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Mild-acid-assisted thermal or hydrothermal dealumination of zeolite beta, its regulation to Al distribution and catalytic cracking performance to hydrocarbons

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ABSTRACT

The synthesized nanoscale beta zeolites (SiO_2/Al_2O_3 = 25, nanocrystals of 50 nm) were treated by two different sequential procedures called acid-steaming and acid-calcination treatment: that is, dilute HCl aq. solution (less than 1 mol/L) treatment followed by either steaming or calcination. These successive treatments were applied two times. The effect of both acid-steaming and acid-calcination treatment of beta zeolite on framework Al at different T-sites, extra-framework Al (EFAL) of different types, and acidity was studied. It was found that nearly 70% of Al was removed in these processes, the location and state of Al in zeolite beta are regulated by different combinations of treatments. ^{27}Al (MQ) MAS NMR, IR, XPS, and XRF data showed that steaming dominated dealumination in the acid-steaming treatment, and Al atoms on T2, T5, T6, and T7 sites were almost completely removed. More EFAL species were formed and migrated to external surfaces of zeolite beta. In acid-calcination treatment, dealumination was completed stepwise by calcination and acid treatment, framework Al atoms on T5, T6, and T9 sites were removed, and more monomeric EFAL species were formed, leading to a more homogeneous Al distribution. The resultant zeolites beta treated by acid calcination and by acid steaming show similar bulk SiO_2/Al_2O_3 ratios but different acidity distributions. Acid-calcination treatment results in more Brønsted acid sites and stronger Brønsted acidity than acid-steaming treatment, leading to higher conversion in *n*-octane catalytic cracking and higher gasoline yield in vacuum gas oil catalytic cracking.

1. Introduction

Gasoline and diesel are primary fuels for vehicles and engines, and one of the important energy fuels production processes is fluid bed catalytic cracking (FCC), [1] in which heavy oil is used as a feedstock. The catalytic cracking conversion of heavy oil need favorable accessibility and adequate acidity of the catalyst [2,3]. Zeolites possess ordered micropores and available acidity plays a dominant role in FCC catalysts [4]. However, intracrystalline diffusion limitations and irregular distribution of acidic sites limit the performance of zeolites in macromolecular catalysis. Therefore, numerous strategies are used to modify the channels and acid sites of zeolites, such as dealumination and desilication, for better diffusion and more proper acidity [5,6]. Acidity can be altered by dealumination of zeolites, which is always achieved by steaming, acid treatment, $(NH_4)_2SiF_6$ and $SiCl_4$ treatment, and calcination [7], while the intracrystalline mesopores can be formed especially in Al-rich zeolites [8]. For silica-rich zeolites, desilication is a promising approach to enhancing diffusion, giving meaningful catalytic performance [9].

On the other hand, nanoscale zeolites with shorter diffusion paths, which are beneficial for resistance to deactivation derived from coke and for reducing secondary reactions [10,11]. Therefore, dealumination or desilication of nanosized high-silica zeolites shows multiple effects. Unfortunately, the dealumination of silica-rich zeolites, such as zeolite beta, are always referred to the concentrated acid [12,13] because of the high acid resistance

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ability of their frameworks [14], which is harsh and environmentally unfriendly. It is worthwhile to study the dealumination of high-silica zeolites under mild acid conditions and to obtain highly dealuminated zeolites.

Zeolite beta has three-dimensional 12-ring channels connected by four-, five,- and six-rings. Nine nonequivalent crystallographic tetrahedral sites (see Fig. S1 in the Supporting Information) were resolved in zeolite beta [15–17]. The nine T-sites can also be found in a single 12-ring, so they are all accessible for reactants. T1 to T4 sites are in the four-ring, T7 to T9 sites are in the five-ring, and T5 and T6 sites are in the six-ring, respectively. In previous studies, ^{27}Al MAS NMR resonance at nearly 54 ppm are assigned to Al atoms on T1 and T2 sites, and resonance between 56 ppm and 58 ppm corresponds to Al atoms on T3 to T9 sites [14,18]. According to recent theoretical calculations and Al extended X-ray absorption fine structure (EXAFS) analysis, the nine T-sites on beta zeolite framework were grouped in three sets. T1, T2, T5, and T6 sites are grouped as Set A, T3 and T4 as Set B, and T7, T8, and T9 as Set C [19,20]. T1 and T2 sites are located at the 12-member ring pore intersections; they are highly stable with regard to dealumination by steaming treatment [21,22], but are selectively hydrolyzed in hot liquid water [23]. It can be seen that dealumination is selective by different post-treatments.

The catalytic activity of zeolite beta is affected by various dealumination treatments, since the acidity of zeolites and the accessibility of active sites are different [24–27]. Generally, the zeolite-beta-containing cracking catalysts for FCC processes produced more C3—C4 olefins and coked faster [28,29]. This is a drawback for catalytic cracking of heavy oil to gasoline and diesel oil fractions, which are the most desired products for the FCC process. Therefore, modulating the acidity and porous structure of zeolite beta could be a way to improve the performance of zeolite-beta-containing FCC catalysts.

