

Structured ZSM-5 Coated SiC Foam Catalysts for Process Intensification in Catalytic Cracking of *n*-Hexane

Electronic Supplementary Information (ESI)

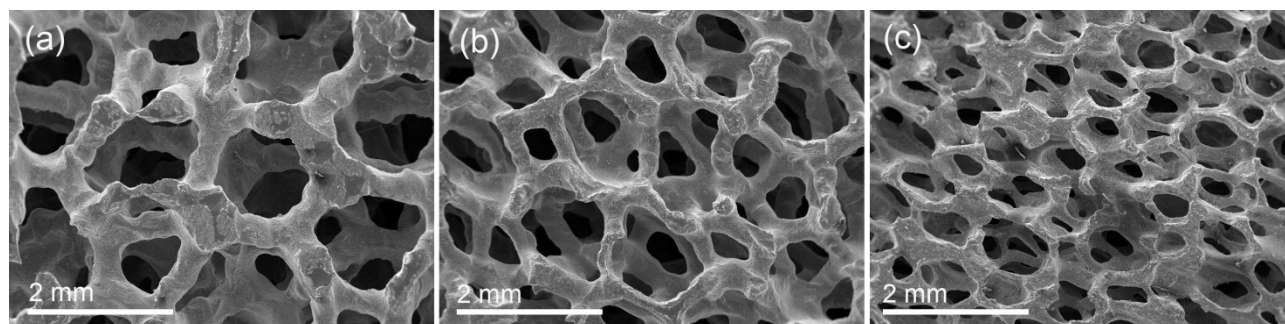


Fig. S1. SEM micrographs of SiC foam supports with different cell densities of (a) 10 ppi, (b) 20 ppi and (c) 45 ppi. The open porosity of SiC foams was estimated by the displacement methods *via* measuring the fluid (water at room temperature) volume displaced by the sample.

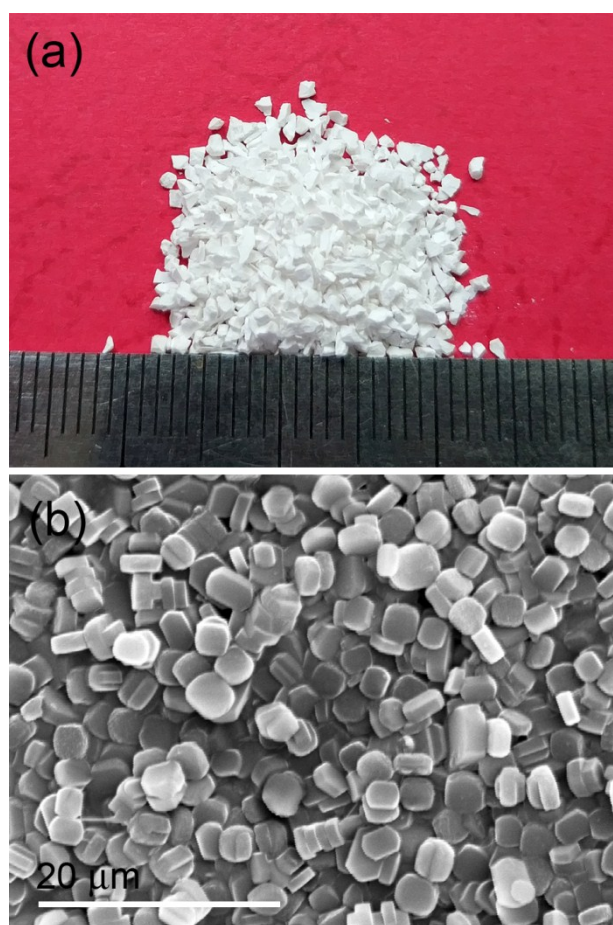


Fig. S2. (a) Optical graph and (b) SEM image of ZSM-5 pellets.

Table S1. Acidic properties of catalysts by the NH₃-TPD analysis.

