Electronic Supplementary Information

Boosting Turnover Number of Core-Shell Al-ZSM-5@B-ZSM-5 Zeolite for Methanol to Propylene Reaction by Modulating the Gradient Acid Sites Distribution and Low Consumption Diffusion

Yanliang Zhai[a], Shaolong Zhang[a], Yunshan Shang[a], Yu Song[a], Wenxuan Wang[a], Tong Ma[a], Luoming Zhang[a], Yanjun Gong[a], Jun Xu[b], and Feng Deng[b]*

[a]State Key Laboratory of Heavy Oil Processing and the Key Laboratory of Catalysis of CNPC, China University of Petroleum, Beijing 102249, China

[b]Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, China

Synthesis of Al-ZSM-5@Al-ZSM-5 (AA) core-shell reference zeolite: To get the Al-ZSM-5@Al-ZSM-5 core-shell zeolite, deionized water, $NaAlO_2$, TPAOH and silica sol were mixed to prepare a gel with the molar composition of 1.0 SiO_2: 0.004 Al_2O_3: 0.1 $(TPA)_2O$: 30 H_2O. The gel was stirred for 1h and then a desirable amount (25 wt% of SiO_2 mass in the gel) of premade nanocrystallines aggregated Al-ZSM-5 (A sample) was added into the gel. After stirring 3h, the mixture was

transferred to a Teflon-line autoclave and crystallized at 170 ℃ for 48h. The solid products were gathered by filtration, washed with deionized water, and dried overnight at 100 ℃. The obtained sample was denoted as AA and its H-type sample was denoted as H-AA.

Synthesis of high Si/Al conventional Al-ZSM-5 (C) reference zeolite: To get the high Si/Al conventional Al-ZSM-5 reference zeolite, deionized water, $NaAlO_2$, TPAOH and silica sol were mixed to prepare a gel with the molar composition of 1.0 SiO_2: 0.0008 Al_2O_3: 0.1 $(TPA)_2O$: 30 H_2O. The gel was stirred for 3h and then the mixture was transferred to a Teflon-line autoclave and crystallized at 170 ℃ for 48h. The solid products were gathered by filtration, washed with deionized water, and dried overnight at 100 ℃. The obtained sample was denoted as C and its H-type sample was denoted as H-C.

Synthesis of 200nm microporous Al-ZSM-5 (A') reference zeolite: To get the 200nm microporous Al-ZSM-5 reference zeolite, $NaAlO_2$, deionized water, TPAOH and TEOS were mixed to prepare a gel with the molar composition of 1.0 SiO_2: 0.004 Al_2O_3: 0.125 $(TPA)_2O$: 10 H_2O. The gel was stirred for 3h and then the mixture was transferred to a Teflon-line autoclave and crystallized at 170 ℃ for 48h. The solid products were gathered by filtration, washed with deionized water, and dried overnight at 100 ℃. The obtained sample was denoted as A' and its H-type sample was denoted as H-A'.

Synthesis of microporous Al-ZSM-5@B-ZSM-5 (AB') core-shell reference zeolite: To get the microporous Al-ZSM-5@B-ZSM-5 core-shell zeolite, deionized water, H_3BO_3, TPAOH and silica sol were mixed to prepare a gel with the molar composition of 1.0 SiO_2: 0.004 B_2O_3: 0.1 $(TPA)_2O$: 30 H_2O. The gel was stirred for 1h and then a desirable amount (25 wt% of SiO_2 mass in the gel) of premade 200nm microporous Al-ZSM-5 zeolite (A' sample) was added into the gel. After stirring 3h, the mixture was transferred to a Teflon-line autoclave and crystallized at 170 ℃ for 48h. The solid products were gathered by filtration, washed with deionized water, and dried overnight at 100 ℃. The obtained sample was denoted as AB' and its H-type sample was denoted as H-AB'.

