Experimental and theoretical study of ZrMo-KIT-6 solid acid catalyst with abundant Brønsted acid sites

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Table S1. The strength of Brønsted and Lewis acidity of KIT-6, Zr-KIT-6, Mo-KIT-6, and ZrMo-KIT-6 samples.

Catalysts	150-250 °C (mmol g^{-1})		250-400 °C (mmol g^{-1})		＞400 °C (mmol g^{-1})	
	Brønsted	Lewis	Brønsted	Lewis	Brønsted	Lewis
KIT-6	0	0.015	0	0.016	0	0
Zr-KIT-6	0.003	0.024	0.012	0.041	0.020	0.067
Mo-KIT-6	0	0.029	0	0.021	0	0
ZrMo-KIT-6	0.028	0.043	0.035	0.076	0.034	0.048

Table S2. The TOF of Zr-KIT-6 and ZrMo-KIT-6 based on the strength of Brønsted acidity.

Samples	TOF (＞150 °C)	TOF (150-250 °C)	TOF (250-400 °C)	TOF (150-400 °C)	TOF (＞400 °C)
KIT-6	—	—	—	—	—
Zr-KIT-6	0.27	3.15	0.79	0.63	0.47
Mo-KIT-6	—	—	—	—	—
ZrMo-KIT-6	0.56	1.94	1.55	0.86	1.60

Table S3. Catalytic performance comparison of ZrMo-KIT-6 catalyst with literature date for anisole benzylation with benzyl alcohol.

Catalysts	Anisole (mmol)	Benzyl alcohol (mmol)	Catalyst mass (mg)	Reaction temperature (°C)	Time (min)	Convesion of BA (%)	Selectivity (o-BA:p-BA)	Reference
ZrMo-KIT-6	100	10	50	130	60	100	49:48	This work
Zr-KIT-5(25)	100	10	100	130	240	100	52:47	1
Zr-KIT-5(25)	100	10	100	170	40	100	53:47	1
W_3Sn_5-KIT-6	100	10	100	130	120	29	31:27	2
$W_{14}Sn_{15}$-KIT-6	100	10	100	130	30	100	49:49	2
KIT-6-SO_3H	50	1	50	100	360	80	38:43	3
HBS-16	20	4	100	120	240	100	54:46	4
H-Beta	20	4	100	120	240	41	33:25	4
SBA-15-S	20	4	100	120	240	49	36:30	4
Amberlyst-15	20	4	100	120	240	100	53:47	4
25% TPA/SnO_2	100	30	100	120	90	95	31:40	5
SO_3H-MSF	100	10	100	100	210	50	—	6
Hf-SBA-15	3	0.5	80	120	360	100	58:38	7
WO_3-ZrO_2-CTAB	50	5	100	124	60	60	—	8
ZrPMo-20	100	10	100	150	60	100	45:45	9
MoO_3/ZrPO	100	10	100	150	60	100	44:43	10

Table S4. Acidity of ZrMo-KIT-6 with different ZrMo contents and calcination temperatures.

Catalysts	Acidity from NH_3-TPD ($mmol\ g^{-1}$)	150-250 °C ($mmol\ g^{-1}$)		250-400 °C ($mmol\ g^{-1}$)		＞400 °C ($mmol\ g^{-1}$)	
		Brønsted	Lewis	Brønsted	Lewis	Brønsted	Lewis
0%-ZrMo-KIT-6-700	0	0	0.015	0	0.016	0	0
1%-ZrMo-KIT-6-700	0.14	0.017	0.164	0.007	0.035	0.017	0.034
3%-ZrMo-KIT-6-700	0.38	0.02	0.095	0.022	0.049	0.027	0.049
5%-ZrMo-KIT-6-700	0.64	0.028	0.043	0.035	0.076	0.034	0.048
7%-ZrMo-KIT-6-700	0.48	0.021	0.085	0.025	0.097	0.025	0.042
9%-ZrMo-KIT-6-700	0.25	0.021	0.096	0.022	0.111	0.022	0.039
5%-ZrMo-KIT-6-500	0.53	0.016	0.086	0.023	0.036	0.023	0.039
5%-ZrMo-KIT-6-600	0.60	0.021	0.142	0.031	0.063	0.026	0.049
5%-ZrMo-KIT-6-800	0.36	0.009	0.109	0.024	0.08	0.026	0.040
5%-ZrMo-KIT-6-900	0.02	0.009	0.025	0.003	0.028	0.011	0

