

# Synthesis of Single Crystal ZSM-5 by Solid-like State Conversion

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**Abstract.** ZSM-5 single crystals were synthesized from fumed silica via solid-like state conversion. The properties of synthesized zeolite samples were characterized by XRD, SEM,  $^{27}\text{Al}$  MAS NMR spectra, XRF and  $\text{NH}_3$ -TPD. The results showed that the amorphous solid phase could be converted into ZSM-5 zeolites with cubic-like crystal morphology at temperature range of 160°C-190°C within 24 h. The optimum synthesis condition is at 180°C for 16 h by considering the crystallinity and uniformity of zeolites. The conversion of toluene in gas phase disproportionation over optimized ZSM-5 catalyst raised to 40.18%, which is higher than commercial ZSM-5 zeolite.

## 1. Introduction

The ZSM-5 zeolites have been studied for a long time as solid acid catalysts in the petrochemical and fine chemical industries due to features such as large specific surface area, excellent shape selectivity, and high hydrothermal stability [1]. However, conventional hydrothermal synthesis of ZSM-5 zeolites involves the use of large amounts of water as solvent, which consumes lots of energy, and causes water pollution. Therefore, considerable efforts have been dedicated to developing a less water synthetic approach to produce ZSM-5 zeolite [2-3].

In 1990, Xu et al. [4] firstly reported the synthesis of ZSM-5 via dry-gel conversion (DGC). The DGC method could obviously reduce the requirement of water, enhance the yield of the products, and shorten the crystallization time [5-6]. In 2012, Xiao et al. [7] synthesized zeolites in the absence of any solvent (solvent-free method) by mixing, grinding, and heating solid raw materials. But, it requires chemical raw agents rich of crystalline water. In 2014, Lu et al. [8] reported a fast route for synthesizing of nano-sized ZSM-5 aggregates from leached metakaolin via solid-like state conversion. Before the crystallization, the solid raw materials were mixed in the presence of small amount of water.

In this work, the crystallization time and temperature of solid-like state conversion were studied to synthesize uniform ZSM-5 single crystals. The samples were characterized using X-ray powder diffraction (XRD), scanning electron microscopy (SEM),  $^{27}\text{Al}$  MAS NMR spectra, X-Ray fluorescence (XRF) spectrometer and temperature programmed desorption ( $\text{NH}_3$ -TPD). The zeolites synthesized showed comparable catalytic performance to commercial zeolite on the toluene disproportionation.

## 2. Experiments

### 2.1. Material

All the reagents used for the preparation of ZSM-5 zeolite were aluminium sulfate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , Tianjin Branch Miou Technology Co., Ltd.), fumed silica (Sigma-Aldrich), tetrapropylammonium bromide (TPABr, Aladdin) and sodium hydroxide (NaOH, Shenyang Xinhua Reagent Factory products) as alkali source. Commercial zeolite (ZSM-5,  $\text{SiO}_2/\text{Al}_2\text{O}_3=45-80$ ) were purchased from Nanjing Jicang Nano Technology Co., Ltd.

### 2.2. Preparation of catalysis

The standard molar ratio of the solid raw materials was  $\text{Al}_2\text{O}_3$ :  $\text{SiO}_2$ : NaOH: TPABr:  $\text{H}_2\text{O}=0.02$ : 1: 0.60: 0.04: 1.0. In a typical synthesis, 1.68 g fumed silica, 0.38 g  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , 0.35 g TPABr, 0.67 g NaOH and 0.50 g  $\text{H}_2\text{O}$  were mixed by grinding, transferred into a 100 mL Teflon-lined autoclave, heated at  $X^\circ\text{C}$  ( $X=160, 170, 180, 190$ ) for  $Y$  h ( $Y=8, 16, 20, 24$ ) and the samples were designated as S-X-Y. After cooling the autoclave to room temperature, the solid sample was washed with deionized water until  $\text{pH}=7$ , then dried overnight at  $80^\circ\text{C}$ , and calcined at  $550^\circ\text{C}$  for 6 h to remove the template. Zeolite sample was ion-exchanged for 3 times in  $\text{NH}_4\text{Cl}$  solution (1.5 mol/L) with the solid/solution weight ratio of 0.1 at  $90^\circ\text{C}$  for 3 h, and then calcined again at  $550^\circ\text{C}$  for 6 h to obtain the corresponding H-type ones.

