Enhancement of catalytic performance in the benzylation of benzene with benzyl alcohol over hierarchical mordenite

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ABSTRACT

Hierarchical mordenites were prepared by a sequential post-treatment method based on a commercial mordenite with a Si/Al molar ratio of 15. The mordenite obtained by acid treatment showed much higher catalytic activity than the parent mordenite in the benzylation of benzene with benzyl alcohol, even a little better than that obtained by acid–base treatment. The apparent reaction rate constant for acid-leached mordenite is six times higher than that for HM. Further, the mordenite with acid–base–acid treatment exhibited the highest catalytic activity among these samples. The apparent reaction rate constant for acid–base–acid-leached mordenite is 15 times that for HM and twice that for acid-leached mordenite and acid–base-leached mordenite. This remarkably enhanced catalytic performance should be attributed to more accessible acid sites and much better mass transfer ability from rich mesoporosity in acid–base–acid-leached mordenite.

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1. Introduction

The liquid-phase benzylation of aromatic compounds by benzyl chloride or benzyl alcohol is one of the important reactions in organic chemistry, because it can be used to produce diphenylmethane and substituted diphenylmethanes, which are key industrial compounds as pharmaceutical intermediates or fine chemicals [1,2]. Generally, such reactions are carried out in the presence of homogeneous acid catalysts such as $AlCl_3$, $FeCl_3$, and H_2SO_4 [3,4]. However, these catalysts meet some problems, such as corrosion and difficulty in separation and recovery. Therefore, there have been many attempts to replace these homogenous catalysts with heterogeneous solid catalysts [5–8]. Zeolites, as solid catalysts, have been studied in benzylation reactions [9–13] because of their strong acidity, large surface area, and regular porous structure with excellent stability. The results indicate that highly acidic zeolite catalysts show poor reactivity, mainly because of diffusion limitation caused by their microporous networks [9,10].

Recently, hierarchical zeolites have received much attention because they cannot only overcome the diffusion limitation of zeolites on the reaction rate but also maintain stability and strong acidity, like conventional zeolites [14–16]. Several preparative

methods have been adopted in the synthesis of hierarchical zeolites with different framework types, such as ZSM-5 [17–22], Beta [19,22], Y [23–25], and SSZ-13 [26]. Of these, the synthesis of hierarchical mordenite is of practical importance because mordenite, with low preparative cost and strong acidity, has been used for hydroisomerization, alkylation, and dewaxing processes in industry. Currently, hierarchical mordenite can be prepared by dealumination with steam and acid [27–33] or desilication with base [34–39]. The studies indicate that dealumination reduces the density of the acidic sites due to the extraction of aluminum from the framework. As a result, the improvement effect of transport ability on catalytic performance is weakened [36]. For example, Boveri et al. showed that the dealuminated catalyst gave a negligibly improved yield of linear alkylbenzene in the alkylation of benzene with ethylene [33]. Van Bokhoven et al. reported that the acid-leached mordenite had a low catalytic activity similar to that of the parent mordenite in the benzylation of benzene with benzyl alcohol [40].

On the other hand, it has been demonstrated that desilication is an efficient route for preparing hierarchical mordenite, with good preservation of the intrinsic acidity [36]. The hierarchical mordenite obtained by desilication exhibited much better catalytic performance than the parent and acid-leached mordenite. However, recent studies suggested that desilication could result in the deposition of part of the Al species on the external surface of the zeolite framework and thus negatively impact catalytic reactivity. After

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subsequent acid washing, the deposited Al species could be removed from the external surface. Then, the catalytic performance could be further improved due to enhanced accessibility [39].

In the present work, with the aim of obtaining a highly efficient catalyst for Friedel–Crafts alkylation based on mordenite, we prepared hierarchical mordenites by a sequential post-treatment method based on a commercial mordenite. Considering that benzyl alcohol is a relatively friendly benzylation reagent due to water as the byproduct, the benzylation of benzene with benzyl alcohol was chosen to evaluate the catalytic performance over the catalysts obtained in each step. The relationship between the structural properties and the catalytic performance will be discussed.

2. Experimental

2.1. Materials

Commercial mordenite was purchased from the Catalyst Plant of Nankai University. HNO_3, $NaOH$, NH_4NO_3, benzene, and benzyl alcohol were purchased from Sinopharm Chemical Reagents Co. and used without further purification.

2.2. Preparation of catalysts

The commercial mordenite was ion-exchanged with a solution of 1 M NH_4NO_3 at 353 K for 1 h, under stirring with a speed of 1000 rpm, followed by calcination at 823 K for 3 h. The obtained sample was labeled HM.

The HM sample was refluxed with a solution of 2 M HNO_3 at 373 K for 2 h with a liquid-to-solid ratio of 20 ml/g, under stirring with a speed of 1000 rpm. Then, the solid sample was filtered, washed with deionized water, dried at 393 K for 12 h, and ion-exchanged thrice with a solution of 1 M NH_4NO_3 at 353 K for 1 h, followed by calcination at 823 K for 3 h. The final product was labeled HM-A.

