Electronic Supplementary Information

Improved Benzene Production from Methane Dehydroaromatization over Mo/HZSM-5 Catalysts *via* Hydrogen-Permselective Palladium Membrane Reactors

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Table S1 Experimental matrix of the permeation study

Effect	Gas Mixtures	$y_{H2,\ feed}$ (mol%)	$Q_{Ar,\ sweep}$ ($cm^3\ min^{-1}$)	Q_{feed} ($cm^3\ min^{-1}$)	T (°C)
Sweep gas flow rate	H_2/N_2	1/5/10/25	50/350/700	50	350
Feed gas flow rate	H_2/N_2	1/5/10/25	350	50/500/2000	350
Membrane temperature	H_2/N_2	10	350	50	350/450/550/700
Presence of CH_4	H_2/N_2, H_2/CH_4	10	350	50	700

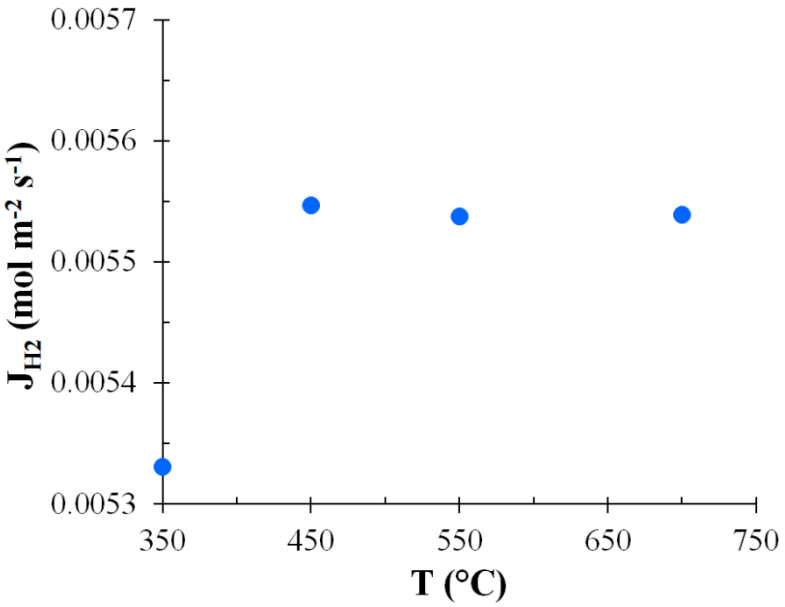

Fig. 1S Effect of temperature on H_2 flux for the Pd membrane packed with HZSM-5. Testing conditions are as follows: T = 350, 450, 550, and 700 °C, Feed = 10% H_2/N_2, Q_{Feed} = 50 cm^3 min^{-1}, $Q_{Ar,\ sweep}$ = 350 cm^3 min^{-1}.

