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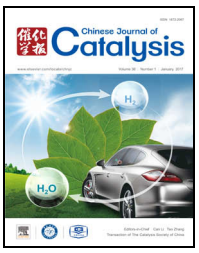

Article

A shaped binderless ZSM-11 zeolite catalyst for direct amination of isobutene to *tert*-butylamine

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ABSTRACT

A shaped binderless and two binder-containing ZSM-11 zeolite catalysts were prepared and characterized by powder X-ray diffraction, N_2 adsorption-desorption, and pyridine adsorption-infrared measurements. The binderless catalyst was synthesized using a dry-gel conversion technique, in which 1,6-hexanediamine and tetrabutylammonium bromide were used as structure-directing agents and no other alkaline materials were added. The catalytic performance of the zeolites in the direct amination of isobutene to *tert*-butylamine was evaluated in a fixed-bed reactor. By virtue of its high crystallinity as well as its good mechanical strength, the shaped binderless ZSM-11 catalyst showed a higher rate of formation of *tert*-butylamine than did the binder-containing catalysts.

1. Introduction

Tert-butylamine is an important raw material and pharmaceutical intermediate, and the direct amination of isobutene over zeolite catalysts to give *tert*-butylamine has been reported to be an environmentally benign and economical process. MFI and BEA have been found to be superior to other materials [1,2]. Zeolites ZSM-5 and ZSM-11 have similar framework densities and pore sizes, but differences in their channels result in a higher selectivity for aromatics in the aromatization of 1-hexene over ZSM-11 compared with that over ZSM-5 [3]. In the case of the direct amination of isobutene, we found that ZSM-11 showed slightly higher activity than ZSM-5 when using similar crystal size, SiO_2/Al_2O_3 molar ratio and acidity.

Zeolites synthesized by conventional techniques are usually obtained in powder form. However, for practical applications, the zeolite powder should be formed into catalyst particles with a certain shape, size, and mechanical strength by using inert materials as binders [4]. Unfortunately, this causes the reduction of the active zeolite component and blocks part of the channel windows in the formed catalysts, which consequently results in a considerable reduction in the catalytic performance

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of the zeolites [5]. It would therefore be interesting to prepare a mechanically stable and self-supporting zeolite catalyst, in which the active components are protected, namely, a binderless zeolite catalyst [6].

Self-bonded ZSM-5 pellets are readily prepared at 170 °C under hydrothermal conditions from a gel with the following composition: a Li_2O : b Na_2O : 2b TPABr : b $A1_2O_3$: 150 SiO_2: 490 H_2O, with $8 \le a \le 9$ and $14 \le b \le 16$ (TPABr = tetrapropylammonium bromide). If the Li_2O is replaced with Na_2O or K_2O, only nonpelleted, powdered ZSM-5 samples can be prepared, which underlines the role of the $LiAlO_2$ binder in the system [7]. Recently, shaped binderless ZSM-5 zeolites have been prepared from aluminosilicate extrudates using a dry-gel conversion (DGC) technique, in which the introduction of amines into the steam favored the formation of nanosized ZSM-5 zeolite. Of particular note, the morphology of these aluminosilicate extrudates was retained in the crystallization process [8]. Self-bonded pellets of ZSM-11 with high mechanical resistance could also be obtained from initial gels with a composition of 1 Li_2O : (3.25–7.5) Na_2O : (3.25–7.5) Al_2O_3 : 150 SiO_2 : (0.65–1.5) TBABr : 490 H_2O [9].

TPABr [10], tetrabutylammonium bromide (TBABr) [11] and 1,6-hexanediamine (HDA) [12] are suitable structure directing agents (SDAs) for the synthesis of ZSM-5, ZSM-11, and ZSM-5/ZSM-11, respectively. However, ZSM-11 synthesized using TBABr and HDA as co-SDAs has not yet been reported. Here, a shaped binderless ZSM-11 catalyst was prepared using the DGC method, using TBABr and HDA as co-SDAs in the synthesis and without adding other alkaline materials. The obtained sample was then employed for the direct amination of isobutene. In addition, the performance of the binderless and binder-containing ZSM-11 catalysts (HZSM-11+Al_2O_3 and HZSM-11+SiO_2) in the amination reaction was compared.

