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Influences of ethylenediamine treatment of Silicalite-1 on the catalytic vapor-phase Beckmann rearrangement of cyclohexanone oxime

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Abstract

Silicalite-1 was modified by organic base of ethylenediamine. The characterization results indicated that after alkaline treatment, the crystal structure of S-1 was not destructed or changed; the silanol nests were maintained, but the terminal silanol groups were eliminated. The modified S-1 exhibited better performance in the vapor-phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam, especially in terms of the stability. It is inferred that the silanol nests are the most suitable centers for the Beckmann rearrangement reaction, while the terminal and vicinal silanol groups might be responsible for the coke deposition.

Keywords: Cyclohexanone oxime; Beckmann rearrangement; Silicalite-1; Base treatment; Ethylenediamine

1. Introduction

Beckmann rearrangement of cyclohexanone oxime (CHO) to ε-caprolactam (CPL) is an important industrial process. In order to solve the problems caused by sulfuric acid as a catalyst in the traditional processes, many solid catalysts have been studied [1–14]. Among these, MFI zeolites with high Si/Al atomic ratios or Silicalite-1 (S-1) have been considered as active and selective catalysts for the Beckmann rearrangement [1,4–12]. Some researchers suggested that the active sites for the Beckmann rearrangement are the very weak acidic or neutral silanol nests, rather than the strong acid sites [5–9]. The solvent of CHO also has strong influences on the activity, selectivity and stability of the catalysts. Ethanol or methanol, with medium polarity, was the most suitable solvent for the Beckmann rearrangement over S-1 [6,8–10]. In order to improve the performances of the zeolites, several methods were used to modify acidity or silanol groups of the S-1 catalyst. Boron was incorporated into H-ZSM-5 to reduce the deactivation rate and acid strength [10]; Mehanol and chlorotrimethylsilane were used to modify the terminal silanol on high silica MFI zeolites [1]; ammonia solution or other organic base [7,11,15], even HF [16] were also applied to modify the silanol groups on S-1.

In the present work, S-1 was modified by ethylenediamine, ammonia mixture solution and HF, characterized with XRD, SEM, FTIR and studied in the vapor-phase Beckmann rearrangement of CHO. The aims are to study the effects of the base treatment on the crystal structure, morphology and the catalytic performance and to reveal the active sites for the Beckmann rearrangement of CHO.

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2. Experimental

2.1. Catalyst preparation

S-1 was synthesized hydrothermally with tetraethyl orthosilicate (TEOS) and tetrapropylammonium hydroxide (TPAOH) aqueous solution (20 wt%). The starting material had the following molar compositions: 1 TEOS: 0.2 TPAOH: 15 H_2O. Crystallization was performed in a PTFE-lined autoclave under static condition at 443 K for 48 h. The product was centrifuged, washed and dried at 383 K overnight. Then it was calcined at 823 K in air for 6 h. The calcined S-1 was designated as S-1A.

S-1A was mixed with ethylenediamine with a mass ratio of S-1A: ethylenediamine = 1: 2. The mixture was statically heated in a PTFE-lined autoclave. The product was also centrifuged, washed, dried and calcined under the same conditions as for the preparation of S-1A. As a result, three samples treated at 443 K for 48 h, at 443 K for 3 h and at 383 K for 48 h were named as S-1B, S-1C and S-1D, respectively.

A mixture solution of ammonium nitrate (7.5 wt%) and aqueous ammonia solution (25 wt%) with the mass ratio of S-1A: mixture solution = 3:1 was used to treat S-1A at 363 K for 1 h and repeated for three times as described in reference [16]. The product was named as S-1E.

Acid treatment by 0.04 wt% HF with the mass ratio of HF to S-1A of 10:1 was also carried out as base treatment procedure at 363 K for 1 h and repeated for three times [16]. This modified sample was named as S-1F.

