Electronic Supplementary Material

Fabrication of surface passivated two-dimensional MFI zeolite for alkylation between toluene with methanol

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Experimental

Materials

$C_{6\text{-}6\text{-}12\text{-}O}Br_4$[$C_6H_{13}$-$N^+(CH_3)_2$-$C_6H_{12}$-$N^+(CH_3)_2$-$(CH_2)_{12}$-O-(p-$C_6H_4$)$_2$-O-$(CH_2)_{12}$-$N^+(CH_3)_2$-$C_6H_{12}$-$N^+(CH_3)_2$-$C_6H_{13}$]·4[$Br^-$] was synthesized following previous literatures [1,[2]. Sodium Silicate (34% wt) was obtained from Shandong Yousuo Chemical Technology Co.LTD. Tetraethyl orthosilicate (TEOS, 98%, Damao Chemical Reagent Factory), tetrapropylammonium hydroxide (TPAOH, 40%, Energy Chemical), sodium aluminate (AR, Aladdin), aluminum sulfate octadecahydrate (AR, Aladdin), ammonium chloride (AR, Macklin), methanol (99.5%, Macklin), sulfuric acid (98% wt, Guangzhou Chemical reagent Factory), toluene (AR, Guangzhou Chemical reagent Factory) were used without further purification, and the water was deionized (DI) water.

Synthesis of pillared 2D MFI zeolites

The ZSM-5 zeolite nanosheets were synthesized by using TEOS as silicon source and sodium aluminate as aluminum source, the $C_{6\text{-}6\text{-}12\text{-}O}Br_4$ as organic template. In a typical synthesis, a gel composition of 2 $C_{6\text{-}6\text{-}12\text{-}O}$: 100 SiO_2 : 1 Al_2O_3 : 30.30 Na_2O : 6000 H_2O was used [3]. Firstly, the organic template was dissolved in deionized water and vigorously stirred for 60 min, and then sodium silicate was added under stirring

conditions and vigorously stirred for 60 min to obtain the mixed solution. The aluminum sulfate octadecahydrate was dissolved in an appropriate amount of deionized water, the aluminum sulfate solution was slowly added into the above mixture under stirring conditions, and then dilute sulfuric was immediately added and stirred vigorously. Finally, the mixture was further stirred at 333 K for 6 h to obtain a gel mixture. The final gel mixture was transferred into a Teflon-lined stainless-steel autoclave for heat treatment at 423 K and 15 rpm for 5 days. The product was filtered, washed and dried at 393 K for 10 h to obtain raw 2D MFI zeolite.

The vapor phase pillarization strategy was employed to fabricate the pillared 2D MFI zeolite [4]. In a typical experiment, 0.1 g raw 2D MFI zeolite was added into a small PTFE bottle (10 ml), then it was transferred into a 100 mL PTFE liner, and 0.05 g TEOS was added into the 100 mL PTFE liner, and then this system was transferred to a stainless-steel autoclave, which was maintained at 423 K for 24 h. After that, the autoclave was cooled to room temperature, then 1.0 g water was added into the 100 mL PTFE liner again, and this system was treated at 353 K for 24 h to obtain the pillared 2D MFI zeolite. Afterwards, the raw pillared 2D MFI zeolite was calcinated at 723 K under N_2 flow for 6 h and finally at 823 K under air flow for 12 h in a furnace to produce P-MFI zeolite.

Synthesis of surface passivated 2D pillared MFI zeolites

The surface passivated 2D pillared MFI zeolite was fabrication following two steps [5]. In the first step, 0.8854 g of TEOS and 1.7794 g of TPAOH were added into 41.68 g of deionized water to form a growth solution with a molar ratio of 17 TEOS : 14 TPAOH : 9500 H_2O, and stirred at room temperature overnight. Subsequently, the above raw pillared 2D MFI zeolite (1 wt% of the mixture) was added into the above growth solution and stirred evenly. Finally, the obtained mixture was transferred into a Teflon-lined stainless-steel autoclave and crystallized for 24 h at 373 K with 20 rmp. The product was filtered, washed and dried at 393 K for 10 h, which was named as P-MFI-S.

In the second step, The TEOS and TPAOH were firstly added into a certain amount

of deionized water to form a growth solution with a molar ratio of *x* TEOS : 14 TPAOH : 9500 H_2O (*x* = 23, 26 and 30) and this mixture was stirred overnight at room temperature. Secondly, the P-MFI-S (1 wt% of the mixture) was added into the above mixture and stirred evenly. Finally, the obtained mixture was transferred into a Teflon-lined stainless-steel autoclave and crystallized at 443 K with 20 rmp for 7 days. Then the obtained product was filtered, washed, and dried at 393 K for 10 h, which were calcined at 823 K for 5 h to remove the organic templates. These samples were donated as P-MFI-*x* according to the value of *x*. Before reaction and acid test, all MFI zeolites were exchanged to H^+ form in 1 mol/L NH_4Cl solution.