2. Experimental

2.1. Preparation

Na-ZSM-11 zeolite powder with a framework SiO_2/Al_2O_3 molar ratio of 61.6, and containing 2.33 wt% Na_2O and 10.4 wt% TBABr was synthesized by following a previously reported procedure [3]. The powder was mixed with silica sol (SiO_2: 30 wt%, Na_2O: 0.31 wt%) to form a cylindrical extrudate that was 1.8–2.2 mm in diameter and 3–7 mm in length. The dried sample containing 30 wt% of silica was denoted S1. For comparison, S2, which contained 30 wt% of alumina, was prepared by using boehmite instead of silica sol as the binder.

S1 was recrystallized using the DGC method. First, 4 g S1 was placed in a stainless-steel tube fixed and supported in a horizontal position in a stainless-steel autoclave with a Teflon lining. Then 1.2 g HDA and 4 mL deionized water were poured into the bottom of the Teflon-lined autoclave taking care that the solid sample did not come into direct contact with the liquid [13]. The autoclave was heated at 175 °C for 10.5 h, and then cooled to room temperature. The solid sample was dried at 120 °C for 2 h and then calcined in air at 540 °C for 5 h. This sample was denoted S3.

All three samples (S1, S2, and S3) were converted to the protonic form by conventional ion exchange in aqueous NH_4NO_3 solution [14], followed by calcination (550 °C, 4 h, air). The resultant samples were denoted Cat-A, Cat-B, and Cat-C, respectively.

2.2. Characterization

The samples were characterized by powder X-ray diffraction (XRD), N_2 adsorption-desorption, temperature-programmed desorption of NH_3 (NH_3-TPD), infrared spectroscopy of adsorbed pyridine (Py-IR), high-resolution transmission electron microscopy (HRTEM) and nuclear magnetic resonance (NMR) techniques as described elsewhere [15]. The side-pressure strength of the samples was tested using a ZQJ-II intelligent particle strength tester.

2.3. Reaction

The direct amination of isobutene to *tert*-butylamine was carried out in a stainless-steel fixed-bed reactor and the mode of operation was down-flow. All the samples were pressed, crushed, and sieved to give a particle size of 0.38–0.85 mm before they were loaded into the reactor. Initially, 5 g of the catalyst was loaded into the center of the reactor and pretreated at 500 °C for 1 h in N_2. The reactor was cooled to 250 °C, and then liquid NH_3 was pumped in from the top to fully fill the reactor before isobutene was introduced. Ma et al. [16,17] have reported that this feeding sequence is favorable for the reaction. After 2 h, it was confirmed that the NH_3/i-C_4H_8 molar ratio remained stable at 4:1 by measuring the concentrations of the educts, and the products were analyzed on-line with an Agilent 7980B gas chromatograph equipped with a flame ionization detector (FID) and a PONA capillary column.

The isobutene conversion ($C_{\text{isobutene}}$), *tert*-butylamine selectivity ($S_{tert\text{-butylamine}}$) and formation rate of *tert*-butylamine ($V_{\text{formation}}$) were calculated according to the following equations:

$$C_{\text{isobutene}} = \frac{x_{tert\text{-butylamine}} + x_{C_8}}{x_{\text{isobutene}} + x_{tert\text{-butylamine}} + x_{C_8}} \times 100\% \quad (1)$$

$$S_{tert\text{-butylamine}} = \frac{x_{tert\text{-butylamine}}}{x_{tert\text{-butylamine}} + x_{C_8}} \times 100\% \quad (2)$$

$$V_{\text{formation}} = \frac{F_{M\text{isobutene}} \times C_{\text{isobutene}} \times S_{tert\text{-butylamine}}}{m_{\text{cat}}} \times 10^6 \quad (3)$$

where $x_{tert\text{-butylamine}}$ is the molar percentage of *tert*-butylamine in the products, x_{C8} is the molar percentage of C_8 hydrocarbons in the products, $x_{\text{isobutene}}$ is the molar percentage of isobutene in the products, $F_{\text{M isobutene}}$ is the molar flow rate of isobutene (μmol/h), and m_{cat} is the mass of the catalyst (g).

3. Results and discussion

3.1. Synthesis of binderless ZSM-11 zeolite catalyst

First, two binder-containing ZSM-11 samples (Cat-A and Cat-B) were prepared, and their XRD patterns are shown in Fig. 1. The relative crystallinity (RC) of the sample was calculated