



Liquid-phase alkylation of benzene with ethylene over postsynthesized MCM-56 analogues

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ABSTRACT

MCM-56 analogues were postsynthesized via a mild acid treatment technique from hydrothermally synthesized MCM-22 lamellar precursors with Si/Al ratios of 15–45. The physicochemical properties of MCM-56 were characterized by XRD, SEM, N₂ adsorption, XPS, ²⁹Si and ²⁷Al MAS NMR, NH₃-TPD and pyridine adsorption IR techniques. In comparison to MCM-22 with 3-dimensional MWW topology, the postsynthesized MCM-56 showed a broad X-ray diffraction of emerged 1 0 1 and 1 0 2 reflections and possessed a structural disorder along the layer stacking direction. Composed of partially delaminated MWW nanosheets, MCM-56 analogues had a larger external surface than MCM-22. The MCM-56 and MCM-22 catalysts were employed in the liquid-phase alkylation of benzene with ethylene. MCM-56 analogues exhibited a higher yield of ethylated benzenes and a higher catalytic stability than MCM-22, proving to serve as promising solid-acid catalysts for processing bulky molecules in petrochemical industry.

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1. Introduction

Alkylation of benzene is an important process in petrochemical industry [1–3]. As one of the most useful alkylbenzenes, ethylbenzene (EB) is used as feedstock for the production of styrene, the raw material for polystyrene, acrylonitrile–butadiene–styrene (ABS), styrene–acrylonitrile (SAN) resins, styrene–butadiene elastomers and latexes, as well as other unsaturated resins [4]. The worldwide capacity of ethylbenzene currently reaches 35 million metric tons per year. Its global demand is estimated to grow by about 4.1% annually in the period of 2009–2014 and by 3.3% per year over the ten years of the forecast.

Nowadays, ethylbenzene is mainly produced by the alkylation of benzene with ethylene or ethanol using acid catalysts [5]. The conventional catalysts for this reaction are mineral acids such as aluminum chloride and phosphoric acid. These homogeneous catalysts cause a number of problems in terms of handling, safety, corrosion, and waste disposal in spite of their relatively high activity and long lifetime [6–8]. An immense endeavor has been put to develop alternative catalytic systems that are more environmentally friendly. As a result, the ethylbenzene production technology has progressively shifted to zeolite-based processes [9]. Using ZSM-5 based catalyst [10,11], the process of ethylbenzene production under gas-phase

conditions was first commercialized by Mobil/Badger. Thereafter, a series of zeolites were investigated to exhibit promising catalytic performances. USY [7,12], Beta [13,14] and MCM-22 [15,16] have been successively commercialized for the liquid-phase alkylation of benzene which is operated at low temperatures and high pressures with the advantage of a better control and a longer catalyst life. With respect to the ethylbenzene production with USY, Beta or MCM-22 as the catalyst, MCM-22 possesses a higher selective for ethylated benzenes at a lower benzene/ethylene molar ratio, which is benefit for reducing the recycling amount of benzene [17].

MCM-22 zeolite with the MWW topology [18], one of the most representative zeolite developed by Mobil [19], is structurally analogous to SSZ-25 [20], PSH-3 [21], ITQ-1 [22] and MCM-49 [23]. Originated from a lamellar precursor, the MCM-22 structure is composed of three pore systems. One is the 2-dimensional (2D) sinusoidal 10-membered ring (MR) channel with elliptical ring cross section of 0.45 nm × 0.55 nm, which runs through the intralayers of the MWW nanosheets. The other interlayer 10-MR channel contains 12-MR supercages of 0.71 nm × 0.71 nm × 1.82 nm. It has also 12-MR side pockets or half cups on the outer crystallite surfaces external, providing more accessible acid sites for catalytic reactions.

