10–15</td>
<td>646</td>
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<td>0.93</td>
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<td>653</td>
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<td>0.84</td>
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<tr>
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<td>1000–5000</td>
<td>268</td>
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<tr>
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<td>353</td>
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<tr>
<td>MTW-CDM2</td>
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<td>1500–2500</td>
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<tr>
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<td>0.29</td>
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<tr>
<td>MFI-CDM3</td>
<td>15–20</td>
<td>549</td>
<td>0.12</td>
<td>0.48</td>
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a Approximately determined from the SEM and TEM images. b BET surface area calculated by BET method. c Micropore volume calculated by Saito–Foley method. d Mesopore volume calculated by BJH method.
BEA yield from water glass (a sodium silicate solution, 29 wt% SiO₂, Na²SiO₂ = 0.6) was approximately 85% based on the silica recovery. Synthesis beyond Na²SiO₂ > 0.6 was not attempted, but it is well expected that the BEA synthesis conditions would be extended to above 0.6. The structure-directing ability of CDM1 for BEA at high concentrations of Na⁺ may be attributed to the molecular dimensions (11.6 × 5.5 × 4.1 Å). The cross-section along the longest molecular axis (5.5 × 4.1 Å) fits well inside the 12-membered ring (MR) channel (6.6 × 6.7 Å along [100] and 5.6 × 5.6 Å along [001] in BEA) during zeolite formation under hydrated conditions. MTW has a 1-dimensional channel structure composed of the same 12-MR channels, in contrast with the 3-dimensional structure of BEA.

Hence, MTW could be obtained by the same organic SDA used for BEA. The formation of MTW zeolite at low Al content in the present work is consistent with the result of Davis and coworkers, who reported that MTW was thermodynamically favored under high-silica synthesis conditions.

CDM2 has two quaternary ammonium groups linked by a biphenyl bridge, instead of the phenyl in CDM1. Despite the difference, the two SDAs gave almost the same phase diagrams as shown in Fig. 1(a) and (b). Furthermore, no significant differences in the SEM and TEM images and N₂ adsorption data were found between products synthesized from CDM1 and CDM2. Similar results may be explained by the geometrical similarity across the cross-sections along the longest molecular axis between CDM1 (11.6 × 5.5 × 4.1 Å) and CDM2 (13.6 × 5.6 × 4.1 Å). The similar cross-section, CDM2 fits well within the 12-membered pore apertures, similar to CDM1 to generate the BEA and MTW structures.

In contrast to CDM1 and CDM2, CDM3 failed to generate BEA or MTW in the pure phase. Instead, pure MFI was obtained as shown in Fig. 1(c). MTW was obtained in a mixture with MFI. The difference of CDM3 from CDM1 and CDM2 may be explained by the molecular rigidity of CDM3, whereas the rigidity of the organic SDA is known as a determinant factor for the resultant zeolite phase. It is reasonable that the two hexamethylene bridges between two ammonium groups in CDM3 would allow much higher flexibility in the molecular structure compared with the aromatic bridges in CDM1 and CDM2. The high conformational variability of CDM3 at the synthesis temperature has indeed been confirmed by our molecular dynamics simulation.

As mentioned above, all the zeolites synthesized with CDM were highly nanocrystalline (less than 30 nm) and included large intercrystalline mesoporosity. In the previous report by Choi et al., the mesoporous structure of BEA-CDM1 was attributed to rapid gelation of silicate by CDM1, which was followed by the pseudomorphic crystallization into BEA zeolite. The pseudomorphic crystallization could take place without significant mass transfer between solid and solution phases (i.e., solid-phase transformation), whereas the pre-organized amorphous gel phase was formed by a local composition similar to that of a crystalline zeolite. In the present study, it was confirmed that the pseudomorphic crystallization mechanism could be extended to the BEA zeolite crystallization using CDM2. In other crystallization processes leading to MTW and MFI phases, the crystalline zeolites exhibited significantly different morphologies from those in the initially developed amorphous phases. The results indicated that the zeolite crystallization occurred via dissolution of the amorphous gel phase and crystal growth at remote sites (i.e., solution-mediated crystallization). It was confirmed that significant compositional changes occurred in the solid phase during the crystallization of MTW and MFI zeolites. For instance, in the MTW crystallization, the organic content of the initially developed amorphous gel was 17 wt%, and then significantly decreased to 7 wt% during crystallization. Such compositional difference would require active mass transfer between solid and solution phases.

All the present zeolites were synthesized at high concentrations of Na⁺ at 170 °C. In the case of CDM SDAs, the nanocrystalline zeolite phases were maintained during 3 d under hydrothermal synthesis at 170 °C, after the crystallization was completed (12 h). The maintenance of such nanocrystallinity without further crystal growths is quite unexpected, as compared with conventional syntheses of BEA and MFI zeolites using tetrapropylammonium (TPA) or tetraethylammonium (TEA) under similar conditions. In the present case of BEA synthesis using CDM1 and CDM2, the nanocrystalline products were obtained through the pseudomorphic transformation route. On the other hand, in the cases of MTW and MFI using CDM1, CDM2, CDM3, and DM363, the products were generated through.

