

Migration-agglomeration-lockup of metal particles in zeolite for ultra-stable propane dehydrogenation catalysts

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Physical Sciences - Article

Keywords:

Posted Date: November 30th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-2231668/v1>

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Additional Declarations: There is **NO** Competing Interest.

Version of Record: A version of this preprint was published at Nature on May 28th, 2025. See the published version at <https://doi.org/10.1038/s41586-025-09168-8>.

Abstract

Propane dehydrogenation (PDH) over Pt catalyst operated in a moving-bed mode is becoming the dominant process for the on-purpose production of propylene worldwide¹⁻³. Sintering and coking deactivations of Pt catalysts, which greatly decrease the durability and efficiency of this scarce and costly noble metal, are the most challenging issues for the sustainable development of the PDH process⁴. Even after over half a century of efforts, the development of long-term durable Pt catalysts that are feasible for more economic and efficient fixed-bed operation remains as a formidable task⁵⁻¹⁰. Herein we report a strategy to modulate the migration-agglomeration-lockup of Pt particles in zeolite silicalite-1 (S-1) for synthesizing highly sintering- and coking-resistant (Pt-Sn₂)₂@S-1 PDH catalysts. It is found that the migration of Pt-Sn₂ clusters in S-1 crystals during the PDH reaction leads to a competition between intra-crystalline agglomeration and external-surface agglomeration of Pt-Sn₂ clusters. We show that, when the *b*-axis length of S-1 crystals is longer than 2 μm, the intra-crystalline agglomeration becomes dominant over the external-surface agglomeration, resulting in the formation of ultra-stable (Pt-Sn₂)₂@S-1 in which the (Pt-Sn₂)₂ dimers are securely locked in the channels of S-1 crystals. The long-term durability (4500 hours or about 6 months on stream without perceptible deactivation tendency) of (Pt-Sn₂)₂@S-1 is at least three orders of magnitude higher than that of the best catalyst reported, which is expected to bring about a breakthrough in revolutionizing the moving-bed operation of the current PDH process to fixed-bed operation. We anticipate that modulating metal migration-agglomeration-lockup within zeolite can act as a general strategy for the synthesis of durable noble metal catalysts, which is beneficial to greatly maximizing the service lifetime of noble metals in industry application¹¹⁻¹⁵.

Full Text

PDH, as the on-purpose propylene production process, is now receiving unprecedented attention, because the shale gas revolution has shifted the feedstock of propylene from naphtha to propane^{1-3,5-10,16-19}. Pt-Sn/Al₂O₃ as the predominating PDH catalyst over the world suffers from fast deactivation arising from severe metal sintering and serious coke deposition under high temperature. Therefore, a moving-bed operation has to be adopted to enable the oxychlorination regeneration for metal redispersion and coke removal every 5-7 days, which gives rise to large capital investment, extensive energy consumption, high operational cost, and harmful halogen-containing gas emission¹⁻³. Therefore, innovation of sintering- and coking-resistant Pt catalysts which are feasible for more economic fixed-bed operation is of both paramount scientific and technological importance. Unfortunately, even after over half a century of efforts, it remains a grand challenge to synthesize long-term durable Pt catalyst for fixed-bed PDH process^{5-10,20-23}.

Herein, we develop an exceptionally stable (Pt-Sn₂)₂@S-1 PDH catalyst, which is achieved by securely locking (Pt-Sn₂)₂ in S-1 crystals via modulating the migration-agglomeration of Pt-Sn₂ in the channels of S-1 crystals with a long *b*-axis. The (Pt-Sn₂)₂@S-1 catalyst with a *b*-axis length of S-1 crystals ca. 4 μm

has been tested in PDH for 4500 hours (more than 6 months), and yet it has not shown perceptible deactivation tendency. The expected durability of this catalyst is 4.6×10^5 hours, which is three orders of magnitude higher than that of the best PDH catalyst reported. Therefore, this catalyst represents a breakthrough in PDH catalyst development, which is anticipated to revolutionize the current PDH process by allowing a shift from moving-bed to fixed-bed operation.

