Synthesis and Characteristics of ZSM-5 Zeolite Prepared from Water Glass

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Abstract: ZSM-5 was synthesized from water glass as the silica source and Al(OH)₃ as Al source. Water glass is an inexpensive silica source, but controlling the reactant composition was difficult because of the high alkali content in water glass. Considering environmental and economic concerns, we propose a new alkali extraction method using methanol to remove the alkali ingredients from water glass. When the MeOH/SiO₂ molar ratio was 3, the maximum extraction of alkali components occurred. After extracting with MeOH, the filtrates were analyzed by UV spectroscopy and titration methods, and we determined the Al₂O₃:SiO₂:Na₂O:H₂O molar ratio to be 1:58:7.55:1510. Crystallization by hydrothermal synthesis was performed at various reaction temperatures and times. Characterizations were carried out by means of XRD and SEM. ZSM-5 display a characteristic MFI peak in its XRD pattern and its crystals have planar shapes and 1~2 μm particle sizes. Alkali extraction using methanol in a template-free system is a better method for controlling the level of Na₂O in water glass used for ZSM-5 synthesis.

Keywords: ZSM-5, water glass, extraction, hydrothermal synthesis, template-free

Introduction

In 1972, the introduction of TPA⁺ (tetrapropylammonium) ions as templates by Argauer and Landolt of the Mobil Oil corporation resulted in the synthesis of ZSM-5, a pentasil, high-siliceous zeolite having especially superior and unique pore structures applicable to combating environmental pollution and for use as catalysts in the petrochemical industry. Subsequently, interest in zeolite synthesis in industry has tended to concentrate on methods for synthesizing superior zeolites that are inexpensive [1-5]. Since then, ZSM-5 (MFI) has been synthesized using organic templates that mediate the formation of the three-dimensional crystalline structure. However, this synthetic method has several problems, including economical and environmental problems related to the toxicity of the organic templates and to wastewater pollution [6-9]. Thus, template-free syntheses of ZSM-5 (MFI) have been investigated keenly and frequently. In template-free systems, the synthetic reaction of ZSM-5 must be controlled carefully because of the very sensitive reaction conditions that are selected in the absence of the organic template. Important variables that influence the reaction mechanism of ZSM-5 include the silica source, the ratio of SiO₂ to Al₂O₃, the content of alkali, the mixing order of the reactants, reaction temperature and time, and the aging time. Among these factors, the silica source (silica sol, amorphous silica, and water glass are the main ones used) is believed to be the most important. Because of the reactivity and treatment of silica sol, low-purity, amorphous fumed silica is used frequently for the preparation of high-purity synthetic zeolites. The expense and low compact density of this material, however, make it not easy to handle and it is rarely used in actual industrial fields.

Water glass is the most inexpensive among the silica sources in its liquefied state; difficulty encountered in its reaction control is ascribed mainly to its high content of alkali ingredients. Synthetic methods that control the alkali content in water glass by using sulfuric/nitric acid treatment require severe conditions. In addition, post-treatment is needed [10-15]. Considering the environmental and economical pro-
blems, in this research we adopt an alkali drowning-out method using alcohol as the extractant as a newly adopted procedure.

**Experimental**

A diagram representative of the overall experimental procedure is shown in Figure 1.

**Raw materials**

Water glass (BDH, SiO₂/Na₂O molar ratio = 3.4), 40% NaOH (DC Chemical Co., 98%), and Al(OH)₃ (Dae Jung, 100%) were used to synthesize ZSM-5 zeolite. MeOH (Jin Chemical Co., 99%) was used to remove the alkali ingredients from water glass. Deionized water was also used.

**Alkali Extraction Procedure**

The extraction of alkali using MeOH was conducted in the absence and presence of Al. The extraction procedure consisted of three steps. First, the water glass was diluted by the addition of distilled water. Concurrently, Al(OH)₃ was dissolved in 40% NaOH aq. solution at 105°C and then cooled to ambient temperature; a prescribed quantity of H₂O was added afterwards. Finally, the Al(OH)₃ and water glass solutions were mixed.

