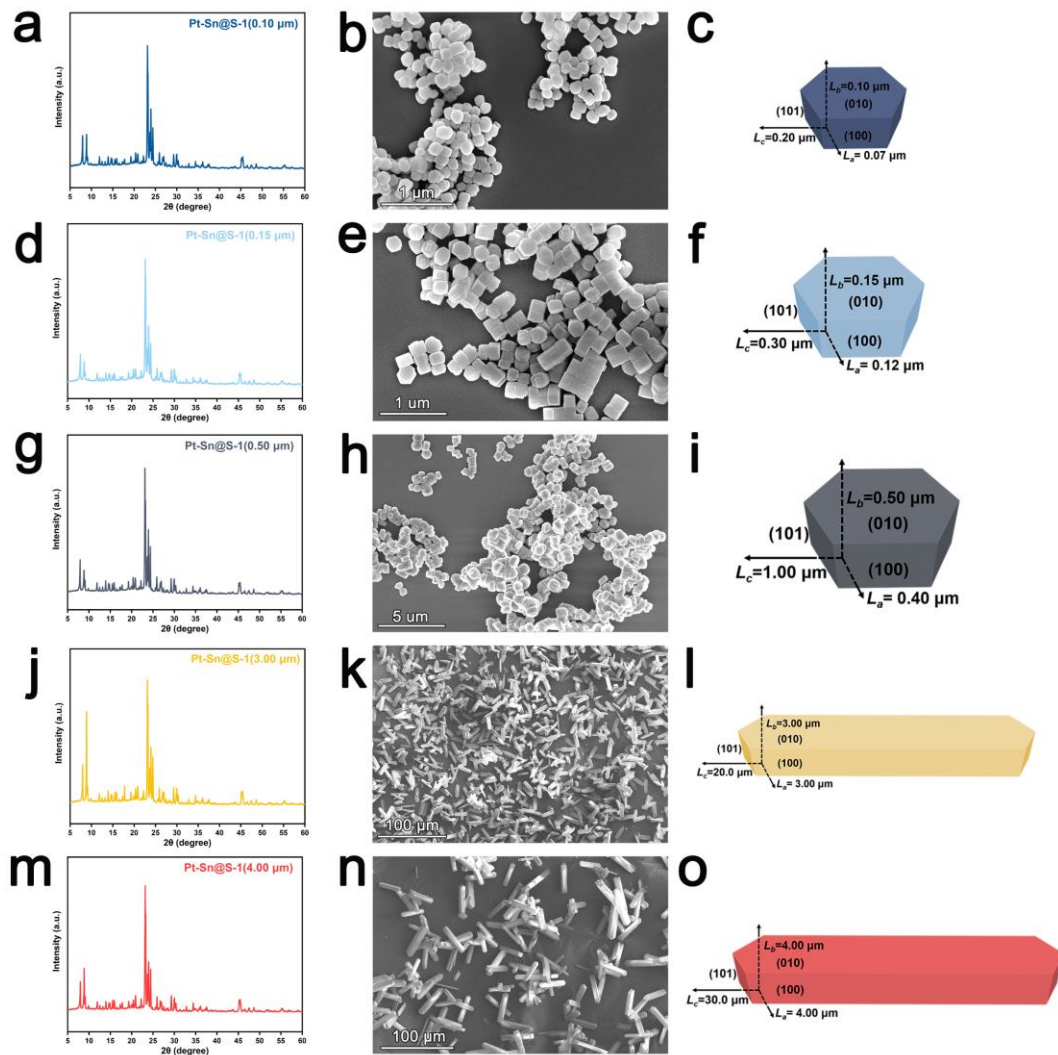
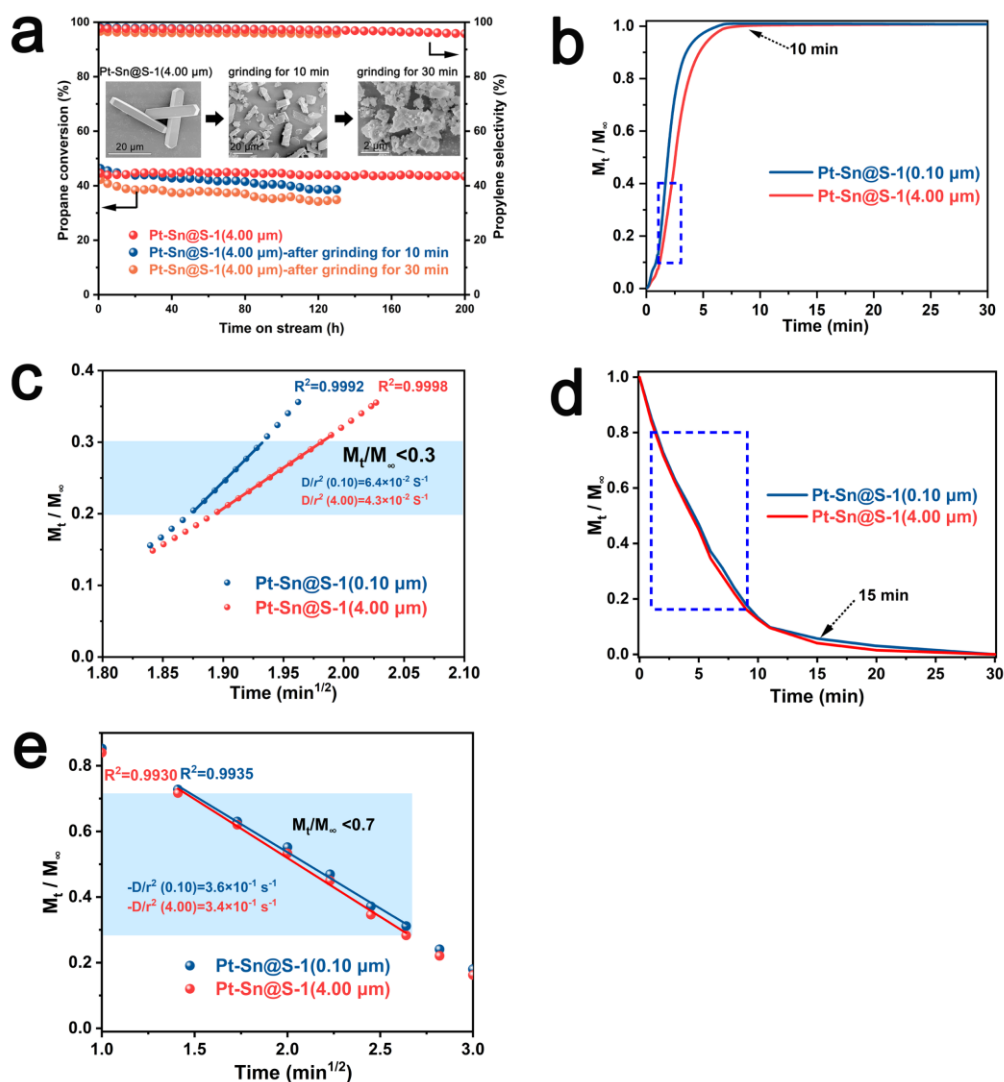