A series of Pt-Sn@S-1 catalysts (0.25 wt.% Pt and 0.30 wt.% Sn with a Sn/Pt atomic ratio of 2) with different lengths of *b*-axis (defined as L_b) were synthesized via a one-pot hydrothermal crystallization in a fluoride-containing system, and the obtained samples are labeled as Pt-Sn@S-1($X \mu\text{m}$) in which *X* denotes the L_b of S-1 crystals. As seen in **Fig. 1a-e** and **Extended Data Fig. 1**, the L_b values of the Pt-Sn@S-1 catalysts can be tuned from 0.10 to 4.00 μm by varying the concentration of fluorine F^- , because F^- acting as a mineralizer can alter the nucleation and growth of zeolite crystals and thus change the crystal size²⁴.

Those Pt-Sn@S-1 catalysts along with an industrial analogue Pt-Sn/ Al_2O_3 were investigated in PDH reaction using pure propane as the feed under the conditions of weight hourly space velocity (WHSV, $\text{kg}_{\text{C}_3\text{H}_8} \text{kg}_{\text{cat.}}^{-1} \text{h}^{-1}$) 5.3 h^{-1} , 600 °C, and atmospheric pressure. **Supplementary Table 1** indicates that the internal and external mass transfer effects are negligible under the reaction conditions. As seen in **Fig. 1f**, Pt-Sn/ Al_2O_3 suffers from rapid drops in both propane conversion (from 43.6 to 6.0%) and propylene selectivity (from 93.8 to 78.9%) within 48 hours, corresponding to a deactivation rate k_d of as high as $5.2 \times 10^{-2} \text{ h}^{-1}$. In sharp contrast, the Pt-Sn@S-1 series exhibit substantially enhanced stability in terms of both propane conversion and propylene selectivity. Notably, **Fig. 1g** shows that Pt-Sn@S-1(4.00 μm) with the longest L_b exhibits no perceptible drop in propane conversion even after 200 hours on stream. Interestingly, the k_d values of these Pt-Sn@S-1 are negatively correlated with the L_b of S-1 crystals as illustrated in **Fig. 1h**, and increasing L_b from 0.10 to 4.00 μm leads to the decrease of k_d by nearly three orders of magnitude. Moreover, by crushing the large Pt-Sn@S-1(4.00 μm) crystals into small ones via physical grinding with different times (**Extended Data Fig. 2a**), the obtained samples exhibit a great loss in stability. This further confirms that the size of S-1 crystals plays a crucial role in determining the catalytic stability of Pt-Sn@S-1. Note that those Pt-Sn@S-1 catalysts exhibit an almost identical initial propane conversion, although they have different crystal sizes. This suggests that the size of S-1 does not affect the mass-transfer of propane and propylene in the reaction, as confirmed by the diffusion measurement results in **Extended Data Fig. 2b-e**.

The best catalyst Pt-Sn@S-1(4.00 μm) was further tested in PDH under harsh reaction conditions. Firstly, Pt-Sn@S-1(4.00 μm) was aged at 600, 700, and 800 °C, respectively, for 4 hours and the resulting samples were tested in PDH. **Fig. 2a** proves that Pt-Sn@S-1(4.00 μm) exhibits high resistance against thermal aging up to 800 °C, and the high-temperature treatment almost has no effect on its activity, selectivity, and stability. By contrast, Pt-Sn@S-1(1.00 μm) shows a great loss in its catalytic performance after being aged at above 600 °C. Secondly, reaction cycles were carried out by allowing Pt-Sn@S-1(4.00 μm) to undergo several reaction sequences of 600-650-550 °C. **Extended Data Fig. 3a, b** shows

that Pt-Sn@S-1(4.00 μm) gives nearly identical propane conversion and propylene selectivity at each temperature during the two reaction cycles. Thirdly, it can work at high WHSV up to 3680 h^{-1} (**Extended Data Fig. 3c**), giving propylene productivity of as high as 329 $\text{kg}_{\text{C}_3\text{H}_6} \text{kg}_{\text{cat.}}^{-1} \text{h}^{-1}$. Finally, **Extended Data Fig. 3d-f** shows that it possesses excellent tolerances to H_2S , H_2O and O_2 (the regeneration atmosphere), whose presence in the feed has only a minor influence on the catalytic performance. On the whole, Pt-Sn@S-1(4.00 μm) exhibits outstanding thermal stability, high propylene productivity, as well as strong resistance to poisoning and oxygen regeneration, and therefore it can serve as a robust catalyst for practical application in industrial PDH.