In this study, the MeOH/SiO₂ molar ratios were varied from 1 to 6 during the synthesis of zeolite. An appropriate MeOH quantity was added to induce gelation. The extraction of alkali ingredients from the water glass then occurred. After filtration, the filtered cake was analyzed to determine the MeOH/SiO₂ molar ratio that resulted in the maximum extraction of the alkali. The filter cake obtained was washed with distilled water. After the extraction, the Si and Na contents in the filtrate were analyzed using UV/VIS spectroscopy and titration methods. From these results, the contents of SiO₂, Al₂O₃, and Na₂O in the filter cake were determined.

To observe the extent of extraction of the alkali ingredients in the water glass as a function of the Al(OH)₃ content, the MeOH/SiO₂ molar ratio was fixed at 3 and various amounts of Al(OH)₃ were added.

**Crystallization**

ZSM-5 was synthesized by the hydrothermal method using alkali-extracted water glass as the silica source. For...
the synthesis of the zeolite, we used an autoclave (a 300-
cc Parr high-temperature and pressure reactor equipped
with a stirrer). The reaction temperature and time ranged
from 170 to 190°C and from 10 to 36 h, respectively. The
crystallinity of the prepared zeolites were examined by
XRD. After crystallization the prepared samples were
treated several times with distilled water to remove
residual substances. To prepare the NH₄ form of ZSM-5,
the obtained zeolites were treated twice with 2 N
NH₄NO₃ the (DC Chemical Co., 98%) at 70°C for 4 h
while stirring. After ion-exchange the prepared samples
were dried at 120°C for 8 h and then finally calcined in
air at 550°C for 4 h.

**Characterization**

X-Ray diffraction analysis (Rigaku, model D/MAX-IIIIB)
was used to observe the crystalline structure of the
zeolite. The crystallinity was determined from the peak
area between 2θ = 22 ∼ 25° using a highly crystalline
ZSM-5 sample (Zeolyst, CBV-5524G) as a reference. The
XRD analysis was conducted using Ni-filtered CuKα
radiation at 40 kV and 40 mA. The ZSM-5 powder was
scanned at a scanning speed of 4°/min, a step size of 0.02
within a 2θ degree range from 5 to 50°. A sample (0.2 g)
was dispersed in 100 mL of ethyl alcohol for 15 min and
then the particle size and morphology of the crystalline
zeolites were investigated. This sample was spread to a
copper specimen plate and dried for 15 min in air and
then put into an ion coater in vacuum and coated with Au
for 3 min. The surface structure of synthesized zeolite
was analyzed by electron microscopy (Scanning Electron
Microscopy, Joel model JSM-840A).

To investigate the structural changes of the extracted
reactant, FT-IR (Jasco, FT/IR-610) analysis was carried
out. The sample was placed in the sample holder in the
form of a pellet after mixing with 10 mg of KBr; 16
scans were recorded within the range 4000 ∼ 400 cm⁻¹.
Nitrogen adsorption isotherms at 77 K were determined
using a volumetric adsorption apparatus (Micrometrics,
model ASAP 2010). From these isotherms, micropore
volumes, the pore size distribution, and the pore surface
areas were calculated by using the Dubinin-Radushkevich
(D-R), Balrett-Joyner-Hahenda (BJH), and Brunauer-
Emmett-Teller (BET) methods, respectively.

**Results and Discussion**

**Effect of Alkali Extraction**

Reactions of water glass are difficult to control because
of its high alkali content, and so it is often neutralized
with sulfuric acid/nitric acid. Although this neutralization
method has been researched for controlling the level of
Na₂O in water glass, it results in the generation of wasted
salt and has a high cost of post-treatment [13-15]. Therefore,
we chose an extraction method in this research using
alcohol as a new approach to the control of Na₂O. That
is, the ingredient in water glass was extracted by the
addition of MeOH. Figure 2 shows the variation of the
SiO₂/Na₂O molar ratio of the filter cake that formed
through the introduction of MeOH to water glass. Before
the addition of MeOH, the SiO₂/Na₂O molar ratio of
water glass was 3.5 whether Al is present or not. After
the addition of MeOH, the formed gel was filtered.
Assuming that all of the Al content is related to reaction
bonds, the Si and Na contents in the filtrate were ana-
lized using UV/VIS spectroscopy and titration methods.
Upon increasing the MeOH/SiO₂ molar ratio, the
SiO₂/Na₂O molar ratio of the filter cake approached its
maximum value in the vicinity of a MeOH/SiO₂ molar
ratio of 3.

