Fabrication of core-shell MFI@TON material and its enhanced catalytic performance for toluene alkylation

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1. Chemicals and reagents

Silica sol (SiO₂ = 40 wt.%, Qingdao Haiyang Chemical Co. Ltd) and sodium silicate (Na₂SiO₃, SiO₂ = 46 wt.%, Zibo Tongjie Chemical Co. Ltd), aluminum sulfate (Al₂(SO₄)₄•18H₂O, 99% Sinopharm Chemical Reagent Co. Ltd), sodium hydroxide (NaOH, 96%, Sinopharm Chemical Reagent Co. Ltd) and potassium hydroxide (KOH, 85%, Xilong Chemical Co. Ltd) were used as the sources of Si, Al and inorganic base, respectively. n-Butylamine (BTA, 99%) and 1,6-diaminohexane (DAH, 99%) were purchased from Sinopharm Chemical Reagent Co. Ltd and used as the organic structure directing agents for ZSM-5 and ZSM-22 zeolites, respectively. Ammonium chloride (NH₄Cl, 99% Tianjin Guangfu Chemical Co. Ltd) was used as the agent in the exchange step. All reagents were used as purchased without further purification.

2. Characterization

The phase compositions and purities of various zeolites were studied by XRD using a Bruker D8 Advance diffractometer with Cu K α (γ =1.5418 Å, 40 kV, 40 mA) radiation. The scan region was set from 5 to 50° with a step size of 0.02°.

After coating with a thin layer of platinum, the morphology and growth process of different samples was determined by field emission scanning electron microscopy (FE-SEM) recorded using FEI QUANTA 400.

High-resolution transmission electron microscopy (HR-TEM) coupled with energy dispersive of X-rays (EDX) were carried out with a 300 kV FEI Tecnai G2 F30 apparatus using a CCD camera. The as-prepared and grated zeolites were dispersed by ultrasonic in ethanol and placed on a micro-grid carbon polymer supported on a copper grid; the crystals remained stable under the electron beam irradiation for at least several minutes.

The Si/Al molar ratios of different samples were determined by X-ray fluorescence spectrometry (XRF).

X-ray photoelectron spectroscopy was measured on a Quantum-2000 K-Alpha ESCA instrument using monochromatic Al K α radiation (*hv*=1486.6 eV) as the X-ray source. The binding energies were referenced to the C 1s peak at 284.8 eV and fitted by the XPSPEAK41 program with Shirley background subtraction and Gaussian/Lorentzian (70/30) as fitting function. Molar fractions were calculated using the normalized peak areas based on the acquisition parameters and sensitivity factors (Si_{sf} = 0.82, Al_{sf} = 0.54) provided by manufacturer.

 N_2 adsorption-desorption was carried on a Micromeritic ASAP 2020 and 2420 analyser to determine the microporous and mesoporous properties, respectively. The surface area and pore volume were determined according to the BET method and τ -plot method, and the most probable pore sizes in the ranges of 0-2 nm and 2-50 nm were calculated by the Horvath-Kawazoe (HK) method and Barrett-Joyner-Halenda (BJH) method, respectively. Prior to measurement, all zeolites were evacuated under vacuum of 5×10⁻³ Torr at 350 °C for 8 h.

Solid-state ²⁹Si and ²⁷Al magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were performed on a Bruker Advance 600 NMR spectrometer. A single 90° pulse of 5.5 μ s duration was applied for ²⁹Si MAS NMR with spin rate at 5 kHz during acquisition and a recycle delay of 45 s. Kaolin was used as the chemical shift reference at -91.5 ppm. A single 16° pulse of 1 μ s duration was applied for ²⁷Al MAS NMR with a recycle delay of 1s. The chemical shifts were referenced to Al(NO₃)₃ solution at 0 ppm.

UV Raman spectra were recorded using a LabRAM HR spectrometer (France, HOROBA Jobin Yvon) using a triple-stage spectrograph with spectral resolution of 2 cm⁻¹. The laser line at 325 nm of a He-Cd laser was used as exciting source with an output of 32 mW. The power of the laser at samples was about 0.8 mW.

Temperature-programmed desorption of ammonia (NH₃-TPD) experiments were carried out using a U-shape quartz tube reactor on a chemisorption apparatus (AutoChem II 2920). The samples were firstly pre-treated in helium flow at 550 °C for 1 h. After cooling down to 100 °C, the NH₃ was injected. Then, the physically adsorbed ammonia was removed in helium flow (50 mL/min), and finally the adsorbed samples

were heated to 600 °C with a rate of 10 °C/min under helium. The signals of desorbed NH₃ were monitored with a thermal conductibility detector (TCD) and a quadrupole mass spectrometer (MS, Pfeiffer Omnistar), simultaneously.

Pyridine-adsorbed infrared (Py-FTIR) spectra were used to discriminate acid type by EQUINOX 70 (Bruker, Germany). Samples (about 15 mg) were pressed into selfsupported wafers and degassed at 400 °C for 1 h in dynamic vacuum (< 10⁻⁴ Pa). Then, the samples were cooled down to 30 °C and saturated with pyridine vapor for 0.5 h. After equilibration, the samples were evacuated at 200 °C and 350 °C to remove the exceed probe molecules, respectively, and the IR spectra were recorded in the range of 1400-1580 cm⁻¹. The density of Lewis (L) and Brönsted (B) acid sites were evaluated from the integrated area of bands at 1454 cm⁻¹ and at 1545 cm⁻¹ using absorption coefficients calculated by Guisnet et al ^[1]. (ϵ_B = 1.13 and ϵ_L = 1.28 cm/µmol).

