Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information for

In situ UV-Raman spectroscopy of coking-caused deactivation mechanism over Mo/HMCM catalyst in methane dehydroaromatization

1. Experimental

1.1.Catalyst evaluation

The MDA test was performed at 700 °C, 1 atm, CH_4:N_2 = 9:1, and a gas hourly space velocity (GHSV) of 1500 mL/(g·h) in a quartz tube fixed-bed flow reactor (i.d. = 10 mm). 600 mg of the sample (20~40 meshes) mixed with 600 mg quartz sand (20~40 meshes) was used in each run, was heated in pure Ar flow (30 mL/min). After flushing with Ar at 700 °C for 30 min, a feed gas mixture of 90 vol.% CH_4/N_2 (N_2 as an internal standard) was introduced into the reactor at a flow rate of 15 mL/min for 10 h. The product gas from the reactor was measured by online analysis using two gas chromatographs (Shimadzu GC-2014 equipped with a TCD detector and Porapak Q column; Shimadzu GC-2014 equipped with an FID detector and HP-INNOWax column) [1]. CH_4 conversion and aromatic yield were calculated according to the carbon balance following a previously reported method [2]. After the MDA reaction, the catalyst was cooled down to room temperature in pure Ar (30 mL/min). The coked catalyst was recovered. The MDA stages were studied using the high-resolution pulse reaction method according to the Hensen's report [3].

1.2.Catalyst characterization

The chemical composition was determined using a Thermo iCAP 7000 spectrometer. XRD was recorded on a PANalytical Empyrean X'pert powder diffractometer with Cu Kα radiation from 5° to 40°. SEM was carried out on a Hitachi-S-4800 microscope. TG was examined on a Rigaku TG instrument from room temperature to 750 °C with a heating rate of 10 °C/min under an air atmosphere (50 mL/min). TPO was determined on a homemade apparatus. 50 mg of coked sample was heated in pure Ar (30 mL/min) from room temperature to 400 °C to remove physically adsorbed CO_2. After cooling down to room temperature, a 10 vol.% O_2/Ar (30 mL/min) was introduced, and the sample was heated from room temperature to 750 °C with a heating rate of 7 °C/min. The evolved species were monitored at m/e = 28 (CO) and 44 (CO_2) by using a GAM200 mass spectrometer. The abundance of CO was corrected by subtracting the

contribution from the CO_2 abundance, and the abundances of CO and CO_2 were corrected by their respective response parameters [4]. In situ UV-Raman spectrum was obtained using a Dilor T LabRAM II spectrometer with a 325 nm excitation source. HRTEM was performed on a JEOL JEM-2100F.

2. Results and discussion

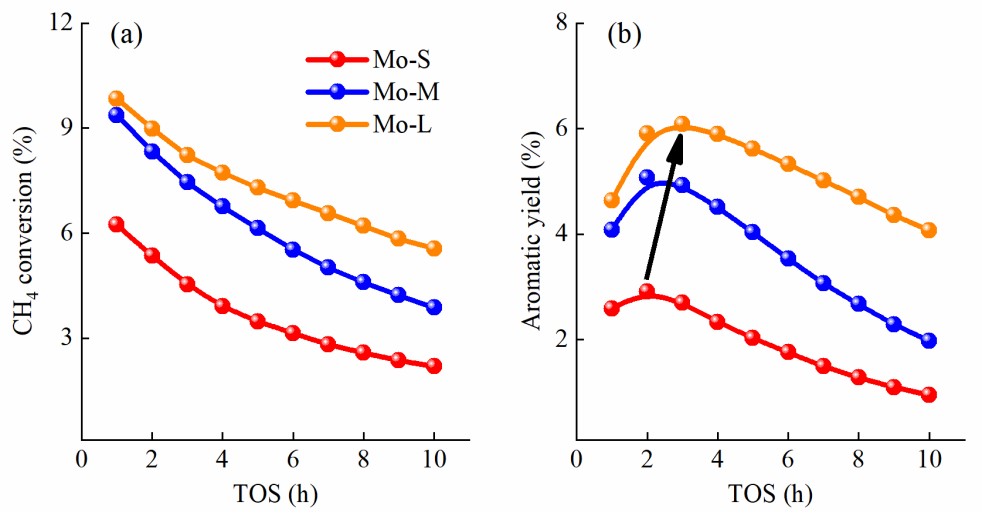

Figure S1. (a) CH_4 conversion and (b) aromatic yield as a function of TOS over the catalysts. (Reaction conditions: 1 atm, 700 °C, 1500 mL/(h·g), and CH_4:N_2 = 9:1)

