The role of external acidity of meso-/microporous zeolites in determining selectivity for acid-catalyzed reactions of benzyl alcohol

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ABSTRACT

A comparison of selectivity in catalytic conversion of benzyl alcohol in mesitylene on hybrid lamellar-bulk MFI (HLBM) zeolite materials containing dual meso-/microporosity showed that the external Brønsted acidity in meso-/microporous MFI zeolites effectively impacts on selectivity of the parallel alkylation and etherification reactions. HLBM zeolites, consisting of crystalline bulk microporous core and lamellar mesoporous shell, not only catalyzed the parallel reactions on the external environments (external surface and mesopore) but also catalyzed the etherification reaction in the internal environment (micropore) as illustrated by the completely suppressed alkylation and retained residual etherification reactions after 2,6-di-tert-butylpyridine (DTBP) poisoning. A systematic study of HLBM zeolites with tunable meso-/microporous domain sizes achieved by a dual template assisted synthesis revealed that parallel alkylation and etherification reactions are tailored by the tunable external surface area and external acidity of the HLBM zeolites. The external alkylation and etherification reaction rates as a function of cumulative DTBP addition suggested the presence of Brønsted acid sites with different strengths on external environments of the HLBM zeolites, which influenced the external etherification reaction, but not as significantly as the alkylation reaction. The evidence shown here for the involvement of external acidity in catalyzing parallel reactions and for the role of external acidity with variable strengths in HLBM zeolite materials extends the scope of observed catalytic behaviors of meso-/microporous zeolite materials beyond those reflecting transport effects and accessibility of acid sites.

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1. Introduction

The meso-/microporous zeolites couple the catalytic features of microporosity and the improved mass transport consequence of mesoporosity in a single material, possessing the capacity of overcoming the mass-transfer constraints and the resultant low catalyst utilization, a major drawback in most reactions catalyzed by the conventional microporous zeolites [1–6]. A variety of zeolites containing structured porosity on micro- and mesopore levels have been created in the past decade [2,7–12] and the catalytic tests showed that the meso-/microporous zeolites have higher reaction rates and/or different selectivity in comparison with their microporous zeolite analogues which consist exclusively of the micropores. The enhanced catalytic reaction rate and/or altered

selectivity on meso-/microporous zeolites has been attributed to the enhanced accessibility to active sites and transport characteristics of these materials [13–16], while the role of external acidity (active sites on external surface and in pore mouth region) and systematically tailoring selectivity of external acid sites in the meso-/microporous zeolite materials have remained rarely accessible.

Recently, we reported a simple one-step synthesis of the hybrid lamellar-bulk MFI (HLBM) zeolite with tunable meso-/microporous domains by a mixed template system (dual templates) [17,18]. The crystalline bulk zeolite core and lamellar zeolite shell were formed simultaneously in the hydrothermal crystallization step with the assistance of dual templates, tetrapropyl ammonium hydroxide (TPAOH) and diquaternary ammonium surfactant ([$C_{22}H_{45}$-$N^+(CH_3)_2$-C_6H_{12}-$N^+(CH_3)_2$-C_6H_{13}]Br_2, ($C_{22\text{-}6\text{-}6}$)), respectively. By tuning the concentration of $C_{22\text{-}6\text{-}6}$ and the synthesis conditions such as aging temperature and time

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of the zeolite synthetic gel in the syntheses, the domain sizes of the lamellar shell and bulk core and thus the meso- and microporosity of the HLBM zeolite particles are simply modulated [17]. The capability of tuning the lamellar and bulk domain sizes of the HLBM zeolite creates the opportunity of designing materials with spatially controlled morphology that have potential advantages for various applications. For example, the similar type of hybrid zeolitic structure, prepared by epitaxial growth of a layered MFI zeolite on the surface of a pre-synthesized bulk MFI, showed enhanced permeability for CO_2 and good CO_2/CH_4 selectivity for gas separations than bare bulk MFI zeolite when they were processed into HLBM zeolite/polyimide and bulk MFI zeolite/polyimide composite membranes [19]. This performance enhancement is due to the highly roughened surface morphology of HLBM zeolite that results in excellent adhesion to a dense glassy polymer. The chemical compositions, particularly acid sites associated with framework Al, could also be spatially modulated. The spatially modulated acid sites would influence the performance of zeolite materials, notably in the area of catalysis.

In this work, we aim to study the physicochemical properties and catalytic behaviors of HLBM zeolites prepared by one-step dual template assisted synthesis method. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), nuclear magnetic resonance (NMR), argon (Ar) adsorption and Fourier transformation infrared (FTIR) spectroscopy of adsorbed pyridine were used to characterize the structural and acidity properties of HLBM zeolite materials. The spatial distribution of acid sites, either on external surface/pore mouth region or in micropores of HLBM zeolite, was identified by organic base titration method. The catalytic behavior of external acid sites in HLBM zeolite catalysts was tested using a parallel reaction, alkylation of mesitylene by benzyl alcohol to 1,3,5-trimethyl-2-benzylbenzene and self-etherification of benzyl alcohol to dibenzyl ether (scheme shown in S2 of the Supplementary Information), respectively. It is shown that fractions of external Brønsted acid sites are modulated when the domain sizes of the lamellar shell and bulk core are varied in HLBM zeolite. The spatially controlled acid site distribution effectively impacts on selectivity of the HLBM zeolite in catalyzing parallel chemical reactions. The study on parallel alkylation and etherification reactions over HLBM zeolite also indicated the potential of HLBM zeolite catalysts in catalyzing bulky molecules involved Friedel–Crafts alkylation/acylation and etherification/esterification reactions.