### 2.3. Characterization

X-ray diffraction (XRD) patterns was performed on a Bruker D8 diffractometer, using  $\text{Cu K}_\alpha$  radiation in the  $2\theta$  range of  $5-50^\circ$  with an angular step size of  $0.02^\circ$ . The relative crystallinity was calculated according to the method described by Paris [9]. The morphology of the samples were characterized by SEM on a scanning electron microscopy (SEM, SU8010, Hitachi).  $^{27}\text{Al}$  magic angle spinning nuclear magnetic resonance (MAS NMR, AVANCEIII, Bruker) spectroscopy characterization was performed on a Bruker DSX 500 MHz spectrometer with a spinning rate of 14 kHz and a length of 1 MS. The acid sites were determined by  $\text{NH}_3$  temperature-programmed desorption ( $\text{NH}_3$ -TPD) on a Pulse Chemisorb 2705 (Micromeritics, USA) instrument. Chemical compositions of the samples were determined using an X-Ray fluorescence (XRF) spectrometer (Epsilon3, Panalytical).

### 2.4. Catalytic activity test

Catalytic reactions were conducted in a quartz tube reactor of 8 mm ID and 600 mm length under atmospheric pressure with a weight hourly space velocity (WHSV) of  $3.3 \text{ h}^{-1}$ . The reaction products (toluene, xylene isomers, etc.) were analysed using a gas chromatograph-mass spectrometer (GC-MS) equipped with a flame ionization detector (FID) for 6 h

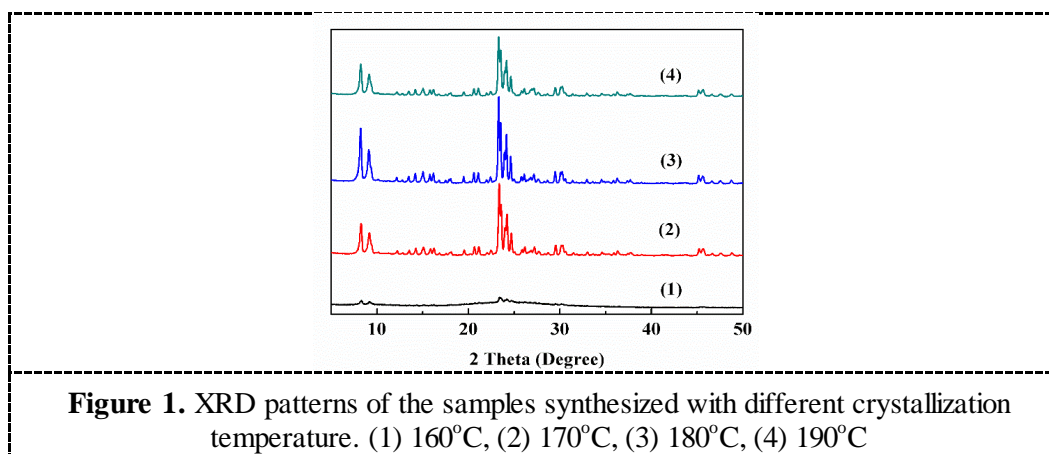
## 3. Results and discussion

### 3.1. Factors affecting the synthesis of ZSM-5 zeolites

#### 3.1.1 Effect of crystallization temperature

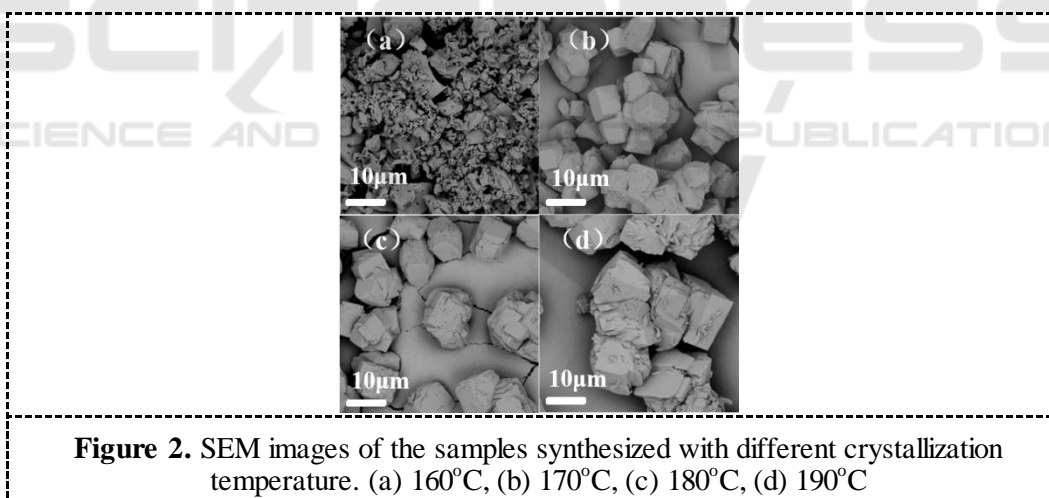
##### 1) XRD characterization results

Crystallization temperature strongly affects the nucleation and crystal growth [10]. Figure 1 shows XRD patterns of the samples synthesized at different temperatures for 24 h. The characteristic diffraction peaks of ZSM-5 ( $2\theta=7-9^\circ, 22-25^\circ$ ) began to appear at  $160^\circ\text{C}$ , and their intensity gradually increased while crystallization temperature was raised to  $180^\circ\text{C}$ , but decreased at further increased temperature of  $190^\circ\text{C}$ .



