

Characterization and catalytic reactivity of mordenite – Investigation of selective oxidation of benzyl alcohol



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ABSTRACT

Commercial mordenite was dealuminated with hydrochloric acid by refluxing at 373 K for different durations to develop a stable catalyst for the selective oxidation of benzyl alcohol. The commercial and dealuminated mordenite samples were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier transform infrared (FTIR) spectroscopy, N₂ adsorption–desorption, high resolution scanning electron microscopy (HR-SEM) and temperature programmed desorption (NH₃-TPD). The results revealed that the external surface area increased with acid treatment while preserving the mordenite structure. The catalytic performance of acid-treated mordenite was evaluated in the selective oxidation of benzyl alcohol with *tert*-butyl hydroperoxide (TBHP) as the oxidant and acetonitrile as the solvent. The influences of the variation in catalyst amount, reaction temperature, TBHP/BzOH ratio and SiO₂/Al₂O₃ ratio (SAR) were investigated. The sample with a SAR of 33, obtained after acid treatment for 3 h, exhibited a higher conversion than the other samples. At the optimum conditions, the benzyl alcohol conversion and benzaldehyde selectivity were about 99% and 98%, respectively, over this sample. This catalyst could be reused at least four times without any significant loss in its activity and selectivity. The selective oxidation of substituted benzyl alcohols is also reported.

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1. Introduction

The selective oxidation of benzyl alcohol (BzOH) to benzaldehyde (BzH) is an important organic transformation in organic synthesis. Benzaldehyde is widely used as a raw material in perfumery, dyestuff, pharmaceutical and agro chemical industries [1,2]. It is commercially produced by the oxidation of toluene (low selectivity) or by the hydrolysis of benzyl chloride. However, benzaldehyde produced by the later method contains trace amounts of chlorine, and hence it is not suitable for perfumery and pharmaceutical applications [3–5].

Selective oxidation of benzyl alcohol has been investigated in both the vapor and liquid phases [6]. While liquid-phase oxidations are generally carried out below 100 °C, vapor phase oxidations with molecular oxygen generally require temperatures above 200 °C, the boiling point of benzyl alcohol being 203 °C [7]. Moreover, a larger variety of oxidants, such as organic and inorganic peroxides, can be utilized for liquid phase oxidations, making liquid phase reactions more attractive [8]. Selective oxidation of

benzyl alcohol in the liquid phase can be performed by both homogeneous and heterogeneous catalysts. Heterogeneous catalysts have major advantages over homogeneous catalysts with respect to the ease of recovery (solid form), reusability, good thermal stability and multiple active sites. Hence, many studies have been reported on the use of heterogeneous catalysts as alternatives to conventional stoichiometric inorganic oxidants, which are harmful, expensive and generate a large amount of hazardous waste [9–12]. The possible oxidants available to perform selective oxidation reactions are air (oxygen), organic peroxides, hydroperoxides, peroxy acids, iodoso benzene and dioxiranes. *tert*-Butyl hydroperoxide (TBHP) is an organic hydroperoxide extensively used in the synthesis of peroxide derivatives, epoxidation and other catalytic oxidation reactions, and is used as a free radical initiator in polymerization reactions. TBHP is a good supplier of active oxygen, is safe to handle and reasonably thermally stable under reaction conditions [1,13].

Zeolites are crystalline, porous aluminosilicates, typically consisting of Si, Al and O atoms in the framework and water molecules inside the pores. Some of the important zeolite types are zeolite A, X, Y, L, mordenite, ZSM-5, MCM-22 and beta [14]. Mordenite is a high-silica, large pore zeolite and has a one-dimensional pore

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system with dimensions of 0.67×0.7 nm, which are connected by tortuous pores (small side-pockets) of 0.26×0.57 nm. It contrasts with the other zeolites with respect to the large amount of aluminum that can be readily removed by dealumination methods without a significant loss in crystallinity. Generally, mordenite zeolites undergo rapid deactivation, due to their one-dimensional pore system that restricts the diffusion of the reactant molecules to the small side-pockets, which ultimately affects catalyst performance. Dealumination is a promising post synthesis modification technique to improve the properties of zeolites by selective removal of aluminum from the framework. Dealumination of zeolites is useful to generate stronger acid sites (a decrease in the total number of acid sites), improve thermal stability and modify the pore structure, which leads to an improvement in both the catalytic activity and selectivity. A number of methods have been developed for zeolite dealumination. These include treatment of zeolites with $(\text{NH}_4)_2\text{SiF}_6$, mineral acids (HCl, HNO_3), organic acids (i.e., acetic acid, oxalic acid) and chelating agents (i.e., EDTA). The factors that influence zeolite dealumination are mainly the zeolite structure and the dealumination treatment method [15–20].

To the best of our knowledge, mordenite zeolite has not been reported for the selective oxidation of benzyl alcohol in the liquid phase with TBHP as the oxidant. In the present work, a commercial mordenite sample is modified by acid-treatment with aqueous HCl for different durations, and the dealuminated mordenite samples are utilized for the selective oxidation of benzyl alcohol to benzaldehyde with TBHP as the oxidant. In addition, the effects of many reaction parameters have been investigated in detail.