In this research, nanosized zeolite beta was dealuminated by treatment with dilute HCl aq. solution (less than 1 mol/L) combined with either steaming or calcination. The acidic properties and structural characters of the treated zeolite beta have been characterized. The catalytic performance of hydrocarbons over the treated zeolite beta has been investigated. In heavy oil cracking, the catalyst containing treated zeolite beta showed better performance than the catalyst containing HBeta.

2. Experimental

2.1. Preparation of the materials

2.1.1. Synthesis and characterization of nanosized zeolite beta

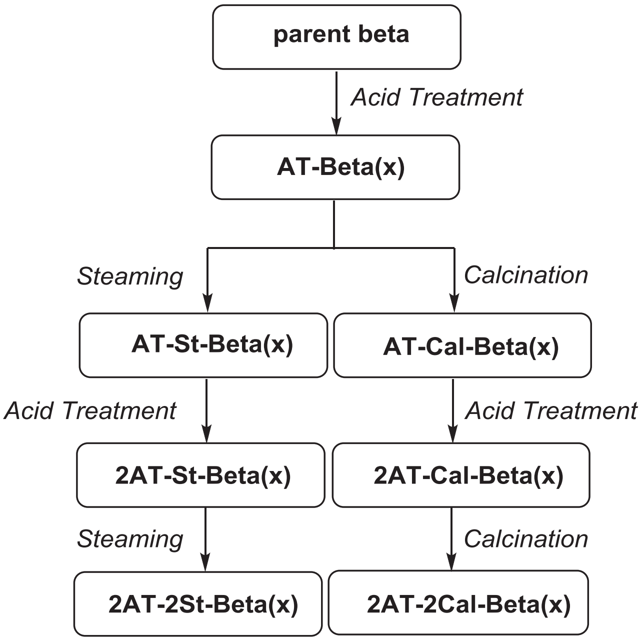
The parent beta was obtained by hydrothermal synthesis using the method reported before [30]. The X-ray diffraction (XRD) pattern shows the typical diffraction for zeolite beta (Fig. S2a in the Supporting Information). The scanning electron microscope (SEM) (Figs. S2b, S2c in the Supporting Information) and transmission electron microscope (TEM) (Fig. S2d in the Supporting Information) images show that all the zeolite beta particles with size around 500 nm are assembled from nanocrystals about 50 nm in dimension. The BET surface areas are 712 $m^2\ g^{-1}$ after the removal of templates under static air, while the external surface area is 194 m^2g^{-1} and the pore size is 10 nm (Fig. S2e in the Supporting Information), which means the synthesized beta are nanocrystals with intercrystalline mesopores. The SiO_2/Al_2O_3 ratio of the parent beta is 25, as determined by X-ray fluorescence (XRF).

2.1.2. Dealumination of beta

The zeolites beta were steamed or calcined after hydrochloric acid treatment at 353 K. The steamed or calcined zeolites were washed with hydrochloric acid solution again, followed by another steaming treatment or calcination (Scheme 1). These two treatments are called acid-steaming and acid-calcination treatment for short. In a typical run, 1 g of as-synthesized parent zeolite beta was added to 10 g of aqueous HCl solution, and the resulting suspension was kept at 353 K for 2 h while being stirred. The slurry was filtered, and the filter cake was washed thoroughly with hot distilled water until it reached a pH of ~7 and dried at 393 K for 5 h. The obtained zeolite beta was named AT-Beta(*x*), where *x* is the concentration of the aqueous HCl solution. In the acid-steaming treatment process, the steaming was executed at 923 K in 100% steam for 2 h; the resulting zeolite was named AT-St-Beta(*x*). In the acid-calcination treatment process, the calcination was carried out at 823 K for 4 h in air; the resulting zeolite was named AT-Cal-Beta(*x*). The steamed and calcined zeolites were leached again by the same aqueous HCl solution described above. The obtained zeolites were named 2AT-St-Beta(*x*) and 2AT-Cal-Beta(*x*). Finally, the samples of 2AT-St-Beta(*x*) and 2AT-Cal-Beta(*x*) were steamed treated and calcined again using the same procedure and named 2AT-2St-Beta(*x*) and 2AT-2Cal-Beta(*x*). NH_4Beta was prepared by twofold ion exchange of parent beta with 0.8 M NH_4Cl solution at 353 K. Calcination of NH_4Beta gave HBeta(Cal) for comparison. The content of Na_2O in all obtained beta was lower than 0.05 wt%.

2.2. Characterization of materials

XRD patterns of all zeolites beta were obtained on a PANalytical X'Pert powder X-ray diffractometer with monochromatized CuKα radiation (40 kV, 40 mA, $k\alpha_1 = 1.5405$ Å). The samples were dried at 393 K for 5 h and ground before the XRD measurements. The samples were continuously scanned from 10° to 50° with a step size of 0.013° and 30 s per step. The crystallinity of zeolite beta was determined by comparing areas of peaks around $2\theta = 21.5°$ and 22.3° and that of the parent beta. Nitrogen physisorption measurements were performed at a Micromeritics TriStar 3020 apparatus. The samples were degassed and dehydrated at 623 K for 8 h before the measurements, while the templates containing zeolite beta (parent beta and AT-Beta) were degassed and dehydrated at



Scheme 1. Stepwise treatment of zeolite beta.