Short communication

Promotion effect of mesopore on the conversion of carbohydrates to methyl levulinate over H-USY zeolite

Lipeng Zhou [a], Huiting Zhao [a], Linlin Cui [a], Yuqi Bai [a], Jingjing Bian [a], Tianliang Lu [b], Yunlai Su [a], Xiaomei Yang [a,*]

[a] College of Chemistry and Molecular Engineering, Zhengzhou University, 100 Kexue Road, Zhengzhou 450001, China
[b] School of Chemical Engineering and Energy, Zhengzhou University, 100 Kexue Road, Zhengzhou 450001, China

A B S T R A C T

H-USY was treated with nitric acid solution to remove Al species and thus adjust the mesoporosity and acidity. Effects of mesopore and acidity of H-USY zeolite were studied on the conversion of carbohydrate to methyl levulinate (MLE). Low concentration of nitric acid mainly removed the extraframework aluminum species with the increase of mesoporosity and resulted in a slight decrease of acidity. Both extraframework and framework Al species were removed to some extent under high concentration of nitric acid, associating with the obvious decrease of acidity. H-USY treated with low concentration of nitric acid showed higher yield of MLE than H-USY-parent. Generated mesopores improved the diffusion limitations, facilitated the accessibility of reactant to the acid sites, and thus promoted the formation of MLE.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

With the gradual consumption of fossil resources and environment concern, utilization of renewable resources has attracted great attention in recent years. Biomass resources are good candidates for sustainable production of biofuels and chemicals with minimal environmental effects [1]. As one of the most important chemicals derived from biomass resources, levulinate esters can be used as plasticizing materials, solvents, odor substances and fuel additives [2]. Additionally, the ester and carbonyl functional groups also enable levulinate esters to be used as substrates for various kinds of condensation and addition reactions in organic chemistry [3].

Levulinate esters are usually produced from biomass resources through alcoholysis of carbohydrates [4,5], esterification of levulinic acid [6,7], or conversion of furfural and its derivatives [8]. Direct conversion of carbohydrates into levulinate esters over heterogeneous acid catalysts offered advantages such as simple purification of products and easy recyclability of catalyst. The reported acid catalysts include mesoporous carbon/silica functionalized with $-SO_3H$ [9], SBA-15–SO_3H [10], heteropoly acids [11], SO_4^{2-}/TiO_2 [12], SO_4^{2-}/ZrO_2 [13], SO_4^{2-}/ZrO_2-TiO_2 [14], zeolite [15,16] ion exchange resins [17], etc. Sulfate materials are efficient catalysts for this process, but the release of SO_4^{2-} from sulfated catalysts is unavoidable which would lead to the

decrease of catalytic activity [12,13]. Zeolites, which are widely used as acid catalysts in petroleum industry, have been used as catalysts for this reaction [15,16]. Unfortunately, the catalytic activity of zeolite is much lower than the sulfate materials, although it is very stable. Adjustable acidity and porous structure are the advantages of zeolites, which are also two important factors associated with the catalytic performance. To improve the catalytic activity of zeolite, it is imperative to understand the effects of pore structure and acidity on its catalytic performance. Ramli et al. reported that the surface area and porosity of Fe/HY could influence the catalytic activity in the conversion of glucose to levulinic acid [16]; the increase of mesoporosity was favorable for the formation of levulinic acid. Saravanamurugan et al. studied the conversion of glucose to alkyl levulinates over aluminosilicate zeolites, and found that the catalysts having acid site density of more than 300 µmol g^{-1} and a proper strong/weak acid ratio of 0.3–1.1 were suitable for obtaining high yield of alkyl levulinates [15].

The size of zeolite micropore and glucose molecule is comparable, so the diffusion of glucose molecules in the micropore of zeolite is inevitable to be limited. This diffusion problem might be resolved through introduction of some mesopores to microporous zeolites, and then the catalytic performance of zeolite might be improved. Herein, mesoporous structure was successfully created for H-USY zeolites through nitric acid treatment. The catalytic performance of the mesoporous H-USY in the conversion of glucose to methyl levulinate (MLE) was investigated. The effects of acidity and porous structure on the catalytic activity were discussed.

* Corresponding author.
E-mail address: yangxiaomei@zzu.edu.cn (X. Yang).

2. Experimental section

2.1. Materials

H-USY, H-ZSM-5, H-β, H-MOR and H-Y powder was purchased from Nankai University Catalyst Co. (China). Nitric acid (AR, 65% solution), glucose, fructose, mannose, sucrose, cellobiose and methyl α-D-glucopyranoside were of analytic grade and used without further purification.

2.2. Preparation and characterization of mesoporous H-USY zeolite

H-USY was treated by nitric acid leaching method to remove some Al species. In a typical procedure, H-USY-parent (4.0 g) and the solution of nitric acid (100 mL) were added in a three-necked flask equipped with a reflux condenser. After being treated at 85 °C for 8 h under stirring, the sample was filtered, washed three times with deionized water, dried at 100 °C for 12 h, and then calcined at 550 °C for 5 h. The acid treated H-USY was denoted as H-USY-x, where x (mol L^{-1}) represents the concentration of nitric acid.