As an important member of MWW family, MCM-56 has been paid more attention because its side pockets on the external surface are easily accessible by large molecules [24]. Consisting of disordered collection of MWW sheets but more exposed side pockets, MCM-56 is claimed to possess a partially delaminated structure in

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comparison to 3D crystalline MCM-22. MCM-56 was once prepared only by hydrothermal synthesis from the synthetic gels similar to MCM-22. The hydrothermal synthesis of MCM-56 usually needs a more careful control for crystallization time and temperature in comparison to the synthesis of MCM-22. Furthermore, the variation of the Si/Al ratios is limited in the direct hydrothermal synthesis of MCM-56 [25].

Recently, we developed a facial postsynthesis method for preparing MCM-56 analogues MWW-type aluminosilicate or titanosilicate precursors with changeable Al or Ti content [26,27], which is based on the fact that 2D lamellar precursors are of soft materials with a structural diversity. In comparison to corresponding 3D MWW counterparts, the obtained MCM-56 analogues exhibit enhanced catalytic activity in the reactions such as alkene epoxidation and 1,3,5-triisopropyl benzene cracking.

With the purpose to develop more active and selective catalysts than 3D MCM-22 for the alkylation of benzene, we postsynthesized MCM-56 analogues having a wide range of Si/Al ratios through a mild acid treatment in this study. The resulting materials were characterized for the structural features and physicochemical properties in detail. Their catalytic performance was investigated in the liquid-phase alkylation of benzene with ethylene.

2. Experimental

2.1. Synthesis MCM-22 precursors and H-MCM-22 samples

MCM-22 lamellar precursors were hydrothermally synthesized using hexamethylenimine (HMI) as a structure-directing agent (SDA) following the literature reported previously [9]. Silica gel (40 wt.%) and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ were used as silicon and aluminum sources, respectively. The precursors were crystallized from the gels with molar compositions of $1.0 \text{ SiO}_2 : 1/n \text{ Al}_2\text{O}_3 : 0.10 \text{ NaOH} : 0.45 \text{ HMI} : 20.0 \text{ H}_2\text{O}$, where n was 30, 40, 60 and 90. The crystallization was carried out in Teflon-lined stainless autoclaves under rotation (200 rpm) at 423 K for 4 days. The precipitates were filtered, washed with deionized water and dried at 373 K overnight. The as-synthesized precursors, denoted as MCM-22(P), were calcined in air at 723 K for 5 h to remove the organic SDA species. Calcined MCM-22 in sodium-form was ion exchanged with 1 M NH_4NO_3 at room temperature for 6 h twice and then calcined at 723 K for 5 h to obtain the proton-type sample, H-MCM-22.

2.2. Postsynthesis of MCM-56 analogues

MCM-56 analogues were prepared from MCM-22(P) by postsynthesis method that we reported elsewhere [27]. Under mild acid treatment conditions, MCM-22(P) was structurally transferred to MCM-56 readily. In a typical preparation, MCM-22(P) was treated with 0.1 M HNO_3 at a solid-to-liquid weight ratio of 1:20 and room temperature for 1 h. The acid treated samples were subsequently calcined and changed into proton-type MCM-56 using the same procedures mentioned above for H-MCM-22.

2.3. Characterization methods

The crystallinity of the samples was characterized by X-ray powder diffraction (XRD) patterns on a Bruker D8 Advance diffractometer equipped with a rotating anode and Cu-K α radiation ($\lambda = 1.5405 \text{ \AA}$). Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 electron microscope. N_2 adsorption was carried out at 77 K on a BELSORP-MAX instrument. The samples were degassed under vacuum at 383 K for 4 h and then at 623 K for 6 h. Fourier transform infrared spectra (FTIR) were obtained with a Nicolet FTIR-380 spectrometer at room pressure. A self-supported wafer (50 mg and $\varnothing 2 \text{ cm}$) was set in a quartz IR cell sealed with CaF_2