The HM-A sample was treated with a solution of 0.2 M $NaOH$ with a liquid-to-solid ratio of 20 ml/g at 343 K for 0.5 h under stirring with a speed of 1000 rpm. The product was filtered, washed with deionized water, dried, ion-exchanged, and then calcined at 823 K for 3 h. The obtained sample was called HM-AB.

The HM-AB sample was treated with a solution of 0.2 M HNO_3 at 323 K for 1.5 h with a liquid-to-solid ratio of 20 ml/g, under stirring with a speed of 1000 rpm. The product was ion-exchanged as described above, followed by calcination at 823 K for 3 h to obtain the sample labeled HM-ABA.

The reused catalyst was obtained by filtering the catalyst after use from the reaction solution, drying, and then calcining at 823 K for 5 h.

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max-2550 diffractometer equipped with a SolX detector—Cu $K\alpha$ radiation with a wavelength of $\lambda = 1.5418$ Å. Relative crystallinity was calculated by the summed intensities of the $(3\,3\,0)$, $(1\,5\,0)$, $(2\,0\,2)$, $(3\,5\,0)$, and $(5\,1\,1)$ reflections. The parent mordenite was assigned a crystallinity of 100%. The crystalline size was determined from the characteristic peak ($2\theta = 22.1°$ for the $(1\,5\,0)$ reflection) using Scherrer's equation, $D = K\lambda/\beta \cos \theta$, where $K = 0.9$, D represents crystallite size, λ represents the wavelength of Cu $K\alpha$ radiation, and β represents the corrected half width of the diffraction peak. SEM images were recorded on a SUPRA 55 operated with an acceleration voltage of 200 kV. Transmission electron microscopy (TEM) images were recorded on a JEOL 2010

with an acceleration voltage of 200 kV. Nitrogen sorption isotherms were obtained at 77 K on a Micromeritics TriStar II 3020 gas sorption and porosimetry system. Samples were normally prepared for measurement after degassing at 423 K under vacuum until a final pressure of 1×10^{-3} Torr was reached. ^{27}Al MAS NMR experiments were performed at room temperature on a Bruker Advance AMS-400 spectrometer at a spinning rate of 12 kHz using a 4-mm probe. In ^{27}Al MAS NMR, a single pulse length of $\pi/6$ and a relaxation delay of 1 s were used, while in ^{29}Si MAS NMR, a high-powered decoupling pulse sequence and a relaxation delay of 6 s were used. The ^{27}Al chemical shift was referenced to (NH_4)-$Al(SO_4)_2 \cdot 12H_2O$ and the ^{29}Si MAS NMR chemical shift to octakis-(trimethylsiloxy)silsesquioxane. X-ray photoelectron spectroscopy (XPS) data were collected on an ESCALAB 250 X-ray photoelectron spectroscope, using Mg $K\alpha$ X-rays as the excitation source. All binding energies were referenced to C1s of 284.6 eV. Temperature-programed desorption of NH_3 (NH_3 TPD) was carried out on a FINESORB-3010 equipped with a thermal conductivity detector. The samples were first outgassed at 823 K for 1 h before the measurement. After being cooled to 303 K, the samples were saturated in an NH_3 stream (5% in Ar) for 1 h and consequently treated in Ar (30 ml/min) for 2 h to remove physisorbed NH_3. Finally, the TPD profile was determined by increasing temperature from 303 to 873 K at a heating rate of 5 K/min while recording NH_3 desorption with a thermal conductivity detector. The adsorption of benzene was performed in an Intelligent Gravimetric Analyzer (IGA-001, Hiden Isochema). Prior to analysis, the powder samples (60–70 mg) were outgassed in situ at 573 K for 4 h under vacuum. When the desired temperature of an experiment was stabilized, the sample was subjected to a pressure step of benzene vapor and the weight change was recorded continuously until equilibrium was reached.

2.4. Catalytic tests

The liquid-phase benzylation of benzene with benzyl alcohol (BA) was carried out in a three-necked round-bottom flask equipped with a reflux condenser and heated in a temperature-controlled oil bath under atmospheric pressure. In a typical run, 14 ml of benzene was added to the catalyst, which had been activated at 773 K in air for 5 h before its use in the reaction. The reaction mixture was maintained for 30 min at the required reaction temperature and then 0.2 ml of benzyl alcohol was added. This moment was regarded as the initial reaction time. Liquid samples were withdrawn at regular intervals and analyzed by gas chromatography on an Agilent 7890A GC with an FID detector using a 30-m packed HP5 column. The products were also identified by GC–MS (5975C-7890A) analysis. Since benzene was in excess, conversion was calculated based on the benzylating reagent, i.e., BA. The selectivity to the product diphenylmethane (DPM) was expressed as the amount of particular product divided by the amount of total products and multiplied by 100.

3. Results and discussion

3.1. Characterization of catalyst

The powder XRD patterns (Fig. 1) of all the samples exhibited well-resolved diffraction peaks, which are characteristic of the mordenite framework structure. Notably, the crystallinity (99%) of HM-A (Table 1) showed a slight decrease from that of HM, although the Si/Al molar ratio increased from 15 to 30 (Table 2). That means that dealumination had a minor influence on the crystallinity of mordenite. A similar result was also observed by another research group [39]. However, after base treatment, the