2. Experimental

2.1. Dealumination of mordenite zeolite

An ammonium exchanged mordenite with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 28 (SAR = 28), (CBV-21A) obtained from Zeolyst International was used in these studies. The commercial zeolite powder was calcined in flowing air at 773 K to convert it from the NH_4 -form into the H-form. The dealumination procedure adopted was as follows: 5 g of the H-form of the parent mordenite sample was dispersed in 100 ml of 6 N HCl solution under stirring. The mixture was then heated to 373 K and kept at this temperature for a stipulated time (0.5, 3 and 6 h). The acid treated (dealuminated) sample was then filtrated, washed repeatedly with distilled water followed by a dilute ammonia solution (pH ~9) to remove any residual acid, and dried at 373 K for 6 h. All the samples were calcined at 773 K for 6 h prior to use in the selective oxidation studies. The calcined zeolite samples were labelled as “xMOR(AT-y)”, where x denotes the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the sample and y denotes the acid-treatment time.

2.2. Characterization of mordenite samples

Powder X-ray diffraction (XRD) patterns were recorded with a Rigaku Miniflex II diffractometer with $\text{Cu K}\alpha$ as the radiation source in the 2θ range of $5\text{--}60^\circ$ with a scan step size of 0.02° . X-ray fluorescence (XRF) analysis was carried out using a Rigaku Primini X-ray fluorescence spectrometer to determine the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. Fourier transform infrared spectra (FTIR, Perkin-Elmer) were recorded in the wavenumber range $4000\text{--}400\text{ cm}^{-1}$ at room temperature using the KBr pellet method. N_2 adsorption–desorption isotherms were obtained with a commercial instrument (Micromeritics ASAP 2020) at liquid N_2 temperature in order to find out the surface areas and pore volumes of the samples. High resolution scanning electron microscopy (HR-SEM) pictures of the samples were obtained using a Hitachi S-4800 instrument to characterize

the surface morphologies. Temperature-programmed desorption of ammonia (NH_3 -TPD) was carried out using a commercial instrument (Micromeritics Chemisorb 2750) to characterize the acidity of the samples.

2.3. Catalytic studies

Liquid phase oxidation of benzyl alcohol was carried out in a batch reactor at atmospheric pressure. In a typical experiment, 0.1 g of the zeolite catalyst (typically, 66MOR(AT-3.0)), 20 mmol benzyl alcohol (BzOH), 25 mmol aqueous *tert*-butyl hydroperoxide (TBHP) as the oxidant and 10 ml of acetonitrile as the solvent were placed in a round-bottom flask equipped with a water condenser and a thermometer. The resulting mixture was kept at 90°C for 4 h under stirring, and then cooled to room temperature. The oxidized products after the catalytic reaction were separated by centrifugation. The products were analyzed in a gas chromatograph with a flame ionization detector, using a SGE BPX70 capillary column (70% cyanopropyl polysilphenylene-siloxane, $30\text{ m} \times 0.53\text{ mm} \times 0.50\text{ }\mu\text{m}$) and N_2 as the carrier gas.

3. Results and discussion

3.1. X-ray diffraction (XRD)

The large-angle powder XRD patterns of the as-received (parent) and acid-treated (dealuminated) mordenite zeolites are given in Fig. 1. They all exhibit the diffraction peaks at $2\theta =$ values around 6.54° , 8.76° , 9.78° , 13.56° , 15.30° , 19.74° , 22.40° , 25.8° , 26.43° , 27.74° and 31.06° , characteristic of mordenite [21]. The diffraction peaks are associated with the [110], [020], [200], [111], [310], [330], [150], [202], [350], [132] and [402] planes, respectively. The diffraction patterns of all the dealuminated samples could be completely indexed to the orthorhombic phase of the (space group Cmc) mordenite structure, corresponding to the JCPDS data; card No.: 43-0171. From Fig. 1, it is seen that the mordenite structure was preserved and no impurity phase is found after the acid-treatment for different durations. Further, the XRD patterns of these samples were analyzed over the 2θ range $5\text{--}30^\circ$, using MDI-Jade 6.5 software [22] to calculate the relative crystallinity of the samples by comparing the peak area under the diffraction peaks around 9.8° , 13.5° and 26.4° . The crystallinity loss of the

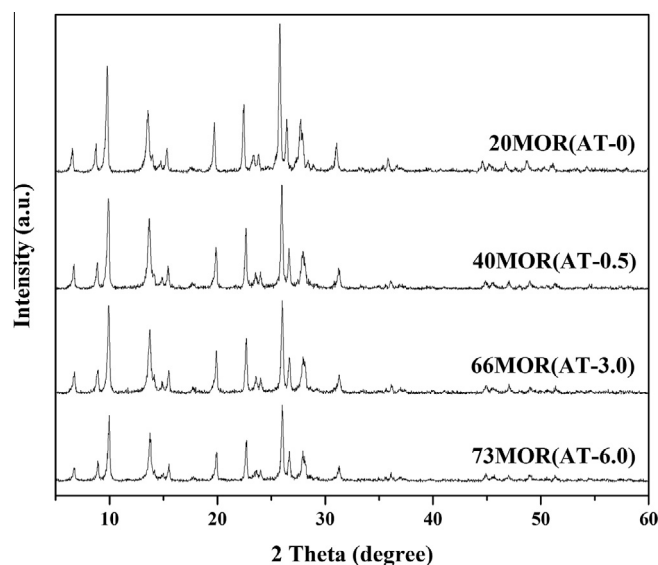


Fig. 1. X-ray diffraction patterns of the parent and acid treated mordenite samples.

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