Characterization

The Bruker D8 ADVANCE diffractometer system was used to examine X-ray powder diffraction (XRD) patterns of samples by using Cu-Ka (wavelength of k = 0.015418 nm) radiation. Micromeritics ASAP2020 physical adsorption instrument was used to determine the pore parameters of the catalysts. Nitrogen adsorption-desorption isotherms were performed at 77 K, and all samples were degassed at 473 K for 6 h before the test. FEI Talos F200X field emission transmission electron microscope was used to observe the skeleton structure of zeolite samples. The Si/Al ratio of the sample was analyzed by OPTIMA 7000DV inductively coupled plasma emission spectrometer. The zeolite samples were analyzed by STA449F5 thermogravimetric analyzer of Netsch GMBH. The pyridine and 2, 6-di-tert-butylpyridine were employed as probe molecules to determine the total Brønsted acid sites and the external surface Brønsted acid sites of samples through the Fourier transform infrared spectroscopy using Bruker VERTEX 70 spectrometer. A multi-station gravimetric steam adsorption apparatus (BSD-VVS) was used to obtain the adsorption kinetic curves. Before test, all sample were degassed in a vacuum at 373 K for 3 h, and then the adsorption experiment of toluene was carried out at 303 K and $P/P_0 = 0.3$ condition.

Catalytic tests

The alkylation between toluene with methanol was carried out in a continuous flow fixed bed reactor. Before the reaction, 0.2 g of 20-40 mesh ZSM-5 zeolite particles

were mixed with quartz sand, which was loaded into a fixed-bed reactor with an inner diameter of 10 mm, the mixture was-treated for 2 h under 723 K and 40 ml/min nitrogen flow to active the catalysts, and then the catalytic test was carried out at 673 K and 0.1 MPa. During the alkylation, the molar ratio of toluene to methanol was 1 : 1 and the WHSV was 39 h^{-1}. The reaction mixture was collected periodically and quantitatively analyzed using a gas chromatograph (GC 7920) equipped with an organosiloxane capillary column (HP-INNOWAX, 60 m, 0.320 mm, 0.50 μm). The conversion of toluene and selectivity of *para*-xylene were calculated based on the following equation: [6]

$$Conversion\ of\ Toluene: C_T = \left(1 - \frac{n_T}{n_A}\right) \times 100\% \quad \text{(Eq.S1)}$$

$$Selective\ of\ para - xylene: S_{PX} = \frac{n_{PX}}{n_X} \times 100\% \quad \text{(Eq.S2)}$$

n_A and n_T were the molar amount of toluene in the mixture before and after the reaction, n_X was the molar amount of xylene in the product, and n_{PX} was the molar amount of *para*-xylene in the product.

Calculation of Diffusion coefficients

The diffusion coefficients of toluene on investigated MFI zeolites are evaluated by adsorption kinetic curves. According to Fick's law, the diffusion equation is defined as below [7]:

$$D\left(\frac{\partial^2 C}{\partial r^2} + \frac{2\partial C}{r\partial r}\right) = \frac{\partial C}{\partial t} \quad \text{(Eq.S3)}$$

where D is diffusion coefficients, C is diffusion concentration, r is radial coordinates, t is the diffusion time.

When zeolite particles are considered as plate-like particles, the mathematical solution of the transient diffusion equation can be defined as follows [8]:

$$\frac{Q_t - Q_0}{Q_e - Q_0} = 1 - \sum_{n=0}^{\infty} \frac{8}{[(2n+1)\pi]^2} \exp\left(-\frac{D_{eff}(2n+1)^2\pi^2 t}{r^2}\right) \quad \text{(Eq.S4)}$$

When the time is short, the transient fraction can be described by the following equation [9]:

$$\frac{Q_t - Q_0}{Q_e - Q_0} \cong \frac{8}{\sqrt{\pi}} \sqrt{\frac{D_{eff}}{r^2}} \sqrt{t} \quad \text{(Eq.S5)}$$

Where D_{eff} is the effective diffusion coefficient (m2·s-1), r is the thickness of ZSM-5 nanosheets (m), Q_0 is the initial weight of the adsorbent (g), Q_e and Q_t (g) are

the amount of adsorbent at equilibrium and time t (s), respectively. When $\frac{Q_t-Q_0}{Q_e-Q_0}$ is plotted versus $\sqrt{t}$, a straight line with a slope ($\frac{8}{\sqrt{\pi}}\sqrt{\frac{D_{eff}}{r^2}}\sqrt{t}$) can be obtained. As a result, the diffusion time constant $\frac{D_{eff}}{r^2}$ (s^{-1}) can be found from the slope of the line.

