Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information of

Highly selective conversion of methanol to propylene: design of an MFI zeolite with selective-blockage of (010) surface

1 Experimental procedure for silica coating and catalyst test

All chemicals were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD and were directly used without further purification. Nano-sized H-ZSM-5 pristine (ZSM-5-P) was synthesized following our previous publications.[1,2] The Si/Al ratio is 64.5, as determined with ICP-AES.

The silica coating process was as follows. Firstly, 15 g of pristine with a particle size between 300-450 μm was put into a quartz fluidized bed reactor to run a methanol conversion reaction. The quartz fluidized bed reactor used has an inner diameter of 16 mm for reaction zone and 56 mm for the expanded zone. The reaction temperature was controlled to 475 ℃, and WHSV of methanol was set to be 0.8 h^{-1}. A nitrogen flow was set at 100 SCCM. After 5 h, the color of zeolite turned into homogeneously grey and such coked pristine was denoted as ZSM-5-CP.

In the second step, 5 g of ZSM-5-CP particles was cracked to 200 mesh and dispersed into 100 mL absolute ethanol with ultrasound. 17.36 g tetraethoxysilane (TEOS) and 3 g water were added. Several drops of hydrochloride acid were added to adjust the pH into ~1. The solution was stirred at room temperature for 8 h. Then the mixture was dried at 80 ℃ with a rotary evaporator. Then, the solids were calcined at 550 ℃ for 5 h in air to remove the coke on the zeolite.

As-synthesized catalyst was tested in an automatic catalyst test system. 1 g catalyst was physically mixed with 5 g of silica and put into a quartz tube. The tube used has an inner diameter of 8 mm and the catalyst was sealed with quartz wool. The reaction temperature was controlled at 500 ℃ with a three-zone furnace. The methanol flow rate was set to 0.02 mL/min, and the nitrogen flow rate was set to 30 SCCM to keep the WHSV=1 h^{-1}.

Outlet gas was kept at over 200 ℃ to prevent condensing and analyzed with online gas chromatography (Shimadzu GC 2014). The specially designed GC was equipped with 2 FIDs and a TCD. A Stabliwax column (30 m) was firstly used to separate aromatics and low carbon hydrocarbon. Then low carbon hydrocarbon were further introduced into an Al_2O_3/KCl column for further separation. Hydrogen and nitrogen were analyzed with TCD. A normalized method was used while dealing with GC data and carbon balance (the mole flow ratio of outlet carbon and inlet carbon) was kept over 98%.

2 Textual properties of mentioned zeolites

XRD and N_2-physical adsorption were used to characterize the properties of samples. Figure S 1 gives the XRD pattern of the two samples. Typical ZSM-5 crystals are recognized, and a wide peak at ~14° indicate the existence of silica blockage layers.

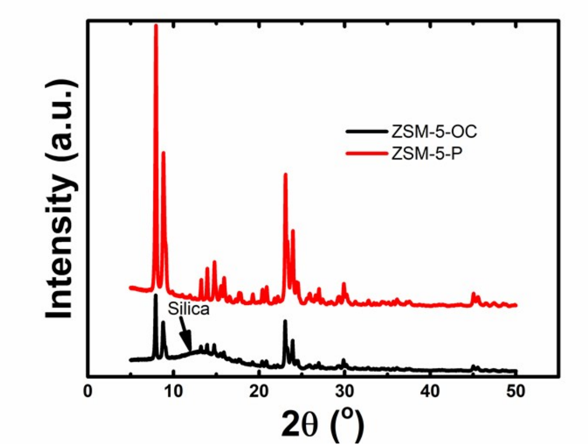

Figure S 1 XRD pattern for ZSM-5-P and ZSM-5-OC.

Table S 1 Physical properties of zeolites

Sample	S_{BET} (m^2/g) [a]	V_{micro} (cm^3/g) [b]	S_{micro} [b] (m^2/g)	$S_{external}$ [b] (m^2/g)
ZSM-5-P	420.16	0.18	371.64	48.51
ZSM-5-CP	418.68	0.16	353.29	65.39
ZSM-5-OC	297.91	0.12	256.89	41.02
ZSM-5-NC	352.73	0.13	310.36	42.38
Spent ZSM-5-OC	156.07	0.06	141.67	14.39

[a] Equivalent surface area was calculated based on BET equation.