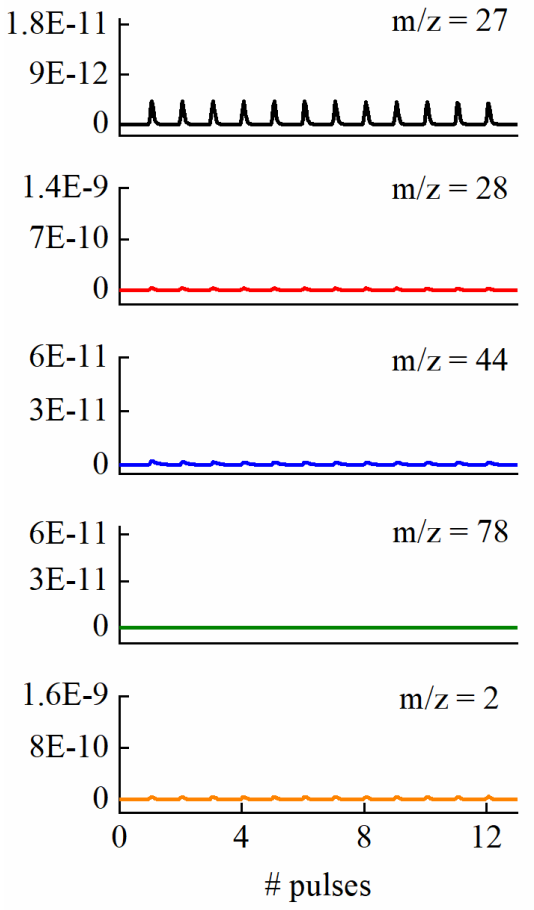

Figure S2. MDA pulse behaviors of pure HMCM-22 zeolite. (Pulse conditions: 700 °C, 1 atm, 200 mg of pure HMCM-22 pulsed 5 mL pure CH_4 with 35 mL/min flow of pure Ar carrier gas every 7 min)

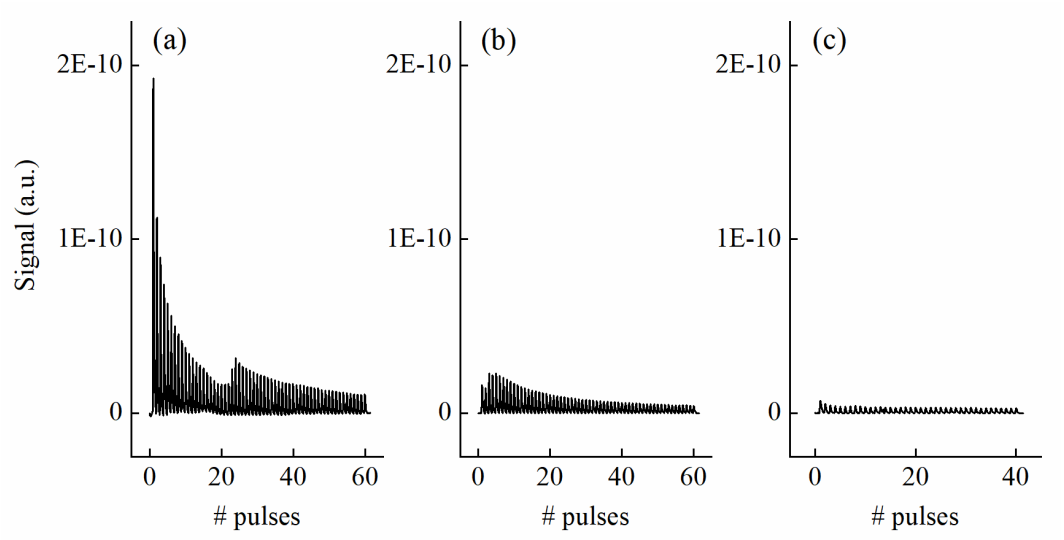

Figure S3. Evolution of H_2O (m/z = 18) over (a) Mo-L, (b) Mo-M, and (c) Mo-S catalysts (Pulse conditions: 700 ^oC, 1 atm, 200 mg of catalyst pulsed 5 mL pure CH_4 with 35 L/min flow of pure Ar carrier gas every 7 min)

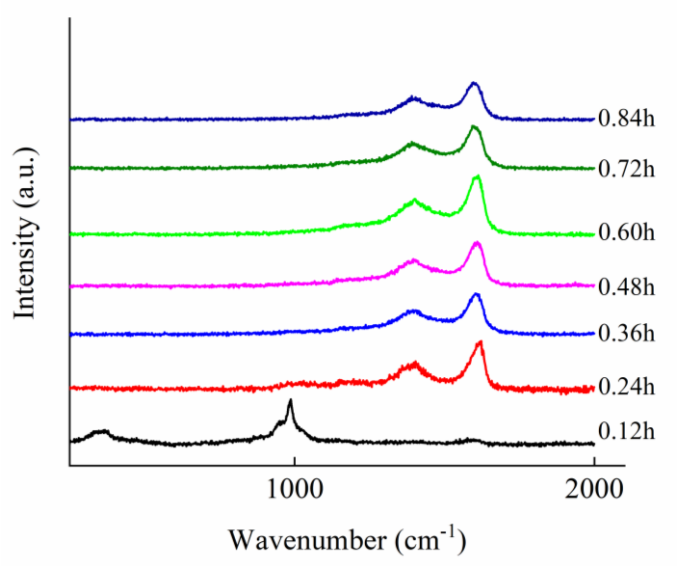

Figure S4. In situ UV-Raman spectras over the Mo-S catalyst during MDA reaction.

