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Effect of post treatment on the local structure of hierarchical Beta prepared by desilication and the catalytic performance in Friedel–Crafts alkylation

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ABSTRACT

Desilication method has been developed to prepare hierarchical zeolites. However, the hierarchical Beta prepared by desilication generally exhibited much poorer catalytic activity than parent one in some acid-catalyzed reactions mainly due to the great loss of acidity. Here, we report that subsequent acid treatment after desilication can greatly recover the acidity of zeolite Beta. As a result, the hierarchical Beta with acid treatment exhibited enhanced catalytic performance in the benzylation of benzene or mesitylene with relatively large molecular size. Additionally, the local structural change in zeolite Beta before and after post treatment was deeply studied by the NMR technique. The results indicated that during the desilication partial tetrahedral coordination Al was transformed into the distorted tetrahedral and pentahedral coordination Al and subsequent acid treatment led to the increase of the proportion of tetrahedral coordination Al. Thus, the number of total Brönsted acid sites in zeolite Beta was decreased after the desilication and subsequent acid treatment may increase the number of total and accessible Brönsted acid sites. These results suggested that acid treatment is helpful for improving the catalytic performance of the desilicated Beta in some acid-catalytic reactions, especially toward large molecules.

1. Introduction

Friedel–Crafts alkylation is an important class of reactions in organic chemistry [1,2]. Among these alkylations, the liquid phase benzylation of aromatic compounds by benzyl chloride or benzyl alcohol is of significance for the production of diphenylmethane and substituted diphenylmethanes which are key industrial compounds used as pharmaceutical intermediates and fine chemicals. Generally, such reactions were carried out in the presence of homogeneous acid catalysts such as $AlCl_3$ and H_2SO_4 [3,4]. However, these catalysts pose several serious problems such as corrosion, handling, toxicity, and separation and recovery of the catalyst. Hence, the replacement of the homogeneous catalysts by heterogeneous solid catalysts has been pursued [5–8].

Several types of zeolites (ZSM-5, Mordenite, Beta, Y) as solid acid catalysts have been widely studied in benzylation reactions because of their strong acidity, large surface area, regular pore array, and excellent hydrothermal/chemical stability [9–16]. The results indicated that zeolite Beta is an excellent catalyst in the benzylation of benzene with benzyl alcohol [11–16]. However, in the benzylation of relatively large molecular reactants like toluene and xylene, microporous Beta was less active due to its small micropore size (ca. 0.7 nm) [16].

The development of hierarchical zeolites can be a good route to solve the above problems because it may not only increase the accessibility of acid sites but also overcome the diffusion limitation [17–32]. Currently, hierarchical zeolites were mainly prepared by direct (soft or hard template) or indirect (desilication, dealumination) method. Thereinto, desilication method is of great interest because of its simple operation conditions and low preparative cost [21–28]. Earlier works showed that hierarchical zeolites including ZSM-5, mordenite and Y prepared by desilication can exhibit enhanced catalytic performance compared with parent ones in many reactions [21,33]. However, zeolite Beta is a special example. Some works have reported that hierarchical Beta obtained by desilication would lead to lower catalytic activity than parent Beta in some reactions, which was attributed to the great loss of acidity in desilicated Beta. It was proposed that aluminum species in Beta framework had relatively low stability and cannot act as a silicon

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extraction moderator and the desilication would negatively affect the acidity [34]. Recently, Tian et al. reported that the Si/Al molar ratio in parent Beta had a big influence on the properties of hierarchical Beta prepared by desilication. The zeolite Beta with a low Si/Al molar ratio less than 30 could well preserve its microporosity and acidic properties after desilication [25,26]. Nevertheless, the catalytic performance of hierarchical Beta has not been evaluated in Friedel–Crafts alkylation involving the reactants with large molecular size.

On the other hand, it was suggested that desilication could result in part of Al species deposited on the external surface of zeolite framework and thus disadvantage the improvement of catalytic reactivity [35]. Acid wash after desilication may remove the deposited Al species to improve the catalytic performance. Some experimental results seemed to support this viewpoint. For example, acid wash after desilication on zeolites like ZSM-5, mordenite, and Y exhibited better catalytic activities than desilicated ones [33,36,37]. However, the effect of such treatment on desilicated Beta has been not presented. Additionally, the study about the local structural change in zeolite Beta before and after post treatment is rare for clarifying this process.

In the present work, we firstly prepared hierarchical Beta by desilication based on a commercial Beta with a low Si/Al molar ratio of 12.5. Then, acid treatment was employed to study its effect on the structure and properties of the obtained hierarchical Beta. The catalytic performance of the catalysts was first evaluated in the benzylation of benzene with benzyl alcohol, then in the benzylation of mesitylene with relatively large molecular size. The change of local structure and acidity in zeolite Beta before and after post-treatment was deeply studied. The relationship between the structural properties of catalysts and catalytic performance was discussed.

2. Experimental

2.1. Materials

Commercial Beta was purchased from the Catalyst Plant of Nankai University. HNO_3, NaOH, NH_4NO_3, benzene, mesitylene, and benzyl alcohol were purchased from Sinopharm Chemical Reagent Co. Pyridine and pivalonitrile were purchased from Sigma company. Both were transferred in glass cylinder in the presence of molecular sieves 3A. Other reagents were used without further purification.

