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Short Communication

# ZSM-5 and ferrierite single crystals with lower Si/Al ratios: Synthesis and single-crystal synchrotron X-ray diffraction studies

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ABSTRACT

Less twinned and high Al-containing ZSM-5 (MFI, $Al_{3.8}Si_{92.2}O_{192}$, Si/Al = 24.1) and high Al-containing ferrierite (FER, $Al_{2.0}Si_{34.0}O_{72}$, Si/Al = 16.7) large single crystals were synthesized by hydrothermal methods using mixed organic structure-directing agents and confirmed by single-crystal X-ray diffraction and SEM-EDX techniques. These large zeolite single crystals with an average size of 100 and 280 μm on an edge for ZSM-5 and ferrierite, respectively, were found to exhibit good qualities for potential use in advanced applications.



## 1. Introduction

Metal exchanged ZSM-5 (MFI) and ferrierite (FER), for example, Co, Mo, Ga, Zn-ZSM-5 and Co, Cu, Fe-ferrierite, are important heterogenous catalysts for petrochemical and environmental industries [1–5]. Therefore, catalytic active metal sites have been extensively studied by various methods such as synchrotron powder X-ray diffraction (XRD), X-ray absorption fine structure, theoretical modeling, and others [1–7]. Especially, some ZSM-5 and ferrierite structures including non-framework cation positions have been determined by powder XRD [5,6,8,9]. Although theoretical studies for NO in Fe-exchanged ferrierite provided some useful but indirect information about NO and Fe interactions [3], the detailed structures and environments of transition metals and adsorbed molecules including reactants and intermediates in metal exchanged ZSM-5 and ferrierite have been rarely confirmed due to some limitations on the analytical methods and materials.

Generally, synchrotron XRD technique using single crystals is one of the most powerful methods to find structural properties of zeolites. However, few or no single-crystal XRD works for metal-exchanged Al-rich ZSM-5 and ferrierite were carried out because it is very difficult to prepare large single crystals of ZSM-5 and ferrierite with high Al content even though they are useful metal-zeolite catalysts. In contrast, lots of crystallographic results including framework and guest molecule structures for these zeolites were obtained using pure-Si or Si-rich single crystals which are much more easily synthesized than Al-rich single crystals [10–14]. For other zeolites, A (LTA), X (FAU) and Y (FAU), the structures and environments of guest cations and adsorbed molecules in the zeolites have been widely studied by using large single crystals of these zeolites with lower Si/Al ratios [15,16]. Some researchers have recently developed special methods using zeolite powders such as synchrotron powder XRD combined with either nuclear magnetic resonance spectroscopy or high-resolution transmission electron microscopy to solve some highly complex zeolite structures. However, the above methods were not enough to find guest molecules, ion-exchanged metal cations and adsorbed species, but useful for framework atoms [17,18]. It means that large single crystals that are suitable for synchrotron XRD experiments are needed for advanced structural works. Additionally, large single crystals (>60 μm on an edge) with higher Al contents can be also used as nano-sized reactors for novel ionic nanomaterial synthesis and as unique materials for single-crystal based microspectroscopic techniques [19,20].

Some previous works using Al-rich ZSM-5 and ferrierite single crystals are also found in the literature [13,21–24]. Crystal structures of large ZSM-5 single crystals with high-Al content and containing structure directing agents were reported prior to 1999 but no additional studies have been reported since then (see below) [21–23]. Also, a ferrierite framework structure including structure directing agents was also found, however, there is no additional work related to metal cations or adsorbed molecules [13]. Very recently we have prepared single crystals of Tl-ZSM-5 and H-ZSM-5 with large size (80 × 20 × 20 μm) and low Si/Al ratio

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(29) with 11% twinning (BASF parameters = *ca.* 0.11) and confirmed them to be single-crystals [24]. The crystals had a twin proportion of *ca.* 11%, which were also suitable for calculation using a crystallographic program, SHELXL97 with TWIN operation. However, ZSM-5 crystals had much less twin proportion and could provide advances for determining detailed structures [24,25].

In this work, we have separated useful large single crystals from synthesized ZSM-5 and ferrierite mixtures and shown that these crystals have enough qualities for further detailed single-crystal XRD works. Additionally, we have tried to find why some ZSM-5 single crystals obtained in pervious works have not been used for determining the structures of adsorbed molecules on metal exchanged ZSM-5 [21–23].

## 2. Experimental

The molar compositions of the final synthesis mixtures for ZSM-5 and ferrierite syntheses were $2(Et_3N{\cdot}3HF){\cdot}0.5TPABr{\cdot}16Pyridine{\cdot}2Propylamine{\cdot}xAl_2O_3{\cdot}2SiO_2{\cdot}yH_2O$ where $x$ is 0.25 or 0.375 and $y$ is 18, 30, 60, 90, 150 or 300 (Table 1). The reagents were $Et_3N{\cdot}3HF$ (98%, Aldrich), tetrapropylammonium bromide (TPABr, 98%, Aldrich), pyridine (99%, Aldrich), propylamine (98%, Aldrich), pseudoboehmite ($Al_2O_3{\cdot}2H_2O$, Catapal B, Vista), fumed silica ($SiO_2$, Aerosil 200, Degussa), and deionized water. After stirring for 30 m at room temperature, the synthesis mixture was charged into a Teflon-lined 45 mL autoclave and then heated at 180 °C for 12 days without stirring under autogenous pressure. The solid product was recovered by filtration, washed repeatedly with deionized water, acetone, and ethanol and treated by ultrasonication in 3% of NaOH aqueous solution to remove residual reagents and amorphous phases. Finally, the resulting materials were washed again with deionized water and then dried at room temperature.