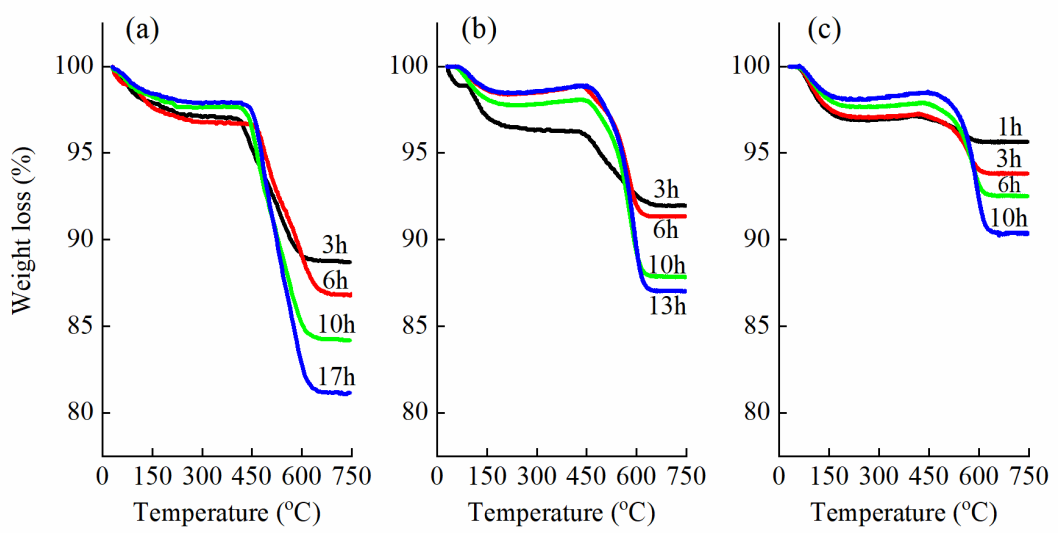

Figure S5. TG profiles of the used (a) Mo-L, (b) Mo-M, (c) Mo-S catalysts after different reaction times.

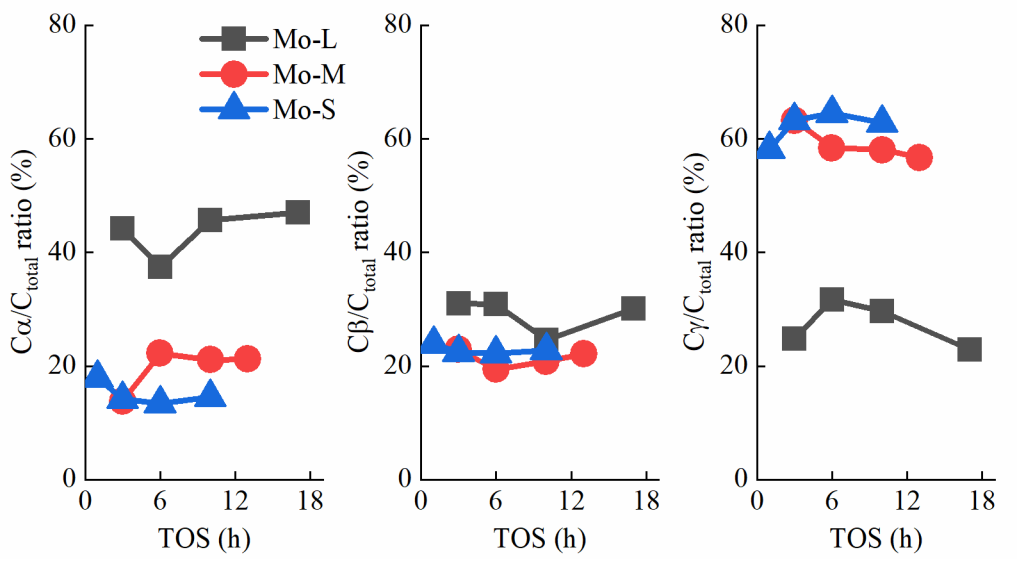

Figure S6. Coke distributions (a) $C\alpha/C_{total}$ ratio, (b) $C\beta/C_{total}$ ratio, (c) $C\gamma/C_{total}$ ratio as a function of TOS over the catalysts