Catalyst	Temperature of desorption peaks [°C]		Weak acidity [mmol g ⁻¹]	Strong acidity [mmol g ⁻¹]	Si/Al ^a [-]
	First peak	Second peak			
ZSM-5/SiC foam (10 ppi)	165.2	308.9	6.6	15.0	24.6
ZSM-5/SiC foam (20 ppi)	159.7	307.0	9.5	19.3	23.8
ZSM-5/SiC foam (45 ppi)	165.0	324.2	10.0	13.8	28.7
ZSM-5 pellets	215.6	412.7	164.8	251.4	25.0

^a based on EDX point elemental analysis (Table S3).**Table S2.** Summary of the element distribution of catalysts by EDX point elemental analysis.

Elements ^a	ZSM-5 pellets	ZSM-5/SiC foam catalysts		
		10 ppi	20 ppi	45 ppi
O	65.9	65.8	65.7	61.1
Si	32.8	33.0	32.9	37.6
Al	1.3	1.3	1.4	1.3

^a atomic percentage of elements at %.**Table S3.** Porosity and zeolite coating properties for ZSM-5/SiC foam catalysts.

Cell density [ppi]	ε ^a [-]	ε ^b [-]	Weight ^c [g]	Weight ^d [g]	Loading ^e [g]	Loading ^f [g]	Coverage ^g [g cm ⁻²]	Mean thickness ^h [μm]	ZSM-5 to SiC ratio ⁱ [-]
10	0.72	0.68	19.7	20.8	1.1	1.0	1.2×10 ⁻³	6–7	0.62
20	0.61	0.56	18.0	19.2	1.2	1.0	1.4×10 ⁻³	7–8	0.84
45	0.58	0.53	20.8	22.0	1.2	1.1	0.8×10 ⁻³	4–5	0.49

^a open porosity before zeolite coating; ^b open porosity after zeolite coating; ^c sample weight before coating; ^d sample weight after coating; ^e based on the weight gain before and after coating; ^f based on the V_{micro} values; ^g based on the zeolite loading and specific surface area; ^h based on the SEM analysis; ⁱ based on the XRD analysis.

Comparisons of specific surface area values obtained by X-ray computed tomographic (CT) scan¹ and Xu's model²:

According to Xu's model (Eq. S1), the specific surface area of cellular foams can be calculated using the information of pore diameter (d_p) and open porosity (ϵ).²

$$S_v = \frac{6.702(1 - 1.003\sqrt{1 - \epsilon})}{d_p\sqrt{1 - \epsilon}} \quad (S1)$$

Previously, we have reported the specific surface area values of two cellular SiC foams based on CT scan ($S_{v, CT}$). The specific surface area values obtained by calculations and CT scans are listed in Table 1. By using Eq. S1, the corresponding calculated values ($S_{v, calc.}$) of the two SiC foams were determined as well. The comparison of S_v values by the two methods is presented in Table S4, showing that the $S_{v, CT}$ and $S_{v, calc.}$ values are comparable, thus validating Xu's model for estimating

the specific surface area values for SiC foams studied in this work.

Table S4. Specific surface area values of SiC foam samples.

SiC foam	E [-]	d_p [mm]	$S_v, calc.$ [m ⁻¹]	S_v, CT [m ⁻¹]
13 ppi	0.762	2.61	4007	3448
30 ppi	0.787	1.48	7716	8826

Estimation of zeolite coating quantity (loading) on SiC foams using the micropore volumes by N₂ physisorption:

$$\text{Coating quantity} = \frac{V_{micro}(\text{ZSM-5/SiC foam})}{V_{micro}(\text{ZSM-5 bulk})} \times \text{Weight of ZSM-5/SiC foam} \quad (S2)$$

For example: for ZSM-5/SiC foam (45 ppi)

- coating quantity (or loading) = (0.0175/0.0081) × 22.0 = 1.1 g

Estimation of zeolite coverage on SiC foams:

$$\text{Coating coverage} = \frac{\text{loading}}{(\text{volume of SiC foam} \times S_v)} \quad (S3)$$

For example: for ZSM-5/SiC foam (45 ppi)

- volume of SiC foam = ((2.5/2)² – (0.035/2)²) × 3.14 × 5 = 24 cm² (cylindrical foam, 25 mm diameter with a 3.5 mm diameter hole in the centre)
- surface area = (24/1000000) × 6.35×10³ = 0.152 m²
- coverage = 1.2/0.152 = 7.9 g m⁻² ≈ 0.8×10⁻³ g cm⁻²

Modelling of catalyst deactivation:

The deactivation of catalysts under study was modelled by the first-order decay law of catalyst in its natural logarithmic form, as in Eq. S4.

$$\ln\left(\frac{C_t}{C_0}\right) = -k_{dec}.t \quad (S4)$$

where C_t and C_0 represent the *n*-hexane concentration at time t and 0 in the stream, k_{dec} is the deactivation rate constant (h⁻¹), and t is the reaction time in h.