2. Experimental

2.1. Synthesis of HLBM zeolite catalysts

The composition of $100SiO_2/xC_{22-6-6}/36TPAOH/0.5Na_2O/yAl_2O_3/4000H_2O$, where the template molar ratios (C_{22-6-6}/TPAOH, $x/36$) were 0/36, 1/36, 3/36, and 5/36, respectively, and y varied from 0.1 to 0.7 for HLBM-3/36 zeolite sample, was used for HLBM zeolite synthesis. The as-obtained zeolite samples were named after the C_{22-6-6}/TPAOH ratio, which are HLBM-0/36, HLBM-1/36, HLBM-3/36, and HLBM-5/36, respectively. HLBM-0/36 is simply a conventional microporous MFI zeolite. For consistency in nomenclature, HLBM-0/36 is designated for conventional MFI zeolite in this paper.

The method for synthesis of HLBM zeolite catalysts was similar to our previous work [17]. The HLBM zeolite was prepared by dissolving 0.0111 g sodium hydroxide (NaOH, ⩾97% purity) in 11.5 g deionized water (DI) followed by addition of 5.075 g tetrapropylammonium hydroxide (TPAOH, 40% (w/w)) to the solution. Then, 0.0567 g of aluminum isopropoxide was dissolved in the solution using sonication at room temperature for 0.5 h. Afterward, 5.78 g

tetraethyl orthosilicate (TEOS, 98% purity) was added, and the resultant mixture was stirred vigorously at room temperature for 8 h. The C_{22-6-6} solution that was prepared by dissolving the desired amount in 8.5 g of DI water at 333 K was added to above mixture. The resultant zeolite synthesis gel was continuously stirred at room temperature for 2 h before transferring it into a Teflon-lined stainless-steel autoclave. Finally, crystallization of zeolite was conducted for 5 days in the autoclaves tumbling vertically in an oven heated at 423 K. After crystallization, the zeolite sample was filtered, washed with DI water, and dried at 343 K overnight.

The as-synthesized HLBM zeolite was then calcined at 873 K for 6 h in flowing air (1.67 mL s^{-1}, ultrapure air, Airgas), ion-exchanged three times using 1 M aqueous ammonium nitrate (NH_4NO_3) (weight ratio of zeolite to NH_4NO_3 solution = 1:10) at 353 K for 2 h, and subsequently, collected by centrifugation, washed with DI water three times, and dried at 343 K overnight. All zeolite samples in their NH_4^+ form were treated in air (1.67 mL s^{-1}, ultrapure air, Airgas) by increasing the temperature from ambient to 823 K at 0.167 K s^{-1} rate and holding them at this temperature for 4 h. All catalytic reactions were carried out after converting zeolites into the proton-form.

2.2. Characterization of HLBM zeolite catalysts

SEM images of the HLBM samples were recorded on a Hitachi SU-70 electron microscope. TEM images were collected by a JEM 2100 LaB6 electron microscope. Powder XRD patterns were recorded using a Bruker D8 Advance Lynx Powder Diffractometer (LynxEye PSD detector, sealed tube, Cu K$_\alpha$ radiation with Ni β-filter) in the 2θ range from 1.25° to 40°. The Ar sorption isotherms were measured using an Autosorb-iQ analyzer (Quantachrome Instruments) at 87 K. Si and Al contents of each sample were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 4300 DV instruments, Perkin–Elmer). The magic angle spinning NMR (MAS NMR) spectra were recorded at a field of 9.4 T (Bruker DSX 300) and 11.7 T (Bruker Avance 500) for ^{29}Si and ^{27}Al, respectively. ^{29}Si MAS NMR spectra were recorded at 59.63 MHz using 4 mm rotors at a spinning speed of 10 kHz, a dwell time of 19.95 μs, a $\pi/2$ pulse of 5.0 μs and a recycle delay of 60 s. The spectra were referenced with respect to 3-(trimethylsilyl)-1-propanesulfonic acid salt (0 ppm). ^{27}Al MAS NMR spectra were recorded at 130.34 MHz using 4 mm rotors at 14 kHz spinning speed, a dwell time of 0.5 μs, a selective $\pi/18$ pulse of 0.3 μs and a recycle delay of 0.1 s. An aqueous solution of aluminum sulfate (0.1 M) was used as the reference (0 ppm). The type and concentration of acid sites in the HLBM catalysts were determined by FTIR spectra of adsorbed pyridine using Nicolet 6700 spectrophotometer (Thermo-Scientific) equipped with high temperature reaction chamber in conjugation with Praying Mantis™ diffuse reflection accessory (Harrick). Prior to the measurement, the zeolite sample was pretreated at 823 K (rate of 4.55 K s^{-1}) under Ar flow of 0.83 mL s^{-1} for 1 h. The catalyst sample was then cooled down to 393 K and exposed to pyridine by flowing Ar through pyridine saturator for 0.25 h. After adsorption of pyridine, the sample was heated to 523 K (rate of 4.55 K s^{-1}) under Ar flow for 1 h in order to desorb the physisorbed pyridine and cooled to the temperature of 393 K, and then FTIR spectra were collected with 32 scans and at an effective resolution of 2 cm^{-1}.

2.3. Determination of external surface, pore mouth and internal Brønsted acid sites

The Si/Al ratio in each HLBM zeolite sample was analyzed by elemental analysis (ICP-OES). The total number of Brønsted acid