Fig. 6  N₂ adsorption isotherms and pore size distributions (insets) of (a) BEA, (b) MTW and (c) MFI zeolites. The isotherms of BEA-CDM1 and BEA-CDM2 in (a) are vertically offset by 200 mL/g and 400 mL/g, respectively. The isotherms of MTW-CDM1 and MTW-CDM2 in (b) are vertically offset by 100 mL/g and 200 mL/g, respectively. The isotherms of MFI-DM363 and MFI-CDM3 in (c) are vertically offset by 100 mL/g and 200 mL/g, respectively.
a solution-mediated crystallization route. The generation of nanocrystalline products through these two different crystallization mechanisms indicates that the presence of two ammonium groups in the same molecule could be the most important factor for the generation of nanocrystalline morphologies and mesoporosity.\textsuperscript{29} The mechanism may be speculated as follows: the diammonium-type SDAs could generate a large number of zeolite seeds as compared with their monoammonium analogues. The crystal ripening process appeared to be very slow in the case of CDM compounds. This may be related to the entropy of the CDM compounds. If the zeolite crystals grow through the Ostwald ripening process, the re-crystallization process would occur through a transition state, in which the zeolite frameworks and SDA are loosely bound (e.g., at crystal surface). It is reasonable that the activation energy to the transition state would be high for a SDA having low entropy (as in rigid cyclic compounds) and high interaction (an enthalpy factor) with the frameworks (as in diammonium). A more systematic modeling would be required to describe the phenomena in greater detail.

As mentioned in the Introduction, zeolites having intercrys-
talline mesoporosity have attracted much attention in recent years, due to interest for applications in catalysis and separation technologies. The short diffusion path length is an important structural parameter affecting molecular diffusion and accordingly catalytic performances (e.g., lifetime, activity, and selectivity). Various synthesis strategies have been proposed for mesoporous zeolites, such as generation of zeolite nanoparticles, post-synthesis demetallation, solid-templating, and supramolecular templating. However, most of the strategies are based on the use of cost-bearing solid templates or surfactants. Since the present synthesis strategy using CDM SDAs is free from the use of solid templates or surfactants, it can provide a highly versatile and economic synthesis route to mesoporous zeolites. In particular, nanocrystalline BEA zeolites (10–200 nm in diameter) were synthesized using TEAOH in the absence of alkali cations.\textsuperscript{10,31} MFI zeolites in the form of stable colloidal suspensions were prepared by hydrothermal treatment of a clear sol containing TPAOH under Na\textsuperscript{+}-free conditions.\textsuperscript{32–33} The synthesis cost for such nanocrystalline zeolites would be much higher than that for conventional zeolites, due to the high cost for the preparation of organic SDAs in the hydroxide form. In addition, such syntheses were performed over a long crystallization period at low temperatures, to minimize crystal ripening. In comparison, our synthesis of BEA zeolites using CDM compounds could be performed under a wide range of synthesis temperatures, with high concentrations of Na\textsuperscript{+}, and various gel compositions and Si/Al ratios. Even water glass proved suitable as a silica source because the synthesis could be performed at a high concentration of Na\textsuperscript{+}. Despite the high concentration of Na\textsuperscript{+}, the product yield calculated by silica recovery was very high (up to 85\% for BEA-CDM1/CDM2, 91\% for MTW-CDM1/CDM2, 90\% for MFI-CDM3 and 82\% for MFI-D363) and the crystallization time was short. In addition, compared to colloidal suspensions having low sedimentation rates, our product was easily collected by filtration.

**Conclusion**

The influence of cyclic diammonium geometry for determining zeolite structure as an SDA has been investigated while constructing phase diagrams at various gel compositions. Rigid CDM compounds containing phenyl or biphenyl bridges were found to be very effective SDAs for zeolites having a 12-membered pore channel, i.e., BEA and MTW, whereas a CDM compound connected with two flexible hexamethylene linkages generated a MFI zeolite having a 10-membered pore channel. With the CDM compounds, BEA, MTW and MFI zeolites were readily generated in pure phases over various Si/Al ratios (10–80, 40–\infty and 60–\infty, respectively). The zeolites thus obtained exhibited nanocrystalline morphologies with high surface areas and large mesopore volumes (i.e., mesoporous zeolite). The presence of the mesopores between adjacent nanocrystals is known to be an important factor, leading to significantly improved molecular diffusion and hence catalytic performance (e.g., lifetime, activity and selectivity). Since the present synthesis strategy for mesoporous zeolites is free from the use of solid templates or surfactants, it is expected to provide a highly versatile and economic synthesis route to mesoporous zeolites.

**Acknowledgements**

This work was supported by the National Honor Scientist Program of the Ministry of Education, Science and Technology in Korea. Electron microscopic studies were performed by supports from Measurement and Analysis Team in National NanoFab Center, and Research Supporting Team at KAIST.

**References**