

Supplementary information for

Highly Selective Synthesis of Large Aromatic Molecules with Nano-zeolite: Beyond the Shape Selectivity Effect

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Experimental

ZSM-12 was synthesized by hydrothermal method. In detail, solution of 0.410 g $\text{Na}_2\text{Al}_2\text{O}_4$ in 10.1 g deionized water were mixed with 13.37 g TEAOH under continuous stirring of 1000 rpm for 10 min. Then 30.0 g colloidal silica and 10.0 g of deionized water were added in as keeping stirring to make the mixture uniform. The as prepared precursor, with a composition of $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2:\text{TEAOH}:\text{H}_2\text{O}=1:1:80:12.7:1040$, was transferred into a Teflon-lined autoclave and was crystallized at 160 °C for 5.5 days. After cooling, the solids in the autoclave was centrifuged and washed with deionized water for 3 times, then dried at 110 °C overnight and finally calcined at 550 °C in air for 5 hrs to get rid of the template. Then H-ZSM-12 were made by the ion-exchange with 1 mol/L ammonium nitrate (NH_4NO_3 , Beijing Chemical Works) solution at 80 °C for 6 hrs and calcined at 550 °C for 5 hrs, with above steps repeated for 3 times.

As used for the catalyst of MTA reaction, it was impregnated with $\text{Zn}(\text{NO}_3)_2$ solution and dried with continuous stirring of 1000 rpm. The mass ratio of metal Zn and ZSM-12 was 3%. The impregnated catalyst was dried at 110 °C overnight and calcined in air at 550 °C for 4 hrs. The as-obtained catalyst was designed as Zn/ZSM-12. MTA reaction was operated at 475 °C and atmosphere pressure. Space velocity of methanol is 0.8 h^{-1} . Coke information was investigated by thermogravimetric analysis (TGA, TA2020). The organic in coke is obtained by the extraction of coke-deposited catalyst using CH_2Cl_2 . Coke structure is obtained by dissolving coke-deposited catalyst using 15% HF solution. The coke content deposited on the external surface was calculated by subtracting the internal coke content from the total coke content.

Zeolite and coke structure was characterized by SEM (JEOL2010) and/or TEM (JSF6700). Surface area and pore size distribution of zeolite was tested by N_2 -adsorption. Acidity information of catalyst was analyzed by NH_3 -TPD and FT-IR. The acidity of the external surface was measured by a gravimetric method using 2,6-di-tert-butylpyridine (DTBPy) as the probe molecule. Methods for N_2 -adsorption, FT-IR, NH_3 -TPD and DTBPy detection followed that in previous works.¹

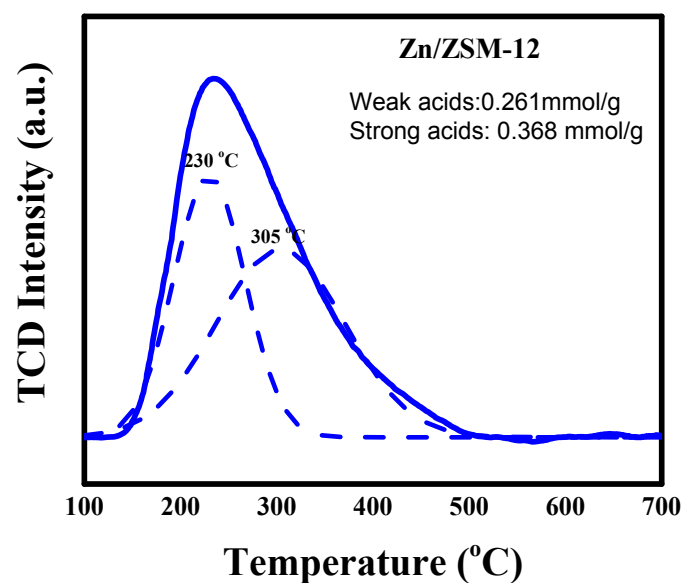


Figure S1†. NH₃-TPD profile of Zn/ZSM-12 and the peaks obtained using Gaussian peak deconvolution.

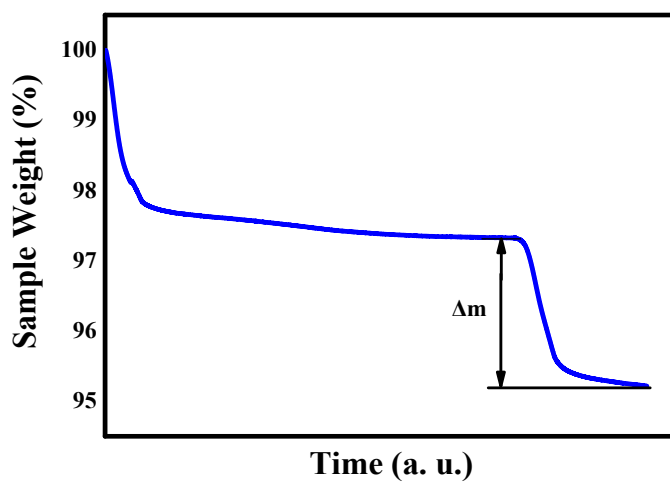


Figure S2†. TGA of samples which adsorbed DTBPy. The first stage means the weight of sample when physically adsorbed DTBPy were desorbed, and the second stage means the weight of samples when total adsorbed DTBPy were desorbed. The value Δm between the first and second stage means the weight of chemical adsorbed DTBPy on samples, related to the external acid density.

