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Electronic Supplementary Information

Impact of hierarchical pore structure on catalytic performances of MFI zeolites modified by ZnO for the conversion of methanol to aromatics

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1. Catalytic performances of ZnO/H-ZSM-5 catalysts prepared by ion-exchange, impregnation and ball-milling methods

Table S1. Catalytic performances of ZnO/H-ZSM-5 catalysts prepared by different methods.

Catalyst	CH_3OH conv. (%)	Selectivity[b] (%)								BTX yield (%)
		CH_4	$C_{2-4}^{=}$	C_{2-4}^{0}	C_{5+}	Benzene	Toluene	Xylenes	Aromatics	
ZnO/H-ZSM-5 (impregnation)	100	10	17	16	1.1	7.9	29	14	55	51
ZnO/H-ZSM-5 (ion-exchange)	100	7.4	12	14	1.2	8.7	33	18	65	60
ZnO/H-ZSM-5 (ball-milling)	100	7.1	11	12	1.0	9.3	34	19	69	62

[a] Reaction conditions: T = 733 K, W = 2.0 g, $P(CH_3OH)$ = 80 kPa, F(total) = 25 cm^3 min^{-1}, time on stream, 2 h. [b] $C_{2-4}^{=}$: C_{2-4} olefins, C_{2-4}^{0}: C_{2-4} paraffins, C_{5+}: C_{5+} aliphatic hydrocarbons.

2. XRD patterns

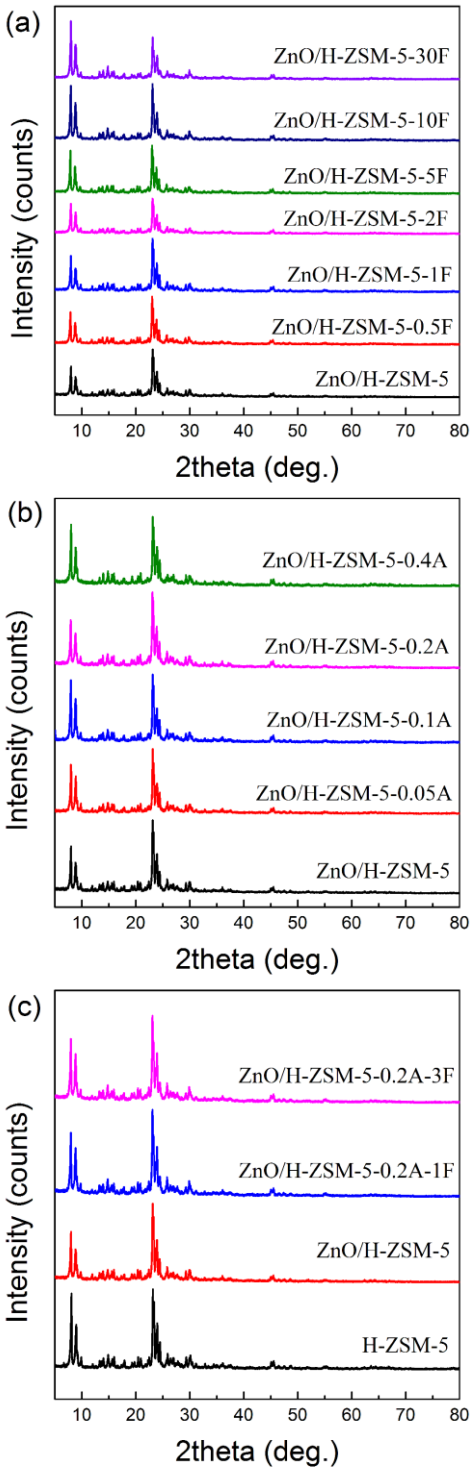

Figure S1. XRD patterns. (a) ZnO/H-ZSM-5−*x*F. (b) ZnO/H-ZSM-5−*x*A. (c) H-ZSM-5, ZnO/H-ZSM-5, ZnO/H-ZSM-5−0.2A−1F and ZnO/H-ZSM-5−0.2A−3F.

3. Pore parameters for ZnO/H-ZSM-5−*x*F and ZnO/H-ZSM-5−*x*A samples

Table S2. Pore parameters for ZnO/H-ZSM-5−*x*F and ZnO/H-ZSM-5−*x*A samples.