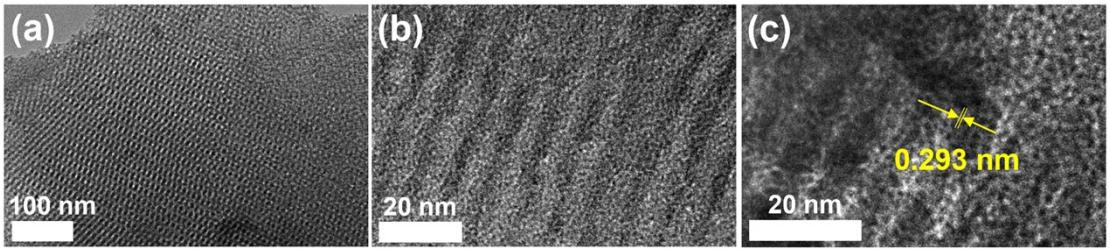

Figure S1. TEM images of **(a)** KIT-6 and HRTEM images of **(b)** Zr-KIT-6 and **(c)** ZrMo-KIT-6.

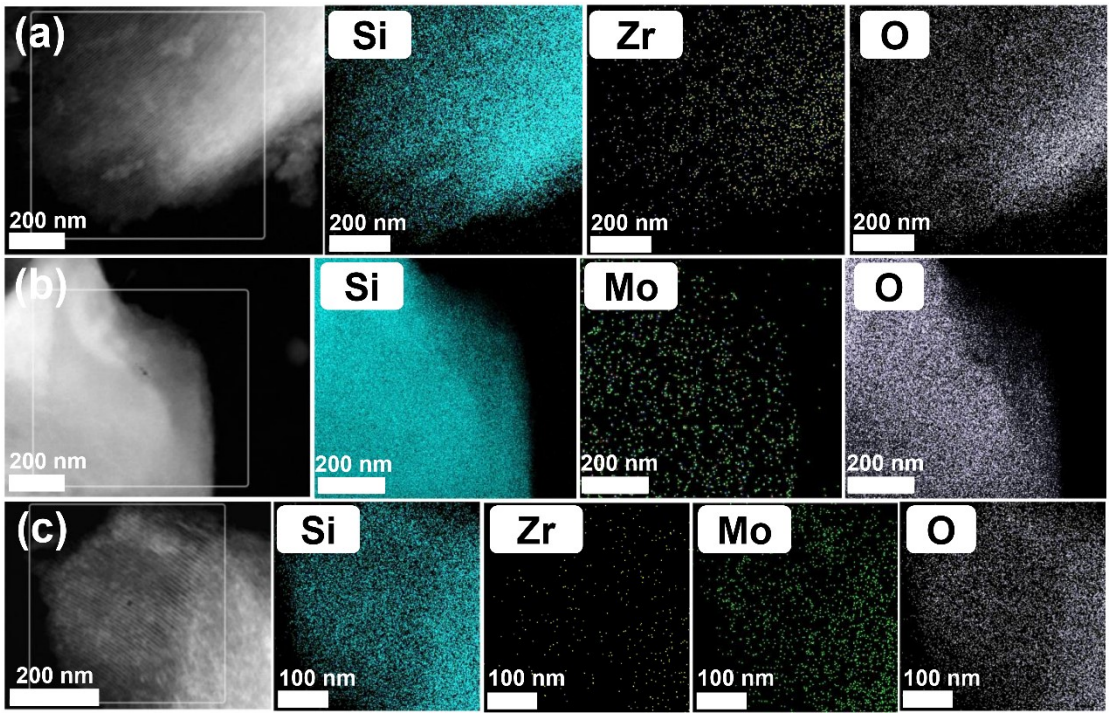

Figure S2. Elemental mapping of **(a)** Zr-KIT-6, **(b)** Mo-KIT-6, and **(c)** ZrMo-KIT-6.