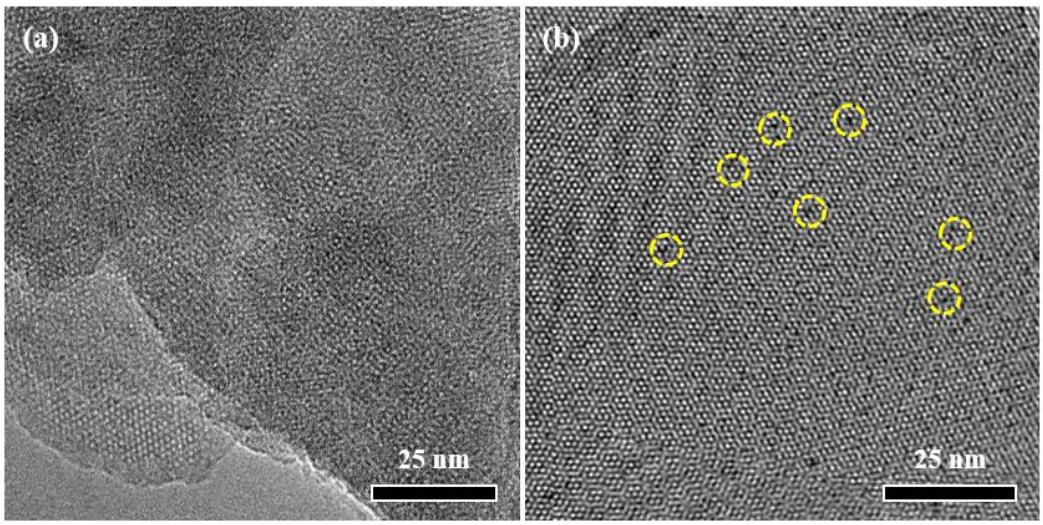

Figure S7. TEM images of (a) fresh Mo-S and (b) used Mo-S catalyst after 10 h MDA reaction.

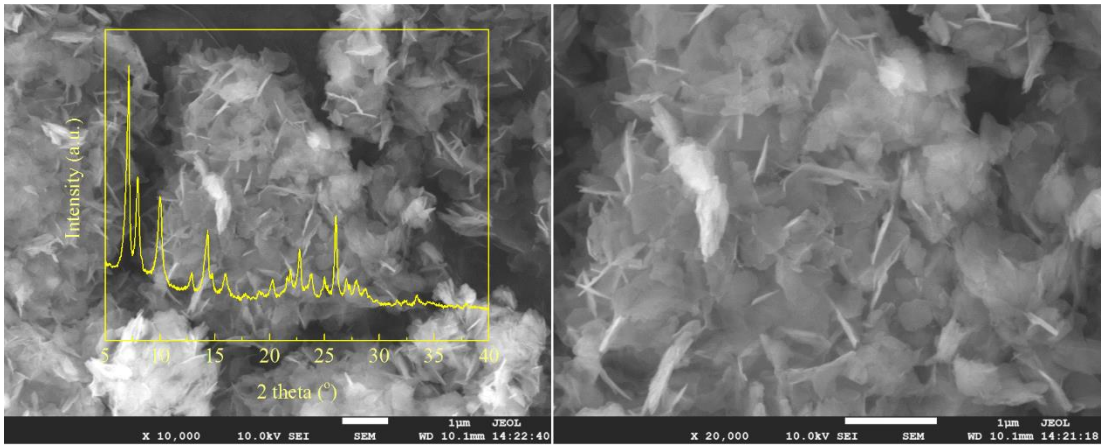

Figure S8. XRD and SEM of HMCM-22 zeolite.

Table S1. Cumulative peak areas of CO_2 and H_2O signal during the carbonization period

Signal	Mo-L [a]	Mo-M [b]	Mo-S [c]
CO_2 (44)	8.11E-11	3.00E-12	1.93E-13
H_2O (18)	2.80E-10	1.60E-11	2.31E-12

[a] cumulative peak areas from 1st to 23th pulses.

[b] cumulative peak areas from 1st to 3rd pulses.

[c] peak area for 1st pulse.

References

[1] C. Tempelman, M. Portilla, M. Armero, B. Mezari, N. Caluwé, C. Martínez, E. Hensen, *Micro. Meso. Mater*., **2016**, 220, 28-38.

[2] N. Kosinov, F. Coumans, E. Uslamin, A. Wijpkema, B. Mezari, E. Hensen, *ACS Catal*., **2017**, 7, 520-529.

[3] N. Kosinov, E. Uslamin, F. Coumans, A. Wijpkema, R. Rohling, E. Hensen, ACS Catal., 2018, 8, 8459-8467.

[4] D. Ma, D. Wang, L. Su, Y. Xu, X. Bao, *J. Catal*., **2002**, 208, 260-269.