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Electronic Supplementary information (ESI)

Self-supported SS-fiber@meso-HZSM-5 core-shell catalyst *via* caramel-assistant synthesis toward prolonged lifetime for methanol-to-propylene reaction

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Fig. S1 Photograph of the caramel solution with caramelization time of 3 h.

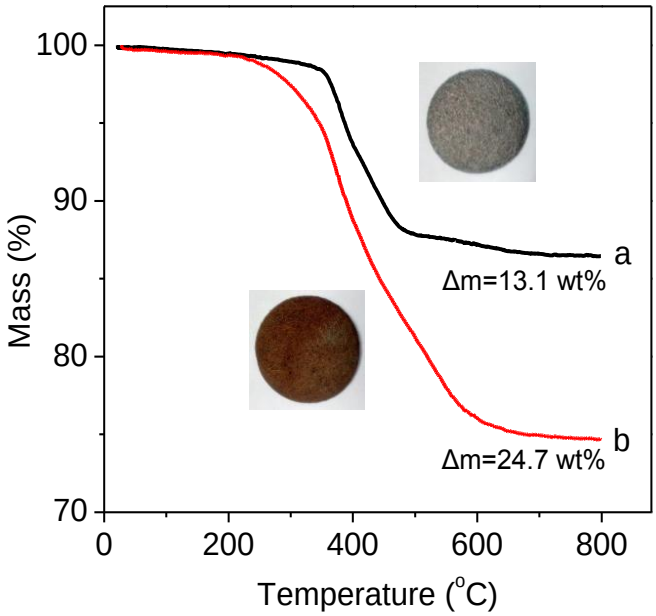

Fig. S2 TGA profiles of shell in the as-synthesized catalysts. (a) SS-fiber@HZSM-5 synthesized with the absence of caramel and without calcination treatment, (b) SS-fiber@HZSM-5(3 h, 1.8) synthesized in the presence of caramel and without calcination treatment. The weight loss of sample (a) was assigned to decomposition of TPA^+, and the larger weight loss of sample (b) was due to the decomposition of TPA^+ as well as caramel.

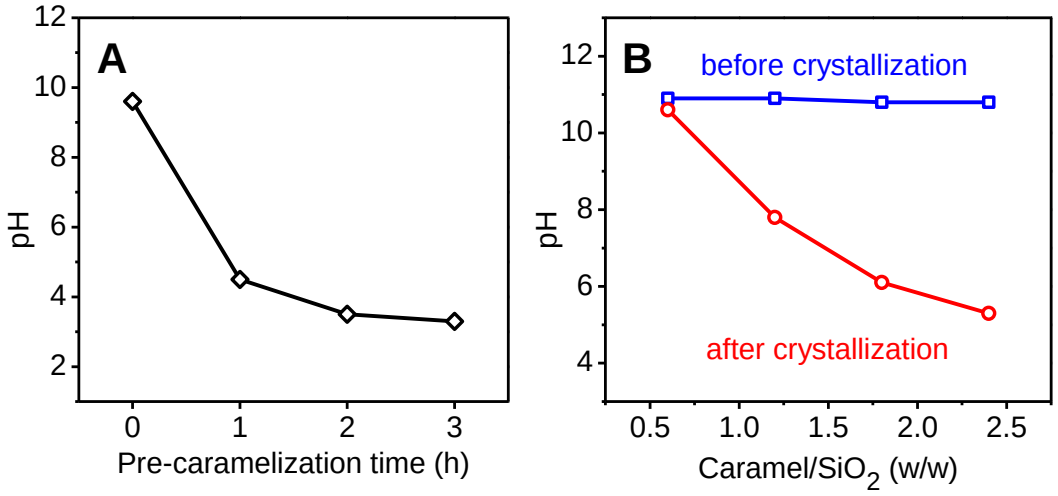

Fig. S3 (A) pH values of the caramel solution (10 wt%) at different pre-caramelization time; (B) pH values of the synthesis sol before and after crystallization with different caramel/SiO_2 mass ratio (pre-caramelization time of 3 h), suggesting caramel is a slow release acid and will be further caramelized during hydrothermal synthesis.

Table S1 Textural properties of the shell in SS-fiber@meso-HZSM-5 catalysts with different pre-caramelization times[a].

