

## Supplementary Information

# Novel ordered hierarchical ZSM-5 zeolite with interconnected macro-meso-microporosity for enhanced methanol to aromatics

Youhe Wang<sup>a,\*</sup>, Tingting Li<sup>a</sup>, Yuqing Ouyang<sup>a</sup>, Jie Zhong<sup>a</sup>, Yu Zhang<sup>a</sup>, Xiaoyun Xiong<sup>b</sup>, Qingxun Hu<sup>b</sup>, Jiacheng

Deng<sup>a</sup>, Hongman Sun<sup>a,\*</sup>, Zifeng Yan<sup>a,\*</sup>

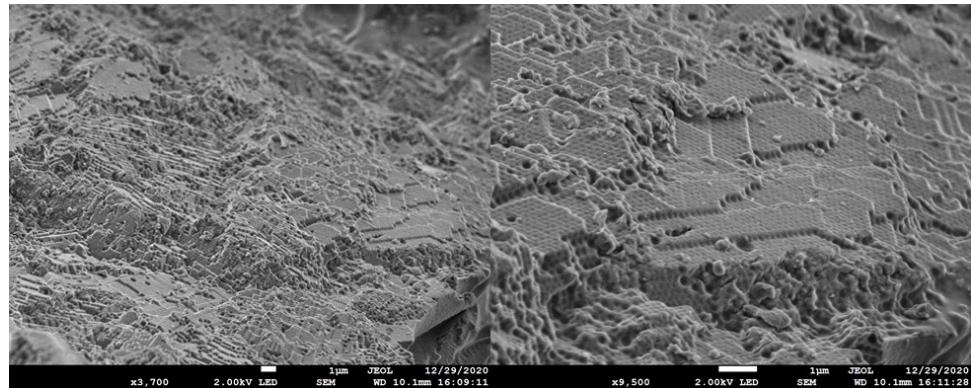
<sup>a</sup> State Key Laboratory of Heavy Oil Processing, College of Chemistry and Chemical Engineering, China

University of Petroleum, Qingdao 266580, China

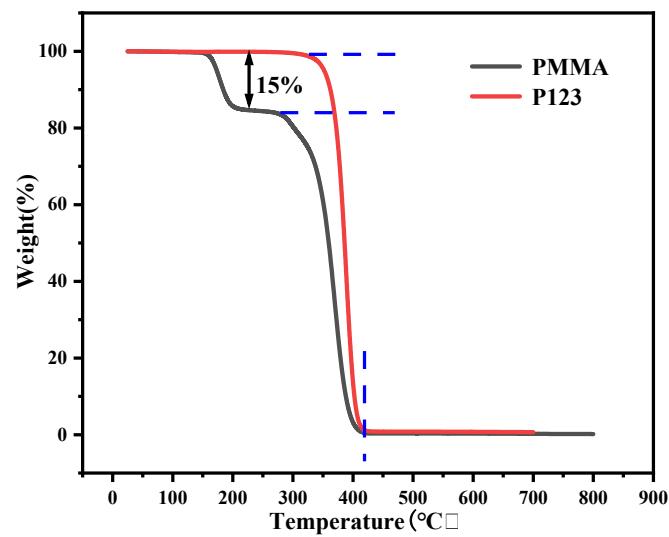
<sup>b</sup> Lanzhou Petrochemical Research Center, PetroChina, Lanzhou, 730060, China

\*Co-corresponding authors.

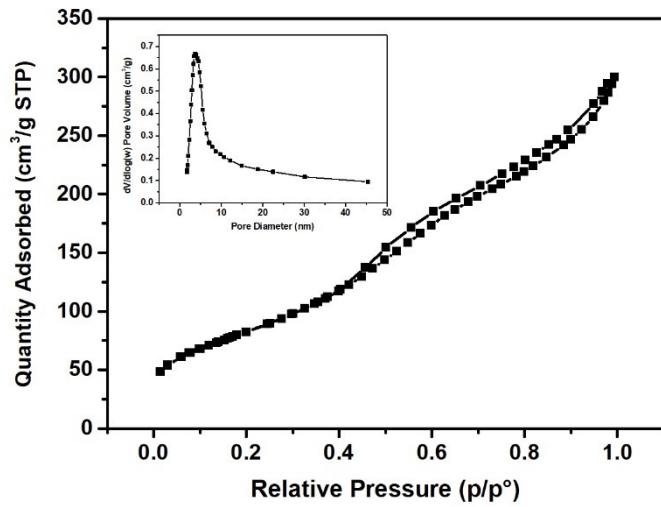
Emails: yhewang@upc.edu.cn; hongman.sun@upc.edu.cn; zfyancat@upc.edu.cn



