

Supporting information for:

Catalytic cracking of endothermic fuels over meso- HZSM-5/MCM-41 coatings

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Synthesis of MCM-41 by recrystallization of desilicated solution

A series of MCM-41 zeolite powder was prepared by recrystallization of desilicated solution with additional aluminium nitrate and iron nitrate. Firstly, 0.4 g of CTAB was dispersed in 10 mL of 0.6 mol/L TEAOH solution. ZC-P tube was filled with the obtained solution, and followed by treated in an oven at 120 °C for 24 h after being sealed. Then, the tube was quenched and the desilication solution was poured out. x mmol of aluminum nitrate and y mmol of ferric nitrate was added into per gram of desilication solution and the pH value of the solution was adjusted to 8.5 by hydrochloric acid, and then the solution (as synthesis gel) was transferred into a Teflon-lined autoclave and recrystallized at 120 °C for 24 h. Finally, the powder was recovered by centrifugation, washed with deionized water, dried overnight at room temperature and calcined at 550 °C for 5 h. The prepared MCM-41 samples are denoted as M41-P, M41-Al, M41-Al/Fe and M41-Fe corresponding to $x=0, y=0$; $x=0.01, y=0$; $x=0.005, y=0.005$; $x=0, y=0.01$; respectively.

Synthesis of ZC-M41 coating

ZC-M41 coating were prepared via sequential desilication and recrystallization of ZC-P without addition of Al or Fe species. The procedure was the same as the synthesis of ZC-Al, ZC-Al/Fe and ZC-Fe, except for the addition of Al or Fe species before recrystallization.

Table S1. Chemical components of MCM-41 powder and ZC-Al/Fe coating.

Samples	Si/Al	Si/Fe	Al/Fe
M41-P ^a	∞	∞	/
M41-Al ^a	51	∞	∞
M41-Al/Fe ^a	102	101	1
M41-Fe ^a	∞	49	0
HZSM-5 in ZC-Al/Fe ^b	57	∞	∞
MCM-41 in ZC-Al/Fe ^b	97	102	1

^a measured by ICP. ^b measured by EDX.

Table S2. Catalytic performance of supercritical *n*-dodecane cracking over hierarchical HZSM-5 coatings^a.

Samples	Reaction temperature (°C)	Load amount (mg·cm ⁻²)	Initial conversion (%)	Average conversion (%)	r_d (%)	Reference
ZC-Al/Fe	500	3.75	58.90	54.05	14.6	/
ZC-M41	500	3.74	43.36	33.51	32.2	/
HZC-0.50	550	1.61	33.0	31.7	5.9	Zhang et al.[1]
HZC-0.2P	500	5.56	52.5	44.41	21.1	Liu et al.[2]
HZM-140	550	4.20	ca. 65	50.1	32.1	Li et al.[3]
MZC-V0.2	500	2.64	ca. 10.6	/	27.2	Liu et al.[4]
HZ-ER	500	5.41	ca. 54	53.32	11.1	Diao et al.[5]
HZ-C16&T	500	5.52	ca. 58	57.97	7.29	Wang et al.[6]
HZCE-62.5-125	500	2.28	55.89	/	/	Wang et al. [7]
HZ-NaOH	550	0.68	ca. 24	/	/	Wang et al.[8]
HZM-C16	550	4.20	ca. 50	ca. 41	ca. 33	Na et al.[9]

^a Reaction condition: 4 MPa, TOS=5 min, feed rate of *n*-dodecane=10 mL/min.

1 **Table 3.** Product mass selectivity (%) of *n*-dodecane cracking over ZC-M41 ^a.

Products	ZC-M41
methane	3.46
ethylene	6.75
ethane	6.87
propane	7.53
propylene	13.95
<i>iso</i> -butane	0.95
<i>n</i> -butane	4.06
<i>trans</i> -2-butene	2.23
<i>iso</i> -butene	3.84
1-butene	5.19
<i>cis</i> -2-butene	1.4
pentene	5.28
<i>n</i> -pentane	4.16
hexene	4.92
<i>n</i> -hexane	3.65
benzene	0.47
heptene	3.44
<i>n</i> -heptane	2.73
toluene	0.71
octene	2.36
<i>n</i> -octane	2.05
nonene	3.34
<i>n</i> -nonane	2.69
decene	3.12
<i>n</i> -decane	1.84
undecene	1.67
<i>n</i> -undecane	0.83
dodecene	0.51
C ₃ [≡] /C ₃	1.85
C ₄ [≡] / C ₄	2.53
Gas products	56.23
Light olefins	33.36

2 ^a Reaction condition: 4 MPa and 500 °C, TOS=5 min.

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Table S4. Texture properties for ZC-Al/Fe before and after cracking reaction.

Samples	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	V_t ($\text{cm}^3 \cdot \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \cdot \text{g}^{-1}$)	Mass loading ($\text{mg} \cdot \text{cm}^{-2}$)
ZC-Al/Fe	796	0.840	0.051	3.75 ± 0.12
ZC-Al/Fe-c ^a	775	0.821	0.052	3.71 ± 0.09

^a ZC-Al/Fe coating after cracking and subsequent calcination.