Sample	S_{BET} ($m^2\ g^{-1}$)	S_{micro} ($m^2\ g^{-1}$)	$S_{external}$ ($m^2\ g^{-1}$)	V_{micro} ($cm^3\ g^{-1}$)	V_{total} ($cm^3\ g^{-1}$)	V_{meso} ($cm^3\ g^{-1}$)
SS-fiber@meso-HZSM-5(0 h, 0.6)	352	334	17	0.15	0.18	0.03
SS-fiber@meso-HZSM-5(1 h, 0.6)	367	349	18	0.16	0.19	0.03
SS-fiber@meso-HZSM-5(2 h, 0.6)	399	380	19	0.18	0.21	0.04
SS-fiber@meso-HZSM-5(3 h, 0.6)	363	340	23	0.16	0.20	0.04

[a] Data calculated excluding the weight of SS-fiber.

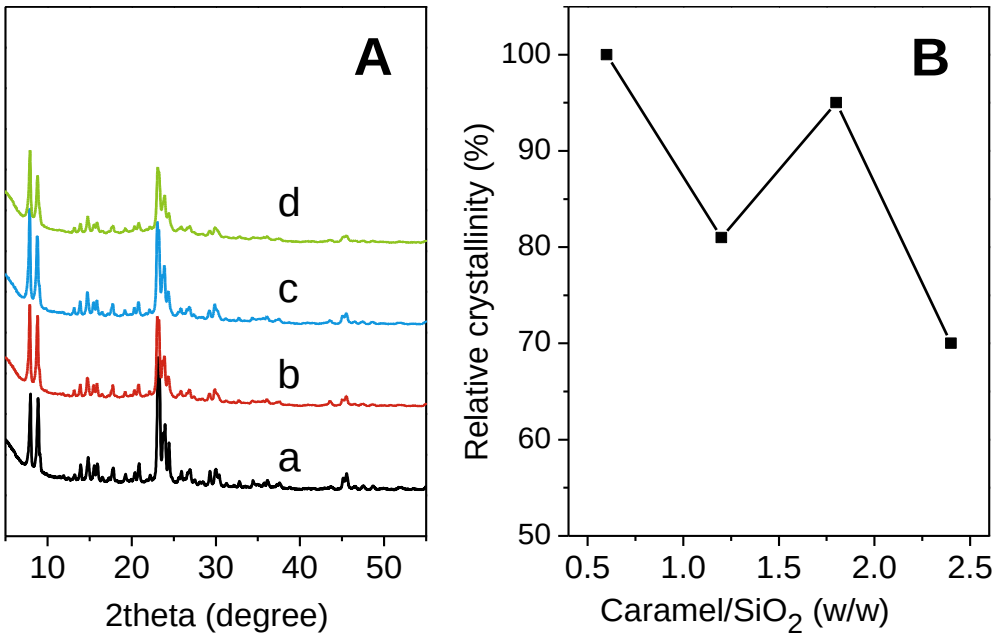

Fig. S4 (A) XRD patterns of powdered ZSM-5 form SS-fiber@meso-HZSM-5 catalysts synthesized with different caramel/SiO_2 mass ratios. To avoid any effect on the calculation of relative crystallinity, such as zeolite content and slight nonuniformity of shell, the composite samples were crashed to destroy the robust core-shell structure to obtain the powdered ZSM-5; (B) Relative crystallinity *vs*. caramel/SiO_2 mass ratio based on the XRD patterns of powdered ZSM-5; (a) SS-fiber@meso-HZSM-5(3 h, 0.6), (b) SS-fiber@meso-HZSM-5(3 h, 1.2), (c) SS-fiber@meso-HZSM-5(3 h, 1.8), (d) SS-fiber@meso-HZSM-5(3 h, 2.4).

