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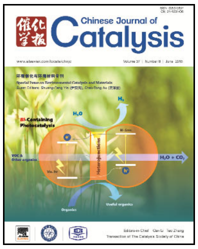

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Effects of acid pretreatment on Fe-ZSM-5 and Fe-beta catalysts for N_2O decomposition

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ABSTRACT

Two series of ZSM-5 and beta zeolites were pretreated in 1.0 mol/L HNO_3 solution at room temperature for various time periods. The catalytic performances of their Fe-exchanged products in N_2O decomposition were evaluated. The Fe-zeolite catalysts were characterized using N_2 adsorption-desorption, inductively coupled plasma optical emission spectroscopy, X-ray diffraction, ultraviolet-visible spectroscopy, temperature-programmed desorption of NH_3, and scanning and transmission electron microscopies. For the ZSM-5 zeolite, acid leaching primarily takes place on the crystal surface and the particle size is reduced, therefore the pore channels are shortened. However, because of the good stability of MFI zeolites, the acid does not greatly penetrate the pore channels and new mesopores are not created. For the beta zeolite, because the amorphous material is inclined to dissolve (deagglomerate), some of the micropores are slightly dilated. The improved catalytic activities can be explained by the increased active Fe loading as a result of structural changes.

1. Introduction

Nitrous oxide (N_2O) is a strong greenhouse gas, and its global warming potential is 310 and 21 times those of CO_2 and CH_4, respectively [1]. In addition, N_2O contributes to stratospheric ozone depletion. The global level of N_2O is increasing by 0.82 ppb/year [2]. Reduction of N_2O emissions is therefore urgent. Exhaust emissions from nitric acid plants and adipic acid installations are the largest industrial sources of N_2O. Consequently, extensive efforts have been made to develop effective methods such as catalytic reduction, and thermal and catalytic N_2O decomposition, for controlling N_2O emissions in these exhausts. Among these methods, direct catalytic decomposition of N_2O to harmless N_2 and O_2 gases is the most effective and economical.

Various types of catalysts for N_2O decomposition have been designed, e.g., noble-metal catalysts, metal mixed oxides, and transition-metal (Fe, Co, Cu)-modified zeolite catalysts [3–8].

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Fe-containing zeolites are attractive catalysts for N_2O decomposition because of their high catalytic activities, good thermal stabilities, and low preparation costs [9–12]. Numerous studies have been performed to clarify the structures of active sites and reaction mechanism, to elucidate the relationship between the physicochemical properties and catalytic performance [13–16]. Fe-exchanged species located in the micropore channels, such as mono- and binuclear Fe species and small oligonuclear $Fe_x^{3+}O_y$ clusters, provide active sites for N_2O decomposition, but FeO_x nanoparticles supported inside and outside the pore channels are inert. A limited amount of active sites is deemed to be one of the key restrictions of catalytic performance. The amount and type of formed Fe species vary depending on the preparation method. Wet ion-exchange is the most popular method, because few steps are involved and the process is easily controlled. However, the main problem with this method is that complete exchange of the zeolite support cannot be achieved because the pore channels obstruct diffusion of Fe species precursors. The exchange degree can be improved by shortening the diffusion paths, e.g., by decreasing the zeolite crystal size or enlarging the pore channels, and this enhances the catalytic activity [17]. Melián-Cabrera et al. [18] reported that the deagglomeration of zeolite crystals caused by mild alkaline leaching treatment improved exchange, but the newly created mesopores did not enhance the catalytic activity. It has also been reported that the catalytic activities of Fe-ZSM-5 materials with hierarchical micro-mesopores are better than that of traditional microporous Fe-ZSM-5 [19–21]. Post-treatments such as alkaline or acid leaching are effective approaches to modify zeolite pore structures. Generally, alkaline treatment preferentially extracts Si from the zeolite framework and acid treatment removes Al [20]. Several works have focused on the effects of alkaline treatment on the catalytic performance in N_2O decomposition. However, few studies of the effects of acid treatment have been reported.

