Microporous and Mesoporous Materials 193 (2014) 61–68

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

The morphology control of zeolite ZSM-5 by regulating the polymerization degree of silicon and aluminum sources

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ARTICLE INFO

Article history:
Received 11 December 2013
Received in revised form 5 March 2014
Accepted 11 March 2014
Available online 19 March 2014

Keywords:
Polymerization degree
Si and Al sources
Morphology
Zeolite ZSM-5
Crystallization mechanism

ABSTRACT

This study was focused on the regulation of the polymerization degree of silica sol and alumina with NaOH and H_2SO_4, and the role of the polymerization degree of Si and Al sources in determining the morphology of zeolite ZSM-5. Results show that, NaOH and H_2SO_4 were useful for decreasing the polymerization degree of silica sol and alumina, respectively. Micro-sized large ZSM-5 crystal can be obtained when the highly polymerized silica sol and alumina (slightly depolymerized by NaOH and H_2SO_4) were used. On the other hand, fine ZSM-5 crystal can be obtained when the highly depolymerized silica sol and alumina (deeply depolymerized by NaOH and H_2SO_4) were used. It is possible to fine tune the polymerization degree of silica sol and alumina by NaOH and H_2SO_4 dosage, and therefore to fine tune the crystal size of zeolite ZSM-5. Raman spectra disclosed that, there existed only very small amount of five-membered structure species in the gels formed by the highly polymerized Si and Al sources. However, monomeric silicate anions could be found in these gels. In contrary, in the gels formed by the deeply depolymerized Si and Al sources, abundant five-membered structure species were seen together with a small amount of monomeric aluminate anions. Such differences of the two kinds of gels accounted for the remarkable distinction of their crystallization processes and product morphologies.

1. Introduction

Zeolite ZSM-5 is a successful aluminosilicate molecular sieve catalytic material. For examples, it has been used as catalysts in petrochemical industry for the synthesis of ethylbenzene, para-diethylbenzene and para-xylene via the shape selective alkylation and disproportionation [1–3], the manufacture of high-octane number gasoline via the fluidized catalytic cracking of heavier distillates (ZSM-5 as additive) [4], and the synthesis of aromatics via the aromatization of short chain hydrocarbons [5]. In recent years, zeolite ZSM-5 has been found with new uses in coal chemical area as catalyst for the processes of methanol to gasoline (MTG) [6], methanol to aromatics (MTA) [7] and methanol to propylene (MTP) [8]. The excellent catalytic performance of zeolite ZSM-5 in different reactions is attributed to its unique lattice structure and high silica framework. The former is related to the zeolitic acidity and micropore diffusion, and the later is related to the framework thermal/hydrothermal stability. However, even when its lattice structure remains unchanged, the acidity, micropore diffusivity and thermal/hydrothermal stability may be substantially different if the crystal morphology (shape and size) of zeolite ZSM-5 changes [9,10]. As compared with large crystals of zeolite ZSM-5, the smaller ones have larger external surface area, more pore openings and shorter channels [11]. This means that the smaller crystals of zeolite ZSM-5 have exhibit higher micropore diffusivity and have more active sites on the external surface and thus, possess higher catalytic activity and improved coke-deactivation selectivity [12,13]. However, the smaller ZSM-5 crystals will have lower shape selectivity. In the case of nano-ZSM-5, the decrease of the framework thermal/hydrothermal stability has been observed [14]. From these reasons, the designing of the crystal morphology is very important step in the optimization of the activity, shape selectivity, anti-deactivation ability and longevity of the zeolite ZSM-5 catalyst used for specific applications. It is well-known that, the crystal morphology of zeolite is determined by its crystallization conditions [15]. Crystal's size of zeolites (including zeolite ZSM-5) decreases with increasing number of nuclei and vice versa [16–18]. The influences of hydrogel chemistry (silicon and aluminum sources, template, cations and anions, molar ratios of OH/SiO_2, SiO_2/Al_2O_3, H_2O/SiO_2, etc.), and crystallization conditions (temperature, agitation, aging, etc.) on the crystallization kinetics and product morphology have been reported [19–23]. As to the influences of silicon and aluminum sources, previous studies were mainly focused on the effect of different kinds of sources.

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http://dx.doi.org/10.1016/j.micromeso.2014.03.015
1387-1811/

Among them, the study by Derouane and Gabelica et al. [24] mentioned that the different silicon sources resulted in different morphology of zeolite ZSM-5 by affecting the rate of nucleation and the crystallization mechanism. When colloidal silica was used, fewer nuclei were produced due to the slow depolymerization of silicon source, the crystallization conducted following liquid transportation mechanism which resulted in large crystals. On the other hand, when water glass was used, a larger number of nuclei were generated by the soluble monomeric (or low oligomeric) silicate ions, the crystallization conducted via direct solid-phase transformation which resulted in small crystals. However, there is no study dealing with the adjustment of the polymerization degree of a silicon source and aluminum source for zeolite ZSM-5 synthesis, so far. Therefore, it is still unclear whether the regulation of the polymerization degree of the silicon and aluminum sources can be a way to the control of zeolite ZSM-5 morphology.

This study focused on regulating the polymerization degree of silica sol and aluminum oxide by using sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) respectively, and investigating the influences of the polymerization degree of the raw materials on the crystallization kinetics and product morphology of zeolite ZSM-5. Significant effect of the polymerization degree of silicon and aluminum sources has been observed, treating with NaOH and H_2SO_4 is a simple way to regulate the polymerization degree of silicon and aluminum sources, and so as to control the morphology of ZSM-5 crystalline.