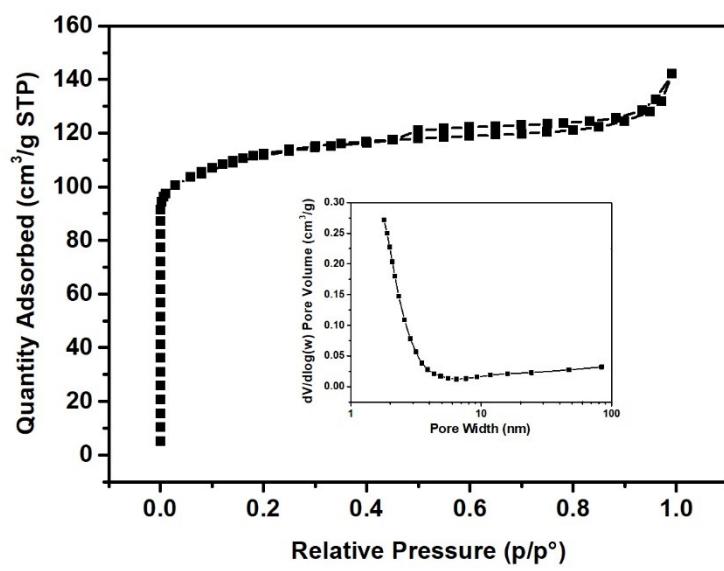
**Fig. S1.** SEM images of PMMA/P123/SiO<sub>2</sub> composite after initial carbonization.



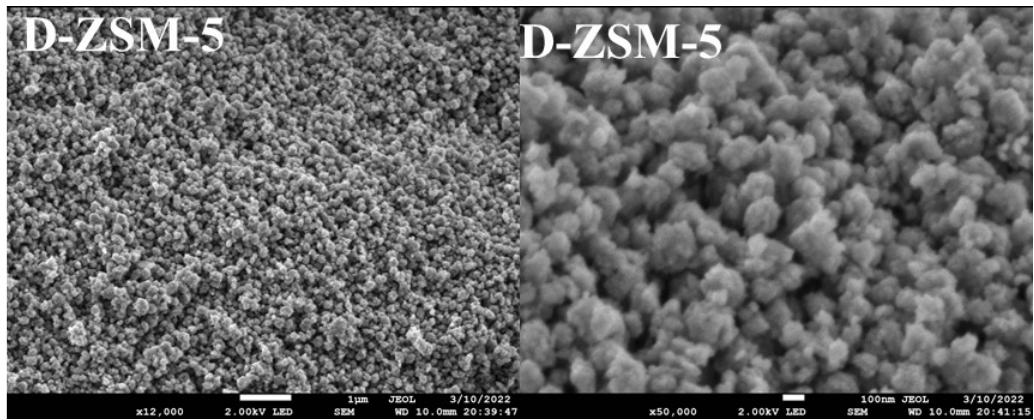
**Fig. S2.** TGA curve of PMMA and P123.



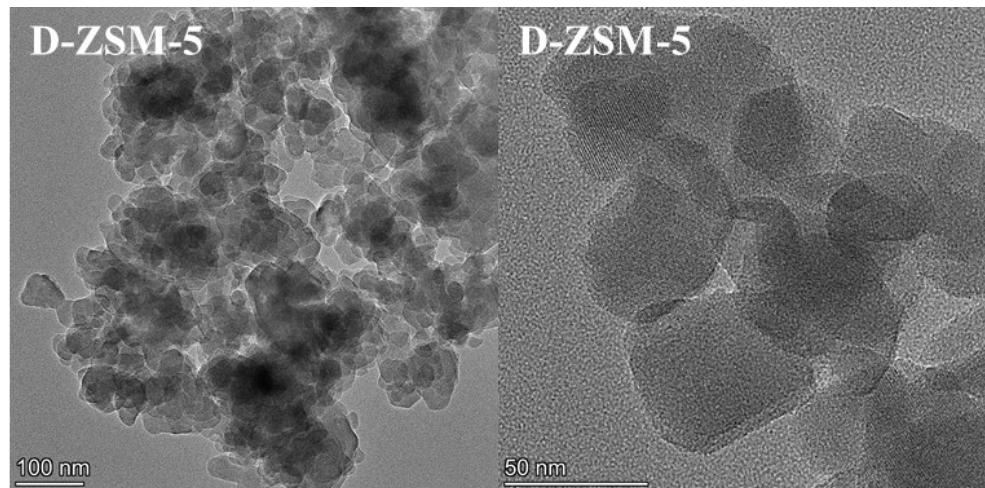
**Fig. S3.** N<sub>2</sub> adsorption/desorption isotherms (c), and BJH pore size distribution (b) of 3DOMmC.