To further demonstrate the potential of Pt-Sn@S-1(4.00 μm) as a practical PDH catalyst, the long-term stability tests of Pt-Sn@S-1(4.00 μm) and industrial analogue Pt-Sn/ Al_2O_3 were conducted. First, a valid stability test was carried out at a lower propane conversion (22.6%) which is far from the equilibrium conversion (33.3%). **Extended Data Fig. 3g** shows that no drop in propane conversion is observed during 30 days. Encouraged by this result, we carried out a long-term stability test at a higher propane conversion, which is of industrial interest but still below the equilibrium conversion. As seen in **Fig. 2b**, Pt-Sn/ Al_2O_3 suffers from a rapid loss of propane conversion from 31.2 to 6.3% within 96 hours. By contrast, after working even as long as 4500 hours on stream, Pt-Sn@S-1(4.00 μm) has not yet shown any appreciable tendency in both propane conversion and propylene selectivity, maintaining propane conversion at 28.4% and propylene selectivity at above 97.1%. To the best of our knowledge, the Pt-Sn@S-1(4.00 μm) catalyst we report here is the first Pt-based PDH catalyst that can survive at least 6 months without detectable deactivation tendency, giving an extremely low k_d value of $2.0 \times 10^{-6} \text{h}^{-1}$. The expected durability t was estimated according to and compared with those of the representative catalysts reported in literatures. As shown in **Fig. 2c** and **Supplementary Table 2**, the expected durability (4.6×10^5 hours) of Pt-Sn@S-1(4.00 μm) is three orders of magnitude longer than the best catalyst in the literature. The ultra-long durability of Pt-Sn@S-1(4.00 μm) enables it to be applicable in a fixed-bed operation, and as summarized in **Extended Data Table 1**, this revolutionary PDH process has great advantages over the current commercial moving-bed process using Pt-Sn/ Al_2O_3 catalyst.

The extraordinary catalytic performance of Pt-Sn@S-1 in PDH greatly arouses our interest to understand its structure-activity relationship, so we used various advanced techniques to investigate the atomic-level structure of the fresh and spent Pt-Sn@S-1 catalysts. The fresh catalyst Pt-Sn@S-1_{fresh} was obtained by reducing the as-synthesized $\text{H}_2\text{PtCl}_6 \cdot 2\text{SnCl}_2$ @S-1 with H_2 at 600 $^\circ\text{C}$. Pt L_3 -edge X-ray absorption near edge structure (XANES) spectra in **Extended Data Fig. 4a** reveal that the reduction of $\text{H}_2\text{PtCl}_6 \cdot 2\text{SnCl}_2$ @S-1 results in the decreased oxidation state of Pt due to the formation of metallic Pt species. Pt L_3 -edge extended X-ray absorption fine structure (EXAFS) results of Pt-Sn@S-1(4.00 μm)_{fresh} in **Extended Data Fig. 4b-e** and **Supplementary Table 3** show the Pt-O (at 2.22 $\text{\AA}$) and Pt-O-Sn (at 3.50 $\text{\AA}$) bands with the average coordination numbers of 6 and $2^{9,10,20}$. These results suggest the possible formation of $\text{Pt-Sn}_2\text{O}_x$ units comprised of one Pt atom with two neighboring Sn atoms, and the O atoms in $\text{Pt-Sn}_2\text{O}_x$ are probably due to the stabilization of Pt-Sn_2 clusters by bonding with oxygen atoms in the

zeolite framework^{9,10,20}. High angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) results in **Extended Data Fig. 4f, g** illustrate that atomically dispersed Pt atoms in Pt-Sn₂O_x are observable in the sinusoidal channels of zeolite S-1 along the [010] orientation^{9,10,20}. Moreover, the PDF $G(r)$ spectrum of Pt-Sn@S-1(4.00 μm)_{fresh} obtained from the synchrotron radiation-based single crystal X-Ray diffraction (SR-XRD) measurement is in good agreement with the modeled structure of Pt-Sn₂O_x in the sinusoidal channels (**Extended Data Fig. 5a, b** and **Supplementary Table 4-5**). On the basis of the above characterizations, we deduce that Pt-Sn₂ clusters are generated in the channels of S-1 in Pt-Sn@S-1_{fresh}.