Powder X-ray diffraction (XRD) was performed on a Panalytical X`pert PRO instrument with Cu Kα radiation. The Si/Al ratio of zeolite was determined by a Philips Margix X-ray fluorescence (XRF) spectrometer. The adsorption/desorption isotherms were measured with a Quantachrome Autosorb using N_2 as adsorbate. Samples were outgassed at 300 °C for 2 h prior to measurements. Total surface area was calculated according to the Brunauer–Emmett–Teller (BET) method, and pore size distributions were calculated from the desorption branch of the isotherm based on the Barrett–Joyner–Halenda (BJH) method. FT-IR spectra of the samples were obtained using a Nicolet IR 200 Spectrometer in KBr media. Acidities of the samples were characterized by temperature-programmed desorption of ammonia (NH$_3$-TPD) on a home-made instrument. Before the adsorption of NH$_3$, the sample (0.1 g) was pretreated at 350 °C in He (40 mL min^{-1}) for 20 min. Then the sample was cooled down to 100 °C and adsorbed NH$_3$ for 10 min. Subsequently, the catalyst was flushed with He until the baseline was steady. The desorption process was monitored with a thermal conductivity detector at a temperature ramp from 100 to 700 °C, with a heating rate of 10 °C min^{-1}.

2.3. Catalytic reaction procedure and product analysis

A teflon-lined stainless steel autoclave reactor (80 mL) was first charged with methanol, and then a certain amount of carbohydrate and catalyst were added under stirring. After the autoclave was sealed, the atmosphere over the solution was replaced four times with N_2, and then the pressure of N_2 was charged to 0.1 MPa. Subsequently, the reactor was heated to the desired temperature under stirring. When the reaction was finished, the reactor was cooled down to the ambient temperature. The products in the reaction solution were identified by an Agilent 6890 N GC/5973 MS and a Shimadzu LC-20AT HPLC analysis system. Conversion of glucose was analyzed with the external standard method on a Shimadzu LC-20AT HPLC analysis system equipped with an Aminex HPX-87H column (300 mm × 7.8 mm) and refractive index detector (RID-10A). 0.005 M H_2SO_4 was used as the mobile phase, which had a flow rate of 0.5 mL min^{-1}. The column temperature was 40 °C. Yield of MLE was analyzed on a GC equipped with an FID detector using naphthalene as the internal standard.

3. Results and discussion

3.1. Characterization

XRD patterns in Fig. S1 show that the crystalline structure of H-USY was preserved after being treated with nitric acid solution. The Si/Al ratio increased with the increase of nitric acid concentration (Table 1), demonstrating that nitric acid is effective to remove Al species from USY zeolite. The Si/Al ratio increased slowly when the acid concentration was ≤0.2 M, and it increased quickly with further increase of acid concentration. Probably, extraframework aluminum (EFAL) was mainly removed at lower acid concentration, whereas both framework Al and EFAL were removed at higher acid concentration. FT-IR spectrum (Fig. S2) of H-USY zeolite treated with 0.5 M nitric acid exhibits an absorption peak at 963 cm^{-1}, which was assigned to the vibration of Si–OH [18]. The formation of Si–OH implies that the framework Al was removed with higher concentration of nitric acid solution.

The results of N_2 adsorption–desorption were supplied in Fig. S3. The treated samples showed type IV isotherms with H3 hysteresis loop, indicating that these zeolites are full of mesoporous structure after acid treatment [19]. The pore size distributions (Fig. S4) also revealed the formation of mesopores. Further, TEM images (Fig. S5) confirm the presence of inhomogeneous mesopores. The average pore size and the most probable pore size increased with the concentration of nitric acid (Table 1 and Fig. S4). The external surface area and the mesoporous volume of H-USY zeolites also increased with the concentration of nitric acid (Table 1), which reached the highest value at nitric acid concentration of 0.3 M. These results suggest that the acid treatment could remove the EFAL to form more mesopores. With further increasing the concentration of nitric acid to 0.5 M, the external surface area and the mesoporous volume decreased due to the destruction of zeolite structure by excessive removal of framework Al.

The acidity of H-USY zeolites was measured by NH$_3$-TPD, and the results are given in Fig. 1 and Table 1. All the NH$_3$-TPD curves show two peaks at temperature lower than 550 °C, corresponding to NH$_3$ desorbing from weak and strong acid sites [20], respectively. When the concentration of nitric acid was lower than 0.3 M, the acid amount of H-USY decreased gradually due to the removal of EFAL. However, the acidity decreased sharply at high concentration of nitric acid

Table 1
Properties of the parent and acid-treated H-USY zeolites.

Sample	n_{Si}/n_{Al}[a]	Acid amount (mmol g^{-1})[b]	S/W[c]	S_{BET} (m^2 g^{-1})	V_{total} (mL g^{-1})	S_{ex} (m^2 g^{-1})[d]	V_{meso} (mL g^{-1})[d]	Average pore size (nm)
H-USY-parent	3.2	2.36	1.0	446	0.316	57	0.116	2.8
H-USY-0.05	4.3	2.24	1.2	458	0.322	73	0.124	2.8
H-USY-0.1	5.0	1.81	1.0	511	0.374	83	0.154	2.9
H-USY-0.2	5.9	1.75	1.1	479	0.373	86	0.172	2.9
H-USY-0.3	14.1	1.29	1.4	554	0.420	100	0.188	3.0
H-USY-0.5	17.6	0.33	1.0	433	0.342	91	0.167	3.2

[a] Measured by XRF.
[b] Determined by NH$_3$-TPD.
[c] S/W is the ratio of strong/weak acid sites, which is calculated from NH$_3$-TPD.
[d] $S_{ex} = S_{BET}$ − micropore surface area; $V_{meso} = V_{total}$ − micropore volume, where micropore surface area and volume were determined by the t-plot method at a relative pressure of 0.05–0.70.