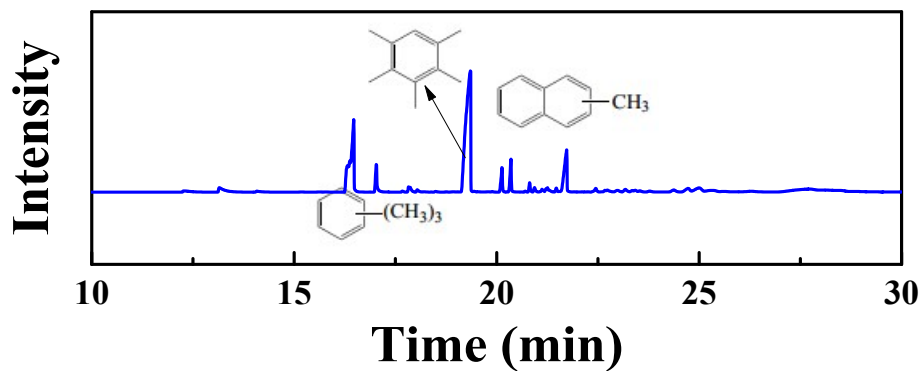


Figure S3†. GC-MS of liquid products for the first 10 hours.

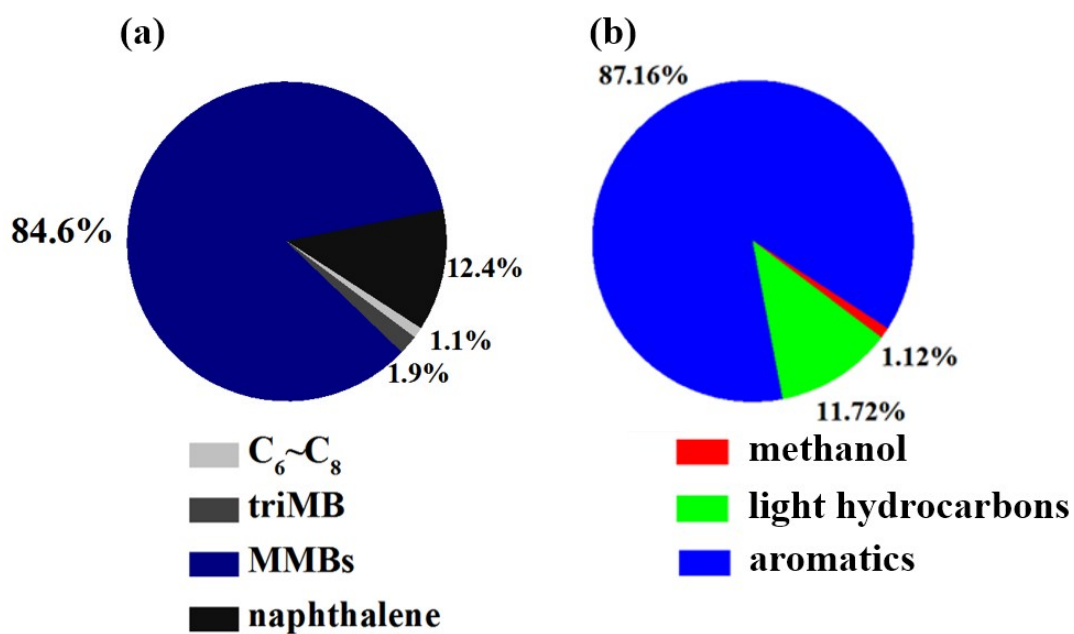


Figure S4†. (a) Selectivity of $C_6 \sim C_8$, triMB, MMBs and naphthalene in aromatics. (b) Methanol conversion and product selectivity of MTA reactions over Zn/ZSM-12. The 11.72% light hydrocarbons contained mainly 5% methane, 1.8% ethylene, and 1.9% propylene and others in lower amount.

