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Synthesis, characterization of hierarchical ZSM-5 zeolite catalyst and its catalytic performance for phenol *tert*-butylation reaction

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Abstract

A hierarchical ZSM-5 zeolite was prepared under hydrothermal conditions through polystyrene (PS) colloidal spheres and tetrapropylammonium hydroxide (TPAOH) dual templates method. The physical and acid properties of the hierarchical ZSM-5 zeolite were characterized by XRD, SEM, N_2 adsorption, ^{27}Al-MAS NMR and NH_3-TPD techniques. Catalytic tests show that the hierarchical ZSM-5 zeolite catalyst exhibits high catalytic activity for alkylation of phenol with *tert*-butanol. The high phenol conversion and 2,4-di-TBP selectivity are mainly assigned to the presence of the hierarchical porosity and strong acidity of the pore walls. The macropores offer easier transport and access to the active sites and the macroporous walls built by nano-ZSM-5 crystals provide the acidic sites for reaction.

Keywords: Hierarchical ZSM-5 zeolite; Alkylation; Phenol; *tert*-Butyl alcohol

1. Introduction

Zeolites as typical porous materials are a class of crystalline solids with intricate channel systems and the pore size is no more than 2 nm. The micropore zeolites are widely applied in industry as heterogeneous catalyst, particularly used in petroleum industry as solid acid catalysts. However, relatively small individual micropores in zeolites strongly influence mass transport to and from the active sites located in them, severely limiting the applied scope in large molecular reactions [1,2]. To overcome this problem, some recent research efforts have been concentrated on introducing mesopores or macropores linked to the zeolite micropores. Compared with conventional zeolites, these hierarchical zeolites combining the benefits of all pore-size regimes would further extend the applications of zeolites [3].

In the past decades, several synthetic routes have been reported for preparation of hierarchical pore materials, such as endo- and exo-templating route [4], phase separation [5–7] and steam-assisted conversion method [8], etc. Recently, hierarchical zeolites prepared by colloidal sphere and structure directing agent dual templates method have attracted much attention, because the hierarchical pore system can be controlled easily. By employing this method, hierarchical zeolites with combinations of micro-/macropores [9–14] or micro-/meso-/macropores [15] have been prepared successfully. Generally, such hierarchical zeolites exhibit well-ordered and interconnected pore structures. To date, most of work has concentrated on the preparation of hierarchical zeolites through dual templates with appropriate reaction solutions or nanoparticle building blocks. However, these studies have mainly focused on the preparation of materials and little on their applications in catalysis.

The reaction of phenol with *tert*-butyl alcohol is typical of Friedel–Crafts alkylation. The alkylated products of

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para-*tert*-butyl phenol (4-TBP) and 2,4-di-*tert*-butyl phenol (2,4-di-TBP) are important intermediates widely applied in industry as raw material for preparation of a variety of resins, antioxidants, varnishes, surface-active agents, ultraviolet absorbers, and as petroleum additives, etc. [16–18]. Therefore, investigating this alkylation reaction has great commercial interests as well as academic interests. It is well known that the phenol *tert*-butylation is a kind of acid-catalyzed reaction. The catalysts used in the alkylation reaction include liquid acid catalyst (Lewis acids or Brønsted acids) [19,20], heterogeneous ion-exchange resins [21] and solid acid catalysts (zeolites or mesopore molecular sieves) [22–26], and so forth. Zeolites as solid acid catalysts to catalyze alkylation of phenol with *tert*-butanol have been studied widely, due to their inherent advantages such as large surface, strong acidity, high thermal stability and recyclability. Additionally, zeolites catalysts are environment friendly. However, the limited pore size makes it difficult for substrates and products to diffuse from the narrow channel of zeolite.

In this work, we report a novel hierarchical ZSM-5 zeolite catalyst prepared by dual templates method. XRD, SEM, N_2 adsorption and ^{27}Al-MAS NMR were performed to characterize the textural properties. NH_3-TPD technique was utilized to evaluate the acidity of the hierarchical ZSM-5 zeolite. The catalytic properties are investigated over the hierarchical ZSM-5 catalyst for the alkylation of phenol with *tert*-butanol.