**Fig. S4.** N<sub>2</sub> adsorption/desorption isotherms (c), and BJH pore size distribution (b) of nano-ZSM-5.



**Fig. S5. SEM images of D-ZSM-5.**



**Fig. S6. TEM images of D-ZSM-5**

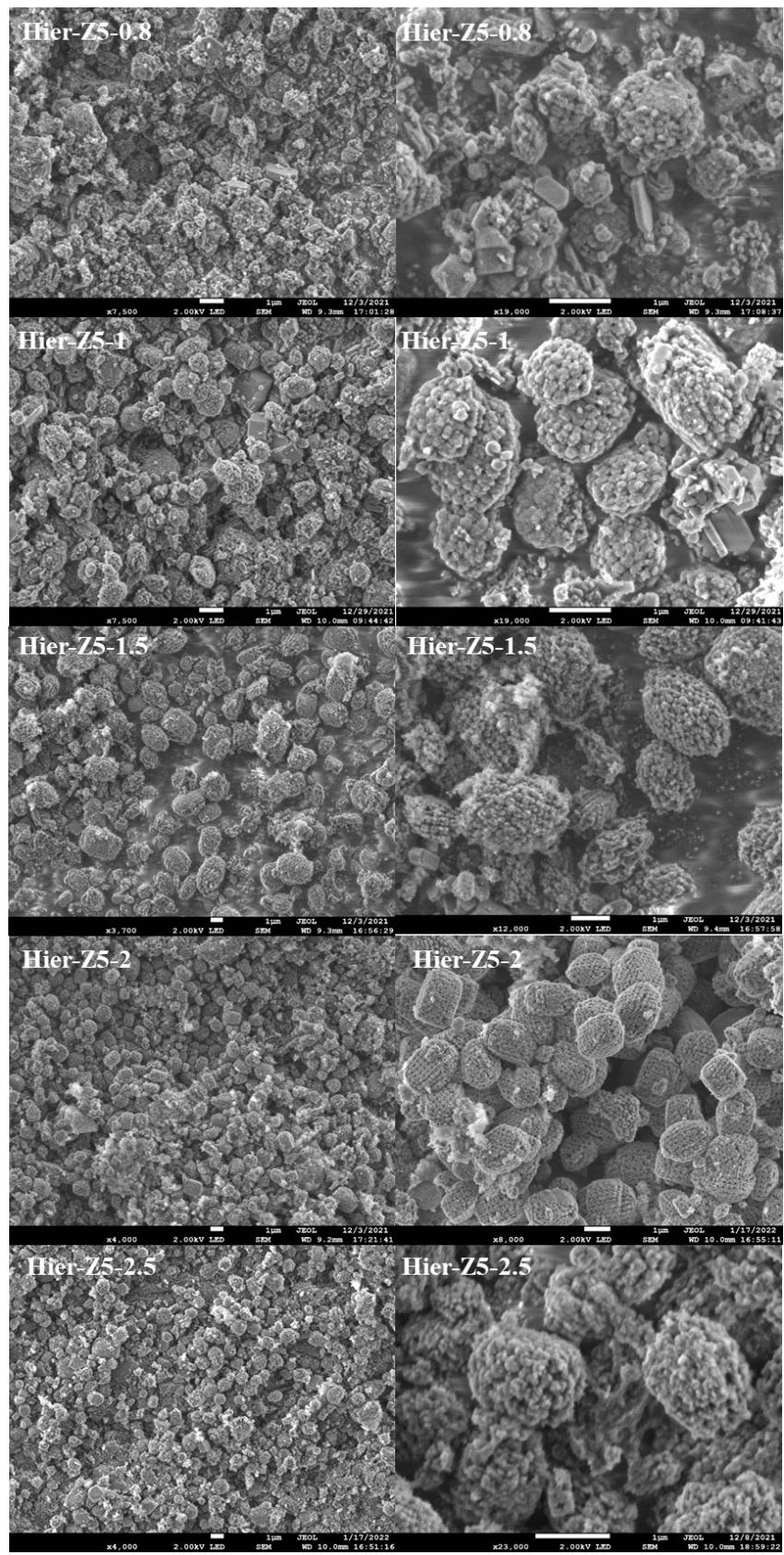
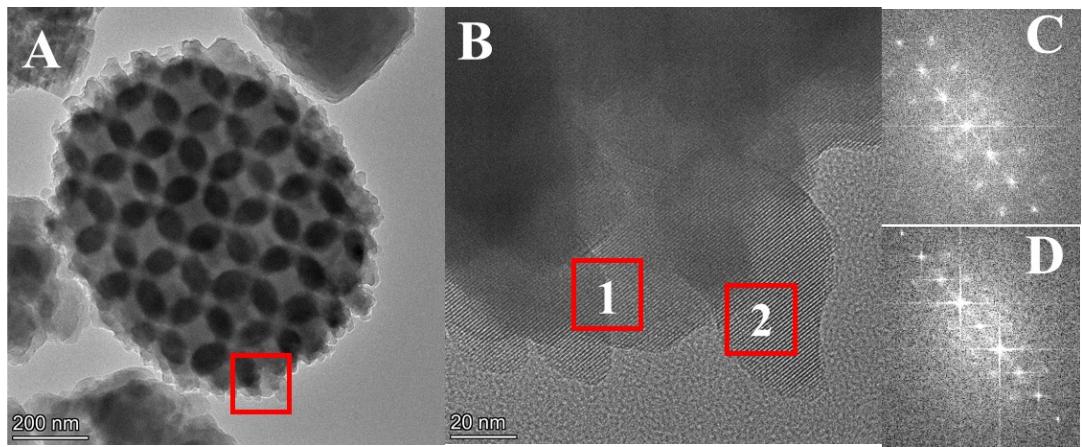
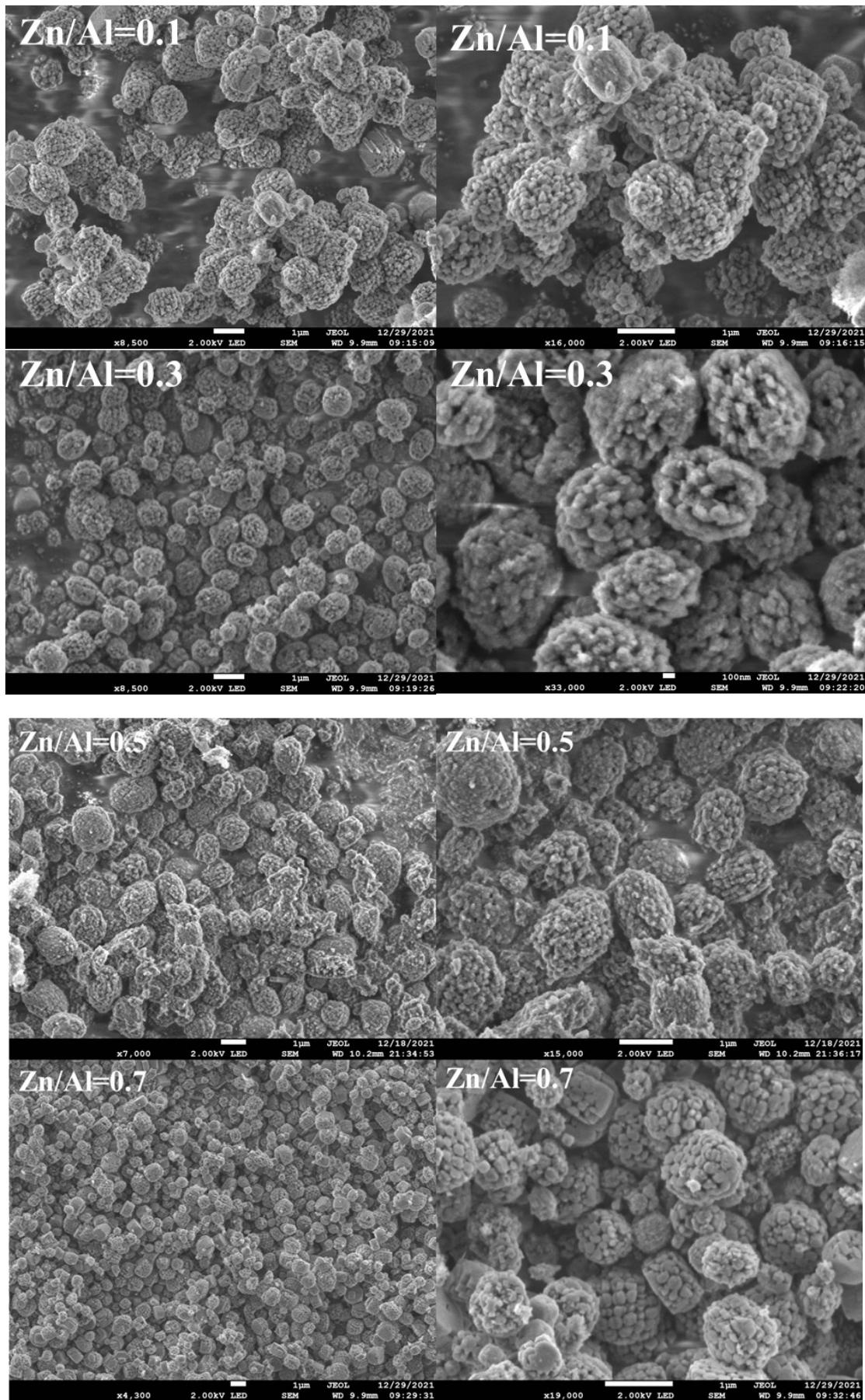


