Coke Relocation and Mo Immobilization in Donut-Shaped Mo/HZSM-5 Catalysts for Methane Dehydroaromatization

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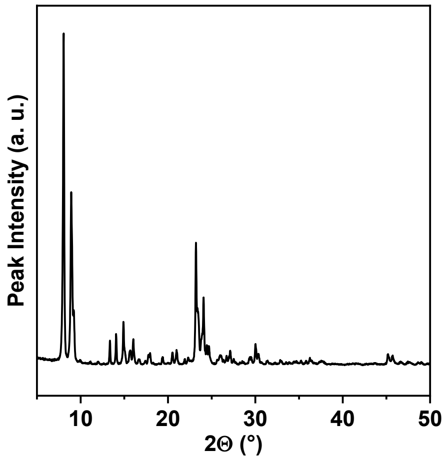

Figure SI.1. XRD patterns of Silicalite-1 seeds.

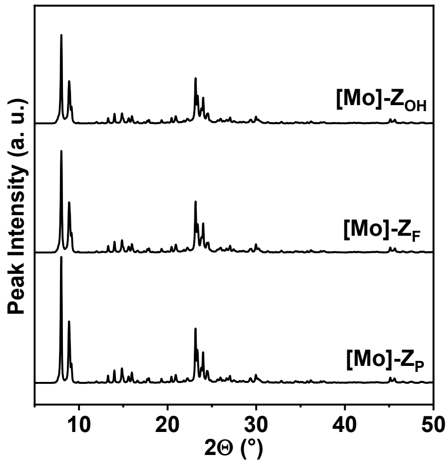

Figure SI.2. XRD patterns of [Mo]-Z_P, [Mo]-Z_F, [Mo]-Z_{OH} zeolite catalysts.

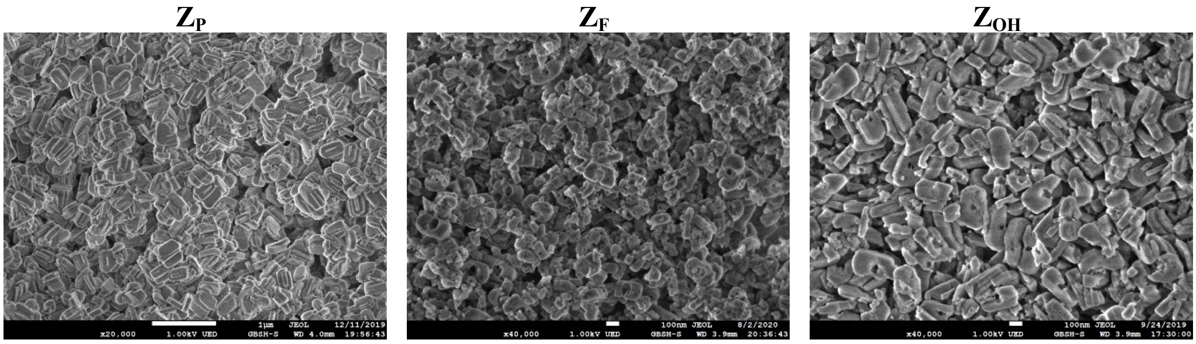

Figure SI.3. SEM images of Z_P, Z_F, and Z_{OH} zeolite catalysts.