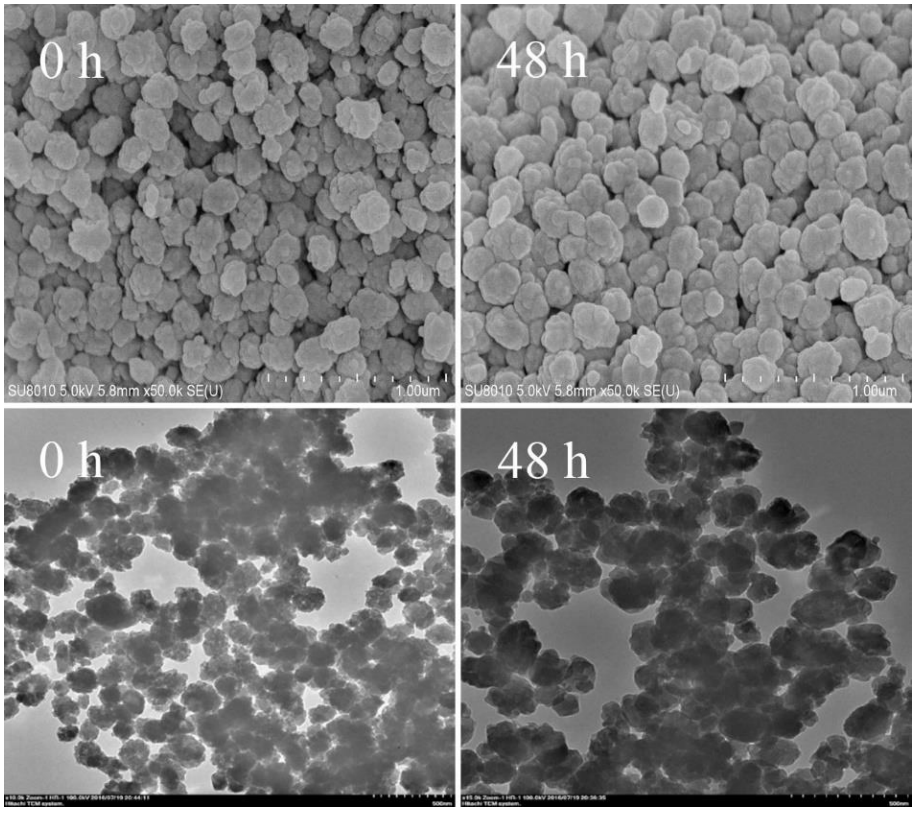

Figure S1. SEM and TEM images of A sample before and after TPAOH treatment

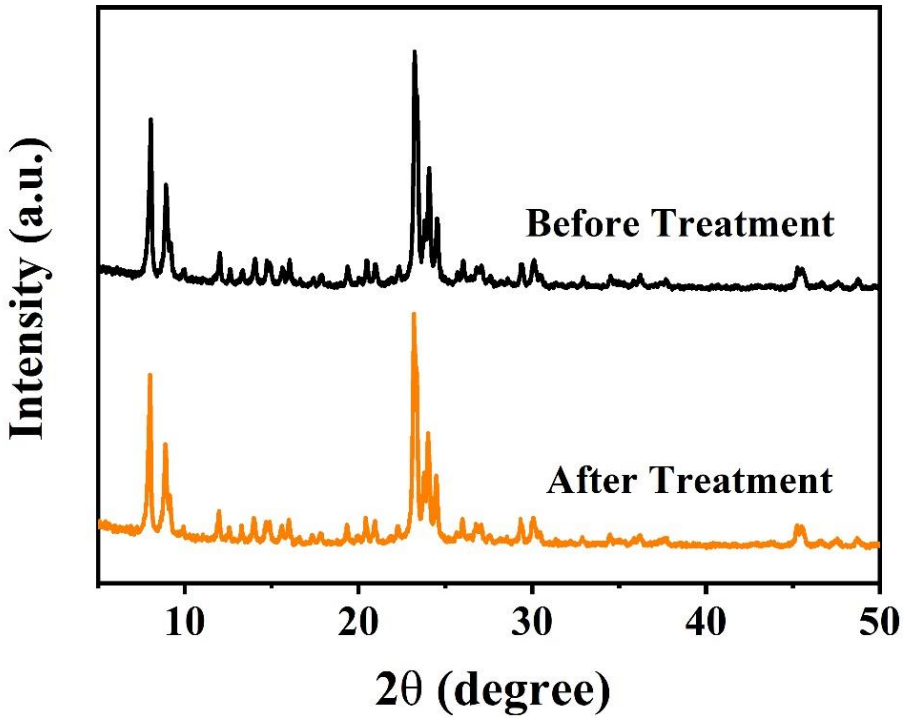

Figure S2. XRD patterns of A sample before and after TPAOH treatment

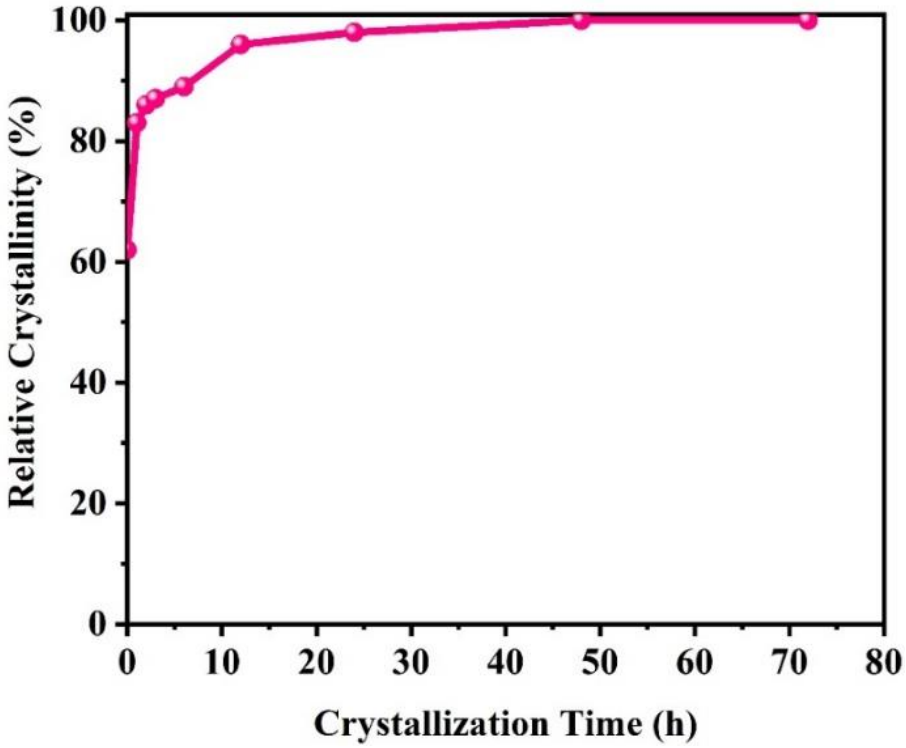

Figure S3. The crystallization profile of AB sample.