The synthesis conditions for each sample are shown in Table 1. Runs 1 to 6 were used for understanding the role of water content and run 7 was done to increase Al content in the crystals. Run 8 was carried out to synthesize ZSM-5, which serves as a reference for morphology by scanning electron microscope (SEM) and chemical composition by SEM-energy dispersive X-ray (SEM-EDX) analysis [24].

Powder X-ray diffraction (XRD) patterns were measured on a PANalytical ẌPert MPD diffractometer with an ẌCelerator detector. Data were collected with a fixed divergence slit (0.50°) and Soller slits (incident and diffracted = 0.04°) and Cu $K_\alpha$ radiation. The step width and scanning speed were 0.0084° and 1.0° $min^{-1}$, respectively. SEM images for each run shown in Table 1 and EDX data for several ZSM-5 and ferrierite single crystals (at least two single crystals for each run of these two zeolites) were obtained using a Hitachi S-4300 with a Koriba EDX-3500 attachment.

ZSM-5 and ferrierite single crystals obtained from runs 4 and 2, respectively (Table 1), were separated by using a needle for single-crystal XRD experiments and are shown in Table 2. ZSM-5 crystals obtained from run 8 were used as control for this work because ZSM-5 crystals with the same recipe had been used for determining crystal structures of Tl-ZSM-5 and H-ZSM-5 in our previous work [24]. Each of the ZSM-5 single crystals used for synchrotron XRD experiment is a well-faceted, coffin shaped crystal (no cruciform twinned crystal was used; the interpenetration of two or three ZSM-5 crystals with long axes at 90° or 60°). Synchrotron XRD data for each ZSM-5 and ferrierite single crystals were collected at 294(1) K on an ADSC Quantum210 detector at Beamline 4A MXW of The Pohang Light Source (PLS), Korea. The basic data

**Table 1**
Representative synthesis conditions and results.

| Run | Gel composition[a] | | | ZSM-5/ferrierite ratio[b] | ZSM-5 | | Ferrierite | |
|---|---|---|---|---|---|---|---|---|
| | $x$ | $y$ | Si/Al | | Size ($\mu$m)[b] | Si/Al[c] | Size ($\mu$m)[b] | Si/Al[c] |
| 1 | 0.25 | 18 | 4.0 | <0.05 | 30 × 10 × 10 | | 175 × 60 × 10 | |
| 2 | 0.25 | 30 | 4.0 | 0.2 | 60 × 15 × 15 | 23.3 | 280 × 80 × 10 | 16.7 |
| 3 | 0.25 | 60 | 4.0 | 1.0 | 60 × 20 × 20 | | 170 × 50 × 10 | |
| 4 | 0.25 | 90 | 4.0 | >5.0 | 100 × 30 × 30 | 24.1 | 200 × 60 × 10 | 16.3 |
| 5 | 0.25 | 150 | 4.0 | Pure ZSM-5 | <10 on each edges | | | |
| 6 | 0.25 | 300 | 4.0 | Amorphous | | | | |
| 7 | 0.375 | 90 | 2.7 | 3.0 | 50 × 15 × 15 | 28.1 | 130 × 60 × 10 | 16.7 |
| 8[d] | 0.5 | 500 | 20.0 | Pure ZSM-5 | 80 × 20 × 20 | 32.3 | | |

[a] Gel compositions for runs 1–7 are $2(Et_3N{\cdot}3HF){\cdot}0.5TPABr{\cdot}16Pyridine{\cdot}2Propylamine{\cdot}xAl_2O_3{\cdot}2SiO_2{\cdot}yH_2O$ where $x$ is 0.25 or 0.375 and $y$ is 18, 30, 60, 90, 150, or 300. The gel composition for run 8 is $2TPABr{\cdot}10NH_4F{\cdot}0.5Al_2O_3{\cdot}20SiO_2{\cdot}500H_2O$.
[b] Estimated and measured from SEM images of the products.
[c] Average Si/Al ratios measured from SEM-EDX experiments.
[d] Prepared as per Ref. [24].

**Table 2**
Crystallogrphic properties of single crystals prepared here.

| Zeolites | Run[a] | No. of reflections ($m$)[b] | Data/parameter ratio ($m/s$)[c] | BASF parameter ($k$)[d] |
|---|---|---|---|---|
| As-made ZSM-5 | 4 | 4526 | 11.3 | 0.051 |
| As-made ZSM-5[e] | 8 | 3826 | 9.6 | 0.243 |
| H-ZSM-5(>500)[f] | 4 | 4427 | 11.1 | 0.037 |
| H-ZSM-5(350)[e,f] | 8 | 4286 | 10.7 | 0.122 |
| As-made ferrierite | 2 | 1114 | 16.1 | |
| H-ferrierite(500)[f] | 2 | 1047 | 15.2 | |
| H-ferrierite(900)[f] | 2 | 1005 | 14.6 | |

[a] The same as the run numbers in Table 1.
[b] Averaged numbers of reflections with $F_o > 4\sigma(F_o)$.
[c] Estimated data/parameter ratio using numbers of variables ($s$), 400 and 69, for ZSM-5 and ferrierite, respectively [5,24].
[d] A refined parameter for the fractional contribution of the second domain of the twinned crystal [24].
[e] References prepared with the same recipe of Tl-ZSM-5 and H-ZSM-5 work [24].
[f] These single crystals were prepared by calcination and then dehydration at 350 °C under vacuum. The numbers in parentheses refer to the temperatures (°C) of calcinations.