It is interesting to note that, during the PDH reaction, the Pt-Sn@S-1_{fresh} catalysts undergo different structural transformations that strongly depend on the L_b of S-1. STEM image of Pt-Sn@S-1(0.10 μm)_{spent} in **Extended Data Fig. 5c** reveals that large Pt-Sn nanoparticles emerge at the external surface of S-1(0.10 μm), suggesting that Pt-Sn clusters migrate from the channels of S-1 crystals and agglomerate at the external surface of S-1 crystals. In sharp contrast, HAADF-STEM image of Pt-Sn@S-1(4.00 μm)_{spent} in **Fig. 3a** indicates that subnanometric clusters of 0.2-0.4 nm are detected in the sinusoidal channels of S-1(4.00 μm) crystals, which could be due to the intra-crystalline agglomeration of Pt-Sn₂ clusters within S-1 crystals in PDH reaction. SR-XRD measurement was used to identify the structure of subnanometric clusters observed in HAADF-STEM, and the obtained PDF $G(r)$ spectrum (**Fig. 3b-c** and **Supplementary Table 6-7**) confirms that (Pt-Sn₂)₂ clusters are formed in the channels of S-1(4.00 μm) crystals. Notably, **Fig. 3d-i** reveals that the *in-situ* formation of (Pt-Sn₂)₂ in the straight 10-membered ring channels essentially deforms the rings from nearly round to elliptical²⁵, which is evidenced by the increased aspect ratio of $d_{\text{max}}/d_{\text{min}}$ from 1.10 to 1.20. The formation of (Pt-Sn₂)₂ dimers within S-1(4.00 μm) crystals is also proven by Pt L₃-edge EXAFS results in **Extended Data Fig. 5d-f** and **Supplementary Table 8**, because the Pt-Pt bond (2.74 Å) in (Pt-Sn₂)₂ becomes detectable. It should be noted that the (Pt-Sn₂)₂ dimers are securely locked in S-1(4.00 μm) crystals and possess extra-high sintering-resistance, which can be proven from the atom probe tomography (APT) and HAADF-STEM analyses of this sample after the thermal treatment at up to 800 °C. APT-3D atom maps of the tip of (Pt-Sn₂)₂@S-1(4.00 μm) calcined at 800 °C in **Fig. 3j, k** show that the Sn and Pt species are still homogeneously distributed²⁶, and HAADF-STEM image in **Extended Data Fig. 5g, h** demonstrates that (Pt-Sn₂)₂ clusters remain in the channels of S-1 crystals even after the thermal treatment at 800 °C. Based on the characterization results above, it can be concluded that the migration-agglomeration of Pt-Sn₂ cluster takes place during the PDH reaction, which leads to formation of large Pt-Sn particles at the external surface of S-1(0.10 μm) crystals and (Pt-Sn₂)₂ clusters in the channels of S-1(4.00 μm) crystals.

Periodic DFT computation was implemented to understand the migration-agglomeration behavior of Pt-Sn₂ clusters within the MFI framework for the formation of securely locked (Pt-Sn₂)₂²⁷. As shown in **Extended Data Fig. 6**, the intersections of the straight and sinusoidal channels of the MFI framework can offer the maximum available space to stabilize Pt-Sn₂ and (Pt-Sn₂)₂ clusters with the lowest adsorption

energies and weak repulsive interactions. The adsorption energies of $(\text{Pt-Sn}_2)_x$ ($x=3$ and 4) at the intersections of the straight and sinusoidal channels are fairly high. As the size of $(\text{Pt-Sn}_2)_x$ clusters increases, the adsorption energies of $(\text{Pt-Sn}_2)_x$ clusters significantly increase, demonstrating that the spatial-confinement imposed by the MFI framework can effectively restrain the over agglomeration of small $(\text{Pt-Sn}_2)_x$ clusters.