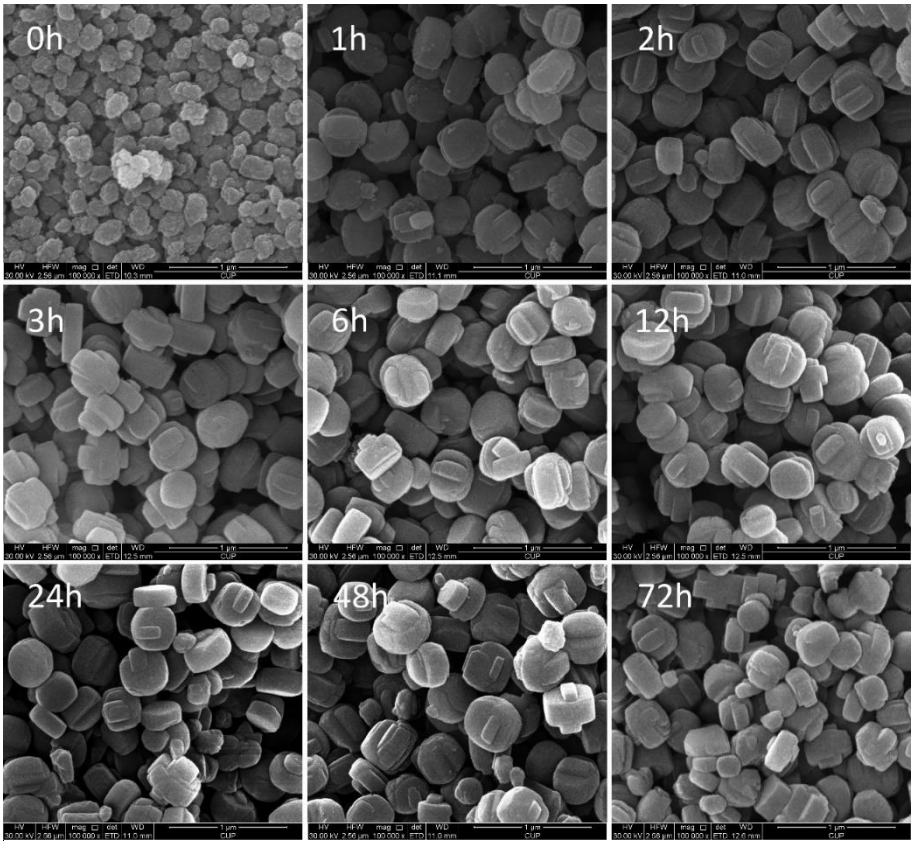

Figure S4. SEM images of AB sample at different crystallization time.

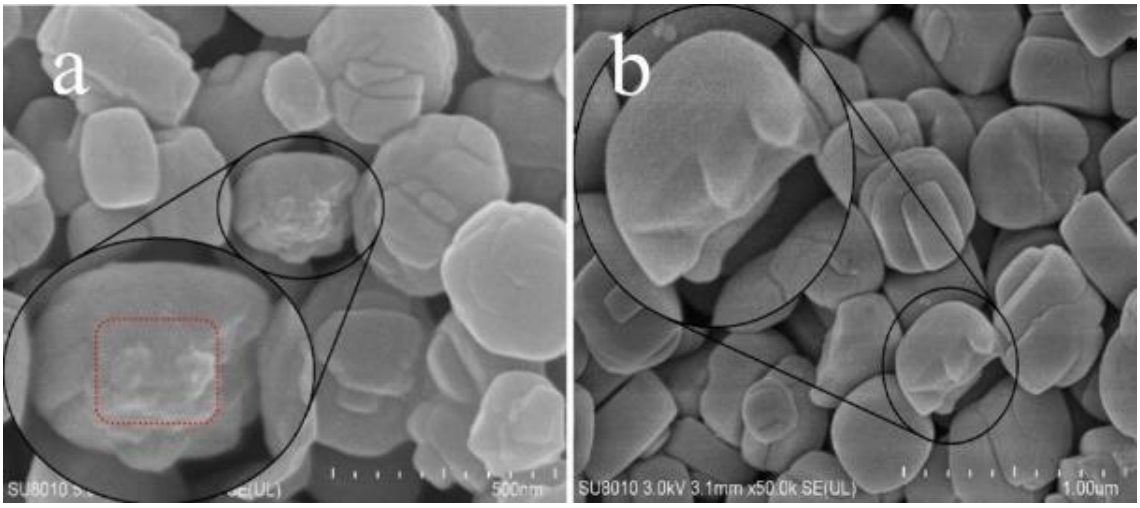

Figure S5. SEM images of fractured particles of (a) AB sample and (b) B sample.

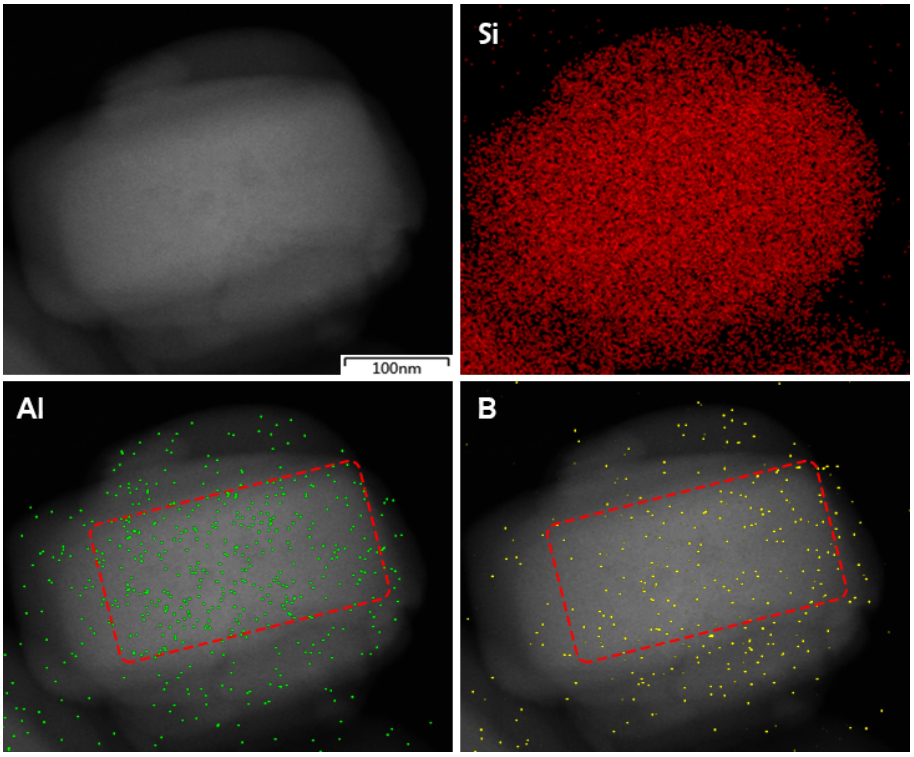

Figure S6. Dark field STEM images and element maps of Al (green), B (yellow) and Si (red) of H-AB sample