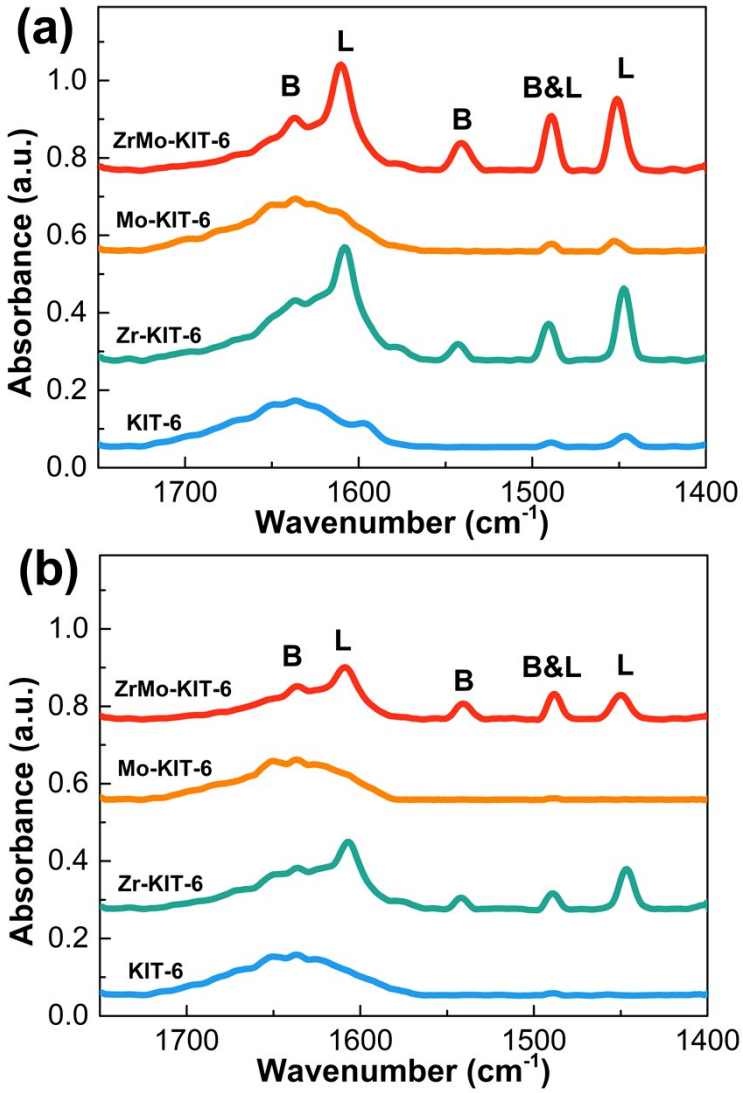

Figure S3. FT-IR spectra for adsorbed pyridine of ZrMo-KIT-6 under different desorption temperature: **(a)** 250 °C and **(b)** 400 °C.

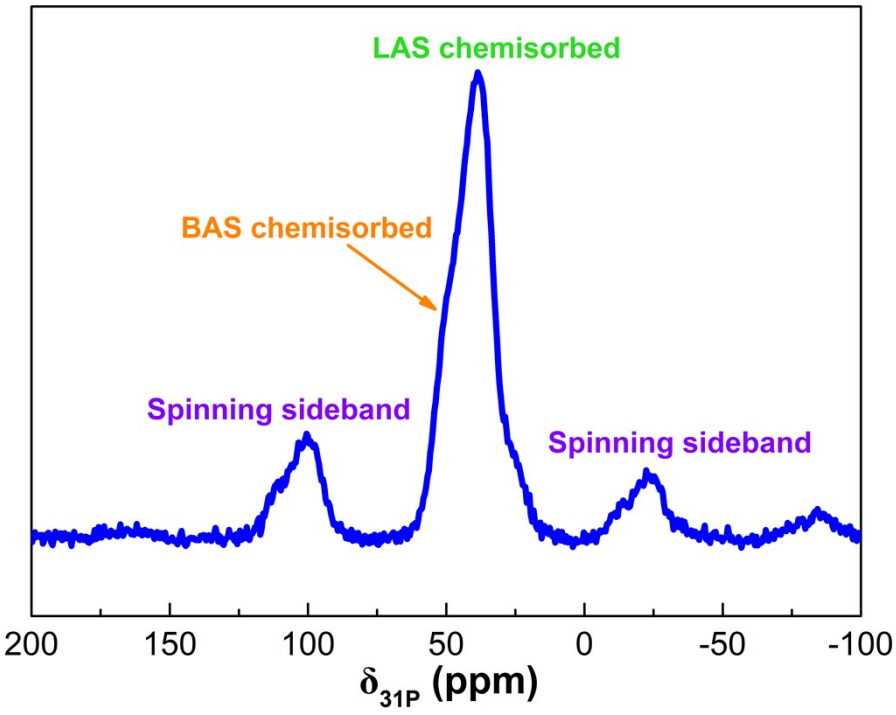

Figure S4. ^{31}P MAS NMR spectra and signal assignment of TMPO adsorbed on ZrMo-KIT-6

