

## Acid properties and catalysis of USY zeolite with different extra-framework aluminum concentration



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### ABSTRACT

USY zeolite was treated by the citric acid. The properties and catalysis of the USY zeolite were studied. The X-ray diffraction has been used to identify and quantify extra framework aluminum (EFAL) in USY zeolite by EFAL extraction using citric acid. The acid character changed depending on the EFAL concentration. The Lewis acid sites can be obtained from the Si/Al ratio. The removing of trace olefins was carried out over kinds USY zeolites with different amount of EFAL. The catalytic performance was correlated with the Lewis acid sites of USY.

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### 1. Introduction

Aromatics hydrocarbon such as benzene, toluene, xylene and ethyl benzene (BTX) are obtained from reforming and cracking processes in the petrochemical enterprises. The conversion of naphtha into BTX stream is always accompanied by the formation of non-aromatic olefins such as hexene and styrene [1–2]. These olefins can poison the adsorbent which is used to separate para-xylene (PX) from aromatics. In order to protect the adsorbent, the bromine index which is an indicator of the presence of olefinic bonds is required to be less than 20 mg Br/100 g. Therefore, these contaminants must be removed before aromatic streams are sent to the petrochemical processes. It has been approved that these harmful impurities can be removed by acid-catalyzed alkylation of the appropriate aromatics [3–4]. In commercial plants, the purification process uses the clay treating [5] or the modified clay treatment. But, both of the two methods pose problems such as limited lifetime, pollution and non-reused. Pressure from legislative and environmental bodies together with a growing awareness within the chemical industry has led to a search for new eco-friendly products and processes to replace polluting reactions.

USY zeolite is one of the most important zeolites applied in industry for petroleum processes, which is the ultrastable counterpart of Y zeolite, and was obtained by steaming treatment of Y zeolite [6–7]. To obtain highly siliceous zeolite Y, it is necessary to have

a post-synthesis treatment (dealumination), in which the Al atom is expelled from the zeolite lattice. As a result, extra-framework Al species is formed. Dealumination can be accomplished by thermal or hydrothermal treatments, chemical treatments and acids leaching [8–10]. The resulting material, USY zeolites, being modified in the framework Si/Al ratio, structure and acidity, usually exhibit improved reactivity, selectivity and coking behavior for a catalytic reaction, which is of great interest to the petroleum industry [11]. It has been suggested that the amount of extra-framework Al species, formed during the process of dealumination, is one of the key factors that influence significantly catalytic activity [12].

Citric acid, as an acid and a chelating agent for metal ion, is effective for the extraction of aluminum from zeolite [11]. The USY zeolite will have a rich acid strength after treating by citric acid. The modified process can change the distribution of the acid in the zeolite. The amount of Lewis (L) acid was increased and the amount of Brønsted (B) acid was decreased. Here the conditions for treatment of USY zeolites by citric acid and the influence of acid treatment on the properties of obtained USY zeolites were systematically studied. Furthermore, removing of trace olefins from aromatics was explored by using the obtained USY zeolite as catalyst.

### 2. Experimental section

#### 2.1. Materials

USY powder was purchased from XinNian Petrochemical Additives Company (China) and was referred as USY-parent. Citric acid

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(AR, 99.8%) was purchased from Sinopharm Chemical Reagent Company, China. Experimental raw materials were aromatic intermediate products without the clay treatment, which were obtained from industrial reforming units of Sinopec Zhenhai Refining & Chemical Company. The main components were C8–C10 which can be seen in Table 1.

## 2.2. Preparation of the USY zeolites

Modified USY was prepared by acid leaching method. In a typical procedure, ten gram of USY zeolites and the solution of citric acid (250 ml) were placed into a three-necked flask equipped with a reflux condenser. After treatment at 363 K for a certain time under stirring, the sample was filtered, washed with deionized water, dried overnight at 493 K.

A series of modified USY zeolites were prepared by the treatment of USY with an acid solution (0.1, 0.2 and 0.3 mol L<sup>-1</sup>) for 4 h. Codes *f* samples reflect their treatment conditions. If the sample was leached by 0.1 mol L<sup>-1</sup> citric acid, it is denoted by USY-0.1, while USY-0.3 means that the USY was treated with 0.3 mol L<sup>-1</sup> acid for 4 h.

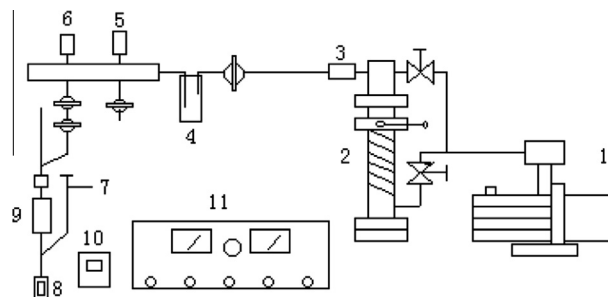
## 2.3. Characterization of USY zeolites

