Electronic Supplementary Information

Vapor-phase transport synthesis of microfibrous-structured SS-fiber@ZSM-5 catalyst with improved selectivity and stability for methanol-to-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 SiO$_2$/Al$_2$O$_3$ 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 M Na₂CO₃ 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 SiO$_2$/Al$_2$O$_3$ 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) N$_2$ 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/P₀ = 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\textsuperscript{S1}:

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

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