Microwave Synthesis of Metallosilicate Zeolites with Fibrous Morphology

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In this paper, we report syntheses of silicalite (Si-MFI) zeolite crystals with tetravalent metal ions incorporated to synthesize metallosilicalite (M-MFI; M = Sn, Zr, Sn/Zr, Ti/Zr) zeolite crystals by using microwave irradiation reactions. β-Diketonate (acetylacetone) was used as a chelating ligand of the metal precursors, in order to reduce their hydrolysis rates and, therefore, to enhance framework incorporation of each metal in the syntheses of M-MFI zeolites. The zeolite crystals formed show puck-like morphology, and these crystals are stacked to form fibers with the degree of self-assembly varied depending on the nature of the tetravalent metal ion used. Importantly, the self-assembly of the zeolite crystals and the resultant fibrous morphology are observed only when the substituting metal ions are present. Powder X-ray diffraction, infrared and ultraviolet diffuse reflectance spectroscopic data all indicate that Sn and Ti atoms are well substituted for Si, but Zr is not well incorporated in the resulting MFI crystals. These results are discussed in terms of the ionic sizes and bulk dielectric constants of the corresponding metal oxides of the substituting metal ions.

Keywords: Microwave Synthesis, Self-Assembly, MFI Zeolite, Metal Incorporation, Fibrous Morphology.

1. INTRODUCTION

Fabrication of nanoscopic and nanostructured materials has attracted much attention with the prospect of miniaturization of chemical systems as one of the applications of nanomaterials. In particular, zeolite molecular sieves and mesoporous materials are promising candidates for designing nanoscopically-engineered materials due to their well-defined pore structures, capability of tailor-made synthesis, and hosting ability for guest species with optical, electronic, and magnetic properties. Many strategies to fabricate the nanostructured materials with various shapes, membranes, or thin films have been reported. Among them, self-assembly of nanoporous materials using chemical glue can offer nanoscopically or microscopically facile manipulation method of the materials.

The microwave technique has been often addressed to offer several advantages over conventional synthesis of inorganic materials such as rapid and homogeneous heating throughout the reaction vessel, the possibility of selective heating of desired materials, homogeneous nucleation, and short crystallization time. Although the microwave method has been successfully applied to the synthesis of nanoporous materials, the main focus of using this technique has been the reduction of crystallization time. However, we found the microwave technique could provide an efficient way to control particle size distribution, phase selectivity, and macroscopic morphology upon the synthesis of nanomaterials.

Silicalite (Si-MFI) and its derivatives with tetravalent and trivalent metal ions substituting Si in MFI (M-MFI) form an important class of zeolite materials that finds many industrial applications mainly as catalysts. Because of their plate-like shape, MFI crystals also have been exploited in fabricating into multiple stacks of layers. In this regard, our recent results of self-assembly of titanium-incorporated MFI crystals (Ti-MFI) in one-dimension into fibers from microwave reactions would be an important addition to work on fabrication of nanostructured materials. In order to explain this peculiar behavior of the Ti-containing system, we have proposed a mechanism in which microwave selectively activates the surface Ti–OH groups to react with Si–OH groups of Si-MFI.
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Composition of the reaction mixture was 1 TEOS : 0.2 at room temperature to get a clear solution. The molar ratio of Si/M (M = Sn and Zr; Sn/Zr and Ti/Zr in 10/3 molar ratio) zeolites with the mole ratio of Si/M = 130 were synthesized under microwave irradiation. In a typical synthesis batch, TEOS and TPAOH were mixed for 1 h, and this solution as added into the other one at room temperature with stirring. The resulting mixture was stirred for 2 h at room temperature to get a clear solution. The molar composition of the reaction mixture was 1 TEOS : 0.2 TPAOH : (1.8 – 7.7) x 10^{-3} M(OR)_{4} : 0.1 isopropyl alcohol : 22.2 H_{2}O : (1.8 – 7.7) x 10^{-3} acac. The mixture was heated for 90 min at 438 K under 600 W of microwave power with the microwave synthesis system (CEM Corp., MARS-5). The solid product was isolated by filtration or centrifugation, washed with doubly distilled water, dried in an oven at 373 K for 10 h and calcined in air under static condition at 773 K.

2. EXPERIMENTAL DETAILS

Tetraethyl orthosilicate (TEOS, Aldrich, 98%), titanium(IV) isopropoxide (Aldrich, 96%), zirconium(IV) isopropoxide (Alfa, 98%), acetylacetonate (acac, Aldrich 99%), and tetrapropylammonium hydroxide (TPAOH, Aldrich, 25%) were purified. Ammonium(IV) isopropoxide (Aldrich, 96%), zirconium(IV) isopropoxide (Alfa, 96%), and tin(IV) isopropoxide (Alfa, 99%) were used as received. M-MFI (M: Sn, Zr, and Ti) samples were obtained by a Rigaku Powder X-ray diffraction patterns of the calcined M-MFI zeolite crystals. Accordingly, we prepared the similar precursors for Ti and Zr to use for metal-incorporated MFI zeolites.

