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Development of hierarchical MCM-49 zeolite with intracrystalline mesopores and improved catalytic performance in liquid alkylation of benzene with ethylene

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ABSTRACT

Hierarchical MCM-49 zeolite with intracrystalline mesopores was prepared through post-treating the conventional MCM-49 zeolite in hexadecyltrimethylammonium bromide (CTAB) and NaOH mixed solution. N_2 adsorption and desorption, XRD, TEM, XRF, ICP and Py-IR techniques were applied to characterize the obtained samples. It was found that uniform intracrystalline mesopores were distributed in the MCM-49 crystals, and the intracrystalline meso-porosity could be modified by changing the post-treatment conditions such as CTAB concentration, NaOH concentration, temperature and time. Based on the characterization results upon the hierarchical MCM-49 zeolite samples obtained by post-treating different time, the formation of intracrystalline mesopores in MCM-49 zeolite was proposed, which followed a CTAB micelle directed desilication mechanism. By virtue of the intracrystalline mesopores, the hierarchical MCM-49 zeolite prepared under proper post-treatment condition exhibited superior stability than the conventional MCM-49 zeolite in liquid alkylation of benzene with ethylene.

1. Introduction

MCM-49 zeolite (MWW topology) has two independent micropore channels [1,2]: one is the intralayer two-dimensional sinusoidal 10 member ring (10 MR) channels; the other is the interlayer 12 MR supercages with 10 MR windows. Besides, numerous hemi-supercages (pockets) with 12 MR openings distribute on the surface of MCM-49 zeolite [2]. This special pore structure endows MCM-49 zeolite with excellent catalytic performance in liquid alkylation of benzene with ethylene [3]. Further study on the role of different micropore systems of MCM-49 zeolite finds that the surface pockets are responsible for c.a. 60% of ethylene conversion at the beginning of the alkylation reaction, the interlayer supercages for c.a. 30% and the intralayer sinusoidal 10 MR channels for c.a. 10% [4]. Additionally, only the interlayer supercages experience a quick deactivation due to coke deposition, while both of the surface pockets and intralayer sinusoidal 10 MR channels exhibit good reaction stability [4]. Therefore, in order to improve the reaction stability of MCM-49 zeolite in liquid alkylation of benzene with ethylene, it is necessary to introduce intracrystalline mesopores into MCM-49 zeolite to facilitate the transportation of reactants and products in the interlayer supercage system.

To our knowledge, little research is reported that the uniform intracrystalline meso-porosity in MCM-49 zeolite is created via post-treatment up to now. Although alkali-treatment using NaOH solution is widely employed to create intracrystalline meso-porosity in some zeolites such as ZSM-5 [5–7], beta [8,9] and mordenite [10], this method is not much suitable for MCM-49 zeolite [11]. Similarly, MCM-22 zeolite, having the same topology structure and morphology with MCM-49 zeolite, is also hard to be introduced remarkable intracrystalline mesopores by traditional alkali-treatment [12,13]. The reason is supposed to be that both MCM-49 and MCM-22 have thin plate-like morphology and are easily cracked into small flakes during the alkali-treatment. Thus, it is necessary to find a way to protect the integrity of MCM-49 crystals in the process of alkali-treatment. Pérez-Ramírez et al.

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[14,15] found that tetrapropylammonium could protect ZSM-5 crystal during the alkali-treatment and enhance the formation of intracrystalline mesopores without severe destruction of the framework. Afterwards, Verboekend et al. [16] demonstrated that hexadecyltrimethylammonium bromide (CTAB) surfactant not only acted as a framework-protection agent, but also created uniform intracrystalline mesopores when Y and beta zeolites were alkali-treated. Chal et al. [17] and García-Martínez et al. [18] drew similar conclusion in the case of alkali-treatment upon Y zeolite in the presence of CTAB. Also, Ji et al. [19] prepared hierarchical MCM-22 zeolite with the mesopore diameter of c.a. 20 nm through organic amine-protective desilication.

Enlightened by the results mentioned above, in this manuscript, MCM-49 zeolite was post-treated in CTAB and NaOH mixed solution, and hierarchical MCM-49 zeolite with uniform intracrystalline mesopores was successfully obtained. The effects of CTAB concentration, NaOH concentration, post-treatment temperature and time on the meso-porosity of the obtained hierarchical MCM-49 zeolite were thoroughly investigated. The formation process of intracrystalline mesopores in MCM-49 zeolite was discussed. Also, the alkylation performances of benzene with ethylene over the prepared hierarchical MCM-49 and conventional MCM-49 were compared.

2. Experimental

2.1. Preparation of hierarchical MCM-49 zeolite

Hierarchical MCM-49 zeolite was prepared via post-treating MCM-49 zeolite in CTAB and NaOH mixed solution. Typically, 9.0 g conventional MCM-49 zeolite (after calcination) with Si/Al molar ratio of 11.5 was treated in 135 mL CTAB (J&K Scientific Ltd.) and NaOH (96.0 wt%, Sinopharm Chemical Reagent Co., Ltd) mixed solution. With the aim of studying the influence of the four factors (CTAB concentration, NaOH concentration, temperature and time) on the meso-porosity of the product, one factor was changed while keeping the others constant. When the post-treatment procedure was done, the product was recovered by centrifugation, washing, drying at 110 °C and calcining at 550 °C. The name of the product was denoted as aCTAB-bNaOH-cT-dt, where “a”, “b”, “c” and “d” represented the values of CTAB concentration (mol/L), NaOH concentration (mol/L), temperature (°C) and time (h), respectively. For example, 0.1CTAB-0.3NaOH-110T-22t meant that the conventional MCM-49 zeolite was treated in 0.1 mol/L CTAB and 0.3 mol/L NaOH mixed solution at 110 °C for 22 h.