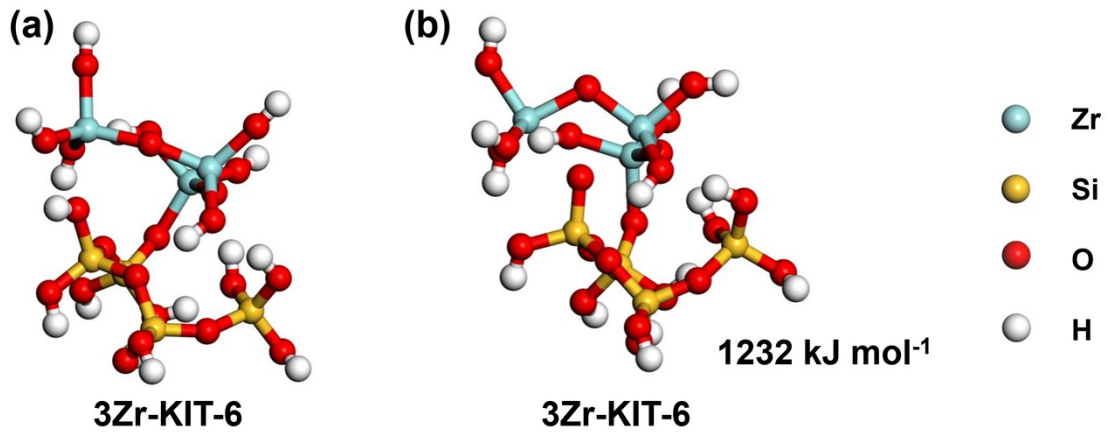

Figure S5. Calculation model of 3Zr-KIT-6 material **(a)** before and **(b)** after removing proton.

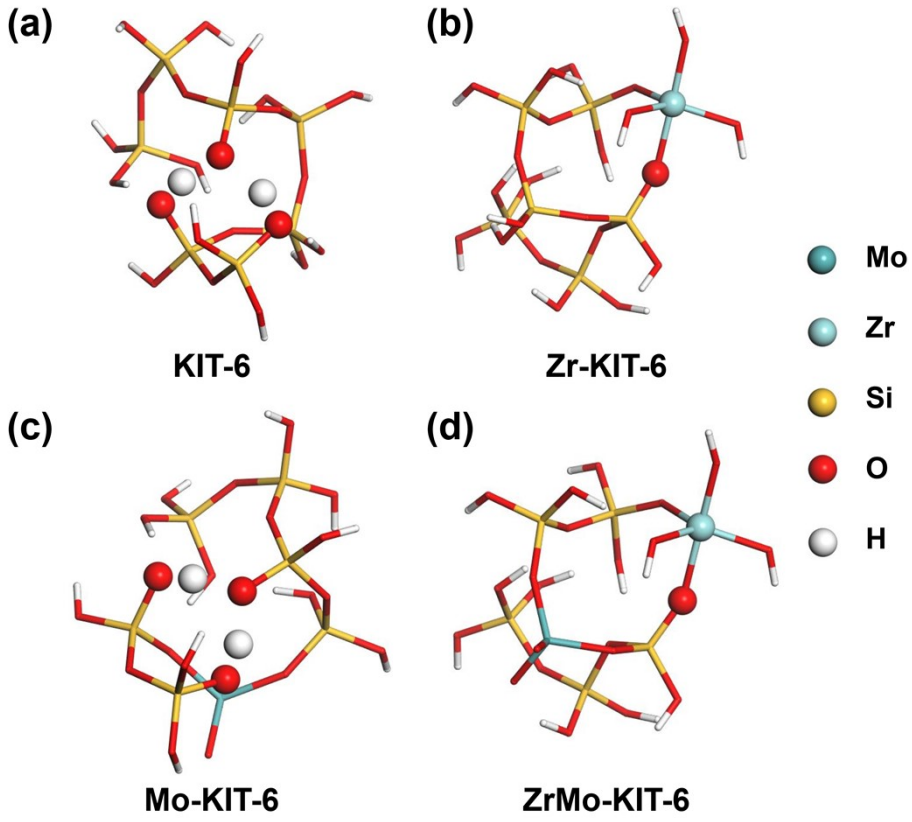

Figure S6. Calculation models after removing proton: **(a)** KIT-6, **(b)** Zr-KIT-6, **(c)** Mo-KIT-6, and **(d)** ZrMo-KIT-6 materials.