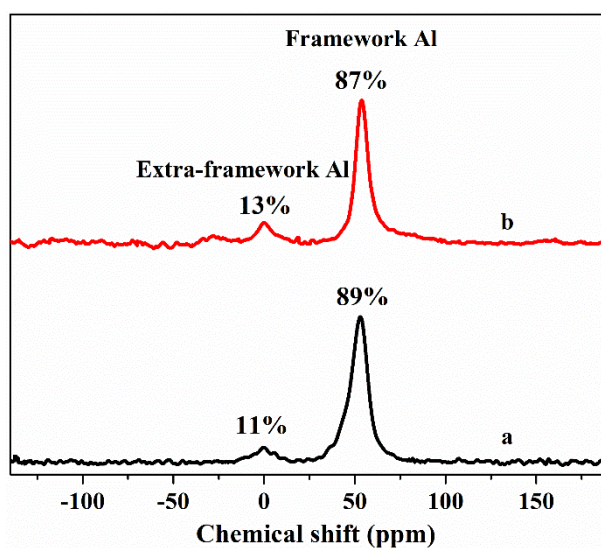


Figure S1. ^{27}Al solid-state MAS NMR spectra for ZC-Al/Fe before (a) and after (b) catalytic cracking.

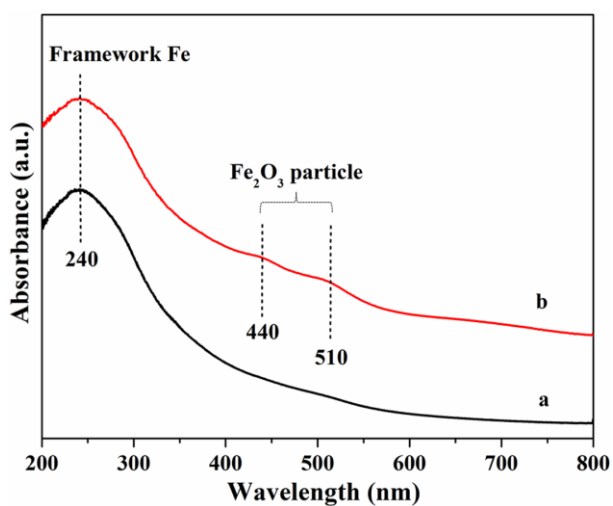


Figure S2. UV-Vis spectra for ZC-Al/Fe before (a) and after (b) catalytic cracking.

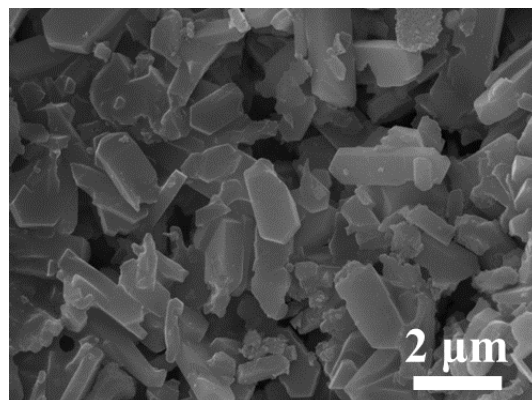


Figure S3. Top-view SEM images of desilicated ZC-P coatings.

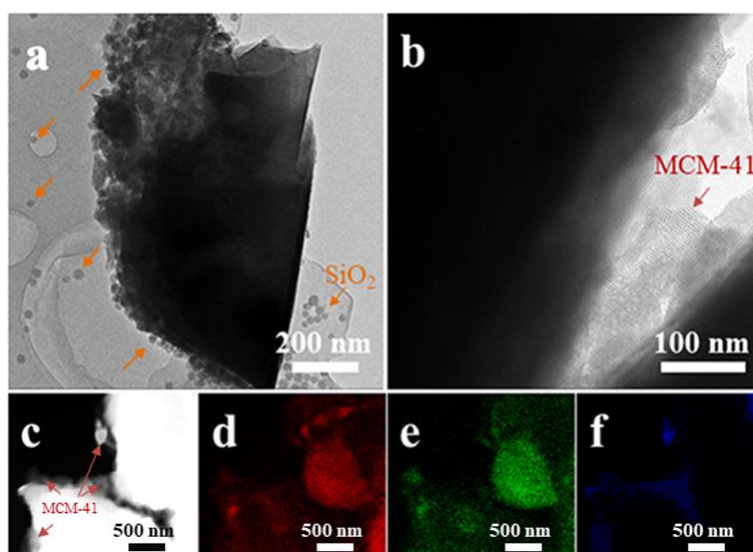


Figure S4. TEM and element mapping images of coatings. (a) TEM image of ZC-P; (b) TEM image, (c) dark-field image, (d) Si, (e) Al and (f) Fe element mapping images of ZC-Al/Fe.

References

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