Based on the stability analysis of $(\text{Pt-Sn}_2)_x$ clusters, the mobility of Pt-Sn_2 and $(\text{Pt-Sn}_2)_2$ clusters and the agglomeration of Pt-Sn_2 clusters into $(\text{Pt-Sn}_2)_2$ ones within the MFI framework were further simulated by *ab initio* molecular dynamics (AIMD) simulations^{28,29}. As seen in **Fig. 4a**, the free energy barriers for the migration of one single Pt-Sn_2 cluster along the straight and sinusoidal channels of the MFI framework are 81.3 and 105.8 kJ mol⁻¹, respectively. This implies that a single Pt-Sn_2 cluster can freely migrate within the MFI framework. Particularly, the straight channels of the MFI framework (i.e. along *b*-axis of S-1) are the dominant migration pathway. However, as shown in **Fig. 4b**, the free energy barriers for the migration of one single $(\text{Pt-Sn}_2)_2$ cluster along the straight and sinusoidal channels are both higher than 140 kJ mol⁻¹, indicating that the migration of $(\text{Pt-Sn}_2)_2$ clusters within the MFI framework is very difficult. The AIMD simulation in **Fig. 4c** indicates that, during the migration of the Pt-Sn_2 clusters within the MFI framework, the agglomeration rate of two Pt-Sn_2 clusters into one $(\text{Pt-Sn}_2)_2$ cluster is relatively fast, because the free energy barrier is only 67.3 kJ mol⁻¹. These results indicate that, once the agglomeration of two Pt-Sn_2 clusters into one $(\text{Pt-Sn}_2)_2$ dimer within S-1 occurs, the formed $(\text{Pt-Sn}_2)_2$ dimer can be securely locked in the channels of S-1. As regarding to the agglomeration kinetics between two Pt-Sn_2 clusters, as demonstrated in **Fig. 4d** and **Extended Data Fig. 7**, extending L_b of S-1 crystals can increase the residence time of Pt-Sn_2 clusters and allow their intra-crystalline agglomeration, avoiding their further migration to the outer surface of the zeolite where they agglomerate into nanoparticles. As shown in **Fig. 4e, f**, in brief, the encapsulation of Pt-Sn_2 clusters within S-1 crystals with $L_b > 2 \mu\text{m}$ is the key to achieving high intracrystalline loading of stable subnanometer $(\text{Pt-Sn}_2)_2$ clusters (> 93% mole fraction of Pt atoms) in the zeolite channels and effectively prevent the formation of metal nanoparticles at the external crystal surface. In such a case, the serious deactivation arising from the severe sintering of Pt particles in high temperature PDH reaction can be largely inhibited.¹⁻³ The migration-agglomeration of Pt-Sn_2 clusters in the channels of S-1 crystals with short and long L_b can be visualized in **movies S1, S2**, respectively, which demonstrate the formation of $(\text{Pt-Sn}_2)_2$ dimers encaged in the zeolite channels or big Pt-Sn nanoparticles at the zeolite external surface.

Periodic DFT computations were also implemented to compare the intrinsic activity of Pt-Sn_2 and $(\text{Pt-Sn}_2)_2$ clusters encaged in S-1 for the elemental steps of the PDH reaction and for coke formation reaction (**Extended Data Fig. 8**). As shown in **Fig. 4g** and **Supplementary Table 9**, for the steps of dehydrogenation from propane to propylene, the adsorption energies of propane, 1-propyl and propylene intermediates at $(\text{Pt-Sn}_2)_2$ clusters are remarkably lower than those at Pt-Sn_2 clusters in the MFI framework. In addition, the energy barriers of the dehydrogenation reactions of propane and 1-propyl at

(Pt-Sn₂)₂ clusters are also lower than those at Pt-Sn₂ clusters within the MFI framework (**Supplementary Table 10**). This reveals that (Pt-Sn₂)₂ clusters are more active than Pt-Sn₂ ones in PDH. Excessive dehydrogenation of propylene to coke precursors at Pt-Sn₂ and (Pt-Sn₂)₂ clusters was also examined. Interestingly, the adsorption energies of propylene and 1-propenyl at (Pt-Sn₂)₂ clusters are higher than those at Pt-Sn₂ clusters. Correspondingly, the energy barrier for the dehydrogenation of propylene at (Pt-Sn₂)₂ clusters is higher than that at Pt-Sn₂ clusters. This further illustrates that the (Pt-Sn₂)₂ clusters encaged in S-1 not only act as the highly active catalytic centers for PDH, but also are unfavorable for coke formation arising from excessive dehydrogenation of propylene.