Samples	S_{BET}[a] [$m^2 g^{-1}$]	S_{micro}[b] [$m^2 g^{-1}$]	S_{meso}[c] [$m^2 g^{-1}$]	V_{total}[d] [$cm^3 g^{-1}$]	V_{micro}[e] [$cm^3 g^{-1}$]	V_{meso}[f] [$cm^3 g^{-1}$]	D_{meso}[g] [nm]
ZnO/H-ZSM-5	327	316	9.0	0.15	0.14	0.01	−
ZnO/H-ZSM-5−1F	328	316	11	0.15	0.13	0.02	−
ZnO/H-ZSM-5−2F	321	304	6.9	0.15	0.13	0.02	−
ZnO/H-ZSM-5−5F	324	306	10	0.15	0.13	0.02	−
ZnO/H-ZSM-5−10F	321	303	16	0.16	0.13	0.03	−
ZnO/H-ZSM-5−0.05A	326	285	33	0.16	0.13	0.03	4.1
ZnO/H-ZSM-5−0.1A	333	284	40	0.17	0.12	0.05	4.6
ZnO/H-ZSM-5−0.2A	341	282	51	0.19	0.11	0.08	6.0
ZnO/H-ZSM-5−0.4A	330	220	96	0.27	0.10	0.17	10

[a]BET surface area. [b]Micropore surface area evaluated by the *t*-plot method. [c]Mesopore surface evaluated by the BJH method. [d]Total pore volume. [e]Micropore volume evaluated by the *t*-plot method. [f]Mesopore volume evaluated by the BJH method. [g]Mean diameter of mesopores evaluated by the BJH method.

4. Pyridine-adsorbed FT-IR results for ZnO/H-ZSM-5−*x*F and ZnO/H-ZSM-5−*x*A catalysts

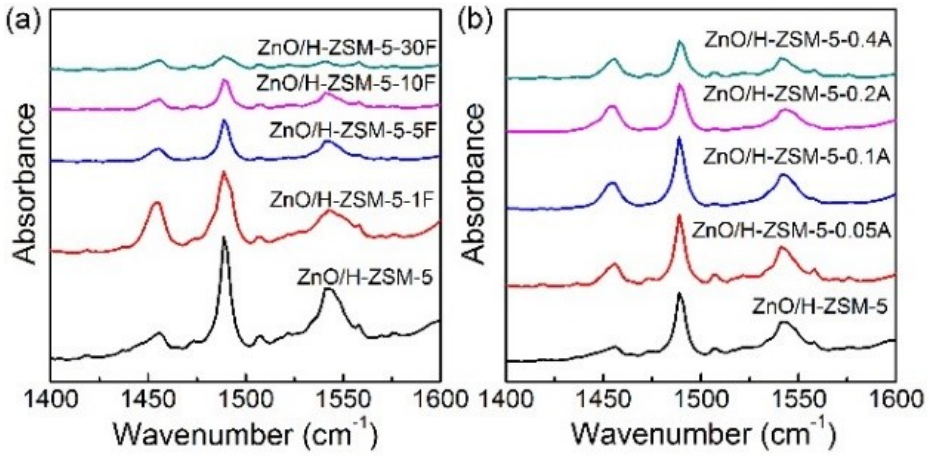

Figure S2. Pyridine-adsorbed FT-IR spectra of. (a) ZnO/H-ZSM-5−*x*F catalysts. (b) ZnO/H-ZSM-5−*x*A catalysts.