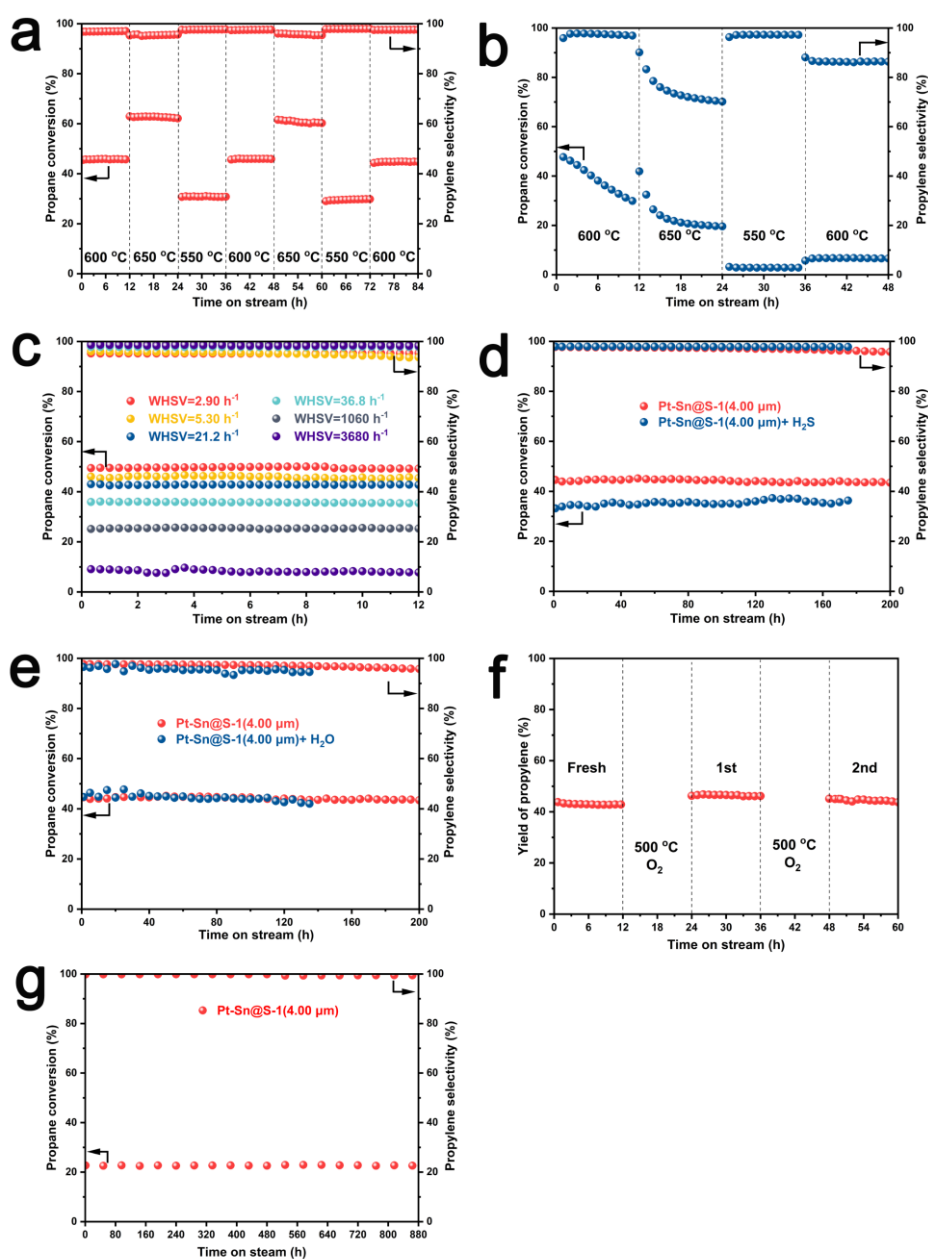


Extended Data Fig. 1 | Crystalline phase and morphology of Pt-Sn@S-1 catalysts. a-c, Powder XRD pattern, SEM image, and morphology parameters of Pt-Sn@S-1(0.10 μm). **d-f,** Powder XRD pattern, SEM image, and morphology parameters of Pt-Sn@S-1(0.15 μm). **g-i,** Powder XRD pattern, SEM image, and morphology parameters of Pt-Sn@S-1(0.50 μm). **j-l,** Powder XRD pattern, SEM image, and morphology parameters of Pt-Sn@S-1(3.00 μm). **m-o,** Powder XRD pattern, SEM image, and morphology parameters of Pt-Sn@S-1(4.00 μm).