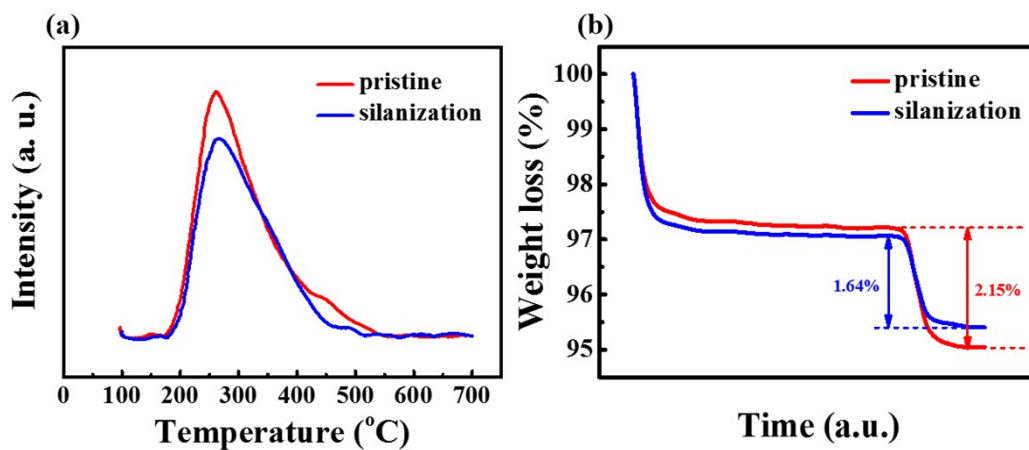


Figure S5†. (a) NH_3 -TPD profile of Zn/ZSM-12 catalysts (pristine and after silanization). The integration area of TPD curve of sample after silanization decreased by 16%, compared to the pristine. (b) TGA of Zn/ZSM-12 catalysts (pristine and after silanization), which adsorbed DTBPy. The amount of external acids decreased by 24% after silanization for ZSM-12.

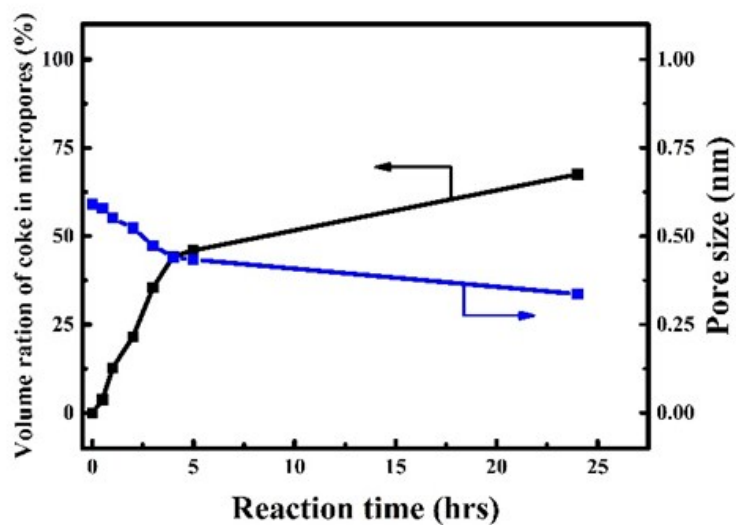


Figure S6†. Time-dependent volume ratio of coke in micropores and pore size. Pore size was calculated by assuming coke formed firstly a cylinder type product inside the channel.

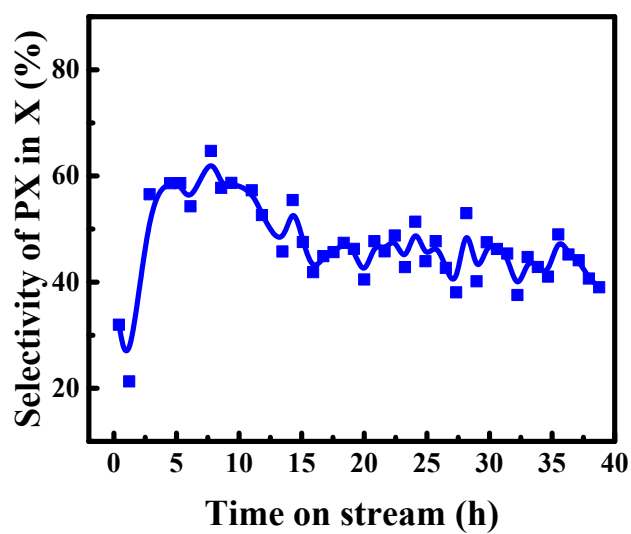


Figure S7†. Time-dependent selectivity of PX in X catalyzed by Zn/ZSM-12.

