Synthesis of nanosized Silicalite-1 in F⁻ media

CrossMark

Kun Jiao [a], Xiangyu Xu [a], Zhi Lv [a], Jiaqing Song [a, *], Mingyuan He [b], Hermann Gies [c]

[a] State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China
[b] Shanghai Key Laboratory of Green Chemistry and Chemical Processes, East China Normal University, Shanghai 200062, China
[c] Institute for Geology, Mineralogy, and Geophysics Ruhr-Universität Bochum, Bochum, Germany

ARTICLE INFO

ABSTRACT

This paper reports on the successful crystallization of monodisperse, highly crystalline, nanosized zeolite Silicalite-1 crystals in fluoride media by using an active silica gel as silica source and tetrapropylammonium fluoride as structure directing agent. The synthesis procedure is hydrothermal dynamic crystallization. The silica/water ratio and synthesis temperature were reduced to optimize the number of crystal nuclei and control the rate of crystallization for obtaining nanosized zeolite crystals. Meanwhile, F⁻ ions were used to partly replace OH⁻ ions in the synthesis system to obtain zeolite products with high crystallinity. Analytical results of XRD-, SEM-, Dynamic Light Scanning- (DLS) IR-, Simultaneous Thermal Analysis- (STA) and N_2 adsorption and desorption experiments show that the average particle size of zeolite Silicalite-1 product is about 45 nm and shows high crystallinity. The F⁻ containing Silicalite-1 zeolite sample was compared with an industrial ZSM-5 zeolite sample and it shows obvious advantages in both reduced particle size and enhanced crystallinity.

1. Introduction

ZSM-5 zeolite is a well-known microporous aluminosilicate having a three-dimensional host framework with intersecting 10-ring channels [1,2]. It is one of the industrially important zeolite catalysts due to its high thermal and chemical stability and its unique channel structure [3,4]. Applications are found in many fields like the separation of gases or liquids [5,6] and the synthesis of fine chemicals [7,8]. It is worth mentioning that as silicalite-1 molecular sieve has no acid sites, it is often used as a selective absorbent to separate gaseous aromatic compounds [9]. Nanometer molecular sieves with large surface areas and shorter diffusion path are advantageous for the adsorption and diffusion of gases. Furthermore, molecular sieves with high crystallinity have few defects and an integrated pore structure. Thus, silicalite-1 molecular sieve with nanoscale particle size and high crystllinity will be a good adsorbent for gaseous aromatic compounds.

An important modification of the original synthesis is the control of the particle size of final zeolite products. Typically, industrial ZSM-5 zeolites are manufactured having micro-sized crystals and high crystallinity. However, nanocrystalline ZSM-5 zeolite with larger surface areas and shorter diffusion pathways in the channels have many advantages in e.g. catalysis and separation. Several groups have successfully developed synthesis methods for preparing nanocrystalline ZSM-5 zeolites, but they all exhibit low crystallinity, i.e. they have defects in their framework structure [10,11]. This leads to a significant loss in performance, since high crystallinity also means high thermal and hydrothermal stability. To obtain zeolites with higher crystallinity than those synthesized through the traditional route hydroxyl anion are replaced with fluoride as mineralizer, making the synthesis possible in neutral and even in acidic media (pH = 5) [14]. However, the crystallite size of ZSM-5 zeolites synthesized in F⁻ media is usually higher than that of the hydroxyl route, increasing it to several 10 or even hundreds of micrometers [12–14].

Our research work is aimed at preparing mono-disperse, nanocrystalline Silicalite-1 zeolite with particle size of less than 100 nm and high crystallinity, which combines the advantages of high thermal and hydrothermal stability of micrometer sized ZSM-5 with the superior performance in catalytic and separation processes of the nanomaterial. Proper fluorine source and processed silica source are reacted under optimized reaction conditions to give highly crystalline, nanosized, monopisderse zeolite products.

Most zeolite syntheses are carried out using the static hydrothermal method. However, large thermal gradients often exist in the bulk solution as no effective convection occurs during the

---

* Corresponding author.
E-mail addresses: songjq@mail.buct.edu.cn, songjq@126.com (J. Song).

process. Meanwhile, large concentration gradient in the bulk solution might change the solution's composition. Thus, the dynamic hydrothermal method with continuous stirring at the speed of 30 r/min was adopted to avoid or reduce the negative influences of inhomogeneities mentioned above [15–17]. Hydrothermal dynamic synthesis is implemented by putting autoclaves into a rotation convection oven.

2. Experimental

2.1. Chemicals

The chemicals used in our study were as following: tetraethoxysilane (TEOS, SiO_2 28 wt%, Guang Dong Fine Chemicals Co., Ltd), silica gel (SiO_2 98.75 wt%, H_2O 1.25 wt%, self-made), fumed silica (SiO_2 99+%, 0.04 micron, Strem Chemicals, Inc.), Ludox (SiO_2 40 wt%, 0.04 micron, Sigma–Aldrich), tetrapropylammonium hydroxide (TPAOH 20–25% in water, TCI), ammonium fluoride ($NH_4F \geq 96$ wt%, Guang Dong Fine Chemicals Co., Ltd), hydrofluoric acid (HF 40 wt%, Sigma–Aldrich), ammonium hydrogen difluoride ($NH_4HF_2 \geq 98$ wt%, Guang Dong Fine Chemicals Co., Ltd), industrial ZSM-5 (LS, Le Shan Trading Co., Ltd) and deionized water.

