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Zeolite with trimodal porosity by desilication of zeolite nanocrystals aggregate

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ABSTRACT

Zeolite with trimodal porosity can be synthesized by desilication of zeolite nanocrystal aggregate. In the desilication process, the originally existed intercrystalline mesopores of zeolite nanocrystal aggregate were enlarged into large mesopore, and the new small intracrystalline mesopore channel was created, thus the Zeolite with trimodal porosity was formed. The structure of resulted zeolite, both on aggregate and mesopore level can be fine tuned by the desilication degree.

1. Introduction

Zeolites are widely used in heterogeneous catalysis, especially in oil refining and petrochemical industries, because of their high acidity and shape-selectivity induced by molecular-sized microporosity [1]. However, the microporous structures of zeolite also result in diffusion limitations on the reaction rate in many applications [2]. To overcome this problem, several novel materials such as ultra-large micropore zeolite [3], ordered mesoporous materials [4], zeolite nanocrystals [5] and mesoporous zeolites have been synthesized [6]. Among these materials, the mesoporous zeolite is considered to be the most effective one because it combines the advantages of both zeolites and mesoporous materials [7], as proved by catalytic and diffusional tests [8–10].

In recent years, various synthetic procedures have been attempted for the fabrication of mesoporous zeolites based on secondary (hard or soft) templates, dealumination/desilication and crystallization kinetics control. Carbon nanomaterials are the mostly used template materials and zeolites with both intercrystalline and intracrystalline mesoporous can be synthesized by this method [11–16]. However, the high cost of carbon materials and the complex synthesis route make the carbon template method unfeasible for large-scale industrial applications. More recently, amphiphilic organosilane or silylated polymers have been successfully used as the secondary template for mesoporous zeolite synthesis [17–20]. The advantage of silane or silyated polymer as secondary template upon carbon materials is the simple synthesis process, however, the organosilane used as the secondary template is also too expensive for large scale applications. Dealumination is a well-known post-treatment method to create mesopores in zeolites with low Si/Al ratio. This technique can improve the catalytic performance of USY zeolites [21], but recent 3D-TEM and PFG-NMR analyses indicated that the mesopores introduced by dealumination do not form an interconnected network and have scarce contributions to molecular diffusions [22,23]. Desilication is reported to be a suitable method for mesopore introducing in zeolite with high Si/Al ratio. However, mesoporous zeolite with excellent diffusion properties can only be obtained when zeolite with suitable Al content and spatial distribution as parent zeolite [24–30]. More recently, we show that mesoporous zeolite (ZSM-5, ZSM-12 and so on) with intercrystalline mesopore structure can be obtained through crystallization kinetics control, for instance, increasing super-saturation degree [31]. Very recently, Moller et al. reported that hierarchical zeolite beta can be synthesized in one-step through network formation of uniform nanocrystals [32]. Such secondary template and post-treatment free mesoporous zeolite synthesis route allows mesoporous zeolites to be synthesized with a cost similar to or even lower than that of conventional zeolites and thus possibly opens a new, cost-effective, and industrially applicable way to the synthesis of mesoporous zeolites.

Up to date, the reported mesoporous zeolites always have bimodal porosity, that is, micropores and mesopores. The mesopore

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can either in small (2–5 nm) or large (10–50 nm) mesopore range. However, based on theoretical consideration it has been proposed that hierarchical pore networks integrate of large mesopore, small mesopore and micropore structure will be optimal for zeolite catalysis. Ideally, large mesopores facilitate mass transfer from the surface of the zeolite crystal followed by transport in small mesopores, finally allowing diffusion into micropores. Consecutive catalytic reactions can thus happen at pore with different size. Recently, Jong et.al reported that zeolite Y with trimodal porosity was obtained by subsequently dealumination/desilication of zeolite HY. The resulted zeolite show better performance as hydro-cracking catalyst support than the parent zeolite. This is the only available example of zeolite with trimodal porosity [33]. However, the dealumination/desilication method cannot be extended to other zeolites with high Si/Al ratio.

Here in this paper, based on the secondary template and post-treatment free mesoporous zeolite synthesis pathway, we further show that zeolite with trimodal porosity can be obtained by desilication of such zeolite nanocrystals aggregate. The structure of resulted zeolite, both on aggregate and mesopore level can be fine tuned by the desilication degree. The desilication mechanism of zeolite nanocrystal aggregate was also discussed.

2. Experimental

2.1. Materials

Chemicals used in this work including Sodium hydroxide (NaOH, min. 99.0%), Sodium aluminate ($NaAlO_2$, $Al_2O_3 \geq 41.0\%$), Fumed silica (SiO_2, min. 99.0%), *n*-Butylamine (min. 99.0%), Sodium chloride (NaCl, min. 99.0%) and Ammonium nitrate (NH_4NO_3, min. 99.0%). All chemicals were purchased from Aladdin Reagent Company and used as received without further purification in this work.