[b] Micropore volume, micropore surface area, and external surface area were got from t-plot method, de Boer model was selected and relative pressure was kept between 0.4 and 0.6.

3 Details of pentene conversion over ZSM-5-OC catalyst

In order to control the flow rate of pentene, we used a 4-stage steam saturation system. 4 containers filled with liquid 2-methyl-2-butene (90%) were kept in 0.00 ℃ and were sequentially connected. A nitrogen flow can sequentially bubble in 4 containers and kept it saturated. The nitrogen flow rate was individually set to 10 SCCM (pass through pentene) and 30 SCCM (directly into the reactor). And other conditions were the same as the methanol conversion test.

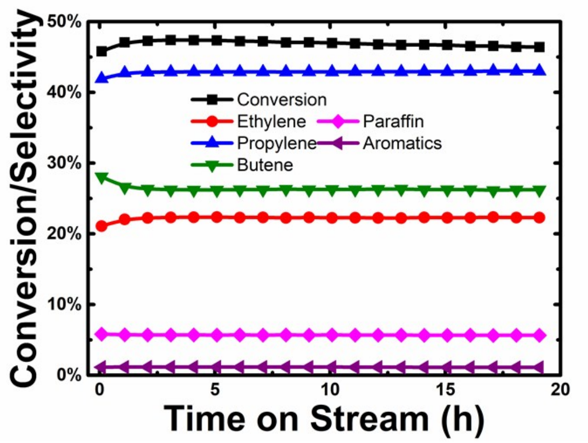

Figure S 2 Pentene conversion over ZSM-5-OC.

Figure S 2 shows the result. Aromatics and paraffin selectivity is even lower than the methanol conversion result, and this indicates a cycling potential for getting more propylene and ethylene.

4 Details of coke rate measurement and calculation

The air flow rate was set at 20 mL/min, and the temperature was controlled from 30 ℃ to 1000 ℃ with 5 K/min rate. And Figure S 3 gives the curves. Weight loss between 300 ℃ and 1000 ℃ was regarded as a mass of coke.

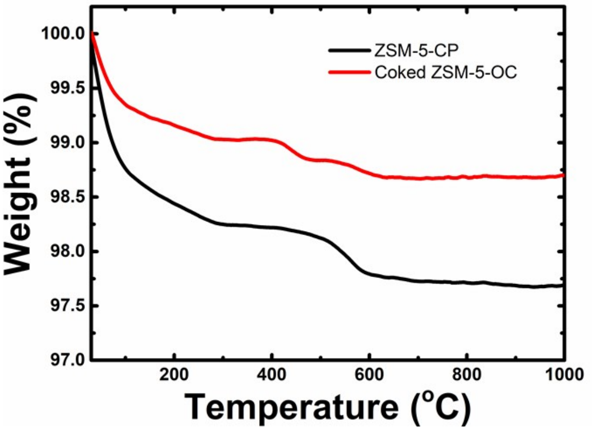

Figure S 3 TGA results for ZSM-5-CP and Coked ZSM-5-OC.

Table S 2 Data of coke rate measurement.

	Time/h	Weight loss/%	Coke rate[a]/(g•gCat.$^{-1}$•h^{-1})	Coke selectivity[b]/%
ZSM-5-CP	5	0.53	0.00107	0.28
ZSM-5-OC	18	0.34	0.00019	0.05
SAPO-34[c]	1	9.00	0.09890	1.70

a. We divided weight loss by mass remained and then by time to get the coke rate.

b. Coke selectivity was based on the coke formula $CH_{0.4}$.

c. Data from reference.[3]

Table S 2 includes the coke rate measured with TGA.

5 Details of xylene adsorption test

All chemicals were purchased from Aladdin Corp and directly used without further purification. Samples were firstly degassed in a vacuum and then impregnated with pure para-Xylene/ meta-Xylene. Then the wet mixture was transferred into a crucible for thermogravimetric analysis.