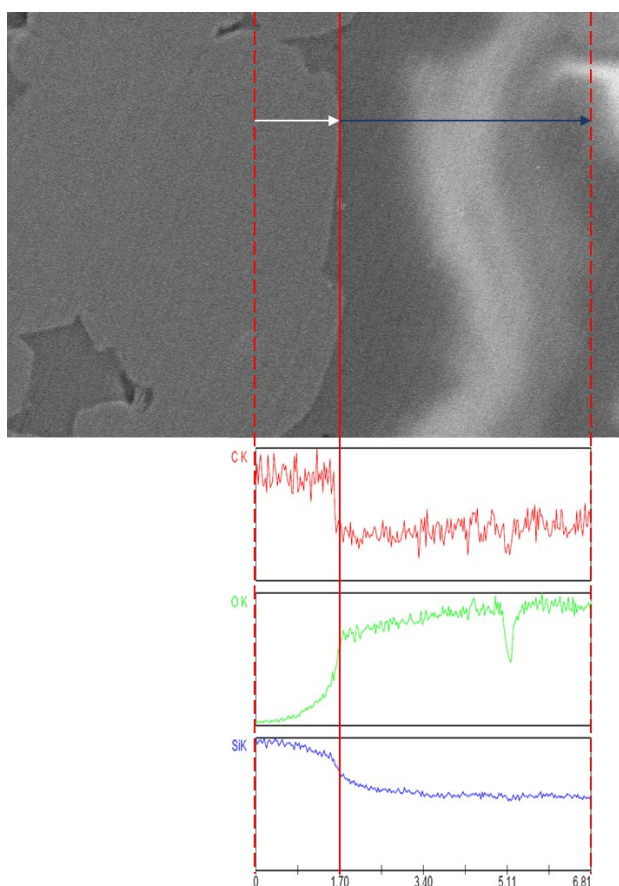


Fig. S3. EDS linescan elemental profile for ZSM-5/SiC foam (20 ppi).

Table S5. Repeatability test for catalytic *n*-hexane cracking (over ZSM-5/SiC foam catalyst, 45 ppi, at 600 °C and 4 h⁻¹).

Experiment	1	2
<i>n</i> -hexane conversion (%)	99.88	99.92
Yield (%)		
C1–C4 alkanes	27.10	25.44
Ethylene	25.71	25.23
Propylene	17.52	16.54
Butylenes	4.72	4.11
Aromatics	24.95	28.67

Table S6. Deactivation rate constants of the catalysts under study determined by the pseudo-first-order plots of $\ln([C_t]/[C_0])$ vs. reaction time.

Catalyst	k_{dec} [h ⁻¹]	R^2 [-]
ZSM-5/SiC foam (10 ppi)	$3.7 \pm 0.2 \times 10^{-3}$	0.97395
ZSM-5/SiC foam (20 ppi)	$4.9 \pm 0.2 \times 10^{-3}$	0.96964
ZSM-5/SiC foam (45 ppi)	$1.9 \pm 0.1 \times 10^{-3}$	0.97451
ZSM-5 pellets (<15 h ToS)	$7.4 \pm 0.5 \times 10^{-3}$	0.97524
ZSM-5 pellets (>15 h ToS)	$44.1 \pm 2.3 \times 10^{-3}$	0.96998

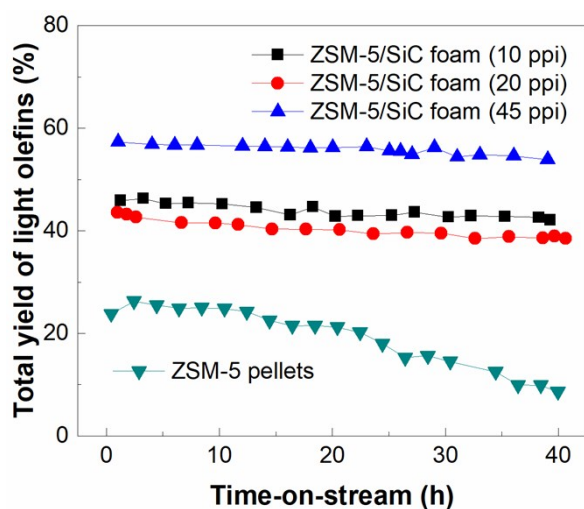


Fig. S4. Total yield of light olefins (ethylene, propylene and butylenes) over ZSM-5/foam and ZSM-5 pellets catalysts at the WHSV of 16 h⁻¹.