Finally, we investigated the coking resistance of Pt-Sn@S-1 in PDH by multi-techniques. As revealed in **Extended Data Fig. 9a**, there is a small amount of carbon deposited in each of the Pt-Sn@S-1 catalysts after the reaction at 600 °C. Interestingly, the amounts of coke deposited in these catalysts are negatively correlated with the zeolite crystal sizes, with Pt-Sn@S-1(4.00 μm) having the lowest coke deposition. **Extended Data Fig. 9b** presents the SEM images of Pt-Sn@S-1(4.00 μm), revealing that carbon fibers or tubes stay around the S-1 crystals without covering their external surfaces. Therefore, it is speculated that coke is mainly generated from the thermal polymerization reaction in gas phase, and it does not cover the external surface and pore entrances of S-1. Structural illumination imaging (SIM) on a single crystal of Pt-Sn@S-1(4.00 μm) exhibits only a weak signal for aromatic hydrocarbons (**Extended Data Fig. 9c**), suggesting very little coke is generated within the S-1 crystals³⁰. STEM characterization (**Extended Data Fig. 9d**) of this sample indicates that carbon species are hardly detected in the channels of S-1. The inhibition of coke formation inside S-1 is mainly attributed to its unique transition state shape-selectivity property^{31,32}. The largest voids (0.64 nm × 0.64 nm) in S-1 are the intersections between the straight and sinusoidal channels, which are still not able to provide enough space for the polycyclic aromatic hydrocarbon formation (**Extended Data Fig. 9e**)³³. As a result, Pt-Sn@S-1 exhibits strong coking resistance in PDH at high temperature.

Our results demonstrate that the migration-agglomeration-lockup of metal clusters within zeolite can produce ultra-stable Pt-based PDH catalyst. (Pt-Sn₂)₂@S-1(4.00 μm) with a *b*-axis length of 4 μm in S-1 crystals exhibits an extremely long durability of more than 6 months without perceptible deactivation tendency in PDH, which is expected to revolutionize the current PDH process by allowing a shift from the most complicated moving-bed to the simplest fixed-bed operation. We anticipate that modulating metal migration-agglomeration-lockup can serve as a general strategy for synthesizing highly sintering- and coking-resistant noble metal catalysts.

Declarations

Acknowledgments: This work was supported by National Natural Science Foundation of China (grants 22178062 and 21878050), National Key Research and Development Project (grant 2021YFA1500302), Industrial Joint Fund of Qingyuan Innovation Laboratory (grant 00422001), 111 Project (grant D17005) and Foundation of State Key Laboratory of Coal Conversion (Grant No. J21-22-620).

We thank Prof. Anhui Lu and Prof. Guangping Hao from Dalian University of Technology for helpful discussion and diffusion measurement. We thank the staffs from the BL06B1 and BL17U1 beamline of National Facility at Shanghai Synchrotron Radiation Facility for assistance in data collection of infrared spectroscopy. We thank the staffs from the 1W1B beamline at Beijing Synchrotron Radiation Facility for assistance in data collection of X-ray absorption fine structure spectra (XAFS). We thank Dr. Zhenghao Jia and Prof. Wei Liu from Dalian Institute of Chemical Physics, Chinese Academy of Sciences, in HR-HAADF-STEM. We thank Prof. Jiangwei Zhang from Inner Mongolia University for his help in data analysis of SR-XRD and EXAFS. We thank Dr. Qinglong Qiao and Prof. Zhaochao Xu from Dalian Institute of Chemical Physics, Chinese Academy of Sciences, in structural illumination imaging are available.

Author contribution: H.B.Z. and X.J.B. designed the study, analyzed the data, and wrote the manuscript. M.B.G. and M.Y. performed the DFT computations. P.F. and J.M.B. analyzed the data and corrected the manuscript. Z.K.X., Y.Y.Y., Z.S.B. and P.Y. prepared the catalyst and carried the catalytic reaction. We declare no competing interests. All data in the main text and the supplementary materials.

Competing interests: The authors do not have any possible conflicts of interest.

Data and materials availability: All data in the main text and the supplementary materials are available.