2. Experimental

2.1. Zeolite ZSM-5 synthesis

Chemical reagents included silica sol (SiO_2 30 wt%), alumina (Al_2O_3 74 wt%), N-butylamine (NBA) (>99 wt%), sodium hydroxide (96 wt%) and sulfuric acid (98 wt%). Zeolite ZSM-5 was synthesized by using silica sol as initial Si source, alumina as initial Al source, and N-butylamine (NBA) as structure directing agent (SDA). Sodium hydroxide and sulfuric acid were used to depolymerize the initial Si and Al sources, respectively. The hydrogel was obtained according to the following procedures:

(1) The depolymerization of silica sol by NaOH:
The aqueous solution of NaOH was added to initial Si source. The mixture was stirred at room temperature for 1 h to obtain solution A
(2) The depolymerization of alumina by H_2SO_4:
The initial Al source was added to the aqueous solution of H_2SO4. The mixture was stirred at room temperature for 1 h to obtain solution B;
The amounts of H_2SO_4 and NaOH were determined by the preset polymerization degree and the basicity of the final hydrogel.
(3) The preparation of solution C:
The solution B was slowly added to solution A. The mixture was stirred at room temperature for 2 h to obtain solution C.

Then, under vigorous agitation NBA was added to solution C to obtain the final hydrogel which had molar composition of 2.0 Na_2O: 1 Al_2O_3: 31.2SiO_2: 800 H_2O: 12 NBA: $x$$Na_2SO_4$ ($x = 0.053$–0.504). Here, Na_2SO_4 was formed by NaOH and H_2SO_4 that used for the depolymerization of the initial Si and Al sources. Finally, the hydrogel was crystallized in the Teflon-lined autoclave at 443 K for 0–48 h. The solid product was recovered by filtration and the sample was obtained by further washing with demineralized water, drying at 383 K and calcining programmatically to 813 K to remove the SDA.

2.2. Characterizations

The polymerization degree of Si species (solution A) was characterized by UV Raman spectra and Liquid-state ^{29}Si NMR spectra. The polymerization degree of Al species (solution B) and the aluminosilicate gel (solution C) were characterized by UV Raman spectra. That is, the entire solution A, B and C which included liquid phase and solid phase were immediately analyzed after prepared. UV Raman spectra were recorded on a home-made DL-2 Raman spectrometer. A 244-nm line of LEXEL LASER was used as excitation source. Acton triple monochromator was used as a spectrometer for Raman scattering. The power of the laser line at the sample was below 3 mw. The spectra were collected by a Prinston CCD detector. Liquid-state ^{29}Si NMR spectra were acquired on a Bruker DRX-400 spectrometer with a 5 mm probe using proton decoupling pulse program. A 400 scans were accumulated with a $\pi/2$ pulse width of 9.5 μs and a 2 s recycle delay. Chemical shifts were referenced to 4,4-dimethyl-4-silapentane sulfonate sodium salt (DSS). The crystallization products were characterized by Field Emission Scanning Electron Microscopy (FE-SEM), Powder X-ray diffraction (XRD), X-ray fluorescence spectrometer (XRF), X-ray photoelectron spectroscopy (XPS) and Nitrogen Physisorp. The FE-SEM images were recorded with a Hitachi S-4800 microscope. The XRD patterns were obtained on a Rigaku D/max-2004 diffractometer with Cu Kα radiation, it worked at the condition of 40 kV, 100 mA with a scanning rate of 0.02° min^{-1} (2θ). The crystallinity of ZSM-5 phase was determined by the intensity of the main peak at $2\theta \approx 23.1°$. The chemical compositions of the solid samples were analyzed using a Bruker SRS 3400 XRF and VG ESCALAB MK2 XPS with an Al Kα(1486.6 eV) X-ray source. Nitrogen Physisorp were performed on Micrometrics TriStar 2020 at 77 K. Prior to the Nitrogen physisorp measurements, all zeolite products were degassed at 350 °C for 3 h.

3. Results and discussion

3.1. The regulation of the polymerization degree of silica sol and alumina

Fig. 1A shows the Raman spectra of Si sources obtained by adding different amount of NaOH into silica sol. It can be seen that, the initial silica sol was characterized by a broad band centered at 440 cm^{-1} (the characteristic of the vitreous SiO_2) [25], and a weak band at 978 cm^{-1} (Si–OH stretching vibrations). These bands are in consistent with the well-known structure of silica sol [26]. The presence of the 978 cm^{-1} band indicates that the surface of SiO_2 particles were covered with -OH groups. When the initial silica sol was depolymerized by NaOH in solution A, the resulting Si sources all showed the signal of monomeric silicate anion at 783 cm^{-1}. [27] In case of the Na_2O/SiO_2 ratio of solution A was 0.064, the monomeric silicate anion was the only visible depolymeric silicate species. As the Na_2O/SiO_2 ratio increased, the SiO_2 particles were further depolymerized which was accompanied by the increase of the monomeric silicate anion concentration (783 cm^{-1} peak intensified), and the appearance of dimeric silicate anion (indicated by 600 cm^{-1} peak when Na_2O/SiO_2 ratio above 0.142), oligomeric silicate anions (indicated by 1040 cm^{-1} peak when Na_2O/SiO_2 ratio above 0.154), and trimeric silicate anion (indicated by 540, 927 cm^{-1} peak at Na_2O/SiO_2 ratio of 0.568) [27–31]. In order to verify these silicate species, the ^{29}Si NMR spectra were taken with the solutions of A1, A3 and A6. The ^{29}Si NMR spectra (Fig. 2) disclosed that, the monomeric silicate (72 ppm) existed together with dimeric (80 ppm), trimeric (88 ppm) and oligomeric (97 ppm) silicate anions in the highly polymerized Si source (the ratio of Na_2O/SiO_2 was 0.064) [32]. As the Na_2O/SiO_2 ra-