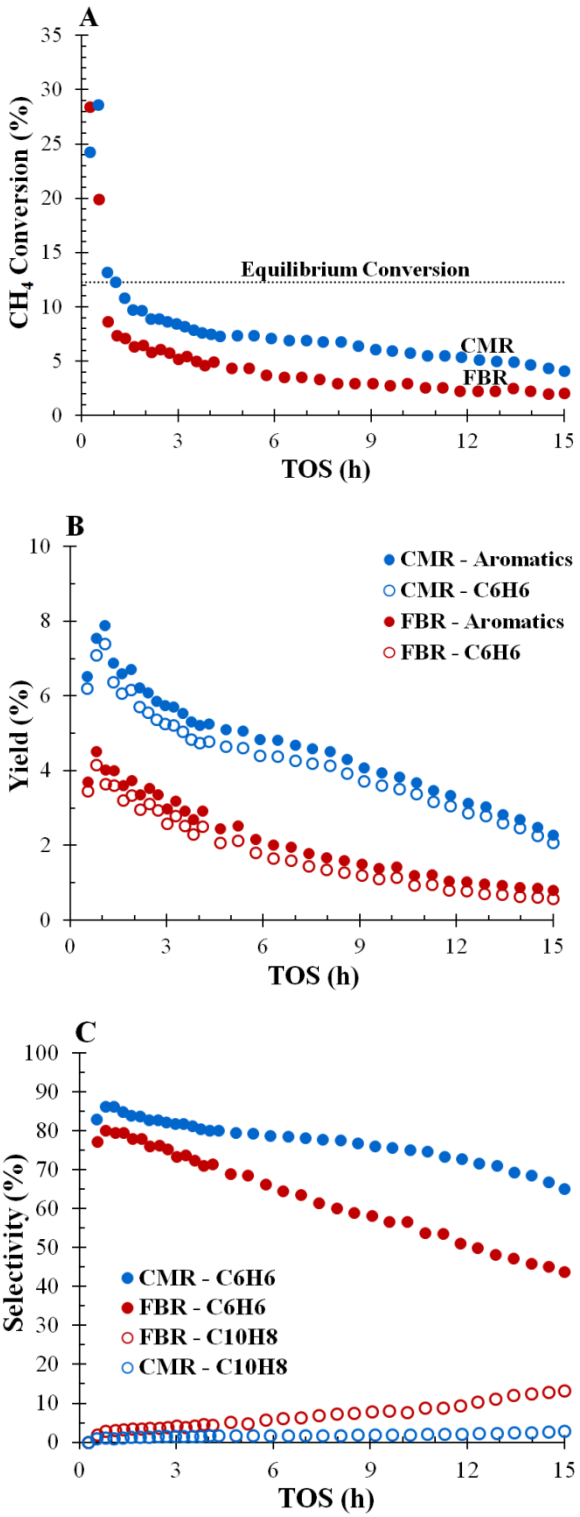

Fig. 2S Comparison of the performance of the 4% Mo/HZSM-5 catalyst in FBR and CMR at 3000 $cm^3\ g_{cat}^{-1}\ h^{-1}$ (A) CH_4 conversion (B) C_6H_6 and aromatic yields (C) selectivity to C_6H_6 and $C_{10}H_8$.