2.2. Zeolite nanocrystals aggregate synthesis and the alkali-treatment

The ZSM-5 nanocrystals aggregate with Si/Al ratio about 38 was crystallized with *n*-butylamine as template according to the procedures in reference [34]. For the synthesis of ZSM-5 nanocrystals aggregate, the NaOH (Aladdin, $>99.0\%$), $NaAlO_2$ (Aladdin, $Al_2O_3 \geq 41.0\%$) and NaCl (Aladdin, $>99.0\%$) was first added into water and stirred to obtain a clear solution, after that pre-calculated amount of SiO_2 (Aladdin, $>99.0\%$) and *n*-Butylamine (Aladdin, $>99\%$) were added under vigorous stirring. The molar composition of synthesis mixture is $80SiO_2/Al_2O_3/3Na_2O/10$ *n*-Butylamine/$15NaCl/800H_2O$. The zeolite crystallization were carried out in a Teflon lined autoclave and heated under static conditions at 423 K for 48 h. The produced solid products were separated by filtration, and then washed with distilled water, dried overnight at 383 K. Finally, 5 g solid products were exchanged with 150 ml 0.1 mol/L NH_4NO_3 solution and washed with deionized water at 363 K, repeatedly. After drying, the samples in NH_4-formwere calcined at in static air at 823 K for 5 h (heating rate of 1 K/min) to convert them into H-form. The resulting sample was used as the parent zeolite and labeled as P.

Alkali-treatment of the ZSM-5 nanocrystals aggregate was performed at 338 K for 120 min with NaOH solution at a concentration of 0.1, 0.2, 0.3 and 0.4 mol/L, and the obtained samples denoted as AT-1, AT-2, AT-3 and AT-4, respectively. The resulting samples were washed with distilled water and dried overnight at 383 K. Prior to further characterization, the alkali-treated samples were ion-exchanged into H-form and calcined following the same procedures as for preparing the parent zeolite.

2.3. Characterizations

X-ray diffraction (XRD) patterns were obtained with a Bruker D8 Advance X-ray diffractometer, using Cu K_α radiation at room temperature and instrumental settings of 40 kV and 40 mA. Data were recorded in the 2θ range 5–50° with a 0.02° step size.

Si and Al concentrations in the zeolites obtained upon alkaline treatment were determined by ICP-OES in Perkin–Elmer Optima 2000DV. Zeolite samples were dissolved in HF/HNO_3 mixture acid prior to the analysis.

Scanning electron microscopy (SEM) images were obtained with a Hitachi S4800 microscope, operating at 10 and 15 kV. Before SEM analysis, each zeolite sample was first placed on a carbon film and subsequently coated with gold by sputtering for 20 min to reduce the charging effects.

Transmission electron microscopy (TEM) measurements were recorded by a Hitachi H-7650 microscope, operating at 100 kV. The sample was suspended in ethanol and dispersed on a copper grid coated with lacey carbon film.

N_2 adsorption and desorption experiments were carried out at liquid nitrogen temperature using a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. Prior to the analysis, each sample was evacuated at 573 K in vacuum for 6 h. The total surface area and micropore volume was calculated according to the BET and the *t*-plot method, respectively. The mesopore size distribution was obtained by the Barrett–Joyner–Halenda (BJH) analysis of the adsorption branch of the isotherm.

Temperature-programmed desorption of ammonia (NH_3-TPD) for acidity analysis was carried out in a Micromeritics Autochem–Chemisorption Analyzer. 50 mg zeolite sample was pretreated at 573 K in an Ar flow of 20 cm^3/min for 1 h. Afterwards, a pure NH_3 flow of 20 cm^3/min was adsorbed at 323 K for 1 h followed by Ar purging at the same temperature for another 1 h. Desorption of NH_3 was monitored in the range of 323–973 K with a ramp of 10 K/min. The curve-fitting analysis was done for the observed profiles to determine the acid strength and its distribution, and the profile resolved according to a simple Gaussian function.

3. Results and discussion

The parent ZSM-5 nanocrystals aggregate was synthesized according to pervious study through the carefully control of crystallization kinetics. Typical SEM and TEM images of parent zeolite are shown in Fig. 1. It can be found that the parent zeolite aggregates are micron-sized particles constructed of primary nanosized zeolite crystals (ca. 50 nm). The primary nanocrystals all have very sharp edges.

The yield and Si/Al ratio of zeolite after alkali-treatment are summarized in Table 1. The zeolite mass yield of AT-1, AT-2, AT-3 and AT-4 was 83%, 60%, 49% and 24%, respectively. Obviously, the yield was decreased evidently with the increasing of the alkali-treatment degree. The elemental composition also changed dramatically after alkali-treatment. The Si/Al ratio of AT-1, AT-2, AT-3 and AT-4 was 30, 24, 19 and 8, respectively. The yield and elemental analysis coincide with each other very well. The Si/Al ratio estimated by the yield for AT-1, AT-2, AT-3 and AT-4 is 30, 25, 16, and 11, respectively, which is very similar to the detected value. These results indicate that the Si species is selective extract out from the zeolite matrix during alkali-treatment, which is coincides with the results drawn in pervious zeolite desilication study.

XRD characterization was used to investigate the crystallinity change of ZSM-5 nanocrystals aggregate upon the alkali-treatment. The XRD patterns of the samples before and after the alkali-treatment are shown in Fig. 2. Only diffraction peaks belong to MFI structured zeolite can be found, indicated that no new phase