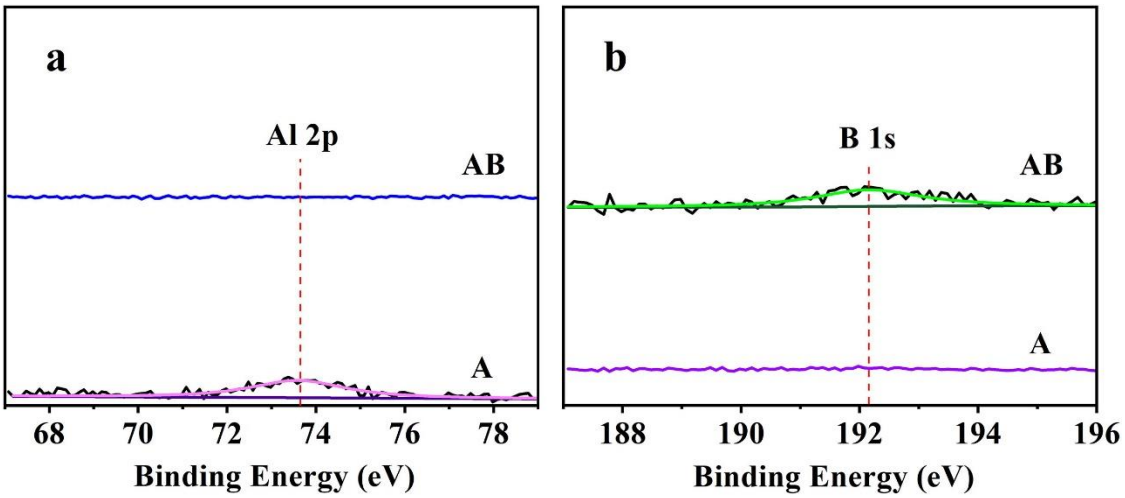

Figure S7. XPS spectra of (a) Al 2p and (b) B 1s peaks for ZSM-5 samples

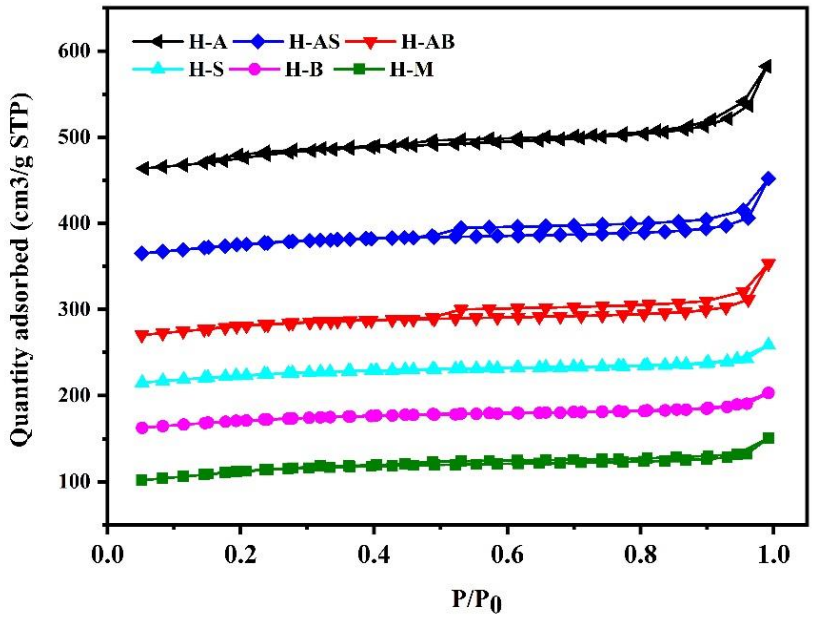

Figure S8. N_2 adsorption/desorption isotherms of ZSM-5 samples.