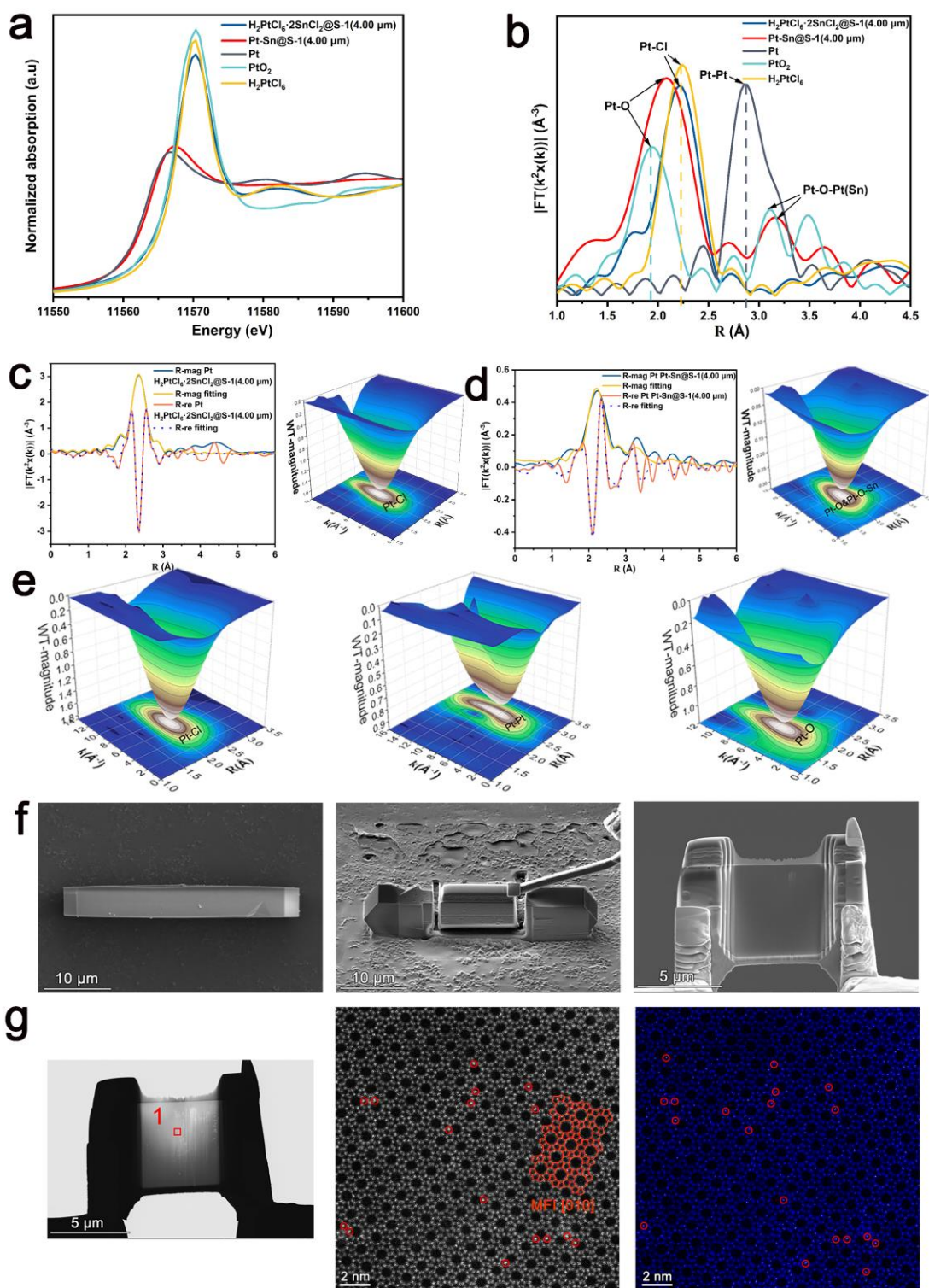


Extended Data Fig. 2 | PDH performance over Pt-Sn@S-1 catalysts and diffusion rate measurements of propane/propylene in Pt-Sn@S-1. **a**, Propane conversion and propylene selectivity over Pt-Sn@S-1(4.00 μm) after physical grinding for different time. Catalytic test conditions: atmospheric pressure, 100% C₃H₈, WHSV = 5.3 h⁻¹, and $T = 600$ °C. **b**, Uptake rates of reactant propane in Pt-Sn@S-1(0.10 μm) and Pt-Sn@S-1(4.00 μm) measured by the intelligent gravimetric analyzer (IGA) at 25 °C. **c**, Effective diffusion coefficients of propane in Pt-Sn@S-1(0.10 μm) and Pt-Sn@S-1(4.00 μm) at 25 °C are $6.4 \times 10^{-2} \text{ s}^{-1}$ and $4.3 \times 10^{-2} \text{ s}^{-1}$, respectively. **d**, Desorption rates of product propylene in Pt-Sn@S-1(0.10 μm) and Pt-Sn@S-1(4.00 μm) by *in situ* FTIR at 25 °C. **e**, Effective diffusion coefficients of propylene in Pt-Sn@S-1(0.10 μm) and Pt-Sn@S-1(4.00 μm) at 25 °C are $3.6 \times 10^{-1} \text{ s}^{-1}$ and $3.4 \times 10^{-1} \text{ s}^{-1}$, respectively.