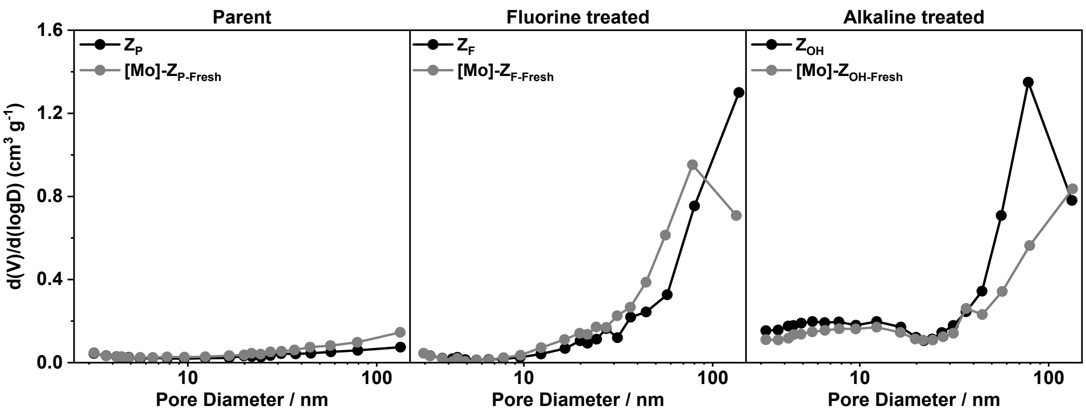

Figure SI.4. BJH pore size distribution of [Mo]-ZP, [Mo]-ZF, [Mo]-ZOH zeolite catalysts (adsorption branches).

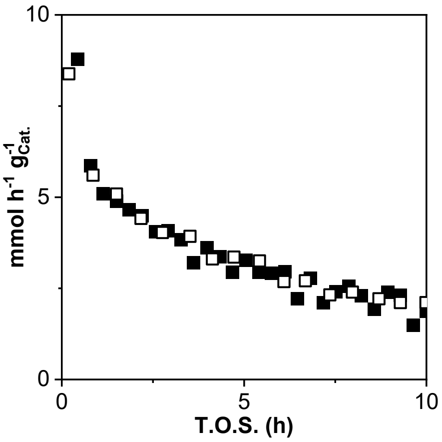

Figure SI.5. Methane conversion as a function of time on stream on [Mo]-Z_P (■) compared to a 3wt.%Mo/ZSM-5 (Si/Al = 40) catalyst reported in the literature[1].

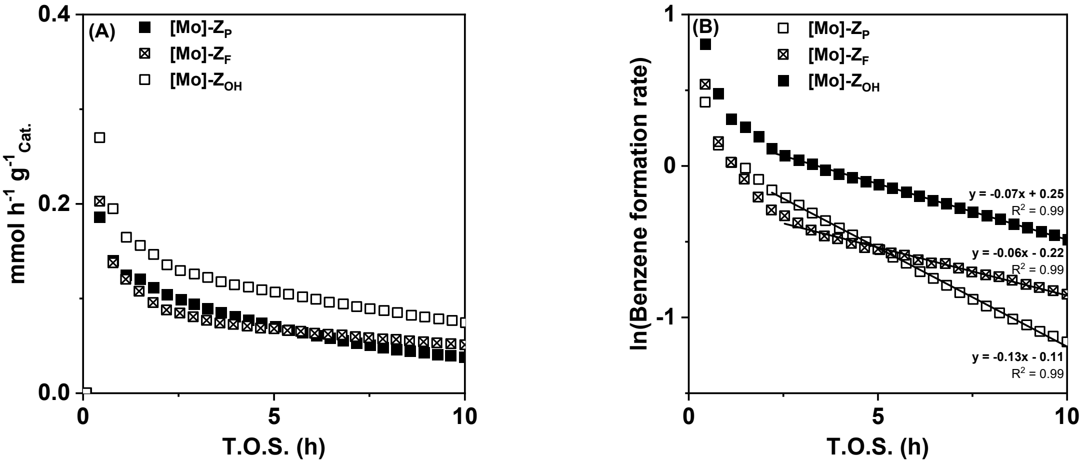

Figure SI.6. (A) Benzene formation rate and (B) logarithm of benzene formation rate as a function of time on stream on [Mo]-Z_P , [Mo]-Z_F and [Mo]-Z_{OH} catalysts.

Determination of cokes distribution

[Mo]-$Z_{P\text{-}Spent}$, assumption: coke only in the micropores

Total coke content: 9.3 wt.%

Loss of microporous volume ($V_{[Mo]-Z_{P-Spent}}^{Micro,\,loss}$): 0.07 cm^3 g^{-1}

The coke molecules are mainly pyrene (ρ_{Pyrene} = 1.27 g cm^{-3}) and benzopyrene ($\rho_{Benzopyrene}$ = 1.24 g cm^{-3})[2].

