Urea-induced platelike ZSM-5 zeolite with Si zoning for efficient alkylation of toluene with ethanol to *para*-ethyltoluene

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Experimental Procedures

Catalysts Characterization

The X-ray powder diffraction patterns (XRD) were recorded on a Bruker AXS-D8 Advance powder diffractometer having Cu Kα radiation foundation (λ = 1.54 Å, 40 KV and 40 mA). The elemental composition of the samples was determined by a Malvern Panalytical multifunctional X-ray Fluorescence spectrometer (XRF), worked on a rhodium target and a power of 3kW. Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDS) elemental mappings were obtained via Hitachi S-5500 and FEI Scios 2 HiVac at 5 kV. Transmission electron microscope (TEM) was carried out on a Tecnai G2 F20 instrument operated at 20kV. NH_3-temperature programmed desorption (NH_3-TPD) was performed using a Micromeritics AutoChem II 2920 equipped with a TCD detector. N_2 adsorption-desorption isotherms were tested using a Micrometrics ASAP 2020 at -196 °C. The Brunauer-Emmett-Teller (BET) was used to calculate the specific surface area and the t-plot method was used to calculate the micropore volumes. Pyridine-adsorbed infrared (Py-IR) were carried out on a Perkin-Elmer 200 FT-IR spectroscope, the adsorption spectra was obtained at 150 °C. The amount of Brønsted and Lewis acid sites was calculated from the corrected integral areas of IR bands at 1540 cm^{-1} and 1450 cm^{-1}, using the extinction coefficients reported by Guisnet et al. [1]. The NMR experiment was carried on a Bruker AVANCE-III 500 MHz spectrometer (11.7 T) operating at a Larmor frequency of 130.4 MHz for the ^{27}Al nucleus. A 4 mm MAS NMR probe was used to approach the ^{27}Al single-pulse experiments. Thermo gravimetric-differential thermal analysis (TG) was carried out using a METTLER TGA/DSC1/1600T instrument at a temperature ramp from room temperature to 800°C in an air atmosphere. A comparison of the external surface acid sites was performed through a cracking reaction on a fixed-bed reactor operating at 350 °C, with a 1,3,5-triisopropylbenzene (TIPB) flow rate of 4.5 h^{-1} mixed with N_2 (80 ml/min). The reaction products were then analyzed in real-time using an Agilent 5890.

The nature of organic species formed on the catalysts during the alkylation reaction was in situ monitored by the Perkin-Elmer 2000 FT-IR spectrometry. 10 mg of sample was pressed into a self-supporting wafer and placed in the chamber. The sample was activated in flowing N_2 (50 mL/min) at 450 °C for 1 h and cooled to 400 °C for taking a background spectrum. N_2 at flow rate of 50 mL/min was used as the carrier gas to transport the feed gas (toluene/ethanol molar ratio of 1:1) into the reaction chamber (WHSV = 2.0 h^{-1}). At the preset reaction temperature, the reaction time was 60 min.

Catalytic Testing

The alkylation of toluene with ethanol was performed in a fixed-bed reactor (50 cm length, 1.5 cm inner diameter) under atmospheric pressure. In a typical run, 2 g of catalyst (sieved to 40~60 mesh) was charged into the reactor, followed by activation at 450 °C for 1 h with a flow of pure N_2 (50 ml/min). Then, a mixture of toluene and ethanol (T/E = 1:1) was fed into the reactor (WHSV = 2 h^{-1}) at 400 °C with a co-fed N_2 flow of 40 ml/min. Analysis of the liquid products was attained using a gas chromatograph (Agilent Technologies GC5890) equipped with a FFAP capillary column (60 m x 0.32 mm x 0.5 μm) and a flame ionization detector (FID). The gaseous product was analyzed in another gas chromatograph (Agilent Technologies GC5890) with flame ionization detector and HP-5 (30 m × 0.32 mm × 0.25 μm) column. The conversion of toluene (C_T) and the product selectivity *(S_i)* were defined as following:

$$C_T\ (\%) = \frac{\text{toluene}_{in} - \text{toluene}_{out}}{\text{toluene}_{in}} \times 100\ \%$$

$$S_i\ (\%) = \frac{n_i}{n_{total}} \times 100\ \%$$

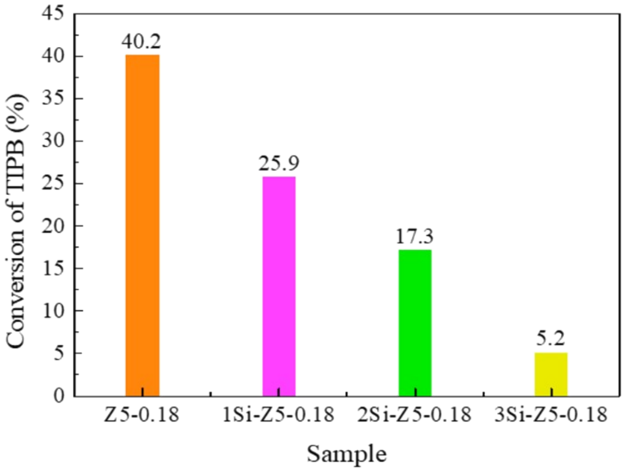

Figure S1. TIPB cracking reaction over the prepared *y*Si-Z5-0.18 catalysts.