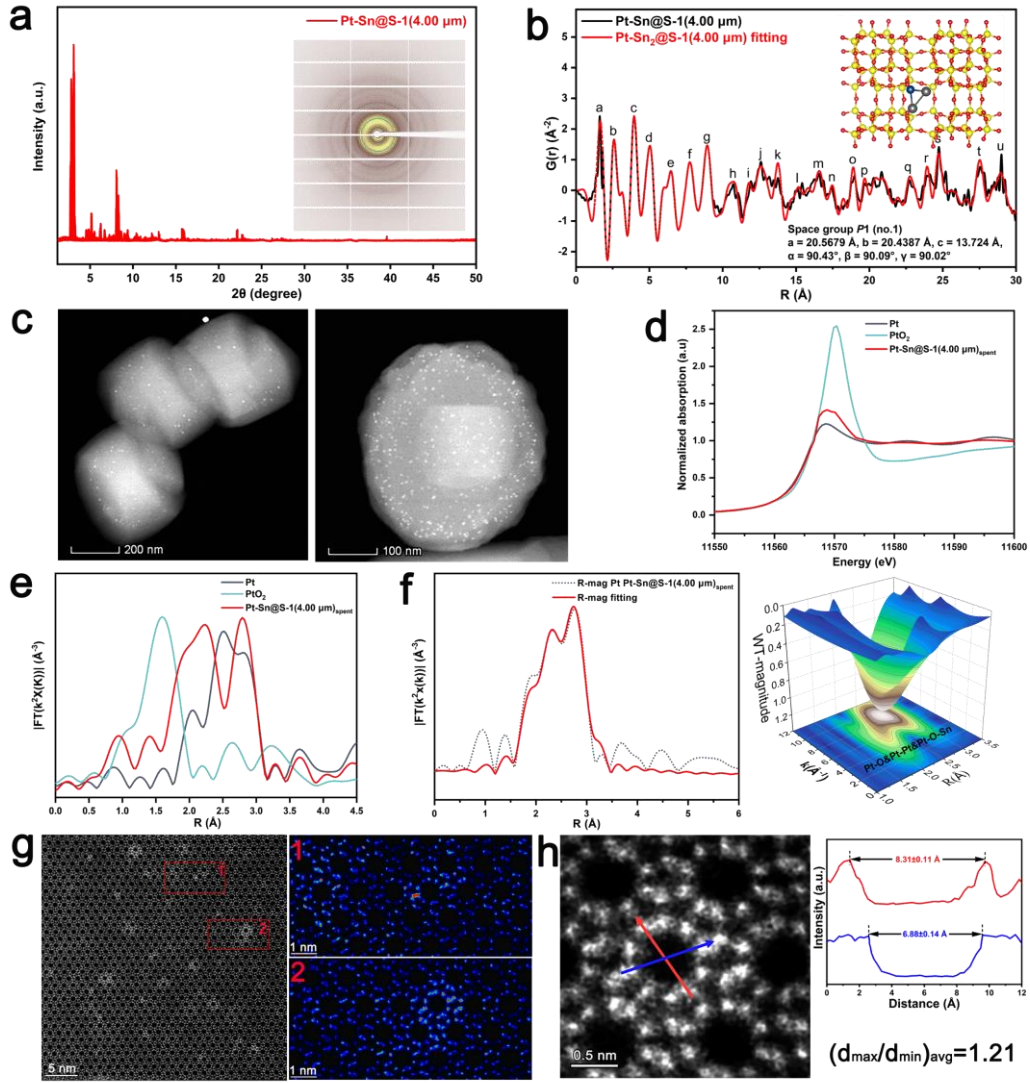
Note: To calculate and compare the diffusion coefficients of reactant propane and product propylene in Pt-Sn@S-1(0.10 μm) and Pt-Sn@S-1(4.00 μm) at low pressure, the experimental data were linearly fitted to calculate the diffusion coefficients. Such a small difference in the diffusion coefficients of Pt-Sn@S-1(0.10 μm) and Pt-Sn@S-1(4.00 μm) indicates that the diffusion of propane and propylene is not limited by the length of *b*-axis of Pt-Sn@S-1 catalysts.