## 2) SEM characterization results

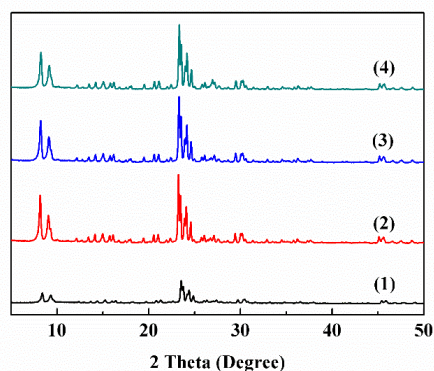
Figure 2 shows the SEM images of the samples synthesized at different crystallization temperatures for 24 h. At low temperature of 160°C, the most phase is amorphous, and it will disappear at higher temperature of 170°C to 190°C. The cubic-like single crystals with smooth surface with the size about 10  $\mu\text{m}$  were observed when the temperature is 170°C and 180°C. In addition, these single crystals were in form of highly dispersed at 180°C. It was also observed that higher synthesis temperature (190°C) led to increasing of crystal sizes, whose average crystal size is more than 10  $\mu\text{m}$ . Because the high crystallization temperature is beneficial for the fast nuclei formation and their continuous aggregation [11].



### 3.1.2 Effect of crystallization time

#### 1) XRD characterization results

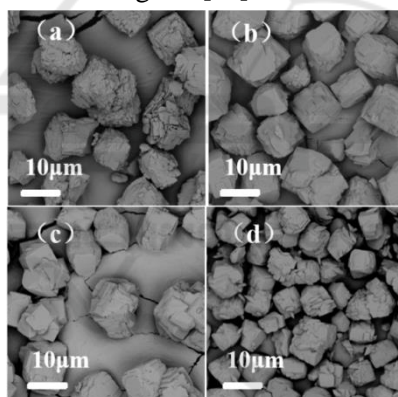
Figure 3 shows XRD patterns of the samples synthesized with different times at 180°C. When the solid materials were heated for 8 h, the characteristic diffraction peaks of ZSM-5 at  $2\theta=7-9^\circ$ ,  $22-25^\circ$  began to appear, and the relative crystallinity was only 33.8%. When prolonged the crystallization time to 16 h, the amorphous phase completely converted into highly crystalline ZSM-5, and the relative crystallinity reached to the high value of 99.5%. With further increase in time, the intensity of the diffraction peaks gradually decreased.



**Figure 3.** XRD patterns of the samples synthesized with different crystallization time. (1) 8h, (2) 16h, (3) 24h, (4) 36h

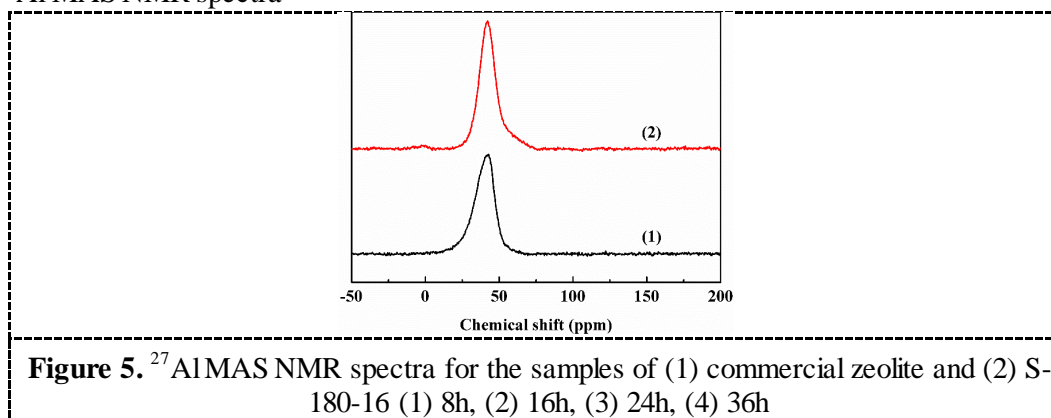
## 2) SEM characterization results

Figure 4 shows the SEM images of the samples. At the short crystallization time of 8 h, the uniform cubic-like morphology of crystals started to appear, but still was the aggregation of small particles. When crystallization time was 16 h, the dispersed single crystals with smooth surface were obtained. The particle size was about 8  $\mu\text{m}$  and the crystallinity of ZSM-5 was 99.5%. As the crystallization time prolonged, the morphology became irregular [12].