In this work, two typical parent zeolite supports, MFI and BEA, were treated in HNO_3 solution. Various characterization techniques were used to investigate the evolution of the porous structure, and the N_2O decomposition activity was evaluated. Possible explanations for the improved activities of the zeolite are proposed.

2. Experimental

2.1. Catalyst preparation

Commercial H-ZSM-5 (Si/Al = 27) and H-beta (Si/Al = 33) zeolites with similar Si/Al molar ratios were purchased from the Nankai Zeolite Company (Tianjin, China). The zeolites were calcined in static air for 4 h at 600 °C before use, to remove organic impurities.

Acid treatment was performed as follows. The parent zeolite (3 g) was added to 1 mol/L HNO_3 solution (50 mL) at room temperature. The mixture was vigorously stirred for 2 or 24 h. We also performed acid treatment for 8 h, but this had no obvious effect on the catalytic activity (Fig. 1). We therefore only discuss the performances of the catalysts pretreated for 2 and 24 h. The sample was thoroughly washed with deionized water and dried at 120 °C overnight. The obtained zeolites were calcined in at 600 °C for 4 h.

Fe was incorporated into the original and modified zeolites using the wet ion-exchange method. All exchanges were performed using $Fe(NO_3)_3$ solution (50 mL) at room temperature for 24 h. The Fe^{3+} concentration in the precursor solution was fixed at 0.1 mol/L. After exchange, the samples were thoroughly washed with deionized water, dried at 120 °C overnight, and calcined in static air at 600 °C for 4 h, with a heating rate of 5 °C/min. The products are denoted by Fe-ZSM-5-*x* and Fe-beta-*x*, where *x* indicates the treatment time (h) or parent zeolite

2.2. Material characterization

X-ray diffraction (XRD) patterns of the samples were obtained using an Ultima IV X-ray powder diffractometer with Cu K_α radiation; the working voltage and current were 40 kV and 40 mA, respectively.

N_2 adsorption-desorption experiments were performed at 350 °C using a Micromeritics TriStar II 3020 gas absorption analyzer after heat pretreatment at 200 °C for 6 h in a vacuum; the specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation.

Scanning electron microscopy (SEM) was performed using a

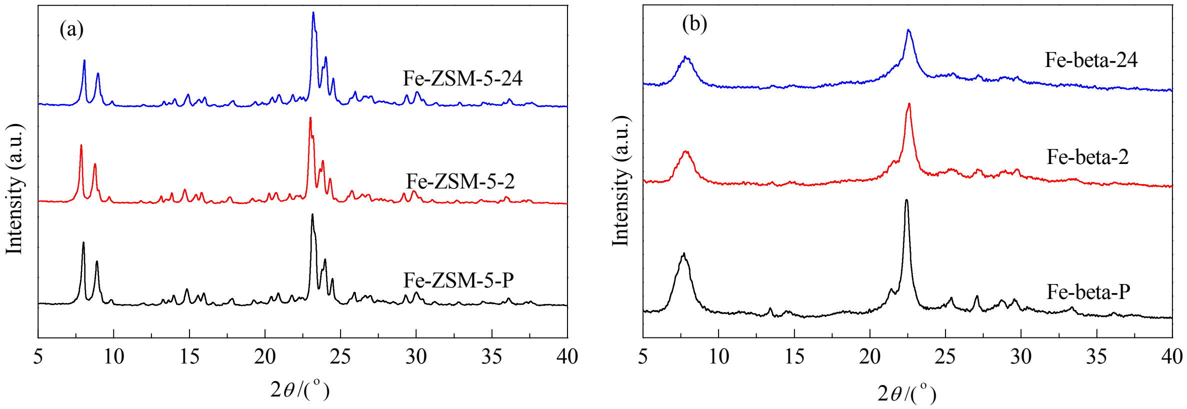

Fig. 1. XRD patterns of Fe-ZSM-5 (a) and Fe-beta (b) zeolites.