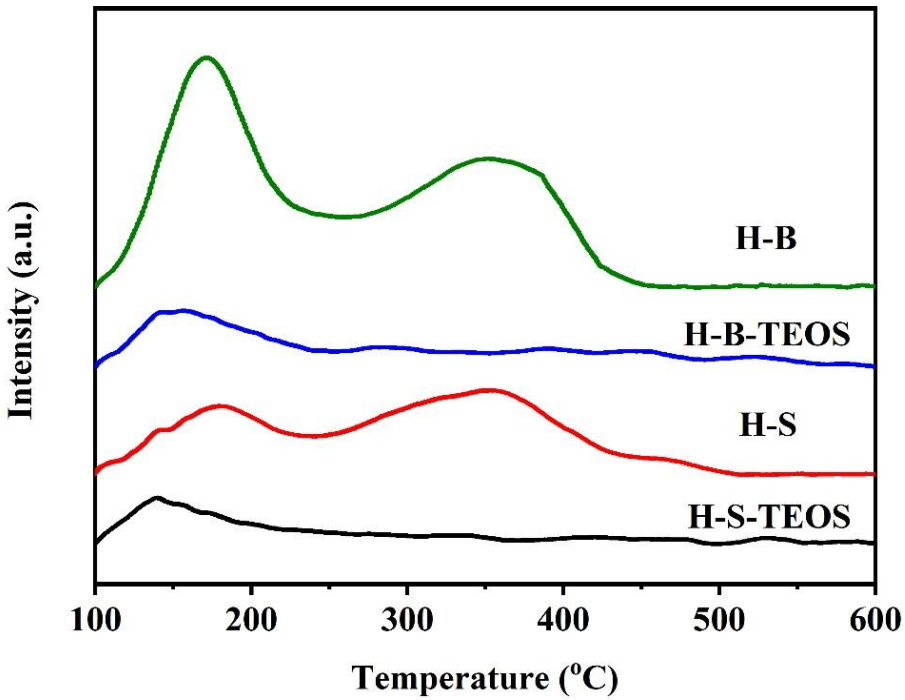

Figure S9. NH_3-TPD profiles of ZSM-5 samples

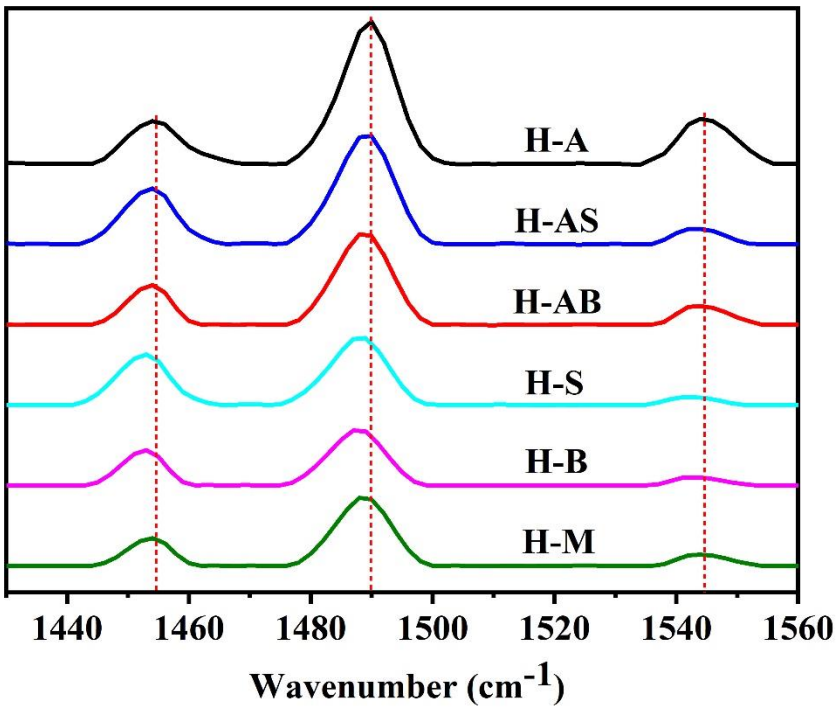

Figure S10. Py-IR spectra of ZSM-5 samples at 200 ℃

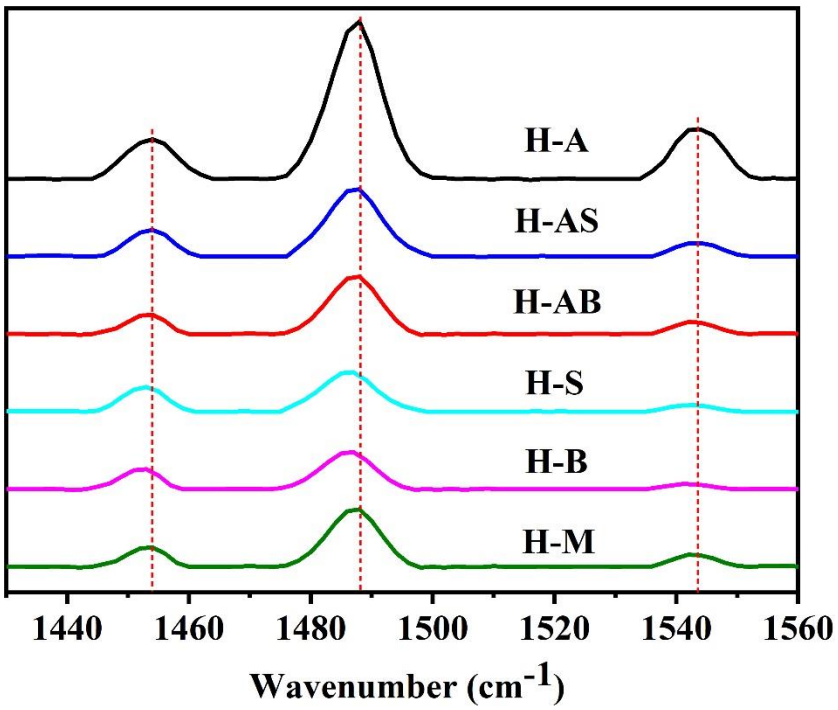

Figure S11. Py-IR spectra of ZSM-5 samples at 350 ℃

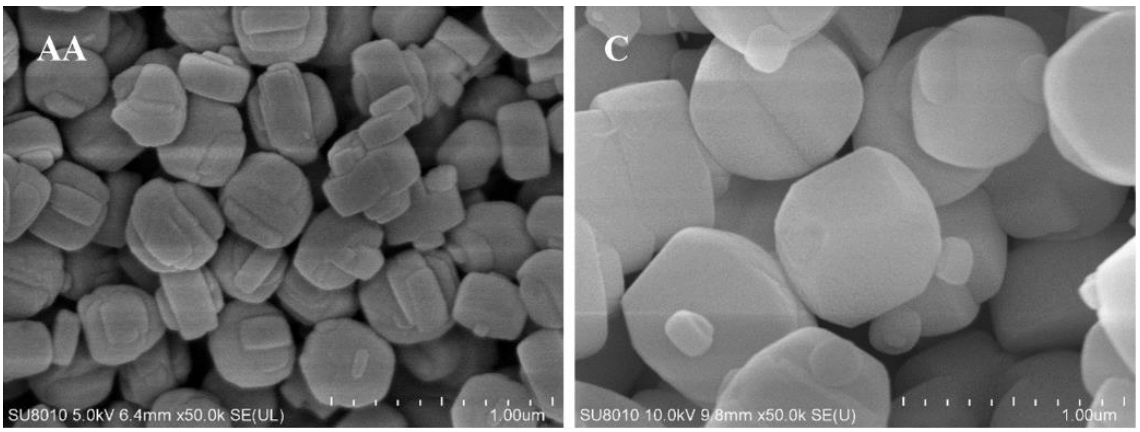

Figure S12. SEM images of AA and C samples

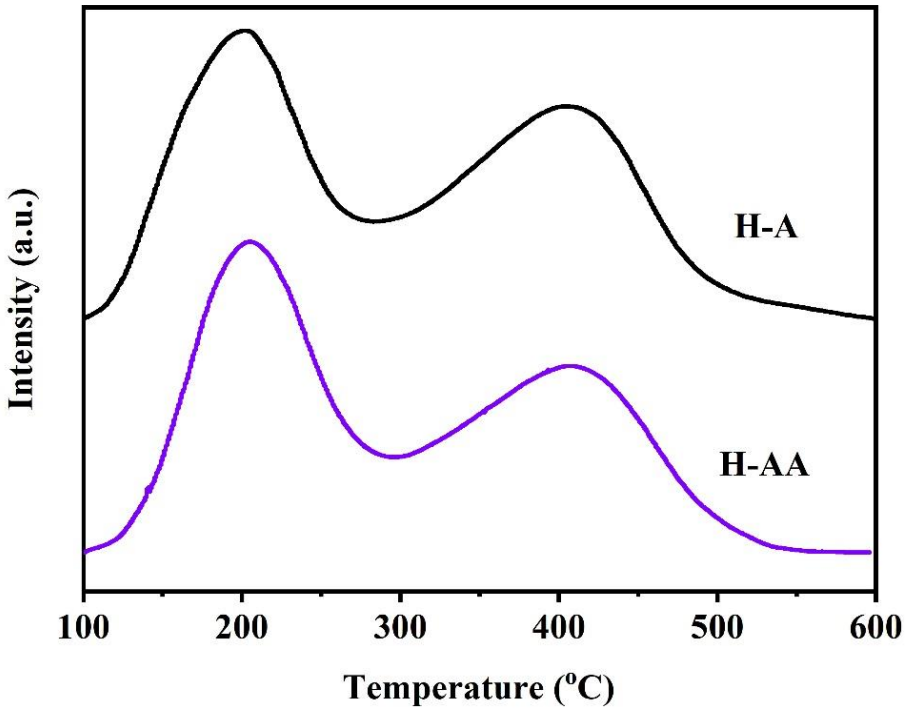

Figure S13. NH_3-TPD profiles of H-A and H-AA samples

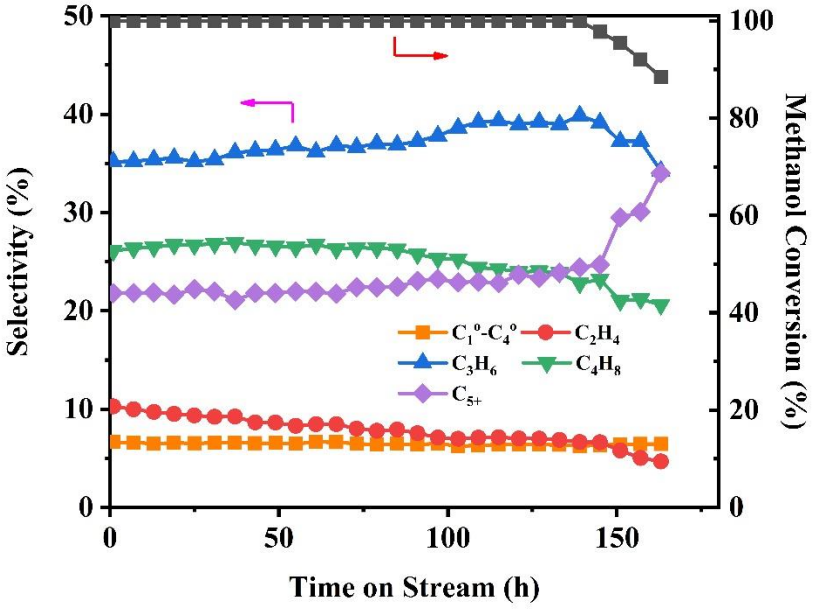

Figure S14. MTP performance of H-AA sample

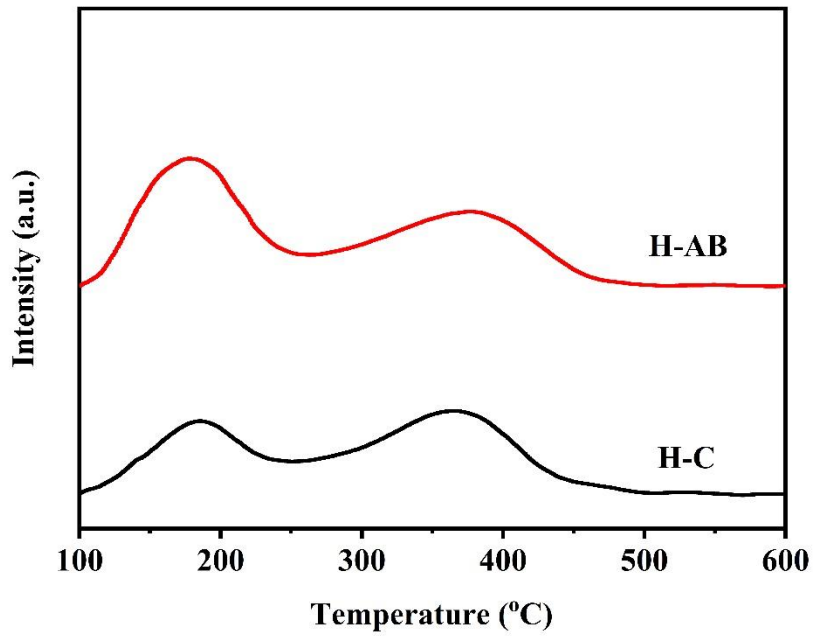

Figure S15. NH_3-TPD profiles of H-AB and H-C samples

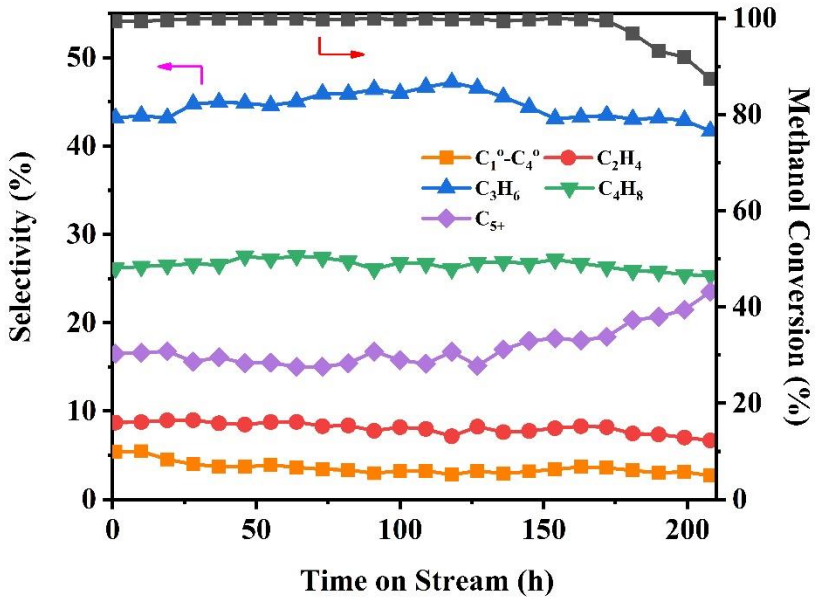

Figure S16. MTP performance of H-C sample

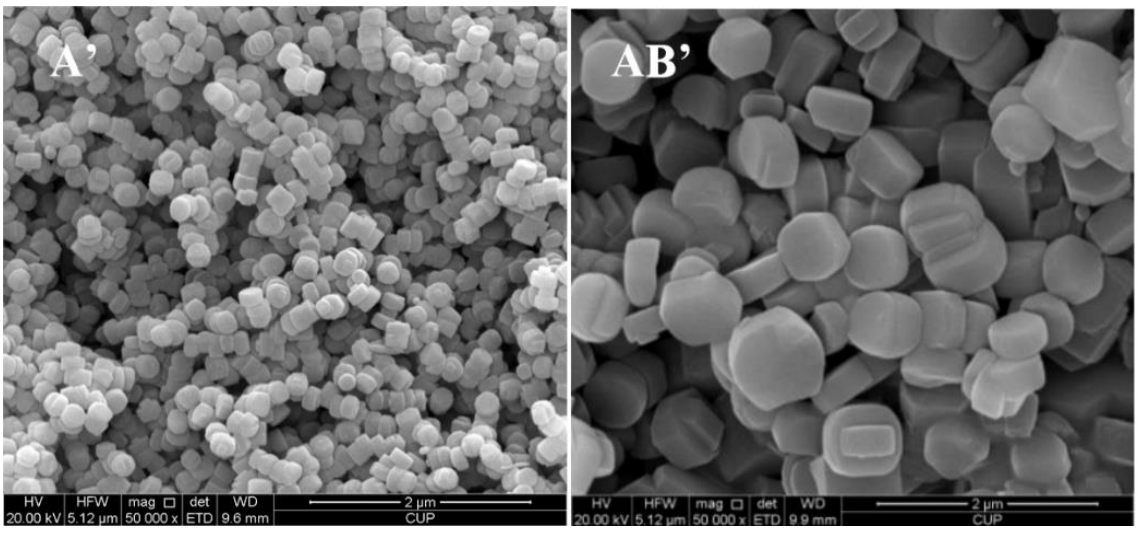

Figure S17. SEM image of A' and AB' samples

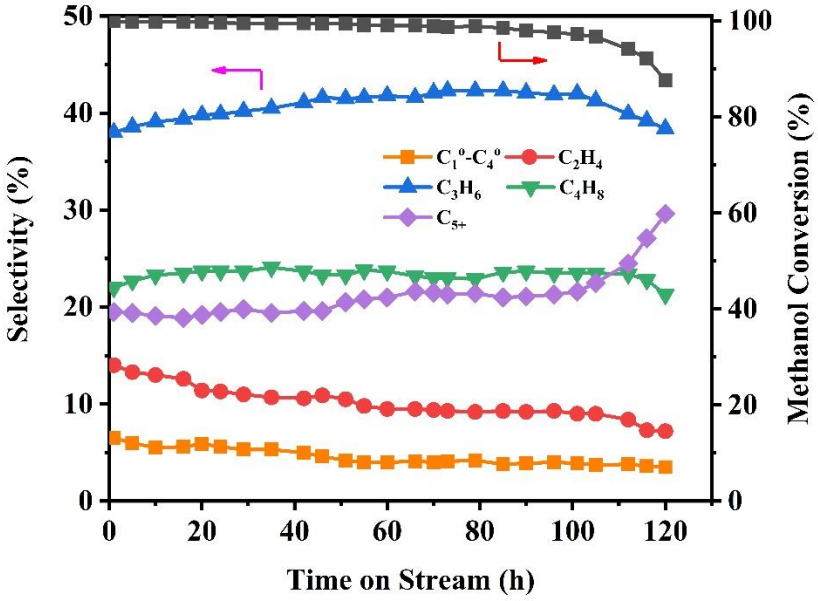

Figure S18. MTP performance of H-A' sample

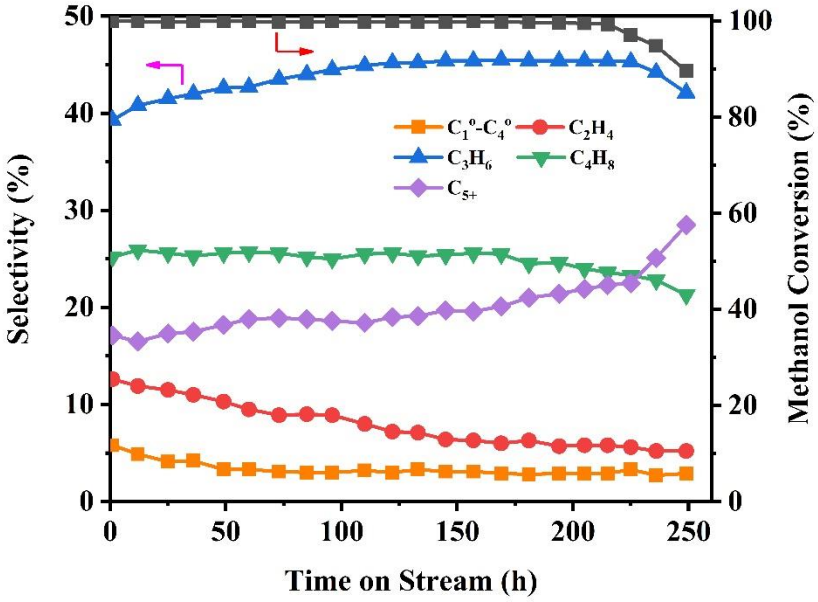

Figure S19. MTP performance of H-AB' sample