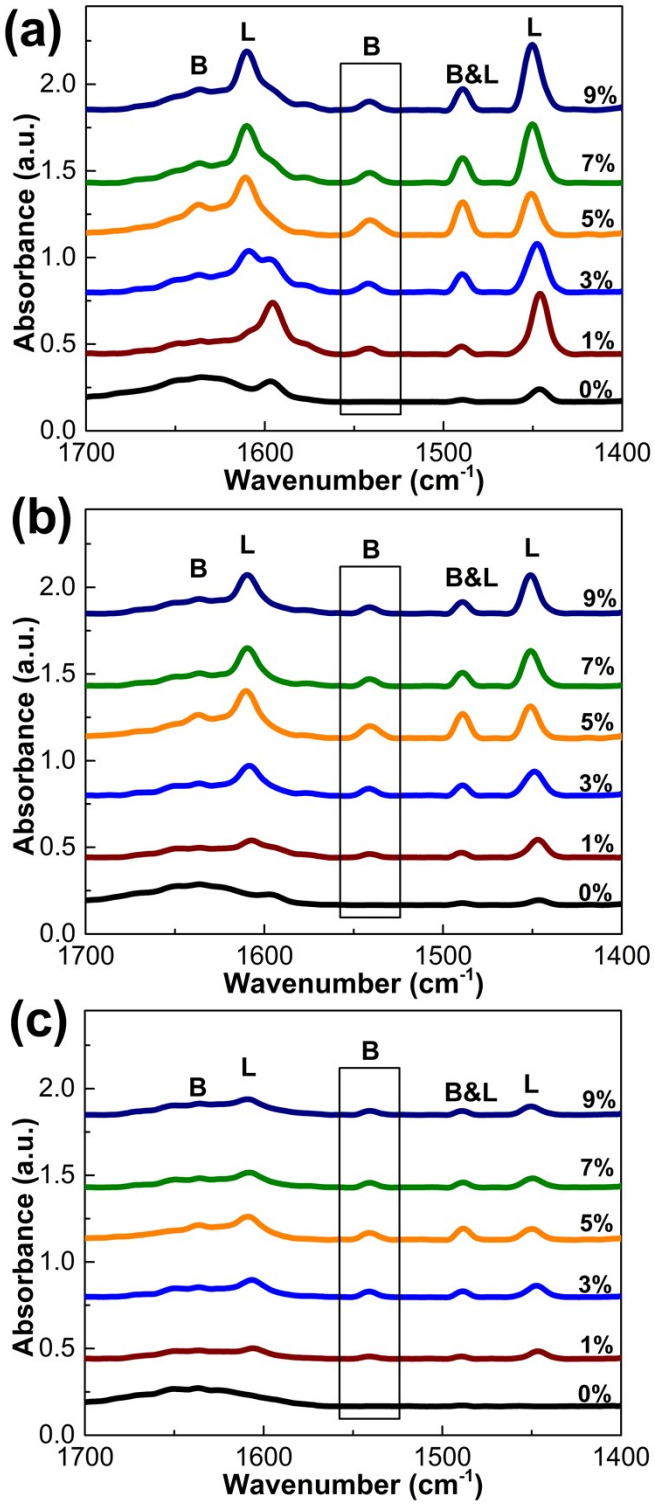

Figure S7. FT-IR spectra for adsorbed pyridine of ZrMo-KIT-6 with different ZrMo contents under different desorption temperature: **(a)** 150 °C, **(b)** 250 °C, and **(c)** 400 °C.