5. Pyridine-adsorbed FT-IR results for catalysts with and without ZnO loading

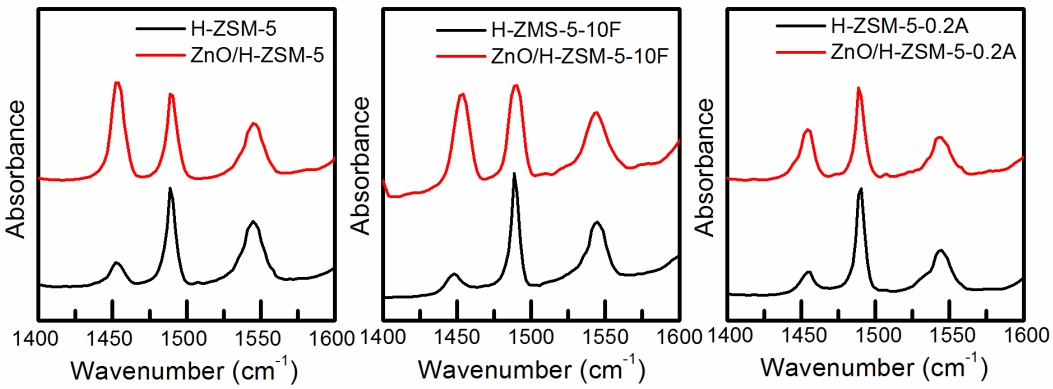

Figure S3. Pyridine-adsorbed FT-IR spectra for catalysts with and without ZnO.

6. ICP, XRF and XPS results for ZnO/H-ZSM-5−*x*F and ZnO/H-ZSM-5−*x*A−*y*F catalysts

Table S3. ICP, XRF and XPS results of the ZnO/H-ZSM-5−*x*F and ZnO/H-ZSM-5−*x*A−*y*F catalysts.

Catalysts	Content (wt%)				
	Al[a]	F[b]	Na[b]	Si/Al[a]	Si/Al[c]
ZnO/H-ZSM-5	1.75	−	−	24.8	23.9
ZnO/H-ZSM-5-0.5F	1.94	0	−	22.3	−
ZnO/H-ZSM-5-1F	2.41	0	−	17.8	−
ZnO/H-ZSM-5-2F	2.46	0	−	17.4	−
ZnO/H-ZSM-5-5F	2.54	0	−	16.8	−
ZnO/H-ZSM-5-10F	2.66	0	−	16.0	19.9
ZnO/H-ZSM-5-30F	2.92	0	−	14.5	−
ZnO/H-ZSM-5−0.05A	2.65	−	0	16.1	−
ZnO/H-ZSM-5−0.1A	2.81	−	0	15.4	−
ZnO/H-ZSM-5−0.2A	2.90	−	0	14.7	11.6
ZnO/H-ZSM-5−0.4A	3.15	−	0	13.4	−
ZnO/H-ZSM-5−0.2A-1F	2.92	0	0	14.5	12.2

[a] Quantified by ICP.

[b] Quantified by XRF.

[c] Quantified by XPS.

7. Possible scheme for the formation of micropores with a larger mean size by fluoride treatment

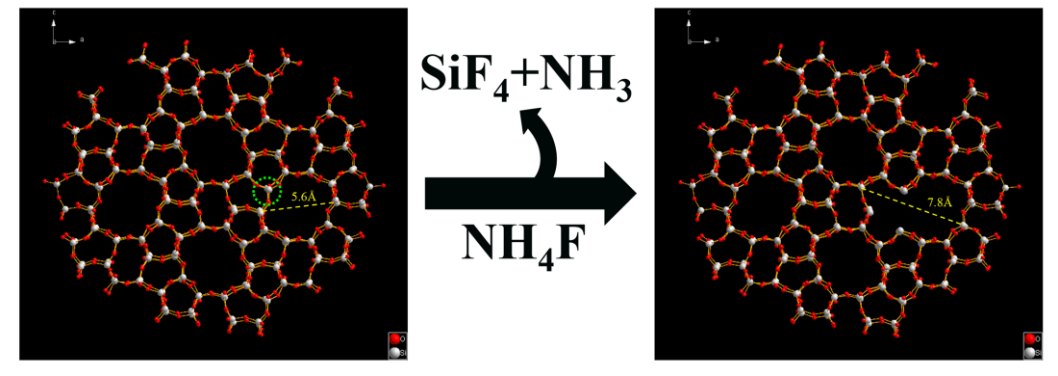

Figure S4. Possible formation mechanism for the micropores with sizes at 0.8-0.9 nm.