The mesopores in the core region of the core-shell material Al-ZSM-5@B-ZSM-5 can reduce the diffusion resistance and enhance the diffusivity of the catalyst, resulting in suppressing secondary reactions, enhancing the propylene selectivity and catalytic lifetime. To confirm this point, we synthesized another Al-ZSM-5@B-ZSM-5 core-shell sample (denoted as AB') whose core was 200 nm microporous Al-ZSM-5 without mesopores (denoted as A') and shell was similar with H-AB sample. The synthesis method, SEM image, texture property and catalytic performance are shown in the Supplementary Information (Figure S17-S19 and Table S5). SEM images show the morphology of A' and AB' is typical coffin with particle size of 200 nm and 600 nm, respectively. N_2 adsorption-desorption measurement shows both A' and AB' samples have almost no mesopores. The catalytic lifetime still increases from 120 h to 250 h under the same MTP reaction condition, and the maximum propylene selectivity also increases from 39.8% to 45.5%. But, without mesopores in the core region, both the catalytic lifetime and propylene selectivity of H-AB' are lower than H-AB sample with mesopores in the core region (350 h, 49%). These results demonstrate that the further enhancement of H-AB sample is attributed to the introduction of mesopores in the core region.

Table S1. Relative crystallinity of A sample before and after TPAOH treatment

Sample	Relative crystallinity %
before treatment	100%
after 1h	98%
after 48h	92%

Table S2. Texture property of deactivated ZSM-5 samples

	surface area ($m^2\ g^{-1}$)			volume ($cm^3\ g^{-1}$)			utilization of pore volume[a]
sample	total	exter.	micro.	total	meso.	micro.	
H-A	309	181	128	0.21	0.13	0.06	36.4%
H-AS	239	142	97	0.15	0.09	0.04	42.3%
H-AB	245	153	92	0.14	0.08	0.04	44.0%

[a]calculated from the decrease in percentage of the total pore volume after MTP reaction.

Table S3. Coking behavior over ZSM-5 samples.

sample	total[a]		inter.[b]		exter.[c]		inter. /total
	carbon (wt%)	carbon deposition rate(mg $g_{zeolite}^{-1}$ h^{-1})	carbon (wt%)	carbon deposition rate (mg $g_{zeolite}^{-1}$ h^{-1})	carbon (wt%)	carbon deposition rate (mg $g_{zeolite}^{-1}$ h^{-1})	
H-A	9.70	0.46	1.73	0.08	7.97	0.38	17.8%
H-AS	9.25	0.37	5.65	0.23	3.60	0.14	61.1%
H-AB	9.10	0.26	5.66	0.16	3.44	0.09	62.2%

[a]Determined by TPO. [b]Coke deposited within the micropores, determined by the method reported in the previous work.[1] [c]Coke deposited on the external surface, calculated from the difference between the total and internal coke.