2.2. Synthesis

The silica gel was made from TEOS by hydrolyzing under continuous stirring in ethanol solution with a certain amount of NH_4F and deionized water. After drying at 60 °C for 2 d and 110 °C for 1 d, the silica gel was calcined at 800 °C for 2 h.

The mixture of TPAOH, silica source, fluorine source and deionized water was directly transferred into a stainless-steel autoclave (25 ml capacity) with open stirring. After the water was evaporated to a certain amount, the mixture was transferred to a homogeneous reactor and reacted under certain condition. The mole ratios were as follows: F^-: TPAOH: SiO_2: H_2O = x: 0.4: 1: y. The as-synthesized crystalline material was filtered, washed with deionized water and dried at 383 K. The template was removed by calcination at 813 K for at least 6 h.

2.3. Characterizations

The specific surface areas (SSA) and the porosity of the zeolites were obtained on Micromeritics TristarII 3020. Before the measurements, samples were calcined for 6 h at 813 K to remove the templates and then heated for 10 h in vacuum at 573 K to remove other impurities. The SSAs (internal + external surfaces) were determined by the BET method and the pore volumes were determined by the t-plot method.

The X-ray diffraction (XRD) data were recorded with an X-Pert Pro diffractometer with graphite monochromatized Cu Kα radiation at 40 kV, 40 mA. All the diffraction data were collected in the range of $2\theta = 5–50°$ with continuous scanning mode at a step of $10°/min$. The standard material was X-Ray Powder Diffraction Intensity Set from National Institute of Standards and Technology (NIST). The patterns were indexed according to the standard ZSM-5 zeolite

diffraction patterns listed on the International Zeolite Association web data base (http://www.iza-online.org/).

Scanning electron microscopy (SEM) was employed to study the morphology of the zeolite crystals. The SEM images were obtained with ZEISS SUPER55 scanning electron microscope (3/30 kV).

Dynamic light scanning (DLS) data were recorded on a Zetasizer Nano ZS 90 laser particle analyzer (Malvern Instruments Ltd.). A small amount of sample was first dispersed ultrasonically in deionized water and then the mixture was transferred into the sample cell for the analysis.

Simultaneous Thermal Analysis (STA) was recorded using a NETZSCH STA449F5. Samples were heated in flowing synthetic air from room temperature to 1300 °C with a heating rate of $20 \,°C \,min^{-1}$. Temperature compensation and correction of alumina crucible were used to avoid baseline drift and enhance signal-to-noise ratio.

Fourier transformed infrared spectroscopy (FT-IR) was performed at room temperature by means of VECTOR 22 spectrometer in the range of $400–4000 \, cm^{-1}$ wavenumbers.

3. Results and discussion

3.1. The effect of fluorine source

HF and NH_4F are conventionally used as fluoride sources. Though both of them are very soluble in alkaline solution, the mixtures result in different pH values——when NH_4F was added, the pH of the initial solution was about 13, while when HF was used, the pH of the initial solution was about 10. The acidity of NH_4HF_2 is close to HF, so the pH of the initial solution was almost the same as with HF except for the influence of NH^{4+} during the synthesis process (Table 1). The near-neutral pH of the medium leads to two important consequences: (i) minimized number of non-bridging ≡SiO- defects; (ii) lower supersaturation of the framework-forming species. As a result, the crystals synthesized in fluoride medium have fewer framework defects [19].

The synthesis conditions of Sample 1–3 are listed in Table 1S (see supporting information). The only difference is the fluorine resource, but, in fact, what matters most is the alkalinity of the initial solution, which greatly affects the performance of F^- ions. It can be seen from Fig. 1 that the relative crystallinity increases with the decrease of the pH value of the initial solution. Meanwhile, the introduction of F^- ions effectively enhances the crystallinity of the samples 2 and 3, which explains that their relative crystallinity is higher than that of the industrial sample (see Fig. 1 and Table 1). This result follows the observation made by Corma and his co-workers, who reported that fluoride ions may catalyze the condensation reaction involved in Si–O–Si bond formation [18]. However, when NH_4F was added as the fluorine source, the relative crystallinity is lower compared to the other sample. The explanation most likely is that there is no contribution to the pH value with NH_4F as the additive, so the alkalinity of the solution remains too high to form F–Si bond. In addition, both the dehydration of Si–OH and the substitution of Si–OH by F–Si will produce more OH^- ions increasing the effect. Fig. 2 presents the SEM images of the three

Table 1
Influence of the fluorine source on the samples' relative crystallinity and particle sizes.

	Fluorine source	Relative crystallinity[a] (%)	Particle size (Scherrer formula, nm)	Particle size (surface area, nm)	The initial pH value[b]
Sample 1	NH_4F	93	50	54	13.15
Sample 2	NH_4HF_2	105	73	76	10.67
Sample 3	HF	124	89	90	10.24

[a] The relative crystallinity of industrial ZSM-5 from Le Shan Trading Co., Ltd (Sample LS) was set as 100%.
[b] The initial pH value was measured by a pH meter, before the silica source was added to the solution.