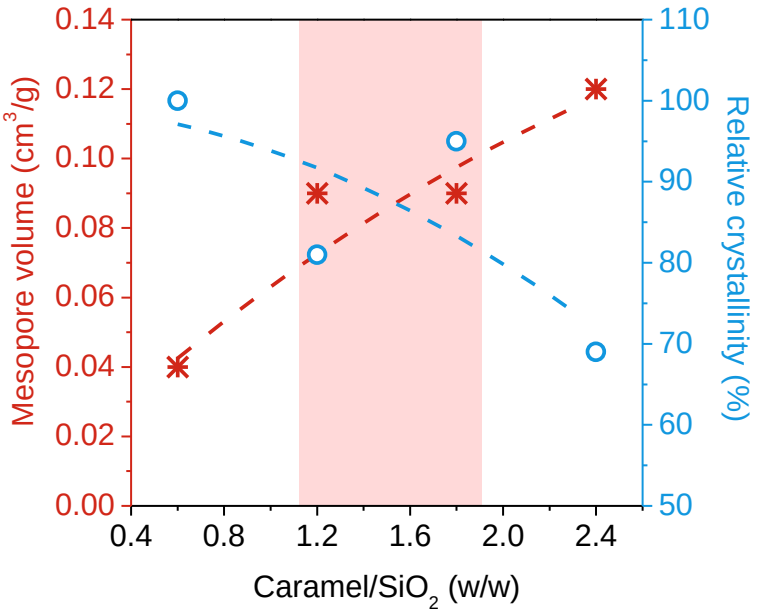

Fig. S5 Mesopore volume and relative crystallinity as a function of caramel/SiO_2 mass ratio.

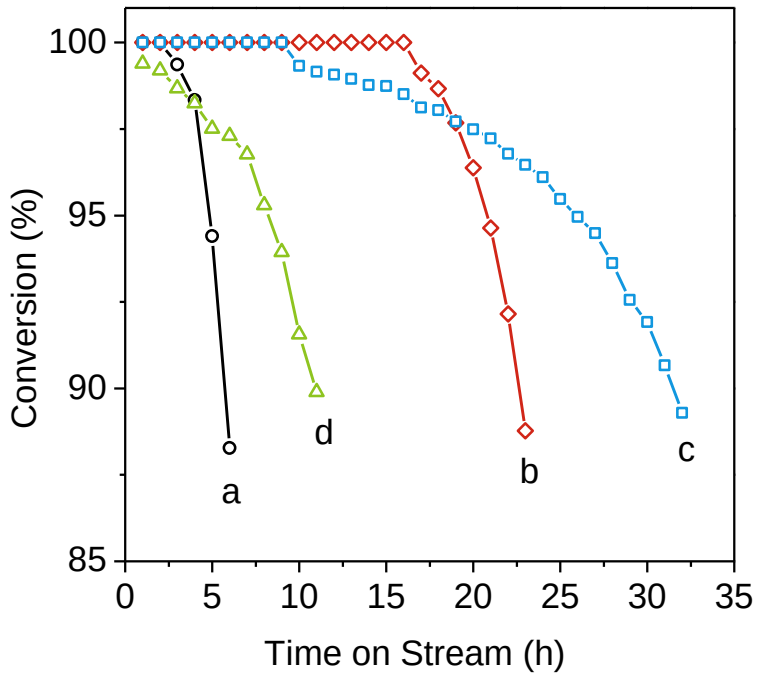

Fig. S6 Methanol conversion as a function of time on stream (TOS) over the SS-fiber@meso-HZSM-5 core-shell catalysts of (a) SS-fiber@meso-HZSM-5(3 h, 0.6), (b) SS-fiber@meso-HZSM-5(3 h, 1.2), (c) SS-fiber@meso-HZSM-5(3 h, 1.8), (d) SS-fiber@meso-HZSM-5(3 h, 2.4). Reaction conditions: 450 ^{o}C, WHSV=10 h^{-1}, 0.1 MPa, 30 vol% methanol in N_2, zeolite 0.4 g. Testing was quitted at ~90% conversion.

Although SS-fiber@meso-HZSM-5(3 h, 1.8) exhibited a longer lifetime compared to SS-fiber@meso-HZSM-5(3 h, 1.2), it was noticed that SS-fiber@meso-HZSM-5(3 h, 1.2) delivered higher methanol conversion during TOS of 10-18 h. Such observation was most likely due to the more Brönsted acid amount and less framework defects of SS-fiber@meso-HZSM-5(3 h, 1.2).

On the other hand, SS-fiber@meso-HZSM-5(3 h, 2.4) delivered a single-run lifetime of only 10 h, and showed a comparable SiO_2/Al_2O_3 molar ratio as well as Al content in zeolite shell with SS-fiber@meso-HZSM-5(3 h, 1.8). However, it should be noted that as active sites, Brönsted acid amount was decreased by 34% (0.024 mmol/g). Considering that the smaller change of WSHV will make a big difference in stability, we believe that lower crystallinity and ultra-low Brönsted acid amount accounted for the shortened lifetime of SS-fiber@meso-HZSM-5(3 h, 2.4).