8. ^{27}Al MAS NMR spectra

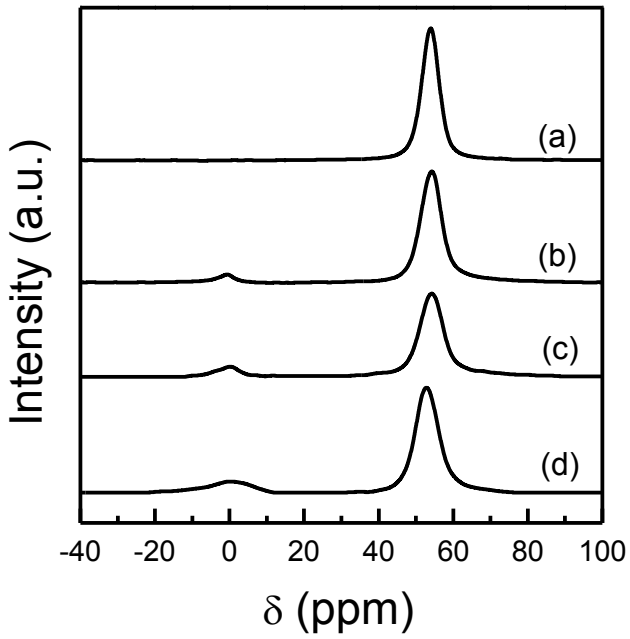

Figure S5. ^{27}Al MAS NMR spectra. (a) H-ZSM-5, (b) H-ZSM-5−1F, (c) H-ZSM-5−0.2A, (d) H-ZSM-5−0.2A−1F.

9. XPS spectra for ZnO supported on hierarchical H-ZSM-5 zeolites

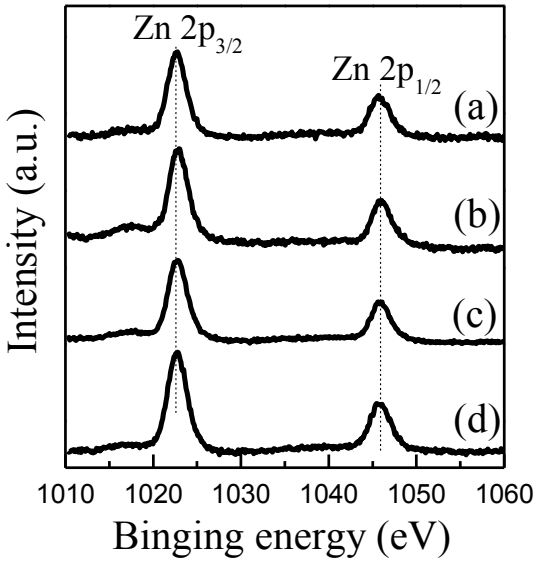

Figure S6. XPS spectra of Zn 2p. (a) ZnO/H-ZSM-5. (b) ZnO/H-ZSM-5−10F. (c) ZnO/H-ZSM-5−0.2A. (d) ZnO/H-ZSM-5−0.2A−1F.

10. Diffuse reflectance UV-vis spectra for hierarchical zeolites

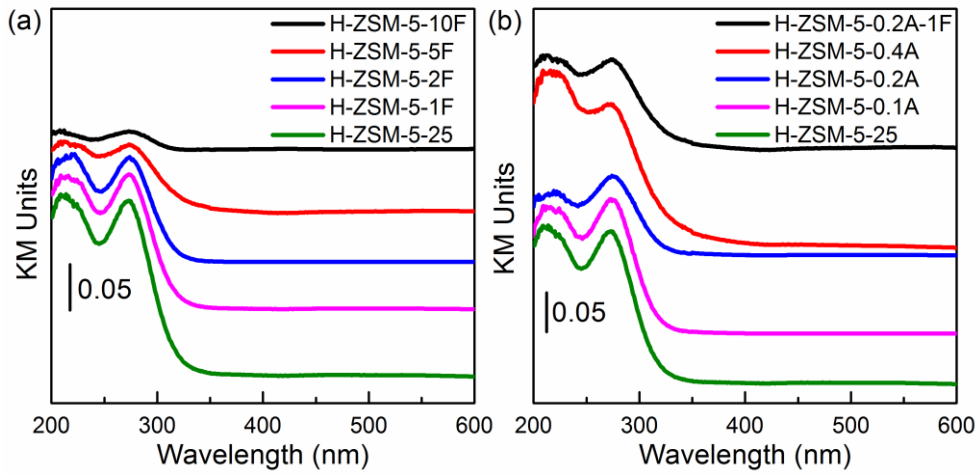

Figure S7. UV-vis DSR spectra for hierarchical zeolites.

11. Space-time yield of BTX over ZnO-containing MFI zeolite catalysts

Table S4. The space-time yield of BTX over ZnO-containing MFI zeolite catalysts.

