



Influence of Br⁻ and Na⁺ in synthesis of Silicalite-1 on catalytic performance in vapor phase Beckmann rearrangement of cyclohexanone oxime

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ABSTRACT

Silicalite-1 was hydrothermally synthesized with tetrapropylammonium hydroxide (TPAOH) as the template in the presence of various Br⁻ and Na⁺ concentrations, characterized by XRD, SEM, BET, XPS, FT-IR and NH₃-TPD and studied in the vapor phase Beckmann rearrangement of cyclohexanone oxime. The characterization results show that the crystal sizes of Silicalite-1 increase with the increase of Na⁺ concentrations in the synthesis; Na⁺ is combined in the Silicalite-1 crystals, but removed by a base treatment. The base treated catalysts exhibit nearly complete conversion of cyclohexanone oxime with above 95% selectivity to ϵ -caprolactam. Catalysts with the addition of up to 20 mol% Br⁻ relative to TPAOH without Na⁺ in the synthesis do not influence the physical and chemical as well as the catalytic properties. The addition of Na⁺ below 2.5 mol% of TPAOH do not influence the catalytic properties either. However, at the concentrations of Na⁺ \geq 5 mol% of TPAOH in the synthesis, the catalysts deactivate faster with the increase of Na⁺ contents, which is attributed to more carbon deposition in the larger Silicalite-1 particles, determined by TGA. The results of this work are of great importance for the industry.

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1. Introduction

ϵ -Caprolactam is the monomer for the production of Nylon-6 [1–4]. The current industrial route for the production of ϵ -caprolactam is a liquid phase Beckmann rearrangement of cyclohexanone oxime using highly concentrated sulfuric acid. Although the process is highly selective, it has several disadvantages such as the corrosion of the reactor, environmental pollutions and by-production of a large amount of ammonium sulfate [1]. In order to solve these problems, strenuous efforts have been devoted to developing vapor phase Beckmann rearrangement of cyclohexanone oxime.

Many solid acid catalysts [5], such as tungsten oxide [6], silicantantalum oxide [7], sulfated zirconia [8], and boron supported on silica [9], zirconia [10], titania–zirconia [11] are investigated for the vapor phase Beckmann rearrangement reaction. However, these catalysts exhibit low catalytic activities or fast deactivation. Molecular sieves have also been widely investigated for this reaction, such as aluminum- or boron-containing M41S [12–14], SBA-15 [15,16], Mordenite [17,18], FAU-type Y (HUSY) [19–21], BEA-type Beta [17,22–25], and MFI-type ZSM-5 [26–32], TS-1 [26,33] and Silicalite-1 (S-1) [4,26,34–45]. Among these, MFI-type zeolites with high Si/Al atomic ratios and S-1 have been found being active and

selective catalysts in the reaction. Sumitomo Chemical Co., Ltd. has commercialized the vapor phase Beckmann rearrangement of cyclohexanone oxime using S-1 as catalyst [4,28,34,35].

In the synthesis of S-1, tetrapropylammonium hydroxide (TPAOH) is used as the template and alkali source. However, Br⁻ and Na⁺ are often found as impurities in TPAOH, which is produced through an ionic exchange process. Intentional addition of sodium to ZSM-5 or TiO₂ led to the increase of the crystal sizes and affected the morphology [46–48]. However, the effects of Br⁻ and Na⁺ in the synthesis of S-1 on the crystal sizes, morphology and the catalytic performance in the vapor phase Beckmann rearrangement of cyclohexanone oxime has not been studied.

In this work, Br⁻ and Na⁺ are added into the TPAOH solution for the synthesis of S-1. The obtained S-1 catalysts are characterized with XRD, SEM, BET, XPS, FT-IR and investigated in the vapor phase Beckmann rearrangement of cyclohexanone oxime. The aims are to study the effects of Br⁻ and Na⁺ in the synthesis on S-1 crystal structure, morphology and the catalytic performance.

2. Experimental

2.1. Materials

Electronic grade tetraethyl orthosilicate (TEOS) was obtained from Tianjin Kermel Chemical Reagents. Sodium hydroxide (NaOH) and methanol were purchased from Tianjin Guangfu Fine Chemical Research Institute. TPAOH aqueous solution (10 wt%, Na⁺ < 4 ppm

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and no bromine was found by Ag^+ testing) was prepared through the ionic exchange of tetrapropylammonium bromide (TPABr), which was purchased from Tianjin Guangfu Fine Chemical Research Institute.

2.2. Catalyst preparation

The starting materials for the hydrothermal synthesis of S-1 had the following molar compositions: $435 \text{ SiO}_2:100\text{TPAOH}:x\text{TPABr}:x\text{NaOH}:20870 \text{ H}_2\text{O}$. First, the required amounts of TPABr and NaOH were dissolved in TPAOH aqueous solution in a polypropylene bottle under stirring, then TEOS was added in TPAOH aqueous solution. The resulting mixture was stirred vigorously at room temperature for 2 h, and the crystallization was performed in a PTFE-lined, stainless steel autoclave under static conditions at 378 K for 96 h. The white solid product was centrifuged and washed with distilled water until the pH reached about 7, then it was dried at 383 K overnight and calcined at 823 K in air for 6 h. The samples are designated as S-1- x , with x varied at 0, 2.5, 5, 10 and 20, respectively. To investigate the effect of Br^- alone, an S-1 sample was synthesized with x of Br^- equal to 20 without the addition of Na^+ with the same procedure. This sample is designated as S-1-20Br.

The samples were treated with a nitrogen-containing basic solution. For this, 4 g samples were treated with a mixture of aqueous ammonium nitrate solution (7.5 wt%, 30 g) and aqueous ammonia solution (25 wt%, 10 g) at 363 K for 1 h for three times. After the treatment, the samples were washed until the pH reached about 7, and then dried at 383 K and calcined at 823 K for 6 h in air.

