

Electronic Supplementary Information (ESI)

## Supporting Information For

### Highly Active and Stable Zn/ZSM-5 Zeolite Catalyst for the Conversion of Methanol to Aromatics: Effect of Supports Morphology

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As the **Supporting Information** of the manuscript “Highly Active and Stable Zn/HZSM-5 Zeolite Catalyst for the Conversion of Methanol to Aromatics: Effect of Supports Morphology”, following materials are provided:

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- (1) The molar composition of ZSM-5 zeolite supports and Si/Al ratios of obtained products.
- (2) Reduction rate of catalyst lifetime with the loading of Zn species, as comparing with the support.
- (3) SEM image (a) and TEM image (b) of Sphere-ZSM-5: (a) overview, and (b) individual crystal; TEM images of Hollow-ZSM-5: (c) overview, (d) fringe in shell.
- (4) (I) Nitrogen adsorption/desorption isotherms and (II) pore size distribution of HZSM-5 and Zn-based HZSM-5 zeolites: (a) Hollow-ZSM-5; (b) Hollow-IM; (c) Sphere-ZSM-5; (d) Sphere-IM; (e) Rod-ZSM-5; (f) Rod-IM; (g) Coffin-ZSM-5; and (h) Coffin-IM.
- (5)  $^{27}\text{Al}$  MAS NMR spectra of ZSM-5 samples: (a) Hollow-ZSM-5, (b) Sphere-ZSM-5, (c) Rod-ZSM-5 (21), and (d) Coffin-ZSM-5.
- (6) Correlation between the medium acid sites and the increase of Lewis sites.
- (7) SEM images of (a) pure ZnO, (b) ZnO macro-particles and (c) ZnO nano-particles in Sphere-IM. (The inset in (b) was the HRTEM image of ZnO macro-particles)
- (8) The variation of carbon mass balances with the time on stream over different catalysts.
- (9) TG curves of Zn/ZSM-5 catalysts with different morphologies: (a) Coffin-IM, (b) Rod-IM, (c) Sphere-IM, and (d) Hollow-IM.

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Table S1. The molar composition of ZSM-5 zeolite supports and Si/Al ratios of obtained products.

Samples	The molar composition	Si/Al <sup>c</sup>
Rod-ZSM-5 <sup>a</sup>	SiO <sub>2</sub> : 0.014 Al <sub>2</sub> O <sub>3</sub> : 0.05Na <sub>2</sub> O: 31H <sub>2</sub> O: 0.15NBA: 0Na <sub>2</sub> -EDTA	31.2
Coffin-ZSM-5 <sup>b</sup>	SiO <sub>2</sub> : 0.014 Al <sub>2</sub> O <sub>3</sub> : 0.09Na <sub>2</sub> O: 31H <sub>2</sub> O: 0.03NBA: 0Na <sub>2</sub> -EDTA	33.7
Sphere-ZSM-5 <sup>b</sup>	SiO <sub>2</sub> : 0.014 Al <sub>2</sub> O <sub>3</sub> : 0Na <sub>2</sub> O: 31H <sub>2</sub> O: 0.15TPAOH: 0Na <sub>2</sub> -EDTA	32.4
Hollow-ZSM-5 <sup>a</sup>	SiO <sub>2</sub> : 0.014 Al <sub>2</sub> O <sub>3</sub> : 0.09Na <sub>2</sub> O: 31H <sub>2</sub> O: 0.15NBA: 0.08Na <sub>2</sub> -EDTA	31.5

a: Without the addition of 1 wt.% silicalite-1 seeds into synthesis gel;

b: With the addition of 1 wt.% silicalite-1 seeds into synthesis gel.

c: Si/Al of obtained products, which was quantified by ICP.

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Table S2. Reduction rate of catalyst lifetime with the loading of Zn species, as comparing with the support.

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Samples	Reduction rate of catalyst life <sup>a</sup> (%)
Rod-IM	46.43
Coffin-IM	30.77
Sphere-IM	27.46
Hollow-IM	16.58

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a: Calculated from  $\frac{t_{\text{HZSM-5}} - t_{\text{Zn/HZSM-5}}}{t_{\text{HZSM-5}}} \times 100\%$ .