2.1. Characterization

Powder X-ray diffraction patterns of the calcined M-MFI (M: Sn, Zr, and Ti) samples were obtained by a Rigaku diffractometer (D/MAX IIIB, 2 kW) using Ni-filtered Cu Kα radiation (40 kV, 30 mA, λ = 1.5406 Å) and a graphite crystal monochromator. The crystal size and morphology were examined using a scanning electron microscope (SEM: JEOL JSM-5400A). The framework IR spectra of zeolite crystals were recorded in the range of 4000–1300 cm^{-1} at room temperature using a Bruker Equinox 55 FT/IR Spectrometer. For the study of surface hydroxyl group, IR spectra were recorded in the range of 4000–1300 cm^{-1} using self-supported CaF_{2} window which were outgassed in vacuo (P ≤ 10^{-3} torr) at 673 K for 1 h and cooled to 298 K with Nicolet FT-IR Spectrometer (IMPACT 420/DSP). UV-visible diffuse reflectance spectra (UV/VIS-DRS) were recorded on a Shimazu UV-Visible spectrophotometer (UV-250 PC) with quartz flat cell at room temperature. The samples were treated at 573 K for 1 h in a vacuo (P ≤ 10^{-3} torr) before the measurements. BaSO_{4} was used as a reference in the range of 200–500 nm. Elemental analyses of M-MFI crystals were performed with Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP: Jovin Yvon Ultima-C). The BET surface area measurements were performed with N_{2} adsorption isotherms at liquid nitrogen temperature (77 K) using a Micromeritics ASAP 2400 analyzer. High Resolution Transmission Electron Microscopic (HR-TEM) studies were performed with a JEOL-3011 electron microscope with an accelerating voltage of 100 kV. The physicochemical properties of M-MFI zeolite crystals are summarized in Table I.

3. RESULTS AND DISCUSSION

The Ti-MFI crystals were synthesized using titanium isopropoxide as a precursor. However, in the case of Sn-MFI crystals synthesis, we tried several metal precursors such as SnCl_{4}-ethanol, SnCl_{4}-acac, Sn(O\text{Pr})_{4}-PrOH, and Sn(\text{OPr})_{4}-acac, and found that only the last one produced fibrous morphology of MFI crystals. This is probably because the chelating ligand, acetylacetonate (acac), forms a stable complex with Sn^{4+}, whose reduced hydrolysis rate prevents the formation of precipitated tin oxide or hydroxide species^{17} and enhances incorporation of Sn into the zeolite crystals. Accordingly, we prepared the similar precursors for Ti and Zr to use for metal-incorporated MFI zeolites.

Powder X-ray diffraction (XRD) patterns of M-MFI (M = Si, Sn, Sn/Zr, Zr, and Ti/Zr) zeolite crystals obtained by the microwave irradiation reactions are identical and show the characteristic peaks of fully crystalline MFI structure (Fig. 1). Though very small in quantity, the substitutions of Si by larger M ions (Shannon radii^{17}: 0.69 Å for Sn^{4+}, 0.73 Å for Zr^{4+}, 0.56 Å for Ti^{4+}, and 0.40 Å for Si^{4+}) shifted the peaks slightly to lower angles and, hence, increased the cell volume as shown in Table I. Assuming that the Vegard’s law holds, one may expect

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/(M1:M2)^a</th>
<th>Shape</th>
<th>Size length (μm)</th>
<th>Cell volume (Å^3)</th>
<th>BET volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-MFI</td>
<td>Flat disk</td>
<td>0.2–0.3</td>
<td>5286</td>
<td>443</td>
<td>0.22</td>
</tr>
<tr>
<td>Sn-MFI</td>
<td>130</td>
<td>Fibrous</td>
<td>5.6</td>
<td>5556</td>
<td>0.24</td>
</tr>
<tr>
<td>Sn/Zr-MFI</td>
<td>130 (100:30)</td>
<td>Fiberous</td>
<td>0.5–1</td>
<td>5334</td>
<td>0.25</td>
</tr>
<tr>
<td>Zr-MFI</td>
<td>130</td>
<td>Fiberous</td>
<td>0.3–0.8</td>
<td>5320</td>
<td>0.26</td>
</tr>
<tr>
<td>Ti/Zr-MFI</td>
<td>130 (100:30)</td>
<td>Fiberous</td>
<td>0.5–1</td>
<td>5317</td>
<td>0.43</td>
</tr>
</tbody>
</table>