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Figures

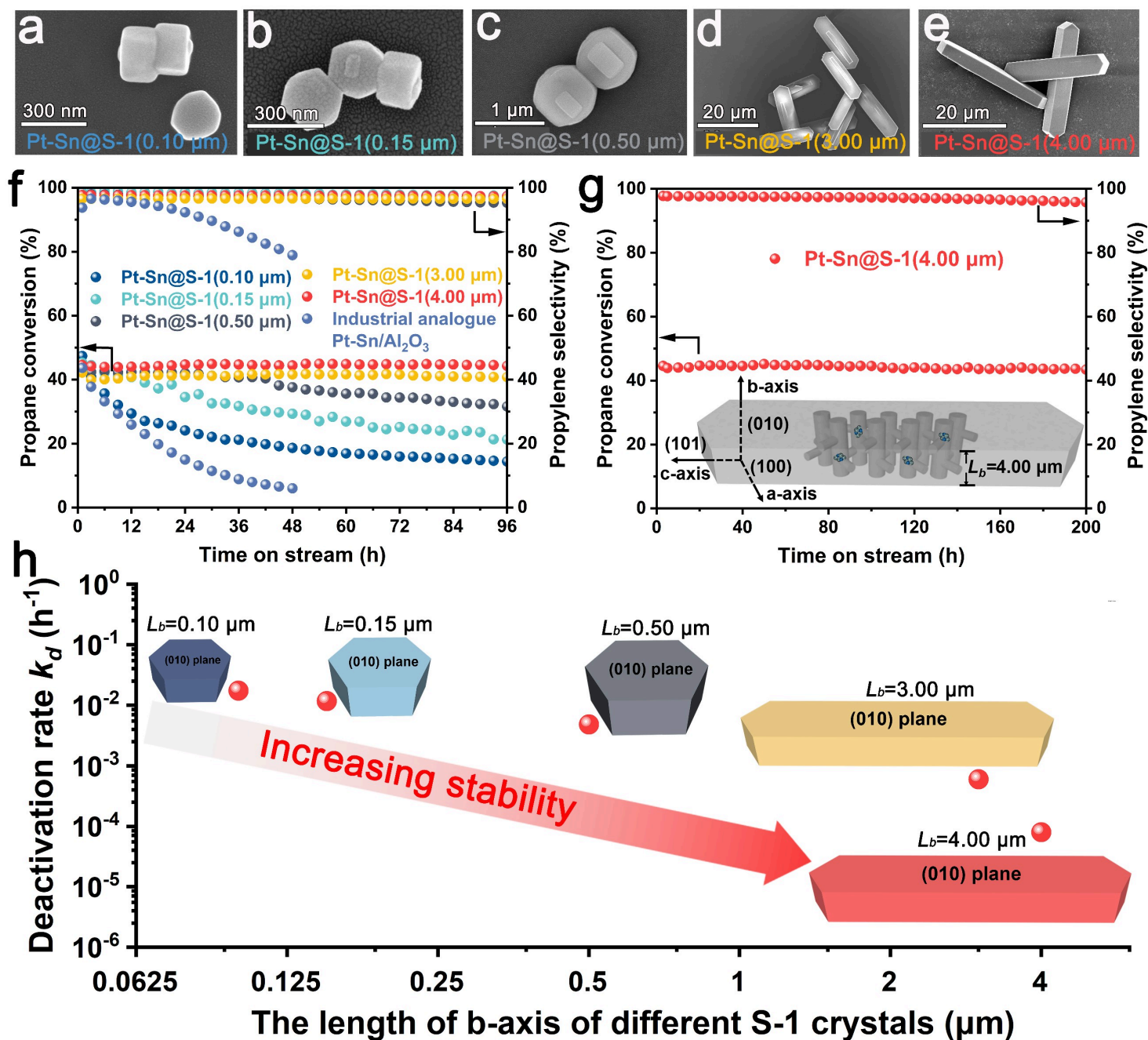


Figure 1

SEM images and PDH catalytic performance of Pt-Sn@S-1. **a-e**, SEM images of Pt-Sn@S-1 with different crystal sizes. **f**, Propane conversion and propylene selectivity for PDH reaction over Pt-Sn@S-1 catalysts. **g**, Stability test of Pt-Sn@S-1(4.00 μm). **h**, Dependence of deactivation rate on the length of b -axis of Pt-Sn@S-1. Catalytic test conditions: atmospheric pressure, 100% C_3H_8 , WHSV = 5.3 h^{-1} , and $T = 600$ $^\circ\text{C}$.

