Creating mesopores in ZSM-48 zeolite by alkali treatment: Enhanced catalyst for hydroisomerization of hexadecane

Miao Zhang[a], Lei Wang[a], Yujing Chen[a], Qiumin Zhang[b], Changhai Liang[a,*]

[a] Laboratory of Advanced Materials and Catalytic Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, Liaoning, China
[b] State Key Laboratory of Fine Chemicals, Institute of Coal Chemical Engineering, Dalian University of Technology, Dalian 116024, Liaoning, China

ARTICLE INFO

ABSTRACT

ZSM-48 zeolites with various Si/Al ratios were hydrothermally synthesized in the $H_2N(CH_2)_6NH_2$ (HDA)-containing media. The obtained samples were highly crystallized with minor mixed phases as evidenced by X-ray powder diffraction (XRD). The alkaline treated ZSM-48 zeolites maintained its structure under different concentrations of NaOH aqueous solution. Micropores remained unchanged while mesopores with wide pore size distribution formed after the alkaline treatment. The surface area increased from 228 to 288 m^2/g. The Brönsted acid sites had little alteration while an obvious increase of Lewis acid sites was observed. The hydroisomerization of hexadecane was performed as the model reaction to test the effects of the alkali treatment. The conversion of hexadecane had almost no change, which was attributed to the preservation of the Brönsted acid sites. While high selectivity to iso-hexadecane with an improved iso to normal ratio of alkanes was due to the mesopore formation and improved diffusivity.

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1. Introduction

Hydroisomerization of long n-alkanes has long been an important process in the petroleum industry. Branching of n-alkanes improves the octane number of gasoline and thus enhances the performance of diesel or lubricating oils at low temperature [1,2]. Properties such as pour point, freezing point, viscosity and viscosity index are significantly improved by introducing side chains along the linear carbon chains. Hydroisomerization and selective hydrocracking of n-alkanes raised much attention in the past years [3–9]. The hydroisomerization of n-alkanes increases the yield of liquid and produce oils with higher quality [10–15].

It is generally accepted that bifunctional catalysts with the metallic sites and acidity sites are essential to hydroisomerization of n-alkanes [16]. Typical metal components are noble metals (Pd, Pt) and transition metals (Ni, Co, Mo). On the metallic sites, the paraffin is (de)hydrogenated and the olefin intermediates are formed [17]. Typical acidic components are amorphous silica-alumina and zeolites. On the acidity sites, the carbenium with rearrangement is formed. The balance between acidity and metallic function of the catalyst are critical to the activity and selectivity. For most bifunctional catalysts on molecular sieve, the number density and strength of acidic sites have a major effect on the hydroisomerization [14,15,18]. Y, β, SiO_2-Al_2O_3, ZSM-5 and SAPO-11 had been compared and we found that these materials with one-dimension pore were the best acidic supports [11]. Many attempts have been made to enhance the isomerization of n-alkanes through the shape selectivity of one-dimension zeolites which suppress the formation of multi-branched isomers, thereby leading to high isomerization selectivity [19]. Acidic zeolites such as SAPO-11 [11] and ZSM-22 [20] with a trace amount of noble metals are excellent hydroisomerization catalysts for n-alkanes, generating high isomerization yield and limiting product losses due to cracking reaction.

ZSM-48 is reported as a kind of high-silica zeolite with low acidic density. It has been reported as the acidic support in the previous researches [21,22], which consists of one-dimensional 10-MR channels with pore diameter 0.53 nm × 0.56 nm [23]. Increasing its acidic property and improving the molecular transportation in the hydroconversion of large molecules are quite urgent. The extraction of silicon in an alkaline medium (typical NaOH) is an effective, versatile, and simple treatment to create accessible mesoporosity, which was successfully applied to ZSM-5, ZSM-12 and β [24–27]. The improved molecular transport and catalytic performance of alkaline-treated zeolites compared to the parent microporous zeolites have been demonstrated decidedly.