2. Experimental

2.1. Catalysts preparation

Initially, non-crosslinked, monodisperse polystyrene (PS) spheres used as macropore templates were prepared, according to the published procedures [27]. Aluminosilicate precursor gel was prepared by mixing $Al_2(SO_4)_3$, H_2O, tetraethyl orthosilicate (TEOS) and tetrapropylammonium hydroxide (TPAOH) following the molar composition: $1.0Al_2O_3$:$100SiO_2$:8TPAOH:$120C_2H_5OH$:$1500H_2O$.

The preparation procedure of the hierarchical ZSM-5 zeolite catalyst included the following four stages. At the first stage, dry PS spheres with an average size of around 580 nm were mixed with required amount aluminosilicate precursor gel under stirring according to the weight ratio of 1:10. In the second stage, the mixture was transferred into centrifugal tubes for centrifugation at 6000 rpm for 1 h to produce close-packed PS/inorganic composite, followed by drying the composite at 333 K for 48 h. In the third stage, the dried solids with amount water were subjected to hydrothermal treatment at 373 K for 16 h to obtain products. The products were calcined at 823 K for 5 h. At last, the protonated form of sample was obtained from ion-exchange with NH_4NO_3, followed by calcination at 773 K for 5 h.

For comparison, conventional ZSM-5 zeolite was also synthesized according to the literature [28].

2.2. Catalysts characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 diffractometer system equipped with Ni-filtered Cu target Kα-ray (operation at 40 kV, 30 mA, wavelength $\lambda = 0.15418$ nm). Diffractions were carried out in the ranges (2θ) of 5° to 35° at the scanning speed of 2°/min.

Scanning electron microscopy (SEM) image was recorded using a JEOL JSM-6700F scanning electron microscope and Iridium (IXRF Systems) software.

N_2 adsorption/desorption isotherms were recorded at 77 K with a Micromeritics ASAP 2020. Before measurements, samples were outgassed at 573 K for 3 h. BET surface areas (S_{BET}) were calculated from adsorption branches in the relative pressure range of 0.05–0.30. Pore size distributions were calculated from adsorption branches by Barret–Joyner–Halenda (BJH) method. The mesopore surface area and pore volume were calculated by *t*-plot method.

^{27}Al-MAS NMR spectrum was determined on a Varian Unity-400 spectrometer operating at a magnetic field of $B_0 = 0.94$ T with NMR frequencies of 104 MHz, at a spin rate of 10 kHz. The chemical shifts were referenced to $Al(H_2O)_6{}^{3+}$.

NH_3-TPD spectra were measured using a fixed-bed reactor connected to a thermal conductivity detector (TCD). Samples (0.05 g) was activated at 773 K for 1 h in pure nitrogen flow, then cooled down to 373 K, and begin to adsorb ammonia for 0.5 h, physically adsorbed ammonia was removed by pure nitrogen flow at 373 K. Ammonia desorption measurements were achieved in the temperature range of 373–773 K at an increasing the temperature at 10 K min^{-1}.

2.3. Catalytic tests

Alkylation of phenol with *tert*-butanol was carried out at atmospheric pressure in a continuous flow fixed quartz bed reactor (i.d. 6 mm) and the weight of the catalyst was 0.5 g. Prior to catalytic reaction, the catalysts were activated in N_2 at 773 K for 1 h to eliminate physically and chemically adsorbed water, then the reactor was cooled to 418 K under a N_2 flow of 20 ml/min. The reaction mixture was injected from the top utilizing a syringe pump. The products were quantified by gas chromatography (GC-8A, Shimadzu) and confirmed by gas chromatography–mass spectrometry (GC–MS).

3. Results and discussion

3.1. XRD results

Fig. 1 shows the XRD patterns of hierarchical ZSM-5 zeolite and conventional ZSM-5 zeolite. Notably, both the hierarchical ZSM-5 zeolite and conventional ZSM-5 zeolite show well-resolved peaks in the 5–35° characteristic for the MFI structure. The peaks of the hierarchical ZSM-5