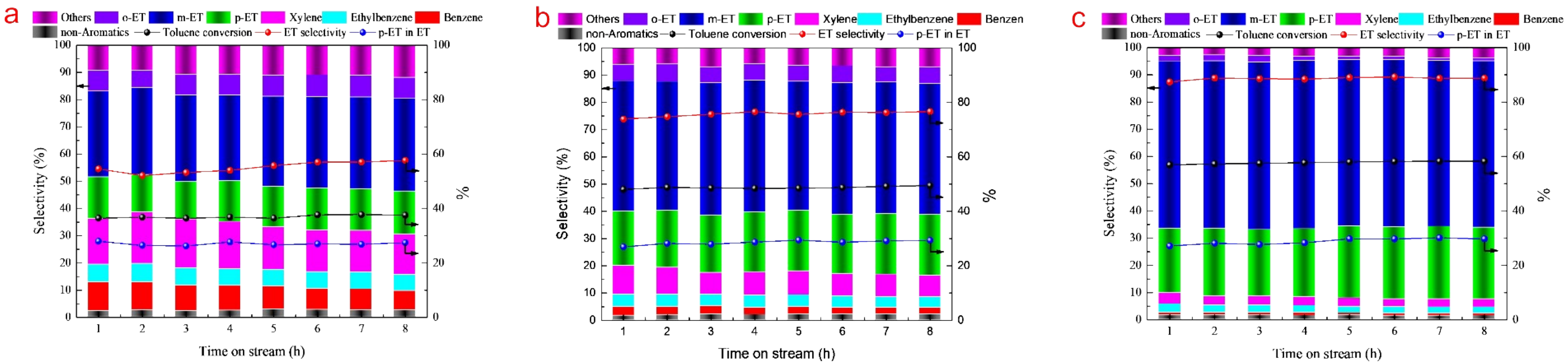

Figure S2. Detailed catalytic performance (including toluene conversion, ethyltoluene selectivity, *para*-ethyltoluene selectivity and products distribution) of ZSM-5 catalysts with different length of *b*-axis. Reaction conditions: 400 ^{o}C, toluene/ethanol ratio = 1.0, WHSV = 2.0 h^{-1}.

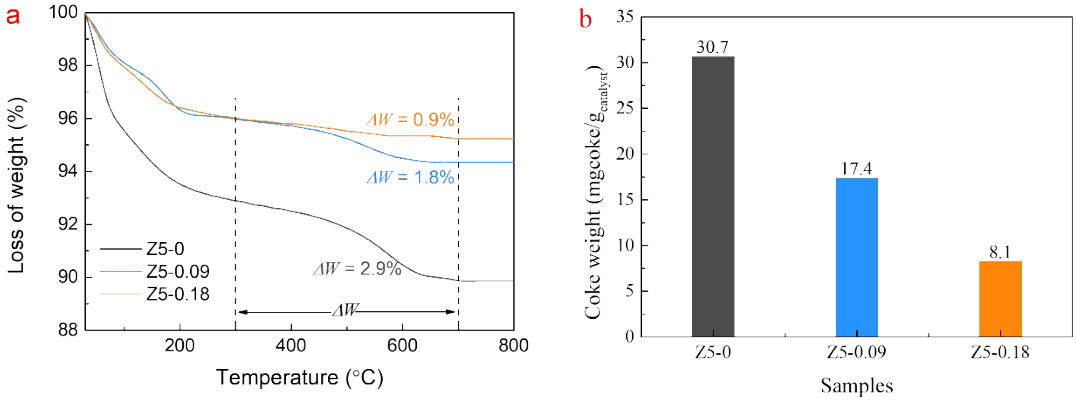

Figure S3. Characterization of coke amount by TG techniques over spent catalysts.

Table S1. The yield of Z5-0.18 samples after each CLD cycle

CLD cycles	Yield of the zeolite product (%)
After 1 cycle	92.5
After 2 cycles	84.2
After 3 cycles	78.5

Table S2. Textural properties of the prepared *y*Si-Z5-0.18 catalysts.