^aSi/(M1:M2) molar input ratio of the gel.
that the increments of the unit cell volume reflect the sizes of the substituting ions. Deviations from this expectation may be interpreted as a substitution at a significantly different concentration, and this appears to be the case for Zr-MFI. Other analysis results to be discussed below also suggest that the Zr-MFI samples have a considerably lower level of Zr-doping in the zeolite crystals. Unfortunately, we do not have any direct evidence for the extraframework zirconium oxide species in the sample because of the low concentration of Zr in the starting gel (Si/M = 130). The unit cell volumes of Sn-MFI and Zr-MFI crystals are increased by 70 Å³ and 34 Å³, respectively, from that of pure Si-MFI, which are considerably larger than the cell volume increments of 1 Å³ and 21 Å³, respectively, reported for the ones under hydrothermal conditions using SnCl₄·5H₂O and ZrCl₄.¹⁸ This result elucidates that the present method is more efficient in substituting Sn⁴⁺ and Zr⁴⁺ ions into the zeolite crystals.

The IR spectra of M-MFI zeolite crystals in the framework vibrational band region (400–1300 cm⁻¹) are compared with that of pure Si-MFI in Figure 2. The series of bands in the 1500–200 cm⁻¹ region are due to overtone modes of fundamental lattice vibrations of the zeolite structure. These are assigned to asymmetric stretching vibrations at 1232 and 1089 cm⁻¹, symmetric stretching vibration at 793 cm⁻¹, double-ring vibration at 555 cm⁻¹ and the T-O bending vibration at 446 cm⁻¹ (Ref. [24]). The absorption band at about 960 cm⁻¹, observed in all M-MFI samples, is assigned to an asymmetric stretching mode of a [SiO₄] unit bonded to a M⁺⁺ ion (O₅Si–O–M).²⁵ This characteristic peak was also reportedly observed for Ti-MFI, Sn-MFI, and Zr-MFI synthesized from hydrothermal reactions.²³

The 3740 cm⁻¹ band of M-MFI crystals, shown in Figure 3, is associated with internal Si–OH species which are free from structural perturbation by the molecular sieve structure. Their vibration frequency thus accidentally coincides with that of terminal Si–OH groups required to terminate the crystalline lattice. The band around 3500 cm⁻¹ is ascribed to free Si–OH groups of H-bonded pairs, isolated vicinal pairs, or geminals that are greatly affected by the molecular sieve structure and subject to
a high degree of hydrogen bonding, which lowers its frequency and broadens the band. The Si-MFI crystals have fully condensed terminal OH-group into Si–O–Si bonds, so the peak intensity at 3740 cm$^{-1}$ is very low. However, as tetravalent metal species are incorporated into the framework, the number of surface hydroxyl groups is increased because of framework distortion and unsaturated coordination of transition metal ions. However, the 3740 cm$^{-1}$ IR peak intensities on M-MFI zeolites synthesized by microwave irradiation are much smaller than those on the corresponding M-MFI zeolites by hydrothermal method (not shown), indicating the consumption of terminal hydroxyl groups due to microwave-induced stacking of MFI zeolite crystals.

UV/VIS DR spectroscopy is a useful tool to characterize different metal species such as framework M, MO$_x$ adsorbed on the framework, and bulk MO$_x$. The diffuse reflectance UV/VIS spectra of our completely dehydrated M-MFI zeolites, shown in Figure 4, show strong peaks at 210–230 nm, that can be assigned to ligand to metal charge transfer (LMCT) transitions of isolated M$^{4+}$ species in the zeolite framework, [M(OSi)$_4$] or Mi(OSi)$_3$(OH)]. It is noted that the pure Si-MFI does not show such a peak in agreement with the assignment. The absence of this peak in the Zr-MFI indicates that there is no or a little Zr in the zeolite framework, probably because Zr is too large to fit into the tetrahedral sites of Si. This contrasts to the reported 212 nm band for Zr-MFI from a hydrothermal reaction.

At any rate, the absence of LMCT in Zr-MFI in the present study corroborates with the observations from the XRD and IR data, which also indicate that Zr-MFI has much smaller degree of Zr substitution in the framework than other M-MFI zeolites in this study. In fact, the LMCT bands for Sn-MFI, Sn/Zr-MFI, and Ti/Zr-MFI all show shoulders in the longer wavelengths. These can be explained with the presence of isolated M(IV) in octahedral environments. Zecchina et al. reported that the electronic transition involving the isolated framework Ti(IV) in tetrahedral coordination occurs at 208 nm and that involving isolated Ti(IV) in octahedral environment at about 238 nm. Likewise, the isolated Sn(IV) in an octahedral environment is reported to exhibit UV absorption at 240 nm. The small band at about 230 nm of Zr-MFI appears to be from ZrO$_2$ which is reported to have a LMCT at 233 ± 2 nm. This also may contribute to the spectra of Sn/Zr-MFI and Ti/Zr-MFI. In addition, the weak band at 325 nm of Ti-MFI can be explained with small TiO$_2$ particles located inside the pore system or anatase particles that are reported to absorb at 325 and 328 nm, respectively.