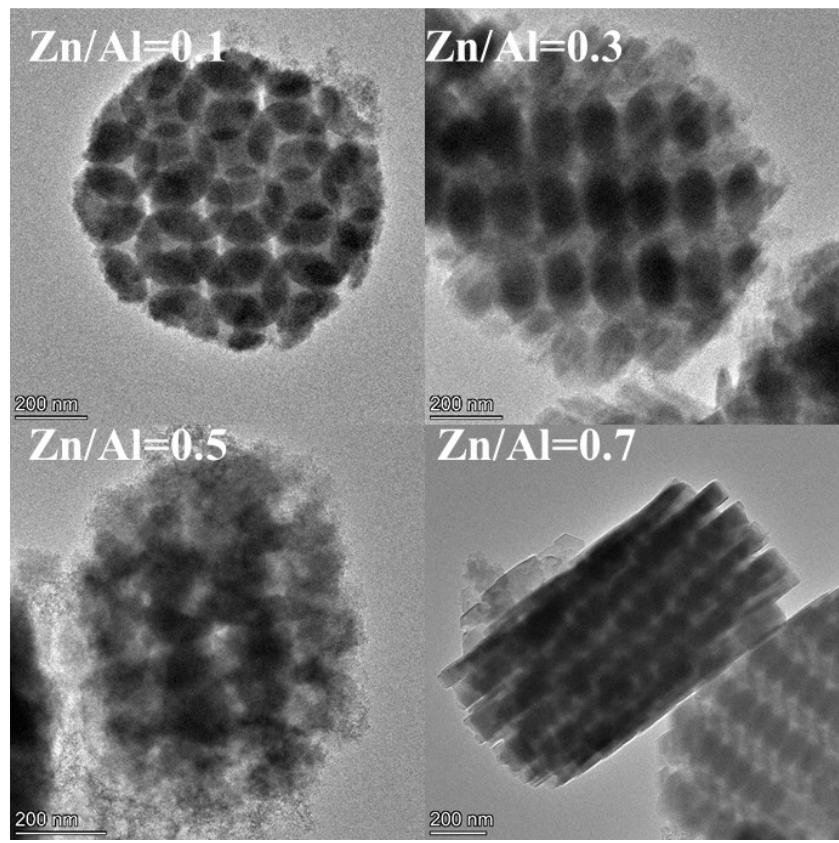
Fig. S7. SEM images of 3DOMmC-Z5 with different  $m(3DOMmC)/m(TEOS)$ .