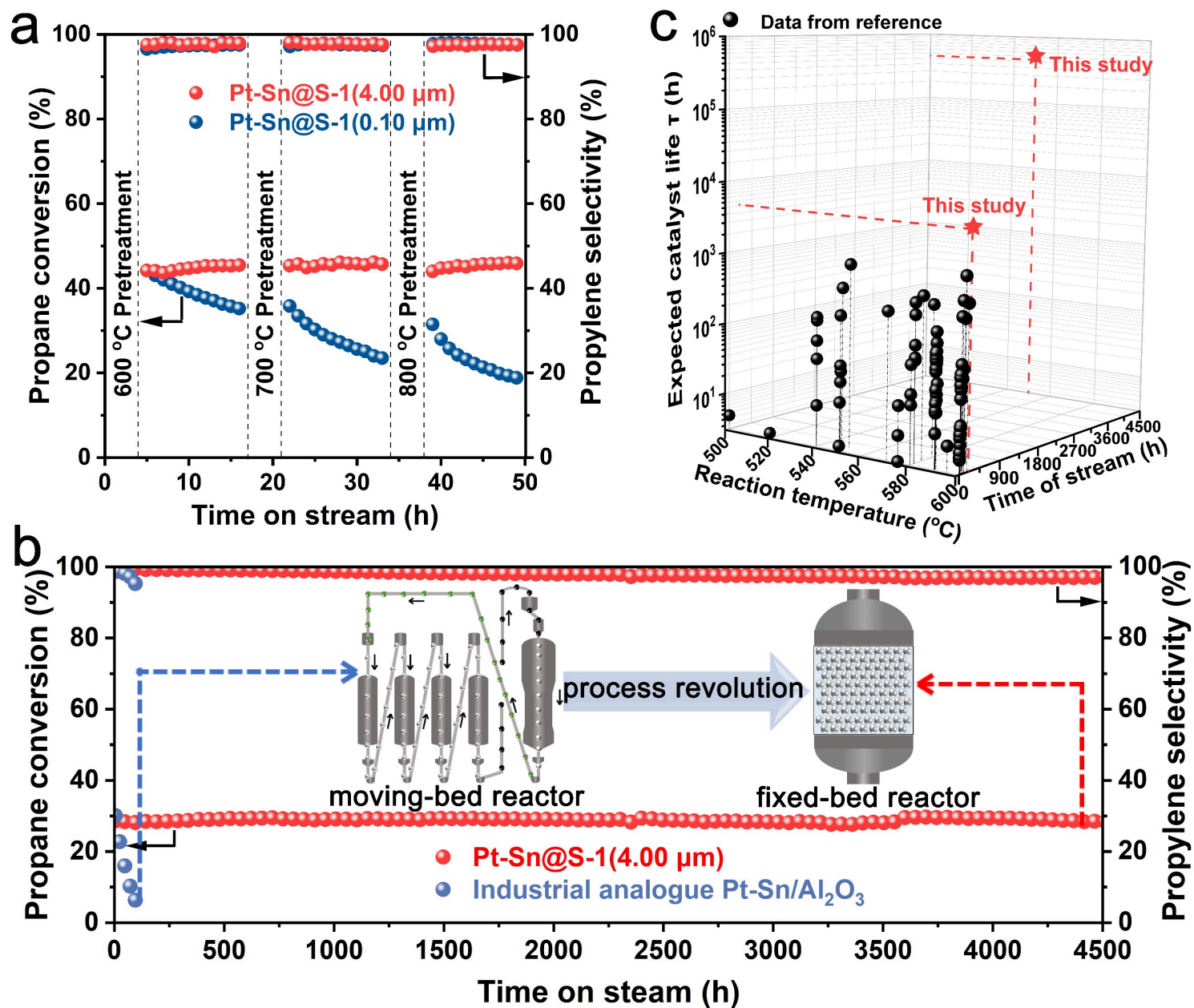


Figure 2

Stability of Pt-Sn@S-1(4.00 μm) in PDH. **a**, Catalytic performance of Pt-Sn@S-1 after pretreatments at different temperatures (test conditions: atmospheric pressure, 100% C₃H₈, WHSV = 5.3 h⁻¹). **b**, Long-term stability test of Pt-Sn@S-1(4.00 μm) and the industrial analogue under the conditions of atmospheric pressure, 100% C₃H₈, WHSV = 5.3 h⁻¹, and $T = 550$ °C. **c**, Catalyst lives for various PDH catalysts reported in literatures and this work (details of this figure are summarized in Supplementary Table 2).

