Supplementary Material for

Resistance against Carbon Deposition via Controlling Spatial Distance of Catalytic Components in Methane Dehydroaromatization

Yan Zeng¹, Ayano Kimura¹, Peipei Zhang^{1,*}, Jiaming Liang¹, Jiaqi Fan¹, Liwei Xiao¹, Chengwei Wang¹, Guohui Yang^{1,2}, Xiaobo Peng^{1,*}, Noritatsu Tsubaki^{1,*}

¹Department of Applied Chemistry, School of Engineering, University of Toyama, 3190 Gofuku, Toyama 930-8555, Japan.

²State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China.

E-mail: zhangpp@eng.u-toyama.ac.jp (P. Zhang); pengxb@eng.u-toyama.ac.jp (X. Peng); tsubaki@eng.u-toyama.ac.jp (N. Tsubaki)

KEYWORDS: spatial distance; molybdenum; HMCM-22; carbon deposition; methane dehydroaromatization



Figure S1. The size distribution of sheet thickness for the Mo/HMCM22-HS, Mo/HMCM22-WI and Mo/HMCM22-MM. (a) Mo/HMCM22-HS; (b) Mo/HMCM22-WI; (c) Mo/HMCM22-MM. Statistical analysis of the thickness distribution was based on 100 sheets for each sample. The average sheet thickness of Mo/HMCM-22-HS, Mo/HMCM-22-WI and Mo/HMCM-22-MM was about 0.118, 0.111 and 0.107 μ m, respectively.



Figure S2. NH₃-TPD analyses for the HMCM-22 zeolite and Mo/HMCM-22-HS catalyst.



Figure S3. SEM images for the spent catalysts of Mo/H-MCM-22-HS, Mo/H-MCM-22-WI and Mo/H-MCM-22-MM.



Figure S4. TG analysis for the spent catalysts of Mo/H-MCM-22-HS, Mo/H-MCM-22-PM, Mo/H-MCM-22-WI and Mo/H-MCM-22-MM.



Figure S5. Raman analysis for the spent catalysts of Mo/H-MCM-22-WI and Mo/H-MCM-22-MM.

The G band is assigned to the first-order scattering of the E_{2g} mode of sp^2 carbon domains, arising from the C-C bond stretching of graphitic materials. The D band is assigned to a disordered structure of graphene [1-4].

Sample	Average distance (µm)
Mo/H-MCM-22-HS ^a	$9.0 imes 10^{-3}$
Mo/HMCM-22-WI ^b	5.6×10^{-2}
Mo/HMCM-22-MM ^c	1.0×10^{-1}
Mo/HMCM-22-PM ^d	$6.0 imes 10^2$
Mo/HMCM-22-DCB ^e	$1.5 imes 10^{4}$

Table S1 Average distance between Mo species and acid sites for Mo/HMCM-22 catalysts.

(a) The average distance was calculated based on uniform distribution of Mo particles in the HMCM-22 zeolite. (b) The average distance was obtained according to the average sheet thickness of Mo/HMCM-22-WI (Fig S1b). (c) The average distance was calculated on the ground of the average sheet thickness of Mo/HMCM-22-MM (Fig S1c) and the size of MoO₃ particles (~100 nm, purchased from Sigma-Aldrich Co., LLC.). (d) The average distance was evaluated on the basis of the particle sizes of HMCM-22 zeolite (20~40 mesh) and MoO₃ (20~40 mesh). (e) The average distance was evaluated based on the bed distance of HMCM-22 zeolite and MoO₃ particles in the quartz reactor.

Sample	$\frac{S_{BET}{}^a}{(m^2 g^{-1})}$	$\frac{V_{total}{}^{b}}{(cm^{3} g^{-1})}$	$\frac{V_{micro}^{c}}{(cm^{3} g^{-1})}$	$\frac{V_{meso}^{}d}{(cm^3 g^{-1})}$
HMCM-22	503.3	0.68	0.17	0.51
Mo/H-MCM-22-HS	298.5	0.51	0.11	0.40
Mo/HMCM-22-WI	315.3	0.56	0.11	0.45
Mo/HMCM-22-MM	364.4	0.51	0.14	0.37
Mo/HMCM-22-PM	424.5	0.70	0.15	0.55

Table S2 Textural properties for the HMCM-22 zeolite and Mo/H-MCM-22 catalysts.

(a) BET surface area, (b) total volume of pores from single point adsorption, (c) t-plot micropore volume, (d) mesopore volume $(V_{meso}) = V_{total} - V_{micro}$.

References

- 1. Ferrari, A.; Robertson, J. Interpretation of Raman spectra of disordered and amorphous carbon. *Phys. Rev. B* 2000, *61*, 14095-14107.
- 2. Ferrari, A. Raman spectroscopy of graphene and graphite: Disorder, electron-phonon coupling, doping and nonadiabatic effects. *Solid State Commun.* **2007**, *143*, 47-57.
- Pimenta, M.; Dresselhaus, G.; Dresselhaus, M.; Cancado, L.; Jorio, A.; Saito, R. Studying disorder in graphite-based systems by Raman spectroscopy. *Phys. Chem. Chem. Phys.* 2007, *9*, 1276-1290.
- 4. Kudin, K.; Ozbas, B.; Schniepp, H.; Prud'homme, R.; Aksay, I.; Car, R. Raman Spectra of Graphite Oxide and Functionalized Graphene Sheets. *Nano Lett.* **2008**, *8*, 36-41.