Comparison of XRD of steam- treated ZSM-12

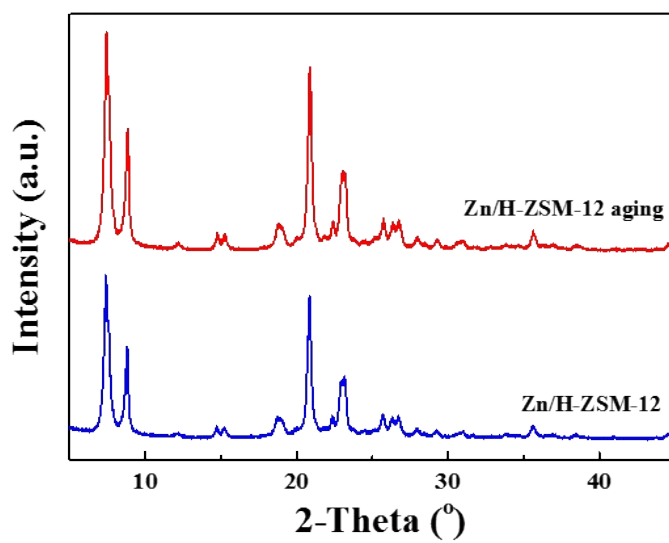


Figure S8†. XRD pattern of ZSM-12 catalyst before and after aging(100% steam, 660°C, 4hrs)

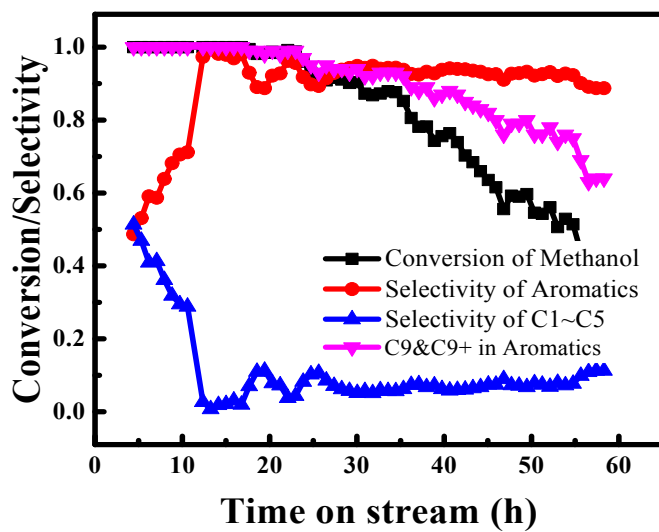


Figure S9†. Time dependent conversion of methanol, product distribution of aromatics, and light hydrocarbon, using pristine catalyst.

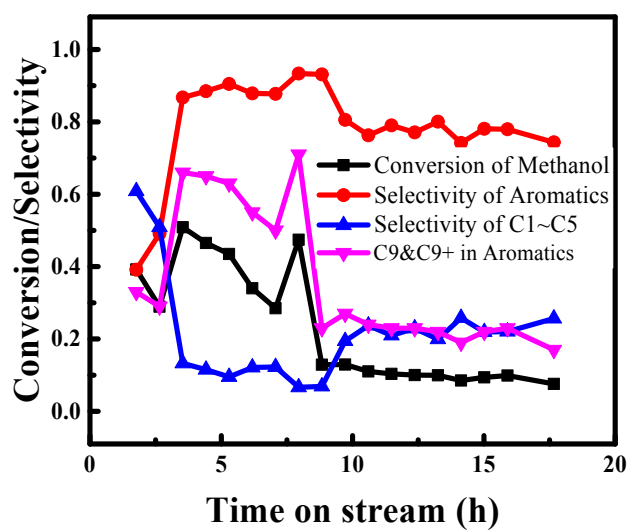


Figure S10†. Time dependent conversion of methanol, product distribution of aromatics, and light hydrocarbons, using catalyst by steam treatment.

Table S1†. Textural properties of ZSM-12, ZSM-5(30) and ZSM-5(60)

Sample name	Si/Al atomic ratio (mol mol ⁻¹)	BET surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Micropore volume (cm ³ g ⁻¹)	Mesopore volume (cm ³ g ⁻¹)
ZSM-12	36.0	310.8	0.56	0.04	0.52
ZSM-5(30)	28.6	484.0	0.73	0.15	0.58
ZSM-5(60)	56.2	441.5	0.72	0.14	0.58

Table S2†. Methanol conversion and product selectivity of MTA reactions over various catalysts used in the present study measured after the reactions were stable

Sample name	Conversion of methanol (%)	Selectivity (%)				
		C ₁ ~C ₅	Benzene	Toluene	C ₉ &C ₉ +	Total aromatics
ZSM-12	98.88	11.72	0.03	0.16	86.20	87.16
ZSM-5(30)	99.47	37.86	0.48	3.71	32.07	62.15
ZSM-5(60)	99.37	32.05	0.32	2.07	50.95	67.94

The sampling time (ZSM-12: 10 h, ZSM-5(30): 1.2 h, and ZSM-5(60): 3.6 h)