2.2. Preparation of catalyst

The commercial Beta calcined at 823 K for 5 h was labeled as HB. The sample HB was treated with a solution of 0.2 M NaOH with a liquid-to-solid ratio of 30 ml/g at 338 K for 0.5 h. Then, the product was filtered, washed with deionized water, dried, ion-exchanged into NH_4-form, and calcined at 823 K for 5 h. The resultant sample was named as HB-B. It was then treated with a solution of 0.1 M HNO_3 at 338 K for 6 h with a liquid-to-solid ratio of 30 ml/g. The product was ion-exchanged as described above, followed by calcination at 823 K for 3 h to obtain the sample labeled as HB-BA.

2.3. Catalyst characterization

X-ray powder diffraction (XRD) patterns were recorded using a Siemens D-5000 diffractometer equipped with the Cu Kα radiation (wavelength of $\lambda = 1.5418$ Å) and at BM01B-SNBL beam line, ESRF, France ($k = 0.5$ A, Si (1 1 1) channel cut monochromatic) using the two cycle diffractometer equipped by six detectors having Si (1 1 1) analyzer crystals and Na-I scintillation counters. The determination of the relative crystallinity value was based on the intensity of the characteristic peaks in the range between 6 and 9°. The parent Beta was assigned a crystallinity of 100%. Nitrogen sorption isotherms were obtained at 77 K on a Micromeritics TriStar II 3020 Gas Sorption and Porosimetry system. Prior to the experiments, the samples were outgassed at 423 K under vacuum for 3 h. SEM images were recorded on Hitachi S-4700 Scanning Electron Microscope system operated with an acceleration voltage of 10 kV. TEM images were recorded on Tecnai microscope operating at 200 kV with a LaB_6 crystal. ^{29}Si NMR experiments were performed at room temperature on a 400 MHz Bruker Advance Avance II 400 spectrometer at a spinning rate of 12 kHz using a 4 mm probe and the ^{29}Si MAS NMR chemical shift was referenced to 0 ppm relatively to tetramethylsilane (TMS). The ^{27}Al MAS NMR spectra [38] were recorded on a 800 MHz Bruker Avance III 800 spectrometer by using single pulse length of $\pi/6$ and a relaxation delay of 1 s. The ^{27}Al chemical shift was referenced to $[Al(H_2O)_6]^{3+}$ (Chemical shift = 0 ppm). The ^{27}Al MQMAS spectra were collected using the Z-filter sequence [39], which consists of two hard pulses of 6 and 1.4 μs at an RF field of 90 kHz, for triple-quantum excitation and reconversion, respectively, followed by a central transition selective pulse of 7 μs at an RF field of 12 kHz. The IR studies of pyridine and pivalonitrile adsorption were carried out to measure the number of acid sites and accessible acid sites, respectively, recorded with a Nicolet Protege System 460 equipped with a DTGS detector. All samples were ground in an agate mortar and were pressed into the form of self-supporting wafers (5 mg/cm^2), then heated at 723 K under high vacuum (10^{-6} mbar) for 2 h before probe molecule adsorption. All recorded spectra were recalculated to a normalized wafer of 10 mg. The concentration of Brönsted and Lewis acid sites was determined by quantitative IR studies of pyridine adsorption experiments. In order to quantify Lewis and Brönsted acid sites, the following bands and absorption coefficients were used: Pyridinium (PyH^+) band at 1545 cm^{-1}, $\varepsilon B = 1.23$ cm/μmol and pyridine (PyL) 1454 cm^{-1}, $\varepsilon L = 1.73$ cm/μmol [40]. The concentration of accessible Brönsted and Lewis acid sites was determined by quantitative IR studies of pivalonitrile adsorption experiments. In order to quantify Lewis and Brönsted sites, the following bands and absorption coefficients were used: pivalonitrile (PiH^+) band at 2274 cm^{-1}, $\varepsilon B = 0.11/f$ cm/μmol and pivalonitrile (PiL) 2302 cm^{-1}, $\varepsilon L = 0.15/f$ cm/μmol [41], where f was a constant depending on the IR system. XPS analyses were performed on an Axis ultra DLD (Kratos analytical) using a monochromatic Al Kα X-ray source ($h\nu = 1486.6$ eV). The emission voltage and the current of this source were set to 15 kV and 10 mA, respectively. Data treatment and peak-fitting procedures were performed using Casa XPS software. Obtained spectra were calibrated in respect of C 1s (C–C bond) at 285 eV. The peaks were decomposed using Gaussian–Lorentzian peak shapes.

2.4. Catalytic tests

The liquid phase benzylation of benzene or mesitylene with benzyl alcohol (BA) (Scheme 1) 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. The reaction temperature for the benzylation of benzene was at 353 K while the benzylation of mesitylene was carried out at 373 K. 160 mmol of benzene (or mesitylene) was added to 100 mg catalyst. The reaction mixture was maintained for 30 min at the required reaction temperature and then 2 mmol 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 6890 GC with an FID detector using a 50 m packed HP5 column. The products were