Table S4. MTP reaction performance of ZSM-5 catalysts in recent works

researcher	WHSV (h^{-1})	propylene (%)	lifetime (h)	converted methanol (mol)	TON[c]
Li[2]	6	40-50	120[a]	22.5	2.8×10^5
Ding[3]	1	35-45	845[a]	26.4	3.8×10^5
Feng[4]	3.8	35-45	24[b]	2.85	0.4×10^5

[a]the time of conversion maintained above 90%. [b]the time of conversion maintained above 85%. [c]TON (Turnover number): number of moles of methanol converted into products per BAS.

Table S5. Texture property of A' and AB' samples

sample	surface area (m^2 g^{-1})			volume (cm^3 g^{-1})		
	total	exter.	micro.	total	meso.	micro.
H-A'	326	42	284	0.21	0.09	0.12
H-AB'	311	35	276	0.19	0.08	0.11

REFERENCES

1. K. Lee, S. Lee, Y. Jun and M. Choi, *J. Catal.*, 2017, **347**, 222-230.
2. J. Li, H. Ma, Y. Chen, Z. Xu, C. Li and W. Ying, *Chem. Commun.*, 2018, **54**, 6032-6035.
3. J. Ding, Z. Zhang, L. Han, C. Wang, P. Chen, G. Zhao, Y. Liu and Y. Lu, *RSC Adv.*, 2016, **6**, 48387-48395.
4. R. Feng, X. Yan, X. Hu, Z. Yan, J. Lin, Z. Li, K. Hou and M. J. Rood, *Catal. Commun.*, 2018, **109**, 1-5.