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Electronic Supplementary Information

Vapor-phase transport synthesis of microfibrous-structured SSfiber@ZSM-5 catalyst with improved selectivity and stability for methanolto-propylene

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Fig. S1 SEM images of dry gel coated SS-fiber.



Fig. S2 TEM images of the zeolite shell of representative EDA-200-5/120 core-shell composite.



Fig. S3 XRD patterns of SS-fiber@ZSM-5 composite synthesized with recycled EDA solution for different times.



Fig. S4 Photograph (A) of SiC-foam substrate and SEM images (B-D) of SiC-foam@ZSM-5 composite synthesized by VPT method.



Fig. S5 (A) XRD patterns and (B-D) SEM images of sample EDA-x-5/3 synthesized

with SiO₂/Al₂O₃ molar ratio of (B) x = 30, (C) x = 200 and (D) $x = \infty$.



Fig. S6 XRD pattern (A) and SEM image (B) of sample EDA-200-0.018T/72.



Fig. S7 XRD patterns (A) and SEM images (B-F) of sample EDA-200-y/72 with varied seeding gel amounts from 2% to 50%, (B) y = 2, (C) y = 5, (D) y = 10, (E) y = 20, (F) y = 50.



Fig. S8 TEM images of sample (A) EDA-200-5/72 and (B) EDA-200-50/72 after alkaline treatment with $0.8 \text{ M} \text{ Na}_2\text{CO}_3$ solution at 80 °C for 36 h.



Fig. S9 XRD patterns (A) and SEM images (B-C) of sample (B) EDA-TEA-200-0/168

and (C) EDA-200-0/168.



Fig. S10 XRD patterns of SS-fiber@ZSM-5 composite synthesized with different types

of seeding gel and SiO₂/Al₂O₃ molar ratios.



Fig. S11 XRD patterns of sample EDA-200-5/z obtained after the VPT for (a) z = 1 h,

(b) z = 2 h, (c) z = 3 h, (d) z = 12 h, and (e) z = 24 h.



Fig. S12 SEM images of the sample EDA-200-5/z obtained after the VPT for (A) z =

48 h, (B) z = 72 h, (C) z = 120 h, and (D) z = 168 h.



Fig. S13 N₂ adsorption-desorption isothermals (A) and Barrett-Joyner-Halenda (BJH) mesopore size distribution curves (B) of the sample EDA-200-5/z with zeolite content of ~23.0 wt% obtained after the VPT for (a) z = 24 h, (b) z = 48 h, (c) z = 72 h, (d) z = 120 h, and (e) z = 168 h.



Fig. S14 Conversion of methanol as a function of time on stream over EDA-200-5/z catalysts. Reaction conditions: 450 °C, WHSV of 10 h⁻¹, 0.1 MPa, 30 vol% methanol in N₂, zeolite 0.4 g. Reaction was quitted at ~90 % methanol conversion.



Fig. S15 Methanol Conversion of and propylene selectivity over EDA-200-5/120 catalyst. Reaction conditions: WHSV = 10 h⁻¹, T = 450 °C, P = 1 atm. Regeneration conditions: 550 °C in air for 5 hours.



Fig. S16 (A) pyridine adsorption IR spectra, (B) N₂ adsorption-desorption isothermals and (C) Barrett-Joyner-Halenda (BJH) mesopore size distribution curves of samples EDA-200-5/120 (~24.4 wt% HZSM-5) and HTS-200 (~16.9 wt% HZSM-5).



Fig. S17 (A) The o-xylene adsorption isotherms by IGA at 298 K, (B) the o-xylene adsorption kinetics curves at 298 K and $P/P_0 = 0.1$ and (C) dependence of normalized o-xylene adsorption on the square root of the adsorption time as well as SEM images for (a) EDA-200-5/120 (~24.4 wt% HZSM-5) and (b) HTS-200 (~16.9 wt% HZSM-5).

Supplementary Text Calculation of diffusion coefficients (D)

Fig. S17 shows the results of o-xylene diffusion measurement. The diffusion coefficient was estimated from the time-dependent adsorption uptake by the following equation^{S1}:

$$\frac{Q_t}{Q_{\infty}} = \frac{2}{\sqrt{\pi}} \sqrt{\frac{D}{L^2}} \sqrt{t}$$

where Q_t and Q_{∞} represent the adsorption uptake of o-xylene at time t and after reaching equilibration respectively. The L denotes the average zeolite shell thickness of SSfiber@HZSM-5, being ~5.0 µm and ~3.5 µm for EDA-200-5/120 and HTS-200, respectively, as estimated as estimated from their SEM images (Fig. S17C). The curve in Fig. S17C was made by plotting the Q_t/Q_{∞} versus the square root of the adsorption time, and the slope of the linear part of the curve $(Q_t/Q_{\infty} = 0.3-0.6)$ was used for estimation of the diffusion coefficient (D)^{S2}.

References

- S1. J. Crank, The Mathematics of Diffusion, Oxford Press, London, 1975, p. 203.
- S2. Y. Li, H. Wang, M. Dong, J. Li, Z. Qin, J. Wang and W. Fan, *Rsc Adv.* 2015, 5, 66301-66310.