2.2. Characterization

Powder X-ray diffraction (XRD) was performed on a RIGAKU D/max-2500 X-ray instrument. Scanning electron microscope (SEM) micrographs were obtained by Philips XL-30 ESEM with 20000 magnitude. FTIR spectra were recorded on a Nicolet Magna 560 spectrometer with a resolution of 2 cm^{-1}. For this, the self-supported wafers (about 10 mg/cm^2) were placed in a cell with CaF_2 windows, heated at 773 K for 1 h under vacuum of 0.1 Pa. When the cell was cooled down to 323 K, the spectra were recorded. The acidity of the catalysts was detected by the FTIR spectra of adsorbed pyridine on the sample wafers as described before [2]. The amounts of coke after reaction were measured using SHIMADZU TGA-50 by heating from room temperature to 973 K at 10 K/min in the flow of oxygen. The weight loss between 623 K and 973 K was attributed to coke [14].

2.3. Catalytic reaction

The vapor-phase Beckmann rearrangement of CHO was carried out at atmospheric pressure in a silica reactor (8 mm i.d.), which was placed inside a temperature-controllable vertical furnace. In a typical run, 0.2 g catalyst was fixed between two layers of quartz wool in the reactor with the thermocouple tip in the quartz well being centered in the middle of the catalyst bed. After the catalyst was preheated for 1 h in a flow of Ar at the reaction temperature, CHO solution in ethanol (33 wt%) was fed by a Series IV Digital HPLC Pump at a constant flow rate into vaporizer before entering the reactor. 20 cm^3/min of Ar was introduced using a mass flow controller. The reaction products were collected in an ice–water trap and analyzed using an Agilent 4890GC with a packed column (PEG-20 M, 2 m) and a flame ionization detector.

3. Results and discussion

3.1. Effects of base treatment on S-1 structural properties

Fig. 1 shows the XRD patterns of S-1A and S-1B, which indicate that both of them have typical MFI structure. For MFI zeolites, there are two reversible phases, monoclinic and orthorhombic structure [7,17]. From Fig. 1, it is seen that both S-1A and S-1B have one peak at $2\theta = 24.5°$, indicating that they have orthorhombic structure [7,17]. The relative crystallinity of the S-1 samples was calculated by comparing the total intensity values of the peaks at $2\theta = 7.9°$, 8.9°, 23.2°, 24.0° and 24.5°. The comparative results indicate that S-1A and S-1B had almost the same crystallinity. Other modified S-1 samples of S-1C, S-1D, S-1E and S-1F also had orthorhombic structure (not shown) and the same crystallinity as S-1A. So the base or acid treatment did not change the structure phase of S-1.

Fig. 2 shows the SEM micrographs of S-1A and S-1B. It is seen that ethylenediamine treatment did not change the crystal size of S-1 significantly and the crystal sizes are both in the range of 100–200 nm. For the milder treated samples of S-1C, S-1D and S-1E, their crystal sizes were almost not changed. But base treatment could form mesopore and extract Si atom [18,19]. Maybe some Si–O–Si bridge bonds in the framework were also broken. Since the desorption of CPL was the rate-controlling step in the vapor phase Beckmann rearrangement of CHO [8], the mesopore could

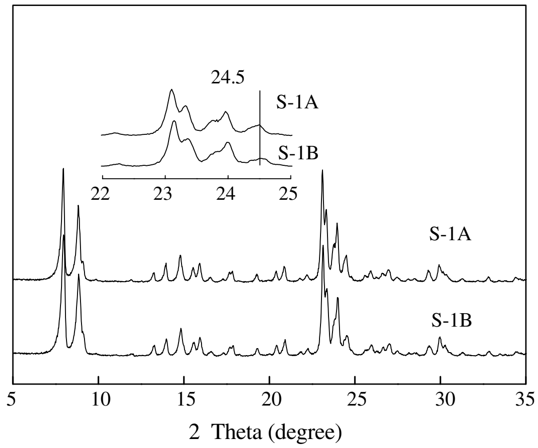

Fig. 1. XRD patterns of S-1A and S-1B.