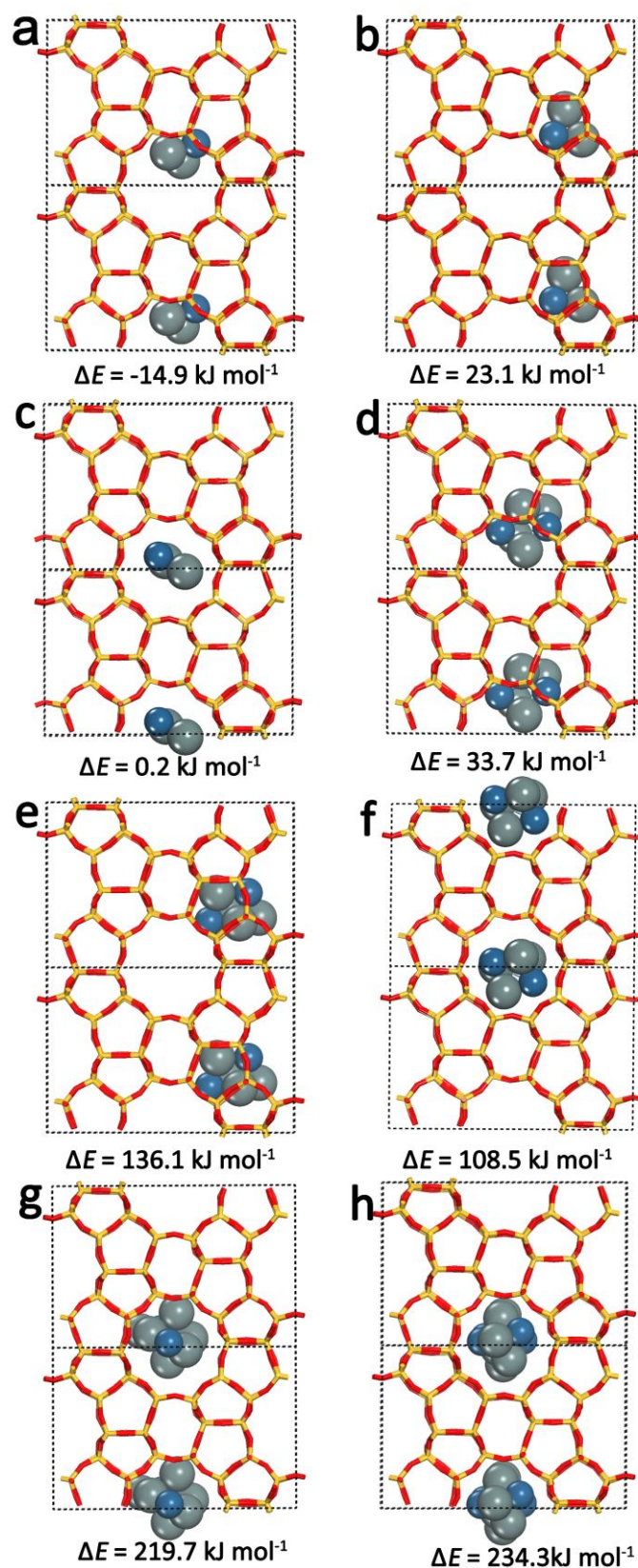
Extended Data Fig. 3 | PDH performance over Pt-Sn@S-1 catalysts. **a, b**, Propane conversion and propylene selectivity over Pt-Sn@S-1(4.00 μm) and Pt-Sn@S-1(0.10 μm) in several reaction sequences of 600-650-550 °C, respectively. Catalytic test conditions: atmospheric pressure, 100% C_3H_8 , WHSV = 5.3 h^{-1} . **c**, Propane conversion and propylene selectivity over Pt-Sn@S-1(4.00 μm) at different WHSVs (2.90, 5.30, 21.2, 36.8, 1.06×10^3 and 3.68×10^3 h^{-1}). Catalytic test conditions: atmospheric pressure, 100% C_3H_8 , and $T = 600$ °C. **d**, Propane conversion and propylene selectivity over Pt-Sn@S-1(4.00 μm) in the presence of H_2S . Catalytic test conditions: atmospheric pressure, WHSV = 5.3 h^{-1} , and $T = 600$ °C. The mixture of H_2S (25 ppm) and propane was used as reactant. **e**, Propane conversion and propylene selectivity over Pt-Sn@S-1(4.00 μm) in the presence of H_2O . Catalytic test conditions: atmospheric pressure, WHSV = 5.3 h^{-1} , and $T = 600$ °C. The mixture of H_2O (37.8 v%) and propane was used as reactant. **f**, Yield of propylene over Pt-Sn@S-1(4.00 μm) after calcination in O_2 for 12 hours. Catalytic test conditions: atmospheric pressure, 100% C_3H_8 , WHSV = 5.3 h^{-1} , and $T = 600$ °C. **g**, Stability test on Pt-Sn@S-1(4.00 μm) for PDH with propane conversion below equilibrium conversion. Catalytic test conditions: atmospheric pressure, 100% C_3H_8 , WHSV = 13.2 h^{-1} , and $T = 550$ °C.