The nitrogen flow rate was set at 50 SCCM. The temperature program was set as follows. Firstly, the temperature was raised from 30 ℃ to 140 ℃ (boil point of PX and MX) with 10 K/min rate. Then the temperature was kept at 140 ℃ for 2.5 h to evaporate liquid xylene totally. Then the temperature was raised from 140 ℃ to 550 ℃ with 10 K/min rate. And finally, it was kept at 550 ℃ for 1 h. The mass loss between 140 ℃ and 550 ℃ was regarded as the adsorption amount, and the mass remained after 550 ℃ calcination was regarded as zeolite weight.

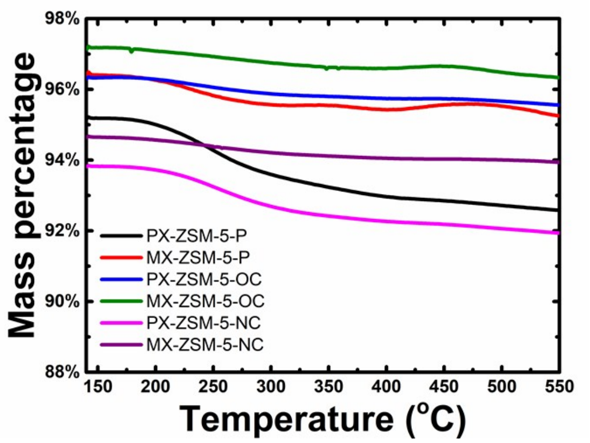

Figure S 4 Temperature Programmed Desorption (TPD) measured by TGA.

Figure S 4 shows the raw results during temperature programmed procedure. 3 unobvious peak can be characterized at ~240 ℃, 400 ℃ and 430 ℃ based on nonlinear regression from an error function. So only mass differences are listed in the main text.

6 Acid properties of mentioned zeolites

We measured the acid properties of mentioned zeolites with ammonia Temperature Programmed Desorption (NH_3-TPD). Measured samples were firstly degassed at 600 ℃ with 100 SCCM helium flow. Then ammonia (5%vol in helium) adsorbed at room temperature, and physically adsorbed ammonia was removed at 100 ℃. The heating rate was set to 10 K/min from 140 ℃ to 700 ℃, and the signal was detected with TCD.

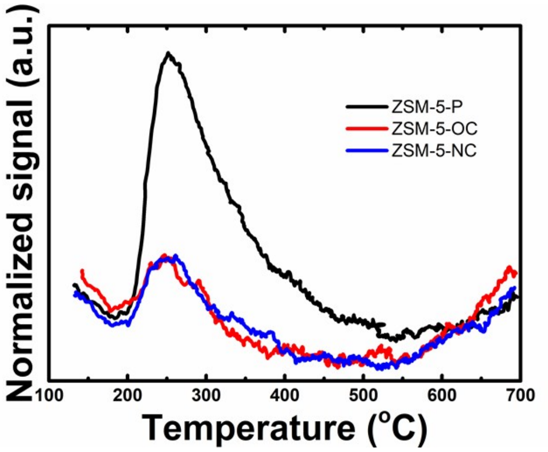

Figure S 5 TPD profile for mentioned zeolites. Signal was normalized to same mass.

Figure S 5 shows the TPD profile, which is the same as our previous work.[1,2] It has been reported that the Lewis acid site plays a major role in this sample. The acid amount is reduced by the silica coating method, but acid strength is almost unaffected. Surface acid sites are killed by silica, and part of the sample is unattached silica particles. The two reasons result in a decrease in acid amount together. No differences in acid properties between ZSM-5-OC and ZSM-5-NC can be noticed.

References:

(1) Ma, Y.; Cai, D.; Li, Y.; Wang, N.; Muhammad, U.; Carlsson, A.; Tang, D.; Qian, W.; Wang, Y.; Su, D.; Wei, F. *RSC Advances* **2016**, *6*, 74797-74801.

(2) Ma, Y.; Wang, N.; Qian, W.; Wang, Y.; Zhang, J.; Wei, F. *RSC Advances* **2016**, *6*, 81198-81202.

(3) Qi, G.; Xie, Z.; Yang, W.; Zhong, S.; Liu, H.; Zhang, C.; Chen, Q. *Fuel Processing Technology* **2007**, *88*, 437-441.