In this work, ZSM-48 zeolites with Si/Al ratio ranging from 200 to 500 were synthesized in the hydrothermal system of Na_2O-SiO_2-Al_2O_3-HDA. ZSM-48 zeolites were treated in an alkaline medium to decrease the Si/Al ratio and the surface area. The

hydroisomerization of hexadecane was taken as a model reaction to test the influence of the modification of ZSM-48 with alkali-treatment.

2. Experimental

2.1. Catalyst preparation

According to the synthesis procedure in literature [28], a series of ZSM-48 samples with different Si/Al ratios were synthesized hydrothermally in a Teflon-lined stainless steel autoclave with the capacity of 1000 mL. Typically, 1.25 g of $Al_2(SO_4)_3 \cdot 18H_2O$ was added into the mixture containing 472 g distilled water, 1.88 g NaOH and 39.3 g hexamethylenediamine under stirring, and then 45 g of fumed silica was added. After stirring for 2 h, the mixture was transferred into an autoclave and crystallized at 160 °C for 72 h. The products were filtered, washed and dried at 85 °C overnight and then calcined at 550 °C for 3 h. Ion exchange was carried out with 5 wt% NH_4NO_3 solution at 85 °C for 8 h for three times. The dried NH_4ZSM-48 zeolites were calcined at 550 °C for 3 h to obtain HZSM-48 with different Si/Al ratios.

Alkali-treatment of the HZSM-48 zeolite with $SiO_2/Al_2O_3 = 400$ was performed with NaOH aqueous solutions. A flask made of polyethylene was used to avoid material dissolution by highly alkaline solutions. In a typical experiment, 3.0 g of HZSM-48 was put into 75 mL of NaOH aqueous solution with various concentration (0.05, 0.1, 0.5, 1.0 and 2.0 M) followed by stirring for 24 h at room temperature. The slurry was filtered, washed and dried at 85 °C for 12 h. After which an ion exchange process similar to the treatment for HZSM-48 was carried out. The code of the samples were designated as ZSM-48 (no alkaline treatment) and ZSM-48-*x* (alkaline treatment), in which *x* denotes the concentration of NaOH.

1.24 g $Ni(NO_3)_2 \cdot 6H_2O$ were added into the solution containing 40 g of distilled water and 0.2 ml concentrated nitric acid and then 2 ml aqueous ammonia was added to the nickel nitrate solution. The mixture was stirred for 20 min at 30 °C. 1 g of alkali-treated ZSM-48 was put into the solution and the mixture was stirred for 2 h at 95 °C. The initial pH of the slurry was about 8.9 [29]. The catalysts were filtered, washed and dried at 85 °C for 12 h. The catalysts were calcined at 400 °C for 3 h under 20% O_2 in Ar at a flow rate of 100 mL/min.

2.2. Catalyst characterization

X-ray diffraction (XRD) analysis of the samples was carried out using a Rigaku D/Max-RB diffractometer with Cu $K\alpha$ monochromatized radiation source ($\lambda = 1.54178$ Å), operated at 40 kV and 100 mA.

Nitrogen adsorption–desorption isotherms were measured with Quantachrome autosorb iQ automated gas sorption analyzer. Prior to measurements, all calcined samples were degassed at 300 °C for 3 h. The surface area was calculated by BET (Brunauer-Emmett-Teller). The surface area and pore volume of micropore were calculated by *t*-plot method at which the points of p/p_0 were chosen from 0.4 to 0.55. Pore volumes were calculated from the volume of liquid nitrogen at $p/p_0 = 0.99$. Pore size distribution was calculated from the absorption branch of N_2-isotherm according to the method of non-local density functional theory (NLDFT).

Element analysis was performed on a Perkin–Elmer Optima 2000DV inductively coupled plasma atomic emission spectroscopy (ICP-AES).