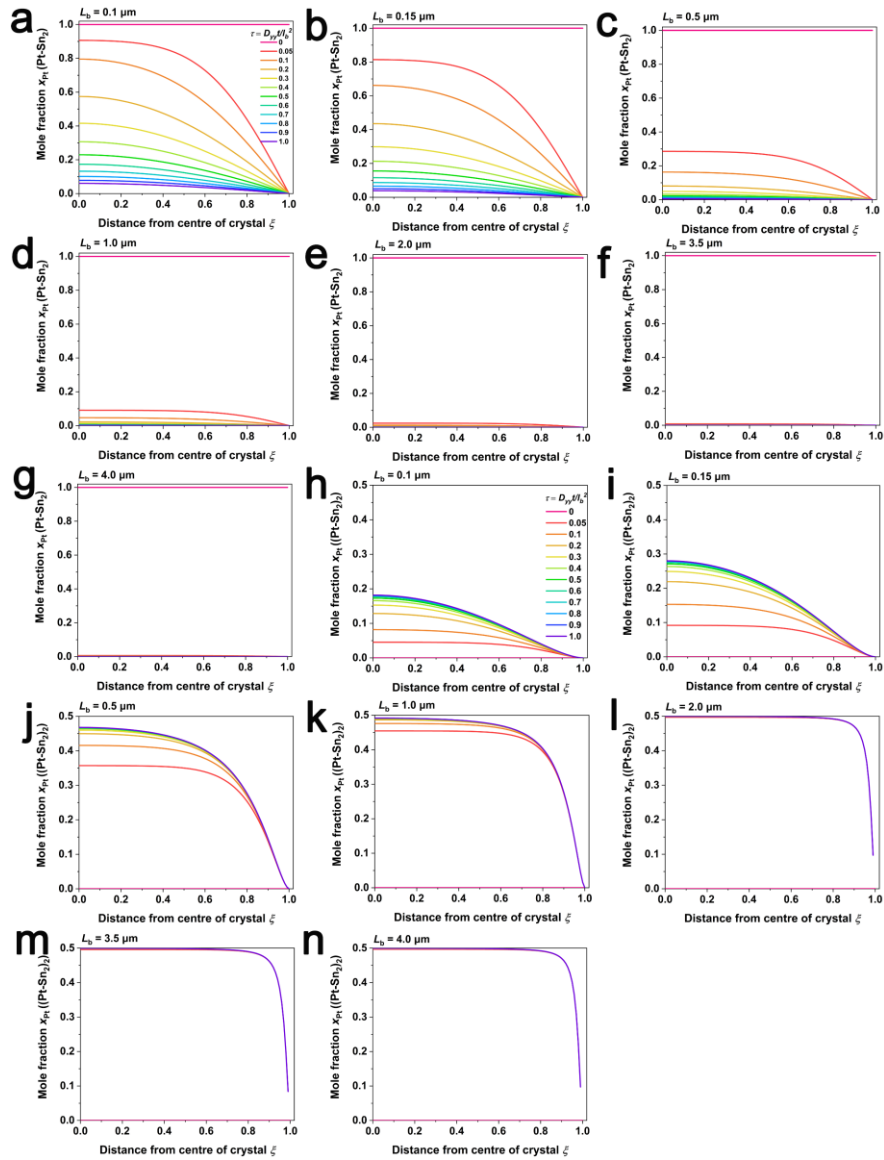
Extended Data Fig. 4 | XAS analysis results and STEM images of Pt-Sn@S-1 catalysts. **a**, Normalized Pt L₃-edge XANES spectra and **b**, radial distance $\chi(R)$ spectra for the Pt L₃-edge of $\text{H}_2\text{PtCl}_6 \cdot 2\text{SnCl}_2 @ \text{S-1}(4.00 \mu\text{m})$ and $\text{Pt-Sn}@ \text{S-1}(4.00 \mu\text{m})$. The quantitative $\chi(R)$ space Pt L₃-edge spectrum fitted curves and 3D contour wavelet transform extended EXAFS maps of **c**, $\text{H}_2\text{PtCl}_6 \cdot 2\text{SnCl}_2 @ \text{S-1}(4.00 \mu\text{m})$ and **d**, $\text{Pt-Sn}@ \text{S-1}(4.00 \mu\text{m})$. **e**, The corresponding 3D contour wavelet transform extended EXAFS map references: H_2PtCl_6 , Pt foil and PtO_2 as the reference samples, respectively. **f**, The FIB-SEM preparation process of fresh $\text{Pt-Sn}@ \text{S-1}(4.00 \mu\text{m})$ single crystal specimens for HAADF-STEM analysis. **g**, STEM images of fresh $\text{Pt-Sn}@ \text{S-1}(4.00 \mu\text{m})$.



Extended Data Fig. 5 | Synchrotron-based single crystal XRD, XAS analysis results, and STEM images of Pt-Sn@S-1 catalysts. a, SR-XRD pattern and 2D XRD image of Pt-Sn@S-1(4.00 μm). **b**, The full-range synchrotron PDF analysis for Pt-Sn@S-1 modelling and the corresponding Rietveld refinement of Pt-Sn@S-1(4.00 μm) (inset: cell unit of the optimized theoretical model). **c**, STEM images of spent Pt-Sn@S-1(0.10 μm) after PDH reaction for 96 hours. **d**, Pt L_3 -edge normalized XANES spectra and **e**, radial distance $\chi(R)$ spectra for the Pt L_3 -edge of spent Pt-Sn@S-1(4.00 μm). **f**, The quantitative $\chi(R)$ space Pt L_3 -edge spectrum fitting curves and 3D contour wavelet transform extended EXAFS maps. **g**, STEM images of Pt-Sn@S-1(4.00 μm) after thermal treatment at 800 $^\circ\text{C}$. **h**, Profile analysis of ten-membered ring from the [010] projection in Pt-Sn@S-1(4.00 μm) after thermal treatment at 800 $^\circ\text{C}$.