The volume occupied by pyrene molecules (V_{Pyrene}) can be estimated as follow based on 1 g of catalyst:

$$V_{Pyrene} = \rho_{Pyrene} \times V_{[Mo]-Z_{P-Spent}}^{Micro,\,loss} = 1.27 \times 0.07 = 0.089\ g$$

For 1 g of catalyst, the coke content measured by TGA (0.093 g) is close to the volume occupied by pyrene molecules (0.089 g).

[Mo]-$Z_{F\text{-}Spent}$, assumption: coke in the micropores and macropores

Total coke content ($Coke_{[Mo]-Z_{F-Spent}}^{Total}$): 7.7 wt.%

Loss of microporous volume ($V_{[Mo]-Z_{F-Spent}}^{Micro,\,loss}$): 0.03 cm^3 g^{-1}

Based on the linear relationship between coke content and loss of microporous volume[3], the amount in the micropores ($Coke_{[Mo]-Z_{F-Spent}}^{Micro}$) can be estimated as follow:

$$Coke_{[Mo]-Z_{F-Spent}}^{Micro} = \frac{V_{[Mo]-Z_{F-Spent}}^{Micro,\,loss}}{V_{[Mo]-Z_{P-Spent}}^{Micro,\,loss}} \times Coke_{[Mo]-Z_{P-Spent}}^{Micro}$$

For 1 g of catalyst, the $Coke_{[Mo]-Z_{F-Spent}}^{Micro}$ is:

$$Coke_{[Mo]-Z_{F-Spent}}^{Micro} = \frac{0.03}{0.07} \times 0.093 = 0.04\ g$$

From coke balance, the amount of coke located in the macropores ($Coke_{[Mo]-Z_{F-Spent}}^{Macro}$) is assessed to be 0.037 g for 1 g of catalyst, according to the following equation:

$$Coke_{[Mo]-Z_{F-Spent}}^{Macro} = Coke_{[Mo]-Z_{F-Spent}}^{Total} - Coke_{[Mo]-Z_{F-Spent}}^{Micro} = 0.077 - 0.04 = 0.037\ g$$

[Mo]-$Z_{OH\text{-}Spent}$, assumption: coke in the micropores, mesopores and macropores

Total coke content ($Coke_{[Mo]-Z_{OH-Spent}}^{Total}$): 10.8 wt.%

Loss of microporous volume ($V_{[Mo]-Z_{OH-Spent}}^{Micro,\,loss}$): 0.03 cm^3 g^{-1}

The loss of microporous volume is similar to the [Mo]-$Z_{F\text{-}Spent}$ catalyst, thus the $Coke_{[Mo]-Z_{OH-Spent}}^{Micro}$ can be estimated to be 0.04 g for 1 g of catalyst.

By assuming a similar deposit in the macropores, as for the [Mo]-$Z_{F\text{-}Spent}$ catalyst, the $Coke_{[Mo]-Z_{OH-Spent}}^{Macro}$ can be estimated to be 0.037 g for 1 g of catalyst. From coke balance, the coke located in the additional mesoporosity ($Coke_{[Mo]-Z_{OH-Spent}}^{Meso}$) is assessed to be 0.031 g for 1 g of catalyst:

$$Coke_{[Mo]-Z_{OH-Spent}}^{Meso} = Coke_{[Mo]-Z_{OH-Spent}}^{Total} - Coke_{[Mo]-Z_{OH-Spent}}^{Micro} - Coke_{[Mo]-Z_{OH-Spent}}^{Macro} = 0.108 - 0.04 - 0.037 = 0.031\ g$$

References

1 M. Rahman, A. Infantes-Molina, A. S. Hoffman, S. R. Bare, K. L. Emerson and S. J. Khatib, *Fuel*, 2020, **278**, 118290.

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3 N. Kosinov, E. A. Uslamin, F. J. A. G. Coumans, A. S. G. Wijpkema, R. Y. Rohling and E. J. M. Hensen, *ACS Catal.*, 2018, **8**, 8459–8467.