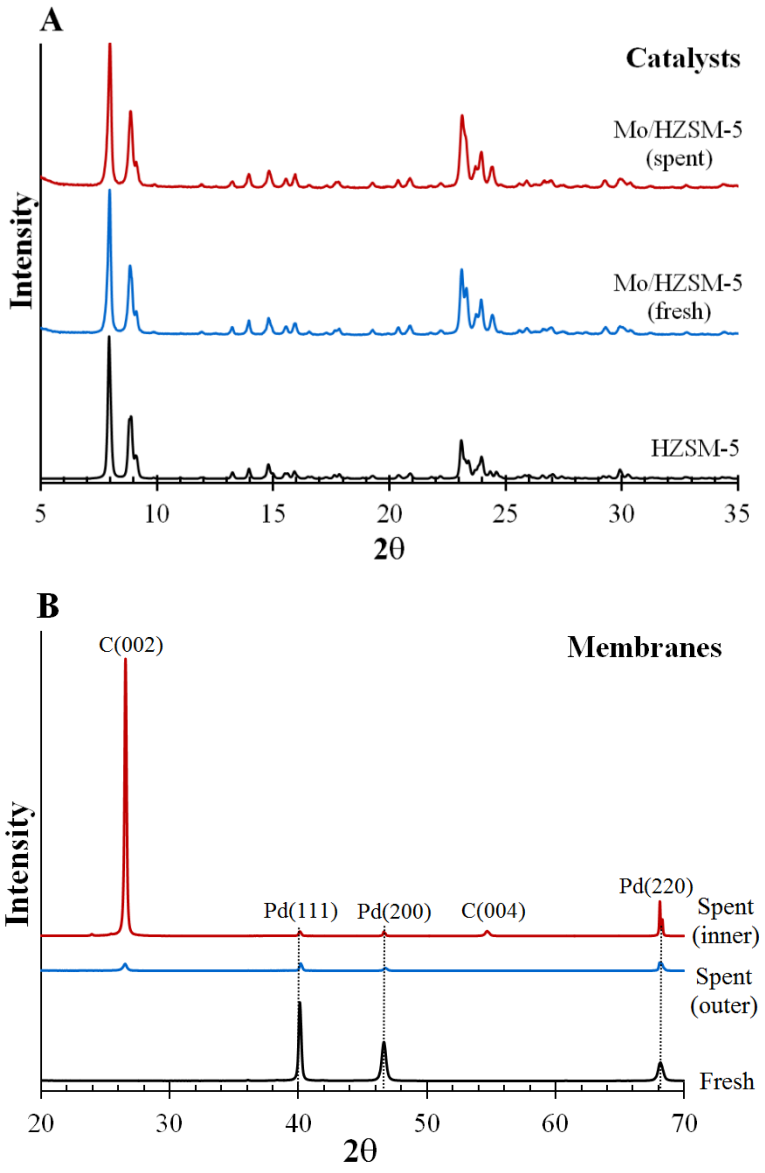

Fig. 3S XRD patterns of fresh and spent materials: (A) Mo/HZSM-5 (B) Pd membranes. The XRD pattern of HZSM-5 is included for comparison.

Mears criterion calculations*

External mass transfer limitations can be neglected if the Mears criterion listed below is satisfied.

$$\frac{-r_{A\,(Obs)}\,x\,\rho_b\,x\,R\,x\,n}{k_c\,x\,C_{Ab}} < 0.15$$

Where $-r_{A(Obs)}$ is the observed reaction rate (kmol kg_{cat}^{-1} s^{-1}), ρ_b is the catalyst bed density (kg m^{-3}), R is the catalyst pellet radius (m), n is the reaction order of reactant A, k_c is the mass transfer coefficient of reactant A, and C_{Ab} is the concentration of reactant A in the bulk gas phase (kmol m^{-3}).

In this study, ρ_b = 1099.2 kg m^{-3} and R = 1.5 x 10^{-4} m for 4 wt% Mo/HZSM-5 catalyst. For CH_4 dehydroaromatization, n = 6.

For flow over a sphere with very low Reynolds number, Sherwood number (Sh) = 2:

$$Sh = \frac{k_c\,x\,2R}{D_e}$$

Where D_e is the estimated diffusivity of CH_4 in the bulk gas phase. At 700 °C, D_e = 4.33 x 10^{-5} m^2 s^{-1}.

$$k_c = \frac{2\,x\,4.33\,x\,10^{-5}}{2\,x\,1.5\,x\,10^{-4}}$$ = 0.289 m s^{-1}.

At T = 700 °C, WHSV = 750 cm^3 g_{cat}^{-1} h^{-1}, TOS = 15 h, $-r_{A(Obs)}$ = 1.014 x 10^{-7} kmol kg_{cat}^{-1} s^{-1}, C_{Ab} =8.878 x 10^{-3} kmol m^{-3}.

$$\frac{1.014\,x\,10^{-7}x\,1099.2\,x\,1.5\,x\,10^{-4}x\,6}{0.289\,x\,8.878\,x\,10^{-3}}$$ = 3.910 x 10^{-5} << 0.15

At T = 700 °C, WHSV = 9000 cm^3 g_{cat}^{-1} h^{-1}, TOS = 15 h, $-r_{A(Obs)}$ = 2.017 x 10^{-7} kmolkg_{cat}^{-1} s^{-1}, C_{Ab} =1.081 x 10^{-2} kmolm^{-3}.

$$\frac{2.017\,x\,10^{-7}x\,1099.2\,x\,1.5\,x\,10^{-4}x\,6}{0.289\,x\,1.081\,x\,10^{-2}}$$ = 6.387 x 10^{-5} << 0.15

Therefore, the Mears criterion calculations confirm the absence of external mass transfer limitations.

***Reference**

W.S. Lee, Z. Wang, W. Zheng, D.G. Vlachos, A. Bhan, *Catal. Sci. Technol.*, 2014, **4**, 2340-2352.