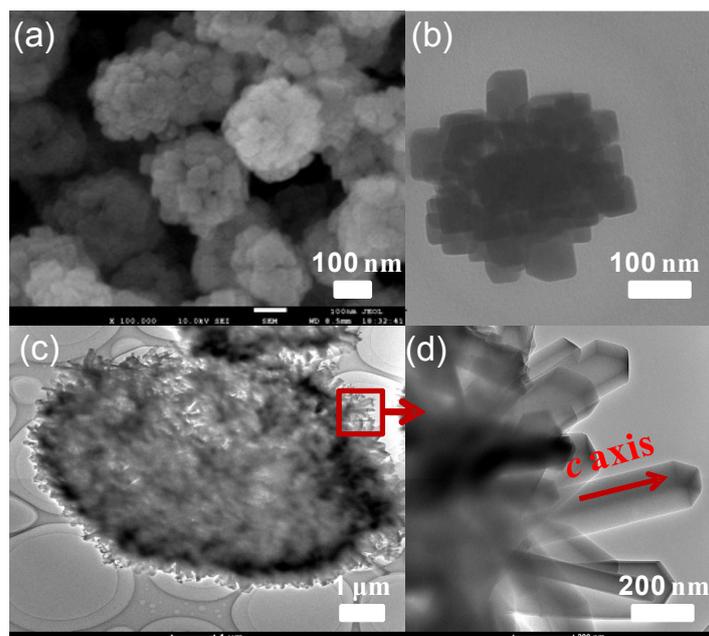


Figure S1. SEM image (a) and TEM image (b) of Sphere-ZSM-5: (a) overview, and (b) individual crystal; TEM images of Hollow-ZSM-5: (c) overview, (d) fringe in shell.