The variation of the SiO₂/Na₂O molar ratio in the filter
cake showed similar trends whether Al was present or not.
Considering the effect of Al addition in water glass,
the maximum value of the SiO₂/Na₂O molar ratio in the
filter cake was 25% larger than it was in the absence
of Al. The initial SiO₂/Al₂O₃ molar ratios [molar ratio of
Al(OH)₃ via SiO₂ in water glass] were chosen in the
range from 106.58 to 59.69. According to the result
above, the prepared gels were extracted with MeOH. The
H₂O/Na₂O molar ratio was fixed at 180. After the com-
positions of the reactants were determined, the products
were synthesized through crystallization.

Table 1 shows the compositions, determined from the
XRD patterns, of samples synthesized under the afore-
mentioned reaction conditions. Before the extraction of
the alkali ingredient, the SiO₂/Na₂O molar ratios remain
almost constant, whether Al is present or not. After
the extraction of the alkali ingredient, however, the SiO₂/
Al₂O₃ molar ratios decreased upon increasing the amount
of added Al(OH)₃. From the XRD analysis, the crystal-
Table 1. SiO₂/Na₂O Molar Ratio of the Extracted Reactant and the Crystal Phase of the Zeolites Synthesized at Various Initial Quantities of Al in Water Glass

<table>
<thead>
<tr>
<th>MeOH/SiO₂ molar ratio</th>
<th>Initial SiO₂/Al₂O₃ molar ratio</th>
<th>SiO₂/Na₂O molar ratio</th>
<th>Crystal phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Before extraction</td>
<td>After extraction</td>
</tr>
<tr>
<td>3</td>
<td>106.6</td>
<td>3.4</td>
<td>9.4</td>
</tr>
<tr>
<td>3</td>
<td>87.8</td>
<td>3.4</td>
<td>9.1</td>
</tr>
<tr>
<td>3</td>
<td>74.6</td>
<td>3.3</td>
<td>7.8</td>
</tr>
<tr>
<td>3</td>
<td>59.7</td>
<td>3.3</td>
<td>5.6</td>
</tr>
</tbody>
</table>

Figure 3. XRD patterns of synthesized samples [(a): SiO₂/Al₂O₃ = 68.5; (b): SiO₂/Al₂O₃ = 58.6; (c): SiO₂/Al₂O₃ = 54.1].

linity of the synthesized zeolite was at its lowest level at an initial SiO₂/Al₂O₃ molar ratio of 106.58. At an initial SiO₂/Al₂O₃ molar ratio of 87.77, both ZSM-5 and mordenite were formed simultaneously. A zeolite having some mordenite structure was synthesized at an initial SiO₂/Al₂O₃ molar ratio of 59.69. For the suitable synthesis of ZSM-5, the Al(OH)₃ content was 74.61.

Characterization from XRD

Table 2 shows the reactant compositions of the filter cake prepared after extraction of the alkali at various initial quantities of Al(OH)₃. The reactant compositions, Si and Na, were determined by analysis using UV spectroscopy and the titration method. After the final reactant composition was decided, the crystallization reaction was carried out. The product synthesized this way was reaction characterized by means of X-ray diffraction analysis. The XRD analysis of the product synthesized at 190°C, with an H₂O/Na₂O molar ratio of 180, and a crystallization reaction time of 14 h is displayed in Figure 3. The peaks at 7.9, 8.8, 23.2, 23.9, and 24.3°(2θ) are known to be the intrinsic diffraction patterns of MFI zeolite [16-18, 20]. Also, the characteristic diffraction patterns of MOR (mordenite) are evidenced by the peaks at 6.5, 9.7, 13.5, 22.3, 25.7, and 26.3°(2θ) [19-20].

As shown in Figure 3(a), when the SiO₂/Al₂O₃ molar ratio was 68, both ZSM-5 and mordenite appear suitably mixed; when the SiO₂/Al₂O₃ molar ratio was 58, the mainly peaks of ZSM-5 appear [Figure 3(b)]. In Figure 3(c), when the SiO₂/Al₂O₃ molar ratio was 58, we see that mordenite was synthesized. The optimized SiO₂/Al₂O₃ molar ratio, which is an important experimental variable to control the synthetic reaction of ZSM-5, was selected to be 58 in this study.