**Fig. S8. (A)**TEM image of 3DOMmC-Z5-1.5, **(B)** HRTEM image of the area indicated by the red box in (A),  
**(C-D)** Corresponding FFT patterns from zone 1-C and zone 2-D



**Fig. S9. SEM images of 3DOMmC-Zn-Z5.**



**Fig. S10. TEM images of 3DOMmC-Zn-Z5.**

**Table S1 Pore structure parameters of 3DOMmC.**

Samples	$S_{\text{BET}}/(\text{m}^2/\text{g})$	$S_{\text{micro}}/(\text{m}^2/\text{g})$	$S_{\text{meso}}/(\text{m}^2/\text{g})$	$V_t/(\text{cm}^3/\text{g})$	$V_{\text{micro}}/(\text{cm}^3/\text{g})$	$V_{\text{meso}}/(\text{cm}^3/\text{g})$
3DOMmC	352	35	307	0.441	0.021	0.420

<sup>a</sup>  $S_{\text{BET}}$  (total surface area) calculated by applying the BET equation using the linear part ( $0.05 < P/P^0 < 0.30$ ) of the adsorption isotherm.

<sup>b</sup>  $V_{\text{total}}$  (total pore volume) calculated by single point adsorption total pore volume of pores at  $P/P^0 = 0.99$ .

<sup>c</sup>  $S_{\text{micro}}$  (micropore area) and  $V_{\text{micro}}$  (micropore volume) calculated using the t-plot method.

**Table S2 Pore structure parameters of samples.**

Sample	$S_{\text{BET}}/(\text{m}^2/\text{g})$	$S_{\text{micro}}/(\text{m}^2/\text{g})$	$S_{\text{meso}}/(\text{m}^2/\text{g})$	$V_t/(\text{cm}^3/\text{g})$	$V_{\text{micro}}/(\text{cm}^3/\text{g})$	$V_{\text{meso}}/(\text{cm}^3/\text{g})$
3DOMmC-Z5-0.8	395	183	212	0.325	0.098	0.227
3DOMmC-Z5-1.0	362	186	176	0.277	0.100	0.170
3DOMmC-Z5-1.5	372	170	202	0.319	0.091	0.228
3DOMmC-Z5-2.0	395	161	235	0.378	0.086	0.292
3DOMmC-Z5-2.5	422	147	275	0.424	0.079	0.345
3DOMmC-Zn-Z5-0.1	411	167	244	0.358	0.090	0.268
3DOMmC-Zn-Z5-0.3	399	182	217	0.315	0.097	0.218
3DOMmC-Zn-Z5-0.5	396	138	258	0.326	0.076	0.250
3DOMmC-Zn-Z5-0.7	373	199	173	0.244	0.107	0.137

<sup>a</sup>  $S_{\text{BET}}$  (total surface area) calculated by applying the BET equation using the linear part ( $0.05 < P/P^0 < 0.30$ ) of the adsorption isotherm.

<sup>b</sup>  $V_{\text{total}}$  (total pore volume) calculated by single point adsorption total pore volume of pores at  $P/P^0 = 0.99$ .

<sup>c</sup>  $S_{\text{micro}}$  (micropore area) and  $V_{\text{micro}}$  (micropore volume) calculated using the t-plot method.

**Table S3 Products Distribution of MTA reactions.**

Samples	B	T	X	BTX	C <sub>9+</sub>	Aromatics
Zn/nano-Z5	0.87%	5.04%	17.50%	23.41%	11.85%	35.26%
JZ-3DOMmC-Z5	0.83%	4.83%	20.65%	26.31%	12.43%	38.74%
3DOMmC-Z5	0.97%	4.67%	18.37%	24.01%	12.18%	36.19%
3DOMmC-Zn-Z50.3	0.99%	4.73%	18.41%	24.13%	12.56%	37.69%
3DOMmC-Zn-Z5-0.5	1.17%	5.82%	22.91%	29.90%	13.65%	43.55%
3DOMmC-Zn-0.7	0.99%	4.96%	20.59%	26.54%	12.98%	39.52%