**Figure 4.** SEM images of the samples synthesized with different crystallization time. (a) 8 h, (b) 16 h, (c) 24 h, (d) 36 h

## 3) $^{27}\text{Al}$ MAS NMR spectra

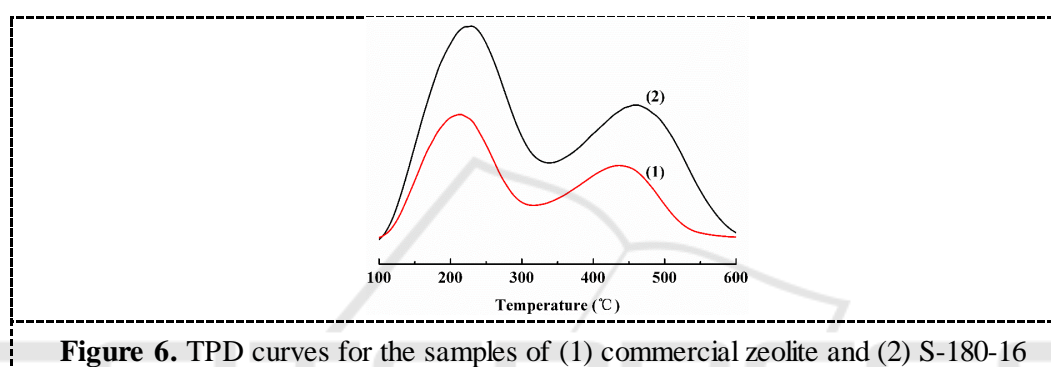


**Figure 5.**  $^{27}\text{Al}$  MAS NMR spectra for the samples of (1) commercial zeolite and (2) S-180-16 (1) 8h, (2) 16h, (3) 24h, (4) 36h

<sup>27</sup>Al MAS NMR spectra of the sample S-180-16 and commercial ZSM-5 zeolite are shown in Figure 5. The spectrum of all the samples exhibit a typical resonance peak at about 50 ppm, which are assigned to Al tetrahedrally coordinated to oxygen (Al<sup>IV</sup>). The absence of resonance peak at 0 ppm indicate that all of the Al species are incorporated into zeolite framework.

#### 4) NH<sub>3</sub>-TPD acidity results

Figure 6 shows the NH<sub>3</sub>-TPD curves of the S-180-16 sample and the commercial ZSM-5 zeolite. All samples showed two desorption peaks centered at 180-210°C and 420-500°C, which correspond to weak and strong acid sites, respectively. The peak at the lower temperature is assigned to the connection between H bonds and O-Si bonds of the weak acid center and non-acid center. The peak at the higher temperature represents the strong acid sites. The area of peaks attributed to amounts acid sites, which are given in Table 1. These results indicated that the sample S-180-16 has higher acid strength and amounts than the commercial ZSM-5 zeolite.



**Figure 6.** TPD curves for the samples of (1) commercial zeolite and (2) S-180-16

**Table 1.** NH<sub>3</sub>-TPD acidity for the samples

Sample	$n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)^a$	Acidity/mmole g <sup>-1</sup>		
		Weak	Strong	Total
Commercial ZSM-5 zeolite	55.2	0.32	0.17	0.49
S-180-16	52.8	0.59	0.34	0.93

<sup>a</sup>Analyzed by XRF

### 3.2. Catalytic performance

Catalytic activity of above zeolite samples on toluene disproportionation is presented in Table 2. The toluene conversion of S-180-16 sample is 40.18%, which is almost 15% higher than that of the commercial ZSM-5 zeolite. And the selectivity towards p-xylene is 23.53% slightly higher than the commercial ZSM-5 zeolite (22.30%), which goes well with acidity observed from NH<sub>3</sub>-TPD experiments. The benzene to xylene (B/X) value of both zeolites is about 1, which is closed to the thermodynamic balance [13].

**Table 2.** Catalytic properties of ZSM-5 for toluene disproportionation

Sample	X <sub>T</sub> <sup>a</sup> (%)	S <sub>PX</sub> <sup>b</sup> (%)	B/X <sup>c</sup> (mol / mol)
Commercial ZSM-5 zeolite	25.91	22.30	0.85
S-180-16	40.18	23.53	1.10

<sup>a</sup> Conversion of toluene.<sup>b</sup> Selectivity to xylene.<sup>c</sup> molar ratio of benzene to xylene.

#### 4. Conclusions

In summary, ZSM-5 single crystals have been synthesized via solid-like conversion. The crystals were in cubic-like morphology with a size of 8 $\mu$ m. Furthermore, Al species were incorporated into the zeolite framework and led to effective acid sites, resulting in a better catalytic performance than commercial ZSM-5 zeolite.

#### Acknowledgements

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#### References

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