X-ray diffraction (XRD) of the representative samples (before the kneading) were performed on a Rigaku-3014 diffractometer with a monochromator using Cu K $\alpha$  ( $\lambda = 0.154$  nm) radiation. The diffractograms were recorded in the  $2\theta$  range 10–80° in steps of 0.04° with a scan rate of 2° per min. The crystallinities of the samples were calculated according to the intensity of the peaks at  $2\theta$  of 11.9°, 15.7°, 18.7°, 20.4°, 23.7°, 27.1° and 31.4°. The nitrogen adsorption of the samples (before the kneading) were performed on a Micromeritics 2010 analyzer at liquid nitrogen temperature (77.3 K) and the samples were degassed at 673 K for 4 h prior to adsorption analysis. The in situ IR spectra of OH groups and pyridine adsorption were run on a Nicolet 6700 Fourier transform IR spectrometer. The surface acidity was investigated by the adsorption of pyridine on the solid surface of samples. FTIR measurements were carried out using pyridine as probe molecule. The Fourier transform infrared spectra was collected with a combined reactor-spectrometer system using a low-volume in situ cell with water-cooled KBr window (see Fig. 1).

For all experiments, 16.5–16.9 mg of finely ground catalyst was pressed into self-supporting wafers with a diameter of 10 mm. The wafer loaded into the cell was pretreated at 653 K in vacuum conditions for 2 h and cool down to 353 K for pyridine adsorption. The physisorbed pyridine was eliminated at 473 K. The total concentrations of Brønsted and Lewis sites able to retain pyridine at 473 K were determined using the absorbance surfaces of the corresponding bands at 1540 and 1450 cm<sup>-1</sup>, respectively [13–14]. Then the sample was subjected to the thermal desorption at 723 K followed by the IR measurement. Through the FTIR spectroscopy, the strong acid sites can be monitored. The difference represents the weak acid sites. The quantification method for Lewis acidic site and Brønsted acidic site was based on Lambert–Beer law:  $A = \xi \cdot C \cdot d$ , where  $A$  is absorbance,  $C$  is the sample concentration,  $\xi$  is extinction coefficient and  $d$  is sample thickness. Surface acid contents of adsorbents for Lewis acid and Brønsted acid were calculated

**Table 1**  
Composition of the aromatics of Sinopec Zhenhai Refining & Chemical Company.

Raw material (with Bromine Index of 1120) w%					
Toluene	Ethyl benzene	Xylene	C <sub>9</sub> aromatics	C <sub>10</sub> aromatics	Others
0.238	7.885	52.207	32.622	6.81	0.238



**Fig. 1.** In situ FTIR reactor system. (1) Rotary vane vacuum pumps. (2) High vacuum oil diffuse pump. (3) Antihunting device. (4) Buffer unit. (5) Vacuum gauge. (6) Thermocouple well. (7) Pyridine entrance. (8) Infrared transmission windows. (9) Heater coil. (10) Temperature controller and solid state relays. (11) Composite vacuum table.

by using empirical formulas which are obtained from the relevant experiments.

$$C_L(\text{mol g}^{-1}) = 3.73 \times 10^{-4} \cdot A_L \quad (1)$$

$$C_B(\text{mol g}^{-1}) = 9.90 \times 10^{-4} \cdot A_B \quad (2)$$

where  $C_L$  and  $C_B$  are respectively Lewis acid contents and Brønsted acid contents (mol g<sup>-1</sup>),  $A_L$  and  $A_B$  are respectively peak areas in 1450 cm<sup>-1</sup> (denoted as L acid sites) and in 1540 cm<sup>-1</sup> (denoted as B acid sites).

## 2.4. Micro-activity test evaluation

The modified sample was powdered, and mixed with alumina (the weight ratio of zeolite/alumina was 4) to prepare modified zeolite catalyst, kneaded with the proper amount of a 10% nitric acid solution, and then squeezed into the form of strips. The moisture was removed in an oven, in an air atmosphere at 393 K for 6 h. Then, the catalyst was activated at 823 K for 6 h. After cooling, the catalysts were crushed and screened to 20–40 mesh for using.

The evaluation of the catalyst was carried out in a fixed-bed tubular microreactor, equipped with a constant-flow pump to control the flow rate and a controlled heating system to maintain the temperature. The treated catalyst was packed between two quartz sands (40–60 mesh) and inserted into the reactor. The reaction was carried out under the following conditions: reaction temperature 448 K; reaction pressure 1 MPa; weight hourly space velocity (WHSV) at 30 h<sup>-1</sup>. Samples of the inlet and effluent liquids from the reactor were analyzed with the bromine index analyzer every 30 min. The value of olefin conversion ( $X$ ) =  $[(n_o - n_i)/n_o] \cdot 100$ , where  $n_o$  is the initial content olefins and  $n_i$  is final content of olefins. Bromine Index is determined according to ASTM D 2710-92, which is a measure of milligrams of bromine consumed by 100 g of the sample under given conditions.

## 3. Results and discussion

### 3.1. Chemical analysis

The XRD patterns of USY and the modified USY zeolites obtained by treatment with different concentrations of citric acid are presented in Fig. 2.

Table 2 gives the Si/Al ratios, crystallinity and cell parameter ( $a_0$ ) for treatments with citric acid. The global and framework Si/Al ratios were determined, respectively, by X-ray fluorescent (XRF) and XRD, the latter using the correlation established by Fichter-Schmittler et al. [15]:

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