Table 2. Compositions of the Extracted Reactant at Various Initial Quantities of Al in Water Glass [(a): SiO₂/Al₂O₃ Molar Ratio, 87.8; (b): SiO₂/Al₂O₃ Molar Ratio, 74.6; (c): SiO₂/Al₂O₃ molar ratio, 59.7].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition of extracted reactant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO₂/Al₂O₃</td>
</tr>
<tr>
<td>(a)</td>
<td>68.5</td>
</tr>
<tr>
<td>(b)</td>
<td>58.6</td>
</tr>
<tr>
<td>(c)</td>
<td>54.1</td>
</tr>
</tbody>
</table>

Figure 4(a) shows the XRD patterns of the zeolites we obtained at various temperature. All of the samples have the same structure, of ZSM-5, at each temperature studied [16-18, 20]. Namely, JCPDS number 37-361 is Na-ZSM-5 [21] and JCPDS number 37-359 is H-ZSM-5 [22]. The XRD peak pattern of synthetic ZSM-5 (Na-form) is the same as that of JCPDS number 37-361. Also, an increase in the crystallization time was accompanied by a slight increase in the crystallinity of the final product [24]. We found that crystallization was complete 36, 24, and 14 h at reaction temperatures of 170, 180, and 190°C, respectively. Also, the extent of crystallization was estimated by using the following formula [22]:

\[
\% \text{ Crystallinity} = \frac{\text{Peak area between } 2\theta \text{ (22-25°) of the product}}{\text{Peak area between } 2\theta \text{ (22-25°) of the reference sample}}
\]

Figure 5 shows the variations in the crystallinity of the zeolites at the three synthesis temperatures. The curves, which show the crystallinity of the zeolite as a function of time, are characteristically S-shaped [24-25]. From the results above, we have found that a reaction temperature of 190°C and a reaction time of 14 h are suitable and economical conditions for ZSM-5 synthesis.

SEM image

During the crystallization of the aluminosilicate gel
Figure 4. XRD peak patterns of the synthesized samples as a function of reaction time at various reaction temperatures [(a): 170°C; (b): 180°C; (c): 190°C].

Figure 5. Crystallization curves of ZSM-5 zeolite prepared at various temperatures.

having a fixed SiO₂/Al₂O₃ molar ratio, we found that the crystallite size varied upon varying the synthetic parameters. Also, the physicochemical properties were found to be influenced greatly by the size of the crystallites. As a consequence, an increase in crystallite size influenced the product yield and selectivity [25]. When the neutralization method producing a salt using sulfuric acid for Na₂O control in water glass, then forming a gel and drying it at 550°C was used to synthesize ZSM-5, a solid-phase transformation occurred involving nucleation and growth processes; this method influences crystallite size [26]. Also, the effect of ultrasound treatment effectively purified the residual gel present on the crystal surface [28]. Thus, we fixed the crystallization time at 14 hr and we used the filtered cake extracted with MeOH as the silica source. The H₂O/Na₂O ratio was 180 and we synthesized the product using the hydrothermal method. The product was analyzed by SEM photography. Figure 6 shows the SEM image of the prepared zeolite; it supports the evidence obtained in the XRD analysis because most ZSM-5 have hexagonal shapes, whereas mordenite has irregular spherical to prismatic shapes. In Figure 6(a), the irregular shape of agglomerated ZSM-5 and mordenite appears. The morphology of ZSM-5 that we identified in the XRD analysis appears in the aggregated particles in Figure 6(b). The particle shape of mordenite is observed in Figure 6(c).

The particle size of ZSM-5 synthesized using sulfuric acid/nitric acid to control Na₂O in water glass with TPA was 0.5~2 μm and its morphology was hexagonal planar [29]. In the template-free system the ZSM-5 crystallites
were 4–6 μm in size and had a cubical crystalline habit [20]. Our particles of the optimal synthetic ZSM-5 extracted using with MeOH are similar to the former synthetic ZSM-5 [27-29]. Figure 7 displays an SEM image of our optimally synthesized ZSM-5. The particle size of this sample of ZSM-5 is ca. 1–2 μm and the particle shape is hexagonal planar.