^{29}Si magic-angle spinning nuclear magnetic resonance (MAS NMR) experiments were carried out on a Bruker 400 NMR spectrometer using a 4 mm probe-head. The relaxation delay was 10 s. All spectra were obtained at a spinning speed of 10 kHz. The chemical shifts were referenced to Q8M8.

^{27}Al magic-angle spinning nuclear magnetic resonance (MAS NMR) experiments were carried out with a Bruker 400 NMR spectrometer using a 2.5 mm double-resonance probe-head. The resonance frequency for ^{27}Al was 400 MHz, and the pulse length was 6 μs. All spectra were obtained at a spinning speed of 10 kHz and had a recycle delay of 1 s. The ^{27}Al chemical shifts were referenced to the Al compound $(NH_4)Al(SO_4)_2 \cdot 12H_2O$.

Pyridine adsorption-IR was carried out on an EQUIOX-55 Fourier transform infrared spectrometer (Bruker Corp.). Self-supporting wafers (15 mm diameter) were made from ca.10 mg of zeolite. The IR cell can hold the wafers of HZSM-48. The pretreatment of the fresh samples was conducted as follows: the cell containing the zeolite wafer was evacuated while slowly increasing the temperature to 450 °C. The sample was finally evacuated at 450 °C for 1 h and then cooled to room temperature to record the background spectra of HZSM-48 zeolite. Infrared spectra were measured at 4 cm^{-1} resolution. After that, the sample was saturated with pyridine and evacuated at 150 °C for 20 min. Subsequently, IR spectra were measured (after cooling to room temperature). The adsorption of pyridine at 300 °C is similar to that at 150 °C.

2.3. Catalytic reaction

The *n*-hexadecane hydroisomerization was carried out at 4 MPa under flow H_2 in a fixed-bed microreactor, loaded with 0.1 g of the catalyst powder. The *n*-hexadecane conversion was monitored at different contact time and temperature. The volume ratio H_2/n-C_{16} was chosen equal to 600. The reaction products were analyzed using a GC with a FID detector and a HP-5 capillary column. The code of the products was designated as *n*-C_i and *y*M-C_i, in which *n*-C_i denotes the straight-chain paraffin and *i* denotes the number of carbon and *y*M-C_i denotes the isomer product and *M* denotes the methyl and *y* denotes the position of methyl.

3. Results and discussion

3.1. Catalyst characterization

XRD patterns of the as-synthesized ZSM-48 zeolite were shown in Fig. 1(a). Only diffraction peaks to ZSM-48 were detected in a series of samples with different Si/Al ratios comparing with the standard pattern of ZSM-48. The crystallinity increased with increasing the Si/Al ratios. This agreed well with the inhibiting role of large amounts of Al during the crystallization process of many zeolites. When the Si/Al ratio increases in the reactant mixtures, it is easy to obtain the pure ZSM-48 product. However, when the Si/Al ratio is below 100, it is hard to obtain the pure ZSM-48 [28].

3.2. Effect of alkali-treatment

From the XRD patterns of ZSM-48 zeolite in Fig. 1(b), the relative crystallinity decreased with increasing alkalinity. The intrinsic lattice structure of samples was destroyed in the highly alkali solution, resulting in a decrease in crystallinity [25]. The crystallinity still exist even treatment with the highly alkali solution. In other words, the as-synthesized ZSM-48 is stable enough to sustain the crystal structure with the alkali-treatment in the selected operating conditions.

The change in surface area and pore volume of ZSM-48 zeolite caused by the alkali-treatment can be analyzed using N_2-adsorption. The results are listed in Fig. 2 and Table 1. In Fig. 2(a), the hysteresis loop revealed the forming of mesoporous after alkali treatment. In Fig. 2(b), it was discovered that new mesopores were generated after alkali treatment. The pore volume of micropore was significantly reduced while mesopores with wide pore size distribution formed after the alkaline treatment.