2.2. Preparation of H-type sample

In order to obtain H-type sample (prefixed by “H-”, such as H-MCM-49), Na-type sample was ion-exchanged in 0.8 mol/L NH_4NO_3 solution at 80 °C for 2 h, followed by drying at 110 °C overnight and calcining at 520 °C for 3 h, respectively.

2.3. Characterization

N_2 adsorption and desorption measurement was carried out at −196 °C on a Micromeritics ASAP 2020 instrument. Pore size distribution was calculated using Barret–Joyner–Halenda (BJH) model applied to the adsorption branch of the isotherm.

Powder X-ray diffraction (XRD) patterns were obtained on an X′ Pert Pro X-ray diffractometer operated at 40 kV and 40 mA using Cu Kα radiation. The wide angle XRD pattern was recorded in the 2θ range of 5°–50°. The relative crystallinity (RC) of the sample was calculated using the total area of the diffraction peak at $2\theta = 7.1, 8.0, 10.0, 14.2$ and 26.0.

The morphology determination of the sample was performed on a FEI Tecnai G^2 spirit transmission electron microscope (TEM) with the accelerating voltage of 120 kV, point resolution of 0.35 nm and line resolution of 0.20 nm. Prior to the measurement, the samples were dispersed in anhydrous alcohol using ultrasonic technique, and then the resultant suspension was dropwise added to a copper grid and dried in air.

The chemical composition of the sample was analyzed on a Philips Magix 601X X-ray fluorescence (XRF) spectrometer.

The concentrations of Si and Al in the collected mother solution were determined on a SHIMADZU ICPS-8100 inductively coupled plasma (ICP) emission spectrometer.

Solid-state ^{27}Al MAS NMR spectra were recorded on a Bruker AVANCE III 500 MHz spectrometer using 4 mm ZrO_2 rotors at 130.3 MHz with a spinning rate of 10 kHz. Prior to the measurements, all the samples were fully hydrated with saturated NH_4NO_3 solution in a desiccator. 1% $Al(NO_3)_3$ aqueous solution was used as the chemical shift reference. A total of 1000 scans were accumulated with a pulsewidth of 0.75 μs and a 2 s recycle delay.

The Brønsted and Lewis acidic site distribution of the samples were determined by pyridine adsorption Infrared (Py-IR) measurements on a Bruker 70 IR spectrometer. The sample power was pressed into a self-supported wafer of c.a. 10 mg, and then the wafer was placed in an in situ cell and outgassed at 450 °C for 30 min in vacuum (10^{-2} Pa). After the wafer in the cell cooled down to room temperature, the background IR spectrum was recorded. Subsequently, the wafer was exposed to pyridine vapor for 20 min at 0 °C followed by being outgassed at 150 °C for 30 min. The IR spectrum was collected at room temperature.

2.4. Catalysts evaluation

Liquid alkylation of benzene with ethylene was carried out in a stainless steel fixed bed reactor at 200 °C and 3.0 MPa. At the beginning, 0.5 g catalyst was loaded in the center of the reactor and pretreated at 500 °C for 1 h in N_2 flow. Afterwards, the reactor temperature was decreased to 200 °C. Benzene was pumped in to fill the entire reactor space, followed by the simultaneous introduction of ethylene with the weight hourly space velocity (WHSV) of 6 h^{-1} and benzene/ethylene molar ratio of 2 into the reactor.

3. Results and discussion

3.1. Development of hierarchical MCM-49 zeolite with intracrystalline mesopores

3.1.1. Effect of CTAB concentration

MCM-49 and aCTAB-0.3NaOH-110T-22t (a = 0–0.2 mol/L) series samples were characterized by N_2 adsorption and desorption technique, and the corresponding N_2 adsorption and desorption isotherms and BJH pore size distributions (derived from the adsorption branches) were given in Fig. S1 and Fig. 1, respectively. It can be seen that almost no mesopores are found in MCM-49. For aCTAB-0.3NaOH-110T-22t series samples, a relatively narrow peak at c.a. 3.0 nm becomes stronger with the increase of CTAB concentration, indicating the presence of intracrystalline mesopores with narrow size distribution. This reveals that CTAB plays a critical role in the formation of intracrystalline mesopores in MCM-49 zeolite. Accordingly, as shown in Table 1, the external surface area of aCTAB-0.3NaOH-110T-22t (a = 0–0.2 mol/L) is larger than that of MCM-49, especially in the case of a = 0.1 and 0.2 mol/L.

Fig. 2 showed the XRD patterns of MCM-49 and aCTAB-0.3NaOH-110T-22t (a = 0–0.2 mol/L). It is found that all the alkali-treated samples have lower relative crystallinity than MCM-49 whether CTAB is present or not, which is due to the partial