Sample	Specific surface area (m^2/g) [a]			Pore volume (cm^3/g) [b]		
	S_{BET}	S_{micro}	S_{ext}	V_{total}	V_{micro}	V_{meso}
1Si-Z5-0.18	373	341	32	0.205	0.161	0.059
2Si-Z5-0.18	326	312	14	0.168	0.157	0.026
3Si-Z5-0.18	225	221	4	0.144	0.131	0.008

[a] Calculated by the BET method and *t*-plot method.

[b] Calculated by the *t*-plot method.

Table S3. The concentration of BASs and LASs on the prepared *y*Si-Z5-0.18 catalysts.

Sample	Acidity by Py-IR (mmol/g)			
	Total (100 °C)		Strong (300 °C)	
	BASs	LASs	BASs	LASs
1Si-Z5-0.18	0.15	0.04	0.09	0.01
2Si-Z5-0.18	0.12	0.02	0.07	0.01
3Si-Z5-0.18	0.08	0.01	0.02	0.01

Table S4. The gaseous product distribution during the alkylation of toluene with ethanol

Catalysts	Gaseous product distribution from methanol (mol %) [a]					
	CH_4	C_2H_6	C_2H_4	C_3H_6	C4-C5	Others
Z5-0	2.7	0.7	80.8	8.6	4.7	2.5
Z5-0.09	1.3	0.4	82.1	9.4	3.5	3.3
Z5-0.18	0.9	0.3	84.7	7.6	4.1	2.4

Reaction conditions: 400 ^{o}C, toluene/ethanol ratio = 1.0, WHSV = 2.0 h^{-1}.

[a] Determined at 8 h time-on-stream.

Table S5. The alkylation performance of toluene with ethanol over different catalysts in literature

Sample	Condition			Catalytic performance			Ref.
	Temperature (°C)	T/E	WHSV (h^{-1})	Toluene conversion (%)	ET selectivity (%)	*p*-ET selectivity (%)	
3Si-Z5-0.18	400	1	2.0	17.9	88.7	96.2	This paper
H-ultraist	400	2	1.0	39.3	77.8	40.1	(2)
MFI-2000	400	1	2.0	14.2	95.0	100.0	(3)
Mg-ZSM-5	400	2	2.0	12.3	80.0	89.7	(4)
Ga-ZSM-5	375	6	7.0	12.0	92.0	70.0	(5)
ZSM-5	375	1	2.0	44.2	86.6	56.6	(6)
Al-MFI	350	6	6.8	15.1	97.0	75.2	(7)
H-B/SIL	350	3	4.2	15.8	99.0	73.1	(8)
A5-ZSM-5	325	6	2.5	17.5	14.9	81.3	(9)

References

(1) Emeis, C. A., Determination of Integrated Molar Extinction Coefficients for Infrared Absorption Bands of Pyridine Adsorbed on Solid Acid Catalysts. *J. Catal.* **1993**, *2*, 341-354.

(2) Aliev, I. A.; Akhmedov, E. I.; Mamedov, E. S.; Gakhramanov, T. O., Toluene ethylation with ethanol on cadmium-promoted high-silica zeolite. *Petroleum Chem.* **2010,** *50* (5), 373-375.

(3) Ogunbadejo, B. A.; Osman, M. S.; Arudra, P.; Aitani, A. M.; Al-Khattaf, S. S., Alkylation of toluene with ethanol to para-ethyltoluene over MFI zeolites: Comparative study and kinetic modeling. *Catal. Today* **2015**, *243*, 109-117.

(4) Bhandarkar, V.; Bhatia, S., Selective formation of ethyltoluene by alkylation of toluene with ethanol over modified HZSM-5 zeolites. *Zeolites* **1994,** *14* (6), 439-449.

(5) Parikh, P. A.; Subrahmanyam, N.; Bhat, Y. S.; Halgeri, A. B., Toluene ethylation with ethanol over Ga-MFI zeolite: a kinetic study. *Ind. Eng. Chem. Res.* **1992**, *31*(4), 1012-1016

(6) Walendziewski, J.; Trawczyński, J., Alkylation of Toluene with Ethanol. *Ind. Eng. Chem. Res.* **1996**, *35* (10), 3356-3361.

(7) Parikh, P. A.; Subrahmanyam, N.; Bhat, Y. S.; Halgeri, A. B., Toluene ethylation over metallosilicates of MFI structure: Effects of acidity and crystal size on para-selectivity. *Catal. Lett.* **1992**, *14* (1), 107-113.

(8) Lee, C. S.; Park, T. J.; Lee, W. Y., Alkylation of toluene over double structure ZSM-5 type catalysts covered with a silicalite shell. *Appl. Catal., A* **1993,** *96* (2), 151-

161.

(9) Bhat, Y. S.; Das, J.; Rao, K. V.; Halgeri, A. B., Inactivation of External Surface of ZSM-5: Zeolite Morphology, Crystal Size, and Catalytic Activity. *J.Catal.* **1996**, *159* (2), 368-374.