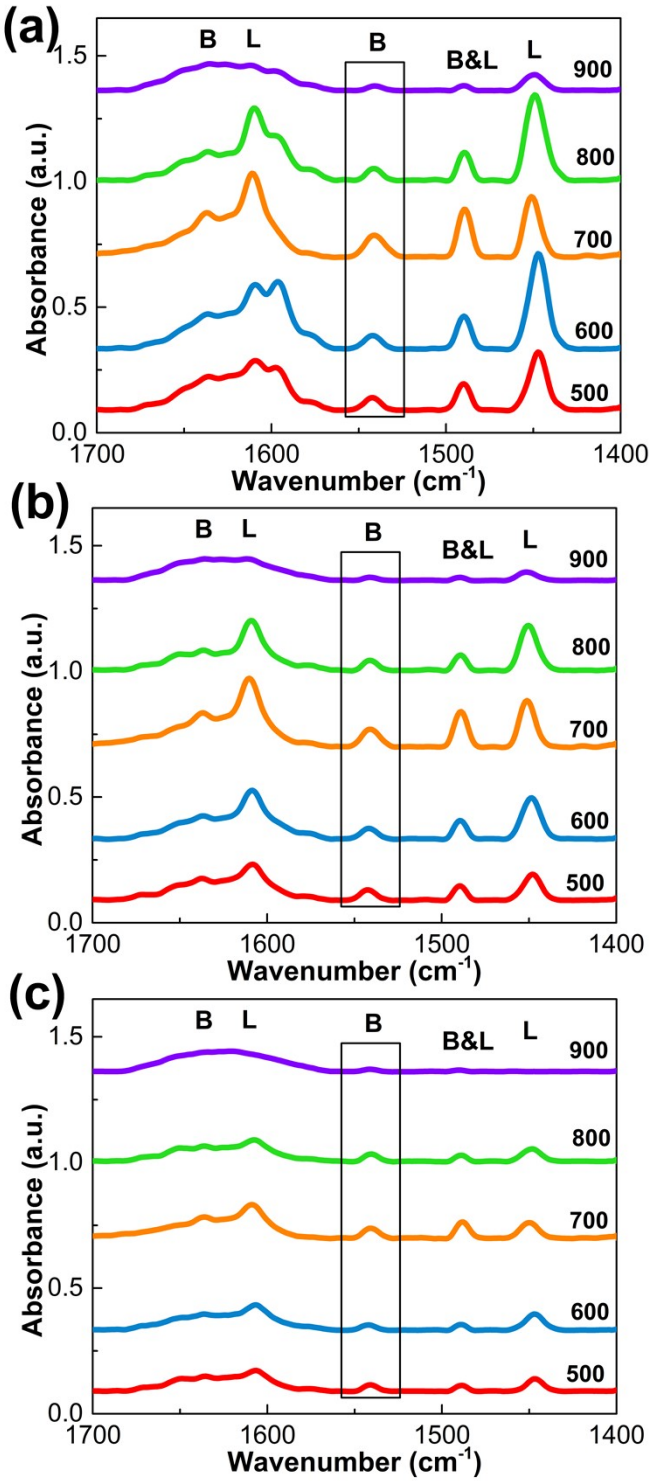

Figure S8. FT-IR spectra for adsorbed pyridine of ZrMo-KIT-6 with different calcination temperatures under different desorption temperature: **(a)** 150 °C, **(b)** 250 °C, and **(c)** 400 °C.