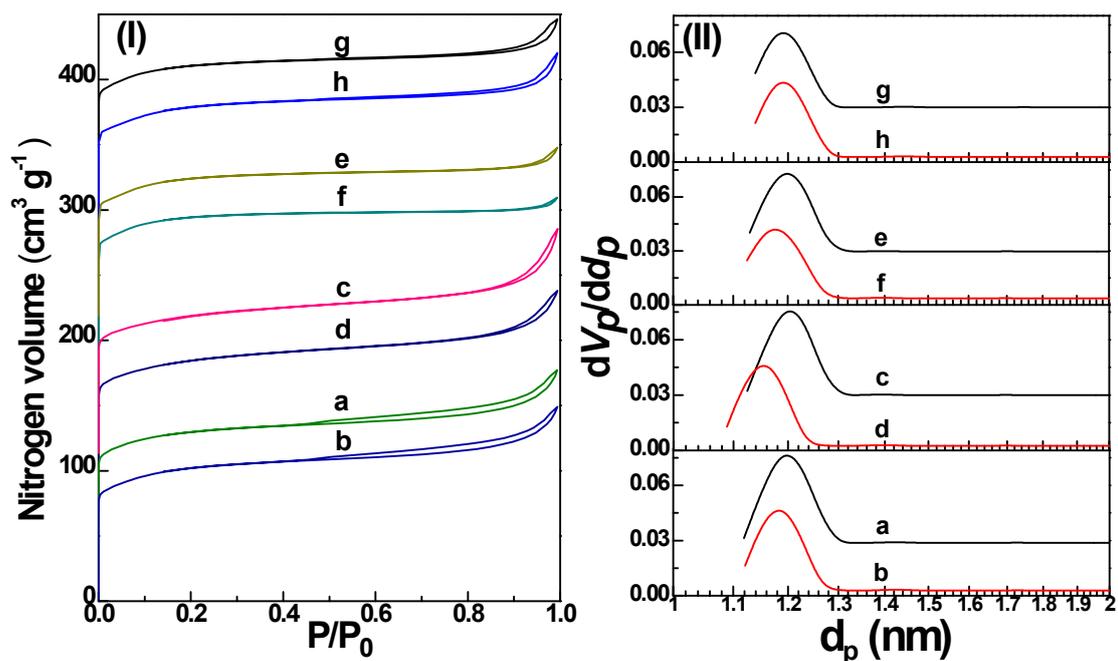


Figure S2. (I) Nitrogen adsorption/desorption isotherms and (II) pore size distribution of HZSM-5 and Zn-based HZSM-5 zeolites: (a) Hollow-ZSM-5; (b) Hollow-IM; (c) Sphere-ZSM-5; (d) Sphere-IM; (e) Rod-ZSM-5; (f) Rod-IM; (g) Coffin-ZSM-5; and (h) Coffin-IM.

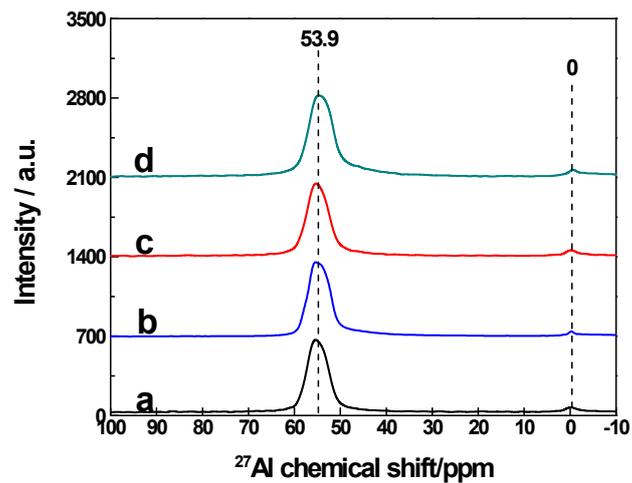


Figure S3.  $^{27}\text{Al}$  MAS NMR spectra of ZSM-5 samples: (a) Hollow-ZSM-5, (b) Sphere-ZSM-5, (c) Rod-ZSM-5 (21), and (d) Coffin-ZSM-5.

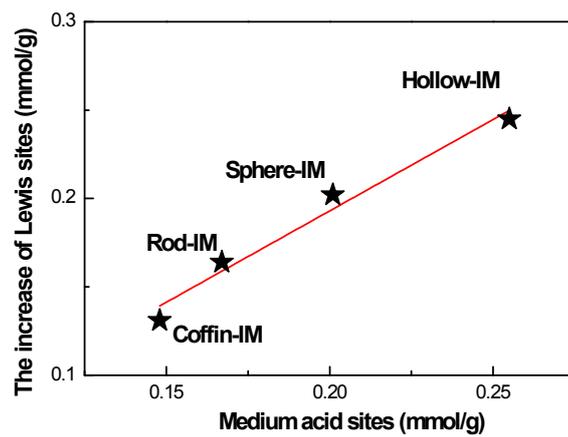


Figure S4. Correlation between the medium acid sites and the increase of Lewis sites.

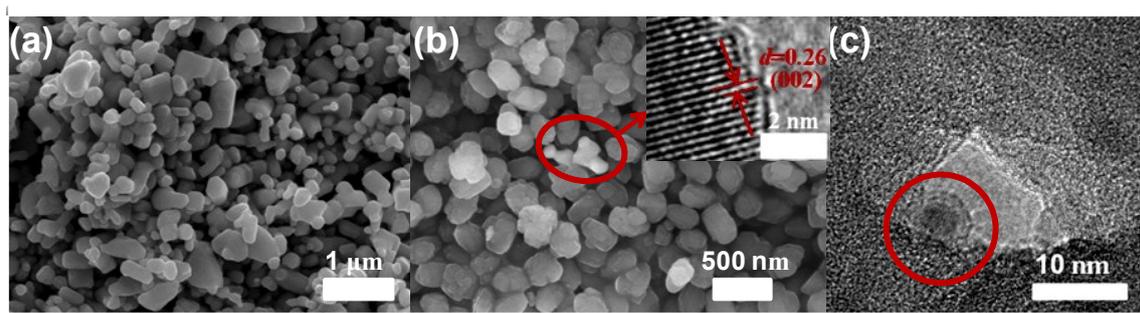


Figure S5. SEM images of (a) pure ZnO, (b) ZnO macro-particles and (c) ZnO nano-particles in Sphere-IM. (The inset in (b) was the HRTEM image of ZnO macro-particles)