Figure 5 shows the SEM images of the M-MFI and pure Si-MFI zeolite samples prepared from the microwave syntheses. The Si-MFI has disc-like morphology of about 0.4 μm in width and 0.2 μm in thickness. All of the M-MFI samples show self-assembly of the disc-like particles along their [010] direction to form rods at varying degrees. Especially, the Sn-MFI shows very long self-assembled fibers up to 5–7 μm in length (Fig. 6). The TEM images of Sn-MFI in Figure 6 clearly show that the fibers are formed by self-assembled connecting preformed zeolite discs with their faces making 90° angles at the joints. These samples were sonicated for 10 min before the SEM examinations, so the stacking of the crystals in the SEM images indicates strong bonds between the bonded crystal faces.

There are several factors that determine the degree of crystal self-assembly. First, the self-assembly is enhanced

![Fig. 4](image)

**Fig. 4.** DR UV-Visible spectra of calcined M-MFI zeolites in the ratio of Si:M = 130. (a) Si, (b) Sn, (c) Sn:Zr = 100:30, (d) Zr, and (e) Ti:Zr = 100:30.

![Fig. 5](image)

**Fig. 5.** Scanning electron micrographs of M-MFI crystal prepared by microwave irradiation at 438 K for 90 min. (a) Si-MFI, (b) Sn-Zr-MFI, (c) Zr-MFI, and (d) Ti-Zr-MFI.
when the bulk dielectric constant of oxide of the dopant metal is high. The lengths of the MFI fibers increase in the order of the dielectric constants of the dopant metal oxides $\text{SiO}_2$ ($\varepsilon = 3.8$) $< \text{ZrO}_2$ ($\varepsilon = 12.5$) $< \text{SnO}_2$ ($\varepsilon = 14$) $< \text{TiO}_2$ ($\varepsilon = 70$–130). Such self-assembly behavior is not observed in pure Si-MFI. Second, the concentration of the M ions in the reaction mixture is very important and often crucial for the fibrous morphology. From our previous study on Ti-MFI,\(^1\)\(^2\) we have found that, for growth of long rods, Si/Ti $= 70$–130 is the optimal condition. For this reason, the reactions in the present work were all carried out with Si/M $= 130$. Third, other chemical factors such as ionic size of M influence the length of the rods synthesized. This point is well demonstrated by the Zr-MFI sample that shows much lower doping level and thereby lesser degree of crystal stacking.

The well-defined fibrous Sn-MFI zeolites give the typical plots of a type I $N_2$ adsorption–desorption isotherm (Fig. 7). The isotherms of Sn/Zr-MFI, Zr-MFI, and Ti/Zr-MFI, different from those of fibrous Sn-MFI, indicate mesopores mostly due to intraparticle spacings (Figs. 7c–e). Pore volume of Ti/Zr-MFI (0.43 cc/g) is the highest value among other M-MFI zeolites, probably because of meso- and macropores between small MFI particles. In addition, Sn-MFI and Zr-MFI crystals possess larger surface areas and pore volumes, than pure Si-MFI crystal.

4. CONCLUSIONS

In this study, we have extended our previous work on the synthesis of fibrous Ti-MFI to other M-MFI systems where M is Sn and Zr, and obtained M-MFI fibers. The lengths of the M-MFI crystal fibers are in the order of the dielectric constants of dopant metal oxides in support of our mechanism of selective activation of the surface M-OH groups by microwave. By the modification with a $\beta$-diketonate chelating ligand (acac), the hydrolysis rates of metal alkoxide precursors were reduced to match that of silicon precursor, which led to successful metal incorporation into the zeolite framework.

Acknowledgments: This work was supported by the Korea Ministry of Commerce, Industry, and Energy (MOCIE) through the Research Center for Nanocatalysts and Institutional Research Program. Y.-U. Kwon thanks the Center for Nanotubes and Nanostructured Composites at SKKU. S.-E. Park thank the Nano Center for Fine Chemical Fusion Technology. The authors thank Mr. D.-K. Kim and Miss Hye-Kyung Kim at KRICT for their helpful assistance.

References and Notes

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Received: 15 October 2005. Accepted: 16 December 2005.