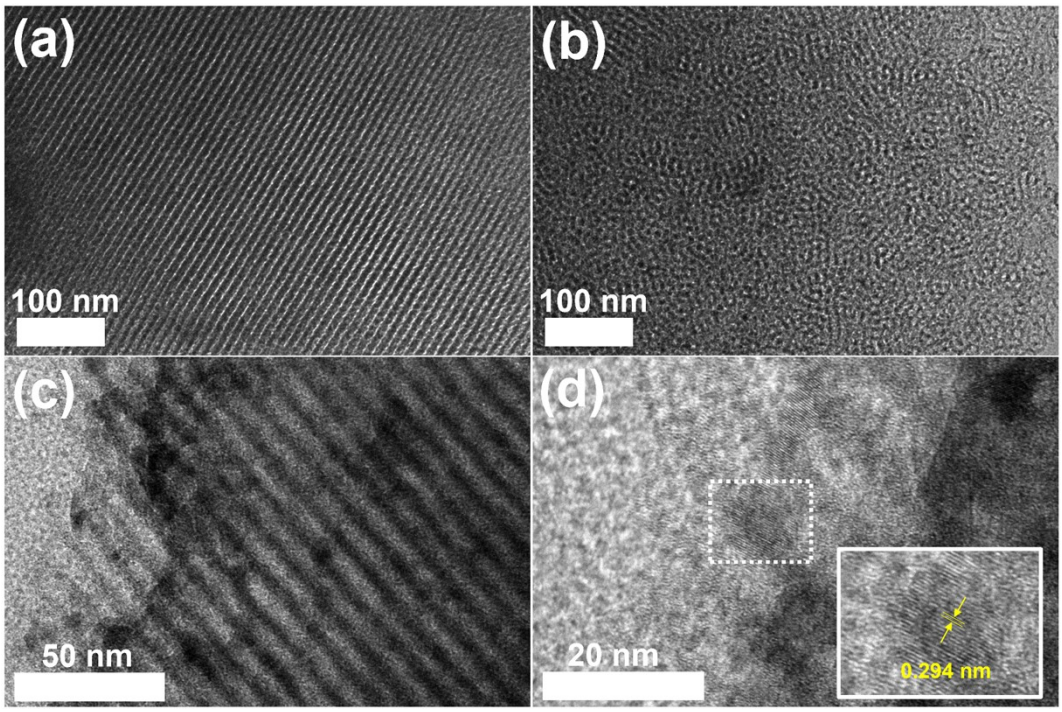

Figure S9. TEM and HETEM images of ZrMo-KIT-6 catalyst after five cycles.

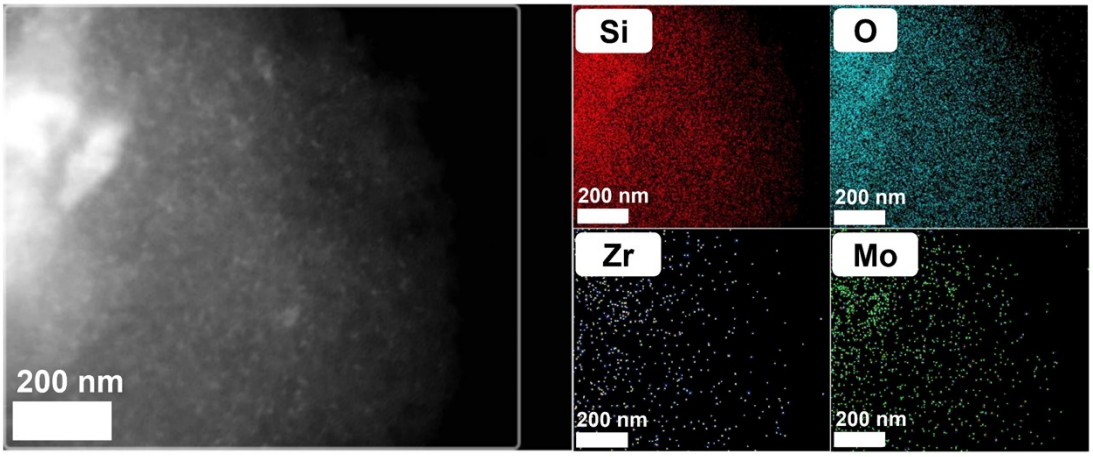

Figure S10. Elemental mapping of ZrMo-KIT-6 catalyst after five cycles.

Reference

1 A. Ramanathan, H. Zhu, R. Maheswari and B. Subramaniam, *Chem. Eng. J.*, 2015, **278**, 113–121

2 R. Maheswari, A. Ramanathan, H. Zhu, A. Araújo do Nascimento Araújo, C. Chapman, Y. Tang, F. Tao and B. Subramaniam, *J. Catal.*, 2020, **389**, 657–666.

3 A. Wawrzyńczak, S. Jarmolińska and I. Nowak, *Catal. Today*, 2021, https://doi.org/10.1016/j.cattod.2021.06.019.

4 J. Li, X. Wang, G. Chen, D. Li, Y. Zhou, X. Yang and J. Wang, *Appl. Catal., B*, Environ., 2015, **176–177**, 718–730.

5 C. R. Kumar, P. S. S. Prasad and N. Lingaiah, *Appl. Catal., A Gen.*, 2010, **384**, 101–106.

6 T. Kamegawa, A. Mizuno and H. Yamashita, *Catal. Today*, 2015, **243**, 153–157.

7 Y. B. Huang, Y. J. Luo and F. Wang, *Nanomaterials*, 2019, **9**, 1128.

8 S. Li, C. Jin, N. Feng, F. Deng, L. Xiao and J. Fan, *Catal. Commun.*, 2019, **123**, 54–58.

9 Z. Miao, Z. Li, D. Liu, J. Zhao, L. Chou, J. Zhou and S. Zhuo, *J. Colloid Interface Sci.*, 2018, **526**, 145–157.

10 Z. Miao, Z. Li, J. Zhao, W. Si, J. Zhou and S. Zhuo, *Mol. Catal.*, 2018, **444**, 10–21.