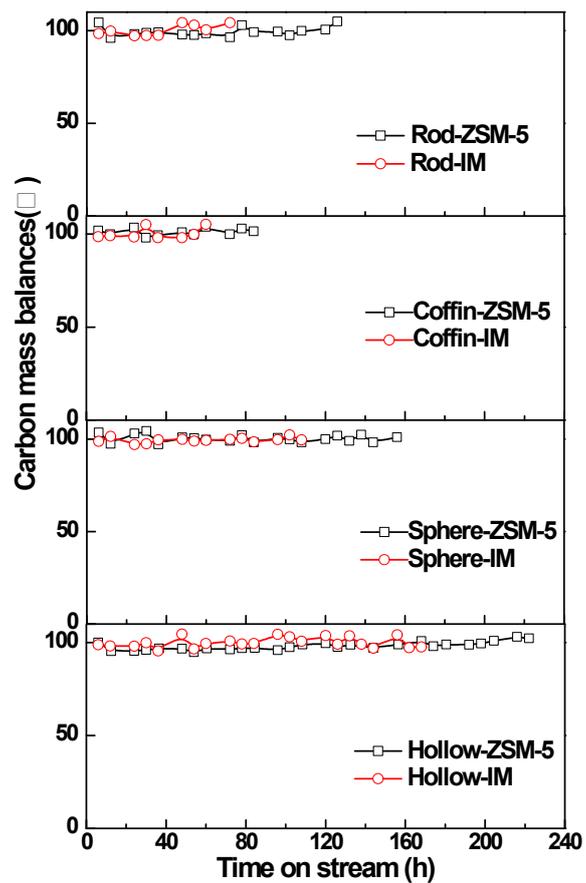


Figure S6. The variation of carbon mass balances with the time on stream over different catalysts.

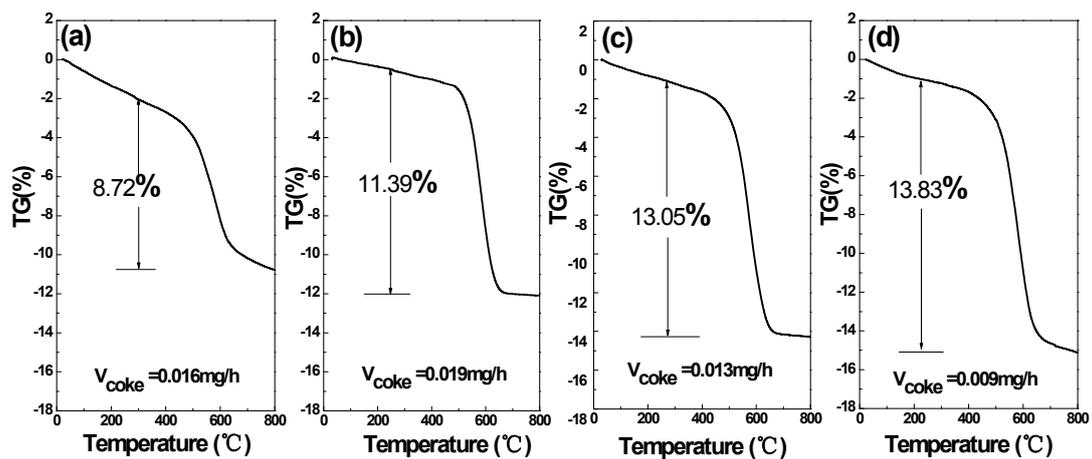


Figure S7. TG curves of four used Zn/ZSM-5 catalysts after MTA process: (a) Coffin-IM, (b) Rod-IM, (c) Sphere-IM, and (d) Hollow-IM.