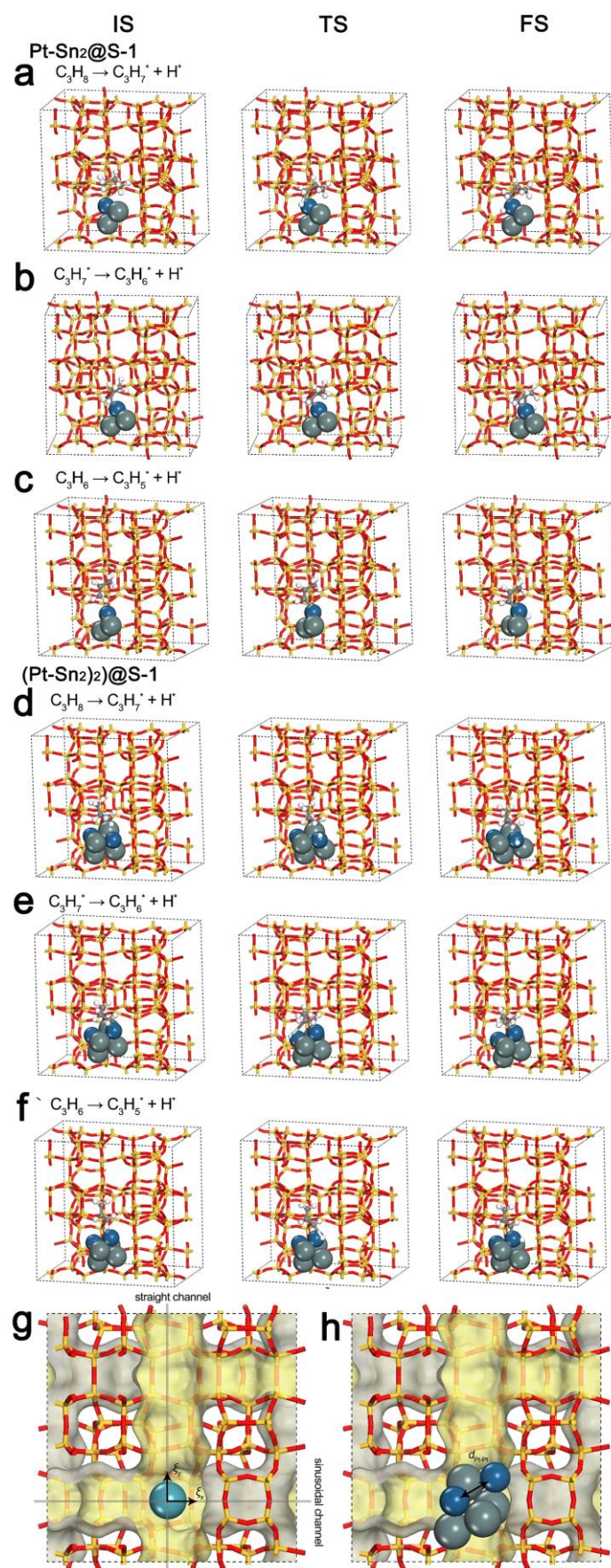


Extended Data Fig. 6 | The adsorption energies of $(\text{Pt-Sn}_2)_x$ clusters within MFI framework. Optimized structure and adsorption energy of one Pt-Sn_2 cluster located at (a) intersection site, (b) zig-zag and (c) straight channels, one $(\text{Pt-Sn}_2)_2$ cluster located at (d) intersection site, (e) zig-zag and (f) straight channels, (g) one $(\text{Pt-Sn}_2)_3$ and (h) one $(\text{Pt-Sn}_2)_4$ cluster located at intersection site of MFI framework.



Extended Data Fig. 7 | Dynamic evolution of agglomeration-migration for Pt-Sn₂ clusters within MFI framework. Dynamic evolution of intracrystalline content of Pt-Sn₂ clusters with mobility and agglomeration properties within S-1 with *b*-axis lengths of (a) 0.1, (b) 0.15, (c) 0.5, (d) 1.0, (e) 2.0, (f) 3.5 and (g) 4.0 μm obtained from agglomeration-migration modelling. Dynamic evolution of formed intracrystalline content of formed (Pt-Sn₂)₂ clusters within S-1 with *b*-axis lengths of (h) 0.1, (i) 0.15, (j) 0.5, (k) 1.0, (l) 2.0, (m) 3.5 and (n) 4.0 μm obtained from agglomeration-migration modelling.

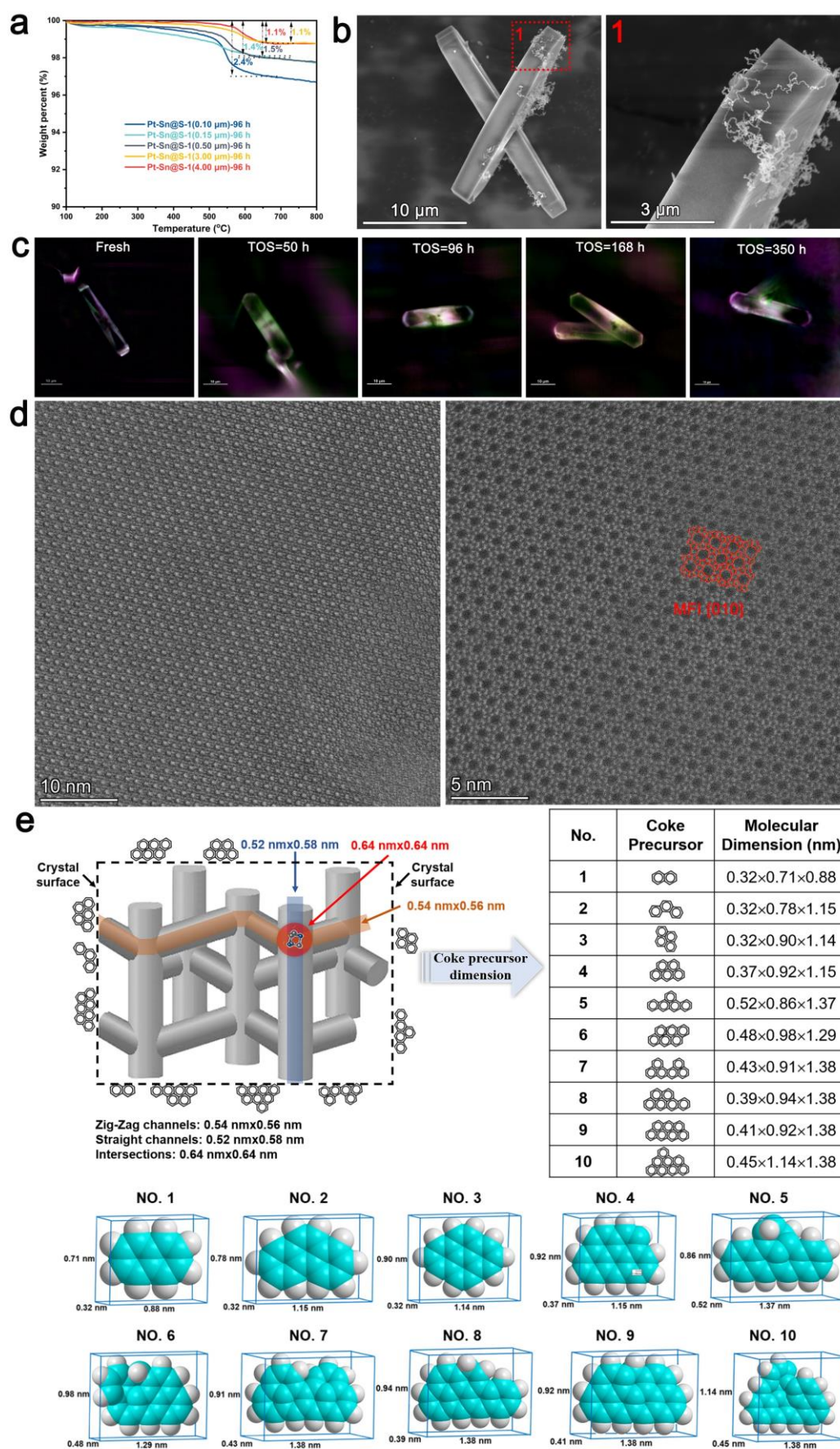
Notes: As time τ increases, the intracrystalline content of Pt-Sn₂ (or (Pt-Sn₂)₂) clusters decreases (or increases) owing to the mobility and agglomeration of Pt-Sn₂ clusters. For S-1 with short length of *b*-axis, the short intracrystalline residence time of Pt-Sn₂ facilitates the agglomeration of Pt-Sn₂ at external surface of S-1. For S-1 with a long length of *b*-axis, the intracrystalline residence time of Pt-Sn₂ significantly increases, which promotes the agglomeration of Pt-Sn₂ within the zeolite framework. The intracrystalline content of (Pt-Sn₂)₂ clusters within S-1 with short *b*-axes are significantly lower than those within S-1 with long *b*-axes.