windows, where it was evacuated at 773 K for 2 h before the pyridine adsorption. The adsorption was carried out by exposing the wafer to a pyridine vapor (1.3 kPa) at room temperature for 0.5 h. The IR spectra of chemically adsorbed pyridine were recorded after evacuation at 473 K, 573 K or 673 K for 1 h. The acid-site distribution was measured with NH_3 temperature programmed desorption (NH_3 -TPD) on an apparatus equipped with a thermal conductivity detector (TCD). A sample of 150 mg was activated in helium flow at 873 K for 1 h. It was then cooled to 373 K where adsorption of NH_3 and desorption physically adsorbed NH_3 were performed. The NH_3 -TPD profile was recorded by heating the sample from 373 K to 873 K at a rate of 10 K min^{-1} and under helium flow at the rate of $30 \text{ cm}^3 \text{ min}^{-1}$. Solid-state MAS NMR spectra were recorded on a Bruker DMX Advance 500 spectrometer. ^{29}Si NMR spectra were recorded at 59.62 MHz with a pulse length of $5 \mu\text{s}$ and a spinning rate of 4 kHz, while ^{27}Al NMR spectra were recorded at 78.20 MHz with a pulse length of $0.31 \mu\text{s}$ and a spinning rate of 12 kHz. Si/Al molar ratios were determined by inductively coupled plasma (ICP) elemental analyses on a Varian 725-ES optical emission spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on ESCALAB 250 (VG) using Al K α ($h\nu = 1486.6 \text{ eV}$) radiation.

2.4. Catalytic reactions

The prepared catalysts, MCM-22 and MCM-56 analogues, were pressed into self-supported tablets under 20 MPa pressure using an electric tablet machine. They were then scrapped to collect the granules with a griddle of 10–20 mesh. The shaped tablets were tested for liquid-phase alkylation of benzene with ethylene in a fixed bed reactor. The catalyst (1 g) was loaded into the middle of the stainless reactor ($L = 750 \text{ mm}$, $D = 10 \text{ mm}$), and it was activated at 673 K under nitrogen flow to eliminate any adsorbed water. The reactor was then brought to the reaction temperature of 463 K where the alkylation was operated continuously at 3.0 MPa, benzene to ethylene molar ratio of 3.0 and weight hourly space velocity (WHSV) of 1.0 or 2.0 h^{-1} for ethylene. The reaction products were collected and analyzed with an Agilent 6820 gas chromatograph equipped with a flame ionization (FID) detector and a HP-FFAP ($50 \text{ m} \times 0.32 \text{ mm} \times 0.25 \mu\text{m}$) capillary column. In poisoning experiments, 2,4-dimethylquinoline (DMQ), employed as a poisonous substance, was co-fed into the reactor continuously at a rate of $50 \mu\text{L h}^{-1}$ by mixing in benzene.

3. Results and discussion

3.1. Postsynthesis of MCM-56 analogues with various Si/Al ratios

The MCM-22(P) precursors were synthesized at various Si/Al ratios (15, 20, 30 and 45) using HMI as SDA. The XRD patterns of these precursors before and after acid treatment with 0.1 M HNO_3 are given in Fig. 1. The precursors all showed the 001 and 002 diffraction peaks in the 2θ region of 3–7°, characteristic of a layered structure with the MWW sheets stacking along the c -direction (Fig. 1A). In addition, the MCM-22(P) samples also showed three well resolved diffractions due to 100, 101 and 102 planes. The diffractions related to the crystalline MWW sheets parallel to the ab -planes such as 310 plane were also clearly observed in higher angle region. The XRD patterns matched well with that of the MWW lamellar precursor reported in the literature [18,28]. Thus, the materials with a pure MWW phase were obtained at different Si/Al ratios. Fig. 1B shows the XRD patterns of directly calcined MCM-22 precursors. They were obviously different from those of corresponding precursors. Upon calcination, the 001 and 002 diffractions shifted to higher angles with reduced intensities,

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