Catalysts	Space-time yield of BTX (g g_{cat}^{-1} h^{-1})
ZnO/H-ZSM-5-300	0.33
ZnO/H-ZSM-5-150	0.43
ZnO/H-ZSM-5-100	0.47
ZnO/H-ZSM-5-50	0.51
ZnO/H-ZSM-5-25	0.60
ZnO/H-ZSM-5-0.5F	0.62
ZnO/H-ZSM-5-1F	0.71
ZnO/H-ZSM-5-2F	0.62
ZnO/H-ZSM-5-5F	0.60
ZnO/H-ZSM-5-10F	0.49
ZnO/H-ZSM-5-30F	0.34
ZnO/H-ZSM-5-0.05A	0.60
ZnO/H-ZSM-5-0.1A	0.55
ZnO/H-ZSM-5-0.2A	0.51
ZnO/H-ZSM-5-0.4A	0.36
ZnO/H-ZSM-5-0.2A-1F	0.55
ZnO/H-ZSM-5-0.2A-3F	0.45

[a] Reaction conditions: T = 733 K, W = 2.0 g, $P(CH_3OH)$ = 80 kPa, F(total) = 25 cm^3 min^{-1}, time on stream, 2 h.

12. TG profiles of some typical catalysts

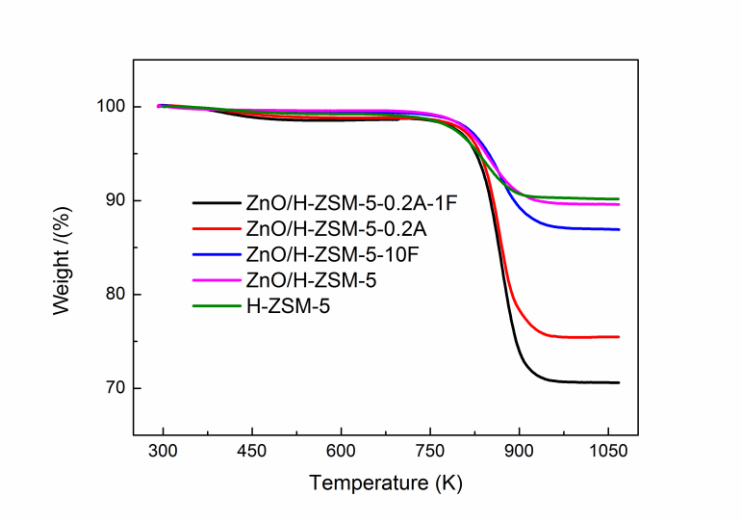

Figure S8. TG profiles of some typical catalysts after deactivation.

13. Pore parameters for some typical catalysts before and after reactions

Table S5. Pore parameters for some catalysts before and after reactions for 30 h.

Samples	S_{BET}[a]	S_{micro}[b]	S_{meso}[c]	V_{total}[d]	V_{micro}[e]	V_{meso}[f]
	[m^2 g^{-1}]	[m^2 g^{-1}]	[m^2 g^{-1}]	[cm^3 g^{-1}]	[cm^3 g^{-1}]	[cm^3 g^{-1}]
			Before reaction			
ZnO/H-ZSM-5 (Si/Al = 150)	325	312	9.00	0.15	0.14	0.01
ZnO/H-ZSM-5−10F	321	303	16.7	0.16	0.13	0.03
ZnO/H-ZSM-5−0.2A	341	282	50.5	0.19	0.12	0.07
ZnO/H-ZSM-5−0.2A−1F	326	265	52.9	0.20	0.12	0.08
			After reaction for 30 h			
ZnO/H-ZSM-5 (Si/Al =150)	7.9	4.5	2.9	0.01	0.002	0.0017
ZnO/H-ZSM-5−10F	120	105	10.9	0.07	0.046	0.02
ZnO/H-ZSM-5−0.2A	192	156	33.6	0.13	0.068	0.06
ZnO/H-ZSM-5−0.2A−1F	230	186	37.2	0.16	0.088	0.07

[a]BET surface area. [b]Micropore surface area evaluated by the *t*-plot method. [c]Mesopore surface evaluated by the BJH method. [d]Total pore volume. [e]Micropore volume evaluated by the *t*-plot method. [f]Mesopore volume evaluated by the BJH method.