When zeolite particles are assumed as the spherical particles, the mathematical solution of the transient diffusion equation (Eq.S3) can be defined as follows:

$$\frac{Q_t-Q_0}{Q_e-Q_0} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-n^2\frac{\pi^2 D_{eff}t}{r^2}\right) \quad \text{(Eq.S6)}$$

When the time is short, the transient fraction can be described by the following equation:

$$\frac{Q_t-Q_0}{Q_e-Q_0} \cong 6\sqrt{\frac{D_{eff}}{\pi r^2}}\sqrt{t} \quad \text{(Eq.S7)}$$

Where D_{eff} is the effective diffusion coefficient ($m^2 \cdot s^{-1}$), r is the particle radius (m), Q_0 is the initial weight of the adsorbent (g), Q_e and Q_t (g) are the amount of adsorbent at equilibrium and time t (s), respectively. When $\frac{Q_t-Q_0}{Q_e-Q_0}$ is plotted versus $\sqrt{t}$, a straight line with a slope ($6\sqrt{\frac{D_{eff}}{\pi r^2}}\sqrt{t}$) can be obtained. As a result, the diffusion time constant $\frac{D_{eff}}{r^2}$ (s^{-1}) can be found from the slope of the line.

Figures and Tables

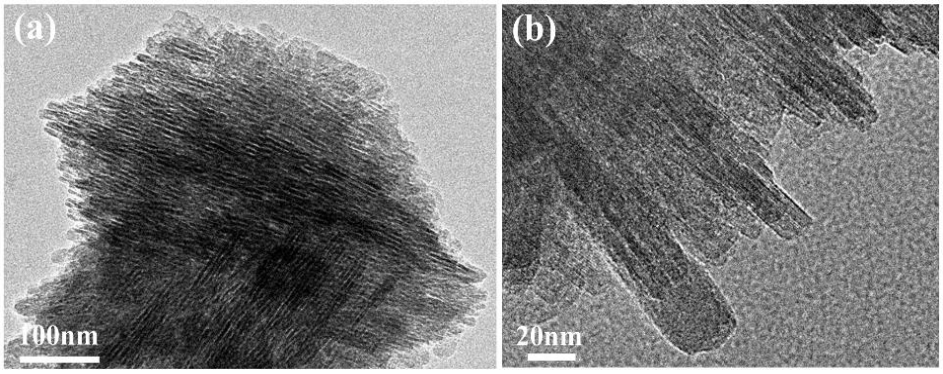

Fig. S1 TEM images of P-MFI (a) and (b) with different magnitudes

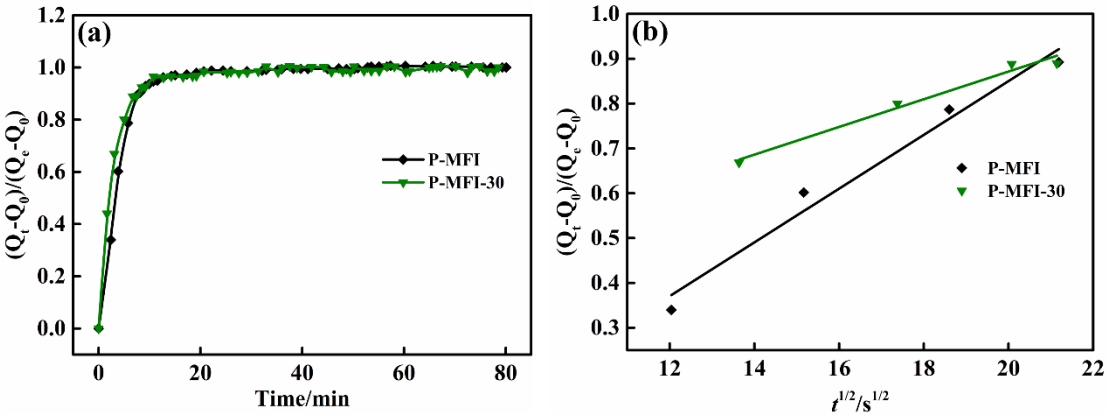

Fig. S2 Toluene transient absorption fraction (a) and toluene fitting adsorption curve (b) of different zeolite samples