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns of the samples were taken on a Rigaku D/max 2500 powder diffractometer using graphite monochromator with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 200 mA with a scanning rate of 8° min^{-1} in the 2θ ranges from 5° to 35° .

Nanosem 430 field emission scanning electron microscopy (FESEM) was utilized to characterize the size and morphology of the samples after sputtering with gold.

BET specific surface areas were measured by N_2 adsorption at 77 K on Micromeritics Tristar 3000. BET specific surface areas were calculated by applying the Brunauer–Emmett–Teller (BET) method.

XPS spectra of the samples before and after the base treatment were measured with a Perkin-Elmer PHI-1600 X-ray photoelectron spectrometer using $\text{Mg K}\alpha$ radiation (1253.6 eV) at 15 kV and 250 W. The binding energies were calibrated by C1s as the reference energy (C1s = 284.6 eV).

FT-IR spectra of the samples before and after the base treatment were recorded on a Nicolet Magna 560 spectrometer with a resolution of 4 cm^{-1} . For this, a self-supported wafer (15 mg/cm^2) was placed in a cell with CaF_2 windows, and heated at 673 K for 1 h under vacuum of 0.1 Pa. When the cell was cooled down to 423 K, the spectra were recorded.

NH_3 -TPD spectra were recorded using Micromeritics 2910 chemical adsorption instrument. The samples were pretreated in a nitrogen flow at 823 K for 1 h, and then cooled down to ambient temperature, and ammonia was introduced with nitrogen as the carrier gas. After 30 min, the flow was switched to nitrogen, and the sample was heated to 873 K at a rate of 10 K/min. The desorbed ammonia was monitored by a thermal conductivity detector.

The amounts of coke formed after the Beckmann rearrangement reaction were measured using Shimadzu TGA-50 thermogravimetric analyzer by heating from room temperature to 1123 K at 10 K/min in the flow of air. The weight loss between 623 K and 973 K was attributed to the burning of coke [44].

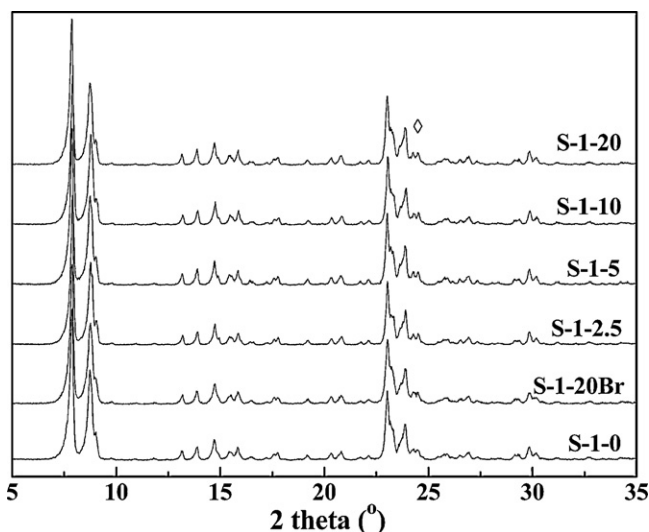


Fig. 1. XRD patterns of base treated samples S-1- x synthesized in the presence of various Br^- and Na^+ concentrations.

2.4. Vapor phase Beckmann rearrangement reaction

The catalytic vapor phase Beckmann rearrangement reaction was carried out at atmospheric pressure in a fixed-bed flow reactor. 0.3 g catalyst (shaped under pressure and sieved at 40–60 mesh) was mixed with 2 g quartz sand (40–60 mesh) and positioned with quartz wool in a quartz reactor with an inner diameter of 10 mm and a length of 400 mm. The reactor was placed inside a temperature-controllable vertical furnace. The thermocouple tip in the quartz well was centered at the middle of the catalyst. After treated in a flow of Ar at 673 K for 1 h, a mixture with 30 wt% cyclohexanone oxime and 1 wt% water in methanol was fed into the reactor at the oxime weight hourly space velocity (WHSV) of 6 h^{-1} by a double-plunger micro-metering pump at the rate of $6 \text{ cm}^3/\text{h}$, and $30 \text{ cm}^3/\text{min}$ of Ar (99.99%) was introduced using a mass flow controller. These optimized conditions were obtained in the previous works [23,25,44]. The reaction products were collected in an ice-water trap and analyzed with an HP 4890GC equipped with an OV-1701 column and a flame ionization detector.

3. Results and discussion

3.1. Characterization results

The powder XRD patterns of the base treated S-1 samples synthesized in the presence of different Br^- and Na^+ concentrations are given in Fig. 1. It is seen that all the samples are highly crystalline, the XRD patterns show all reflections matching well with those reported for S-1 [49], and no peaks corresponding to Na-containing phases are detected. All samples show reflections at $2\theta = 24.4^\circ$, indicating that the typical structures of the S-1 are monoclinic symmetry [36,40]. The relative crystallinity of the base treated S-1 are calculated by comparing the total intensity values of the reflections at $2\theta = 7.9^\circ, 8.9^\circ, 23.0^\circ, 23.2^\circ, 23.7^\circ$ and 24.0° [50] and assuming those of S-1-0 being 100%. The results in Table 1 indicate that S-1 with various Br^- and Na^+ concentrations in the synthesis have almost the same crystallinity, suggesting that the presence of Br^- alone or with Na^+ together in the synthesis does not affect the crystal structure of S-1.

Fig. 2 shows the SEM micrographs of the base treated samples of S-1- x synthesized in the presence of different concentrations of Br^- and Na^+ . The micrographs demonstrate a uniform distribution of the crystal sizes for each sample. With the increase of Br^- and

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