Extended Data Fig. 8 | See next page for caption.

Periodic DFT computations for the PDH steps over Pt-Sn₂ and (Pt-Sn₂)₂ clusters confined within the MFI framework. Geometries of initial (IS), transitional (TS) and final (FS) states for the dehydrogenation of (a) propane, (b) propyl isomer and (c) propylene over Pt-Sn₂ clusters within S-1. Geometries of IS, TS and FS for the dehydrogenation of (d) propane, (e) propyl isomer and (f) propylene over (Pt-Sn₂)₂ clusters within S-1. g, Scheme of collective variables ξ_y and ξ_x for the migration of Pt-Sn₂ or (Pt-Sn₂)₂ clusters through the straight and sinusoidal channels of S-1, respectively. h, Scheme of collective variable $d_{\text{Pt-Pt}}$ for the agglomeration between Pt-Sn₂ clusters within S-1.

Notes: The geometries of TSs for the dehydrogenation steps over Pt-Sn₂ clusters are schematically represented in Extended Data Fig. 9a, b, c. From the data, some general trends are observed: (1) In the activated complex, the propane and monovalent group (1-propyl) prefer to be bound to the atop site, and the divalent group (propylene) is bonded to the bridge site. The H atom that is detached from the C₃ intermediates is relaxed to the atop or bridge site. (2) On the alloyed surfaces, the geometries of TSs are close to FSs on the potential energy surface.



Extended Data Fig. 9 | See next page for caption.

Coking-resistant properties of Pt-Sn@S-1(4.00 μm). **a**, TG analysis of spent Pt-Sn@S-1 catalysts after reaction for 96 hours. Catalytic test conditions: atmospheric pressure, 100% C_3H_8 , $\text{WHSV} = 5.3 \text{ h}^{-1}$, $T = 600 \text{ }^\circ\text{C}$. **b**, SEM images of spent Pt-Sn@S-1(4.00 μm) after PDH reaction for 96 hours. **c**, Spatiotemporal distribution obtained by SIM of aromatic hydrocarbons in a single crystal of spent Pt-Sn@S-1(4.00 μm) for different reaction times. **d**, STEM images of the spent Pt-Sn@S-1(4.00 μm) after PDH reaction for 96 hours. **e**, Coking-resistant mechanism of MFI framework and the scheme of molecular size of aromatic hydrocarbons.

Notes: The fresh samples were reduced by H_2 . Samples with coke species were transferred from the fixed bed reactor after specific reaction time of PDH reaction (i.e. 50, 96, 168 and 350 h). All the samples were exposed to air during measurement of SIM. The dimensions of coke precursors were measured by Materials Studio and presented by van der Waals radius.

Extended Data Table 1 | Comparison of catalytic performance in PDH over the industrial analogue catalyst and Pt-Sn@S-1(4.00 μm) with the propylene production capacity of 0.7 million tons per year.

	Current moving-bed unit	Proposed fixed-bed unit
Catalyst	Pt-Sn/ Al_2O_3	Pt-Sn@S-1
Type of reactor	Moving bed (the most complicated reactor)	Fixed bed (the simplest reactor)
Reaction process configuration	4 radial-flow moving bed reactors, 1 continuous catalyst regeneration unit, 4 catalyst collectors, 5 lift engagers	2-3 fixed bed reactors
Catalyst loading	260 ton	Around 100 ton
Catalyst makeup per year	18 ton (Dusts formed due to catalyst attrition may block the filter in reactor which brings about serious issue)	0
Propylene selectivity	85-88%	97.1-99.5%
$\text{H}_2/\text{C}_3\text{H}_8$	0.40-0.60	0
Feed requirement	H_2S : 75-85 ppm, H_2O < 1 ppm, N_2 < 0.1 ppm	No
Regeneration period	5-7 days	More than 6 months
Regeneration conditions	Cl_2 and air treatment at high temperature (Cl_2 is harmful to environment and corrosive to reactor)	Air treatment at high temperature
Cl_2 gas consumed per year	96 tons	0
Capital investment	Quite high, 500 million US dollars	Reduce by more than 30-50%
Operational cost	High (energy consumption in reaction, energy consumption in catalyst moving, frequent regeneration, catalyst makeup, removal of catalyst dusts, Cl_2 consumption, facility corrosion)	Low (energy consumption in reaction)
Propane consumed for producing one ton of propylene	About 1.18 ton	About 1.07 ton
Estimated CO_2 emission per year	0.342 million tons	0.036 million tons

Note: See reference (1-4) for the detailed information of the commercial catalyst.

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