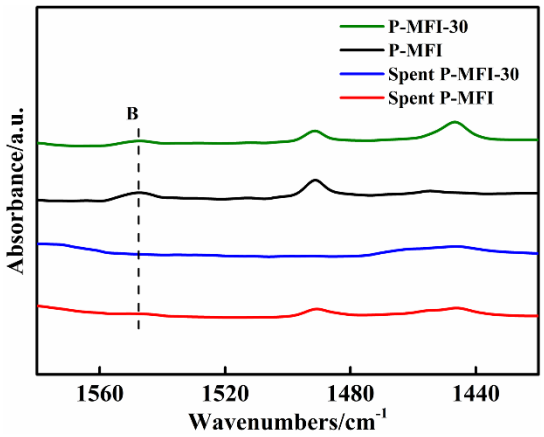

Fig. S3 FT-IR spectra for pyridine adsorbed on fresh and spent zeolites

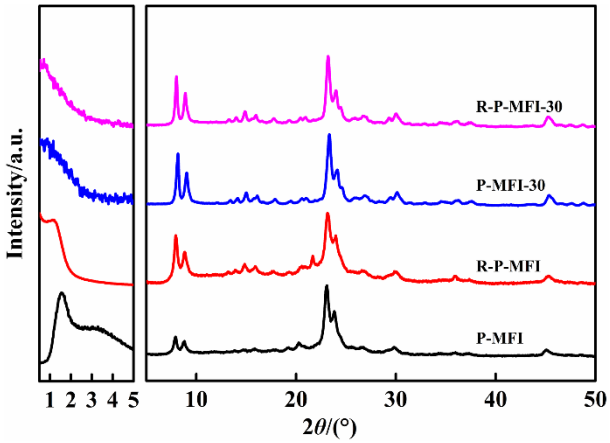

Fig. S4 XRD patterns of fresh and regenerated zeolites

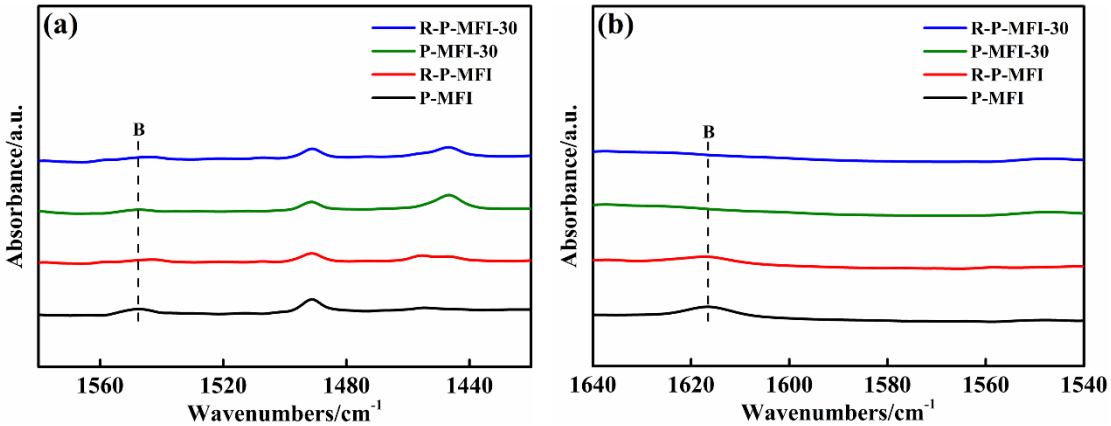

Fig. S5 FT-IR spectra for (a) pyridine and (b) 2,6-di-tert-butylpyridine adsorbed on fresh and regenerated zeolites

Table S1 Diffusion time constant of toluene on zeolites

Catalysts	P-MFI	P-MFI-30
D_{eff}/r^2 /(s^{-1})	1.77×10^{-4}	8.33×10^{-5}

Table S2 Acidity of fresh and regenerated zeolites

Catalysts	Total Brønsted acid sites[a)]/(mmol·g^{-1})	External Brønsted acid sites[b)]/(mmol·g^{-1})	f_B[c)]/(mmol·g^{-1})
P-MFI	0.074	0.059	80 %
R-P-MFI	0.036	0.028	78 %
P-MFI-30	0.035	—	—
R-P-MFI-30	0.020	—	—

a) measured by FT-IR spectra of adsorbed pyridine; b) measured by FT-IR spectra of adsorbed 2,6-di-tert-butyl pyridine; c) the percentage of external Brønsted acid sites over total Brønsted acid.

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