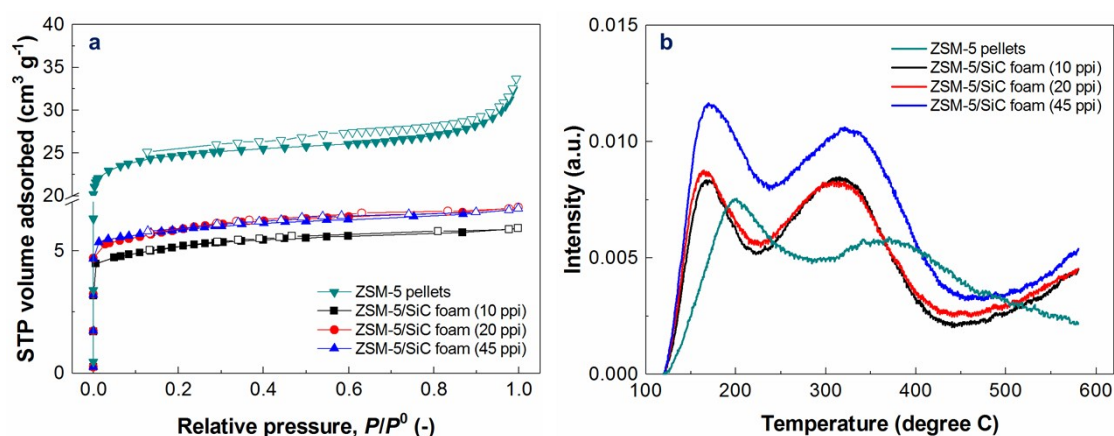


Fig. S5. Nitrogen adsorption/desorption isotherms and NH₃-TPD curves of the spent ZSM-5/SiC foam catalysts (with different cell densities) and ZSM-5 pellets from *n*-hexane cracking.

Table S7. Pore texture properties of the spent catalysts from *n*-hexane cracking.

Catalyst	S_{BET} [m ² g ⁻¹]	S_{micro} [m ² g ⁻¹]	$S_{ext.}$ [m ² g ⁻¹]	V_{micro} [cm ³ g ⁻¹]
ZSM-5/SiC foam (10 ppi)	18.1	17.3	0.9	7.4×10 ⁻³
ZSM-5/SiC foam (20 ppi)	18.4	17.3	1.0	7.5×10 ⁻³
ZSM-5/SiC foam (45 ppi)	18.8	17.7	1.1	7.6×10 ⁻³
ZSM-5 pellets	92.3	87.7	4.6	3.7×10 ⁻²

Table S8. Acidic properties by NH₃-TPD analyses for the spent catalysts from *n*-hexane cracking.

Catalyst			Temperature of desorption peaks [°C]		Weak acidity [mmol g ⁻¹]	Strong acidity [mmol g ⁻¹]
			First peak	Second peak		
ZSM-5/SiC	foam	(10 ppi)	166.7	312.0	7.0	14.0
ZSM-5/SiC	foam	(20 ppi)	164.3	309.6	8.6	14.6
ZSM-5/SiC	foam	(45 ppi)	171.1	325.6	11.0	13.4
ZSM-5	pellets		199.0	363.7	45.8	53.7

References:

1. X. Ou, X. Zhang, T. Lowe, R. Blanc, M. N. Rad, Y. Wang, N. Batail, C. Pham, N. Shokri, A. A. Garforth, P. J. Withers and X. Fan, *Materials Characterization*, 2017, **123**, 20-28.
2. W. Xu, H. Zhang, Z. Yang and J. Zhang, *Chemical Engineering Journal*, 2008, **140**, 562-569.