**FT-IR Spectra**  
The synthesized zeolite, the intermediate reactant during
Table 3. Physical Properties of Synthesized ZSM-5

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area (m² g⁻¹)</td>
<td>396.6</td>
</tr>
<tr>
<td>Micropore area (m² g⁻¹)</td>
<td>364.7</td>
</tr>
<tr>
<td>Micropore volume (m³ g⁻¹)</td>
<td>0.1</td>
</tr>
<tr>
<td>Median Pore Diameter (Å)</td>
<td>5.2</td>
</tr>
<tr>
<td>BJH desorption average pore diameter (Å)</td>
<td>18.5</td>
</tr>
<tr>
<td>Micropore capacity (cm³ g⁻¹)</td>
<td>93.7</td>
</tr>
</tbody>
</table>

the course of crystallization, and the alkali-extracted reactant were scanned in range 4000–400 cm⁻¹ using FT-IR spectroscopy. The IR spectra of the zeolite prepared in the template-free system was obtained and the assignment of the O-H and Si-O bands in each sample were known from Figure 8. After the addition of MeOH, the Si-O band appears weakly at 1026 cm⁻¹. Asymmetric stretching (external) of Si-O band appears at 1220 cm⁻¹ during the course of the crystallization reaction, a strong symmetric stretching (external) was formed at 790 cm⁻¹, and a double five-ring lattice vibration, which is the special peak of MFI-type zeolite, appears weakly in the range 540–560 cm⁻¹ [30-31]. In particular, the absorption bands at 550 and 1220 cm⁻¹ confirm that the crystal of ZSM-5 has a 3D channel structure. Coulrier and coworkers have reported similar experimental results [30]. The absorption band at 550 cm⁻¹ indicates that a D5R structure is formed in the zeolite by combining T04 tetrahedrons, and the band at 1220 cm⁻¹ implies that a chain structure exists four D5R units linked on two surrounding rotation axes [30-31].

The IR spectroscopic analysis of ZSM-5 synthesized by adding sulfuric acid/nitric acid into water glass [32-33] is similar to that of our prepared sample. Also, the synthesized ZSM-5 has the characteristic IR spectral patterns of MFI-type zeolite.

When no template was used, it might be expected that sodium ions having a low volume-to-charge ratio would be occluded in excess of those necessary for charge compensation, in an attempt to fill the available voids. Nitrogen sorption was ca. 300 m²/g because of the presence of the occluded material [34]. The prepared gels were extracted with MeOH and the H₂O/Na₂O molar ratio in the filter cake was fixed at 180. The composition of the synthesized sample that formed under the aforementioned reaction conditions and by crystallization was carried out by BET analysis.

Table 3 displays the results of BET analysis to investigate the specific surface area and pore capacity characteristics of ZSM-5. The BET surface area was calculated from the linear part of the BET surface plot according to IUPAC recommendations [35]. The specific surface area calculated by the BET equation was 396.6 m²/g. The pore size distributions were calculated from the nitrogen adsorption branch using the BJH model. The external surface areas and micropore surface areas of the synthesized ZSM-5 were estimated from t-plots derived from the nitrogen adsorption isotherms [36]. The micropore area of the synthesized ZSM-5 was 364.7 m²/g as deter mined using the BJH equation. The micropore capacity of the prepared sample was 93.7 cm³/g.

Conclusions

A new, “drowning-out” method using methanol was adopted to remove the alkali ingredients of water glass as the silica source for zeolite formation. When the MeOH/SiO₂ molar ratio was 3, the alkali ingredient was extracted to the maximum extent. Filtrates were analyzed by UV spectroscopy and the titration method to observe the effect of the introduction of MeOH to drown out the Na₂O in water glass. From the experimental results, the Al₂O₃:SiO₂:Na₂O:H₂O molar ratio was determined to be 1:58:7.5:5:1510. The optimal reaction temperature and time were 190°C and 14 h, respectively. Hydrothermal treatment of the reactant solution induced the generation of crystalline zeolites. Characterizations was performed by means of XRD and SEM. We observed the typical peak patterns of ZSM-5 in the former and planar shapes of ZSM-5 crystals (1 ~ 2 μm particle) in the latter. From the results of FT-IR spectroscopic analysis, we observed that MeOH addition facilitated the formation of Si-O bands. As the crystallization reaction progressed, a strong Si-O band was formed. The appearance a band at 550 cm⁻¹ strongly supported the MFI structure. Also, the specific surface area, the micropore area, and the micropore capacity of the prepared zeolite were determined to be 396.6 m²/g, 364.7 m²/g and 93.7 cm³/g, respectively.

The alkali extraction method, using methanol as an extractant in zeolite synthesis without a template, is a promising method for controlling the Na₂O content of water glass.

References

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