3 Results and discussion

NH₃-TPD spectra of different materials are depicted in **Fig. S8**. The desorbed amounts of NH3 from the zeolites are fitted by Gaussian deconvolution ^[2] with the density and distribution of acid sites in **Table 2**. Generally, each profile of ZSM-5 and ZSM-22 zeolites exhibit two main types of NH3 desorption in the spectrum. In **Fig. S8**, two peaks assigned to the desorbed ammonia appear, and these are denoted as L- and H-peak, corresponding to the low and high temperature peak, respectively ^[3]. From the desorption peak, the profile of the acid site can be measured ^[4]. The temperature range for strong acid sites of TON, TON-MFI, and TON@MFI samples is set at 400-410 °C, and that for the weak acid sites at 200-210 °C, respectively. However, for MFI sample, the peaks at around 225 °C and 300 °C can be ascribed to the ascrption peak of ammonia on the strong acid sites.

Py-FTIR experiments are used to assist the identification of the different types of acid sites for various samples. In Fig. **S9**, the spectral bands at 1550 cm⁻¹ and 1445 cm⁻¹ are used to quantify Brönsted (B) acid sites and Lewis acid sites, respectively. The adsorption amount of pyridine molecule equilibrated at 200 °C is ascribed to the total acidity, whereas the adsorption amount of pyridine, degassed at relatively high

temperature of 350 °C, corresponded with the amount of strong acidity. The difference of two adsorption amounts between 200 °C and 350 °C is attributed to the weak acidity. The Lambert-Beer Law is used for calculations ^[5].

Crystallization time (h).	Surface areas (m^2/g)			
	Microporous	External	Total	
MFI	229.3	109.5	338.9	
18 h	82.7	71.0	153.7	
22 h	140.2	72.9	213.2	
24 h	172.6	61.3	233.9	
36 h	198.8	44.1	242.9	

 Table S1 Textual properties of various TON@MFI composites prepared at different time.

Crystallization time	Microporous Areas	Microporous Volume	Coverage
(h)	(m ² /g)	(cm ³ /g)	(%) ^a
Core MFI	229.3	0.15	
18 h	150.6	0.10	34.3
24 h	30.9	0.03	86.5
36 h	5.4	0	97.6

Table S2 Textual properties and Coverage of the parent MFI and un-calcined TON@MFI composites prepared at different times.

 $_{a} Coverage (\%) = \frac{(S_{BET} of calcined MFI - S_{BET} of uncalcined MFI@TON)}{S_{BET} of calcined MFI}$

Catalysts	Toluene	Para-xylene	Reaction	Ref.
	Conversion (%)	Selectivity (%)	conditions	
Silicalite/H-ZSM-5	49.9	46.1	400 °C, W/F = 0.20 kg·cat.	[\$6]
ZSM-5	53.7	23.9	hmol ⁻¹	[30]
Silicalite-1	19.3	76.0	$460 ^{\circ}\text{C}$ 5 h ⁻¹ T/M – 2·1	[S7]
ZSM-5	28.6	24.0	400° C, 5° II , $1/M = 2.1$	
ZSM-22	12.2	56.0	$410 ^{\circ}\text{C} 4 \text{h}^{-1} \text{T/M} = 4.1$	[82]
ZSM-23	15.5	45.0	$+10^{\circ}$ C, $+11^{\circ}$, $1/10^{\circ}$ -4.1°	[00]
MCM-22	20.1	56.2	300 °C, 2.56 mol g ⁻¹ h ⁻¹ , T/M	[\$9]
			= 4:1	[07]
ZSM-11	20.0	58.0	300° C, 4.8 h^{-1} , $T/M = 4:1$	[S10]
SAPO-11	11.7	61.4	350 °C 3 h^{-1} time on	[S11]
SAPO-31	17.0	51.7	stream=3 h	[S11]
SAPO-5	21.0	28.8	Sucan 5 n	[S11]

 Table S3 Summary of the catalytic performance of zeolites for toluene methylation in the literature and present work.



Fig. S1 XRD patterns of the MFI@TON composites prepared at different conditions (Synthesis conditions: MFI@TON-a: Si/Al ratios of TON and MFI zeolites in the pre-adsorbed seed are 71.5 and 34, respectively; Si/Al ratio of initial gel is 65; MFI@TON-a: Si/Al ratios of TON and MFI zeolites in the pre-adsorbed seed are 71.5 and 121.5, respectively; Si/Al ratio of initial gel is 110.)



Fig. S2 Crystallization curves of core-shell TON@MFI composites prepared at different temperatures.



Fig. S3 Magnified SEM images for the shell of TON@MFI composites with similar crystallinity synthesized at 140 °C (a) and 180 °C (b).





Fig. S4 Close and general views of the TON@MFI composite prepared at 24 h (a), 32 h (b), and 36 h (c).



Fig. S5 TEM images for the TON shell of the TON@MFI composite.



Fig. S6 XRD patterns of the physically mixed TON and MFI zeolites in various ratios.



Fig. S7 N₂ adsorption-desorption isotherms of TON@MFI composite before and after calcination.



Fig. S8 Micropore (a) and mesopore (b) size distribution of different (protonic form) samples.



Fig. S9 N_2 adsorption isotherms of core-shell composites crystallized at different times.



Fig. S10 NH₃-TPD spectra of TON, MFI, TON/MFI and TON@MFI composite.



Fig. S11 Py-IR spectra of TON, MFI, TON/MFI and TON@MFI composite determined at 200 °C

(a) and 350 °C (b).



Fig. S12 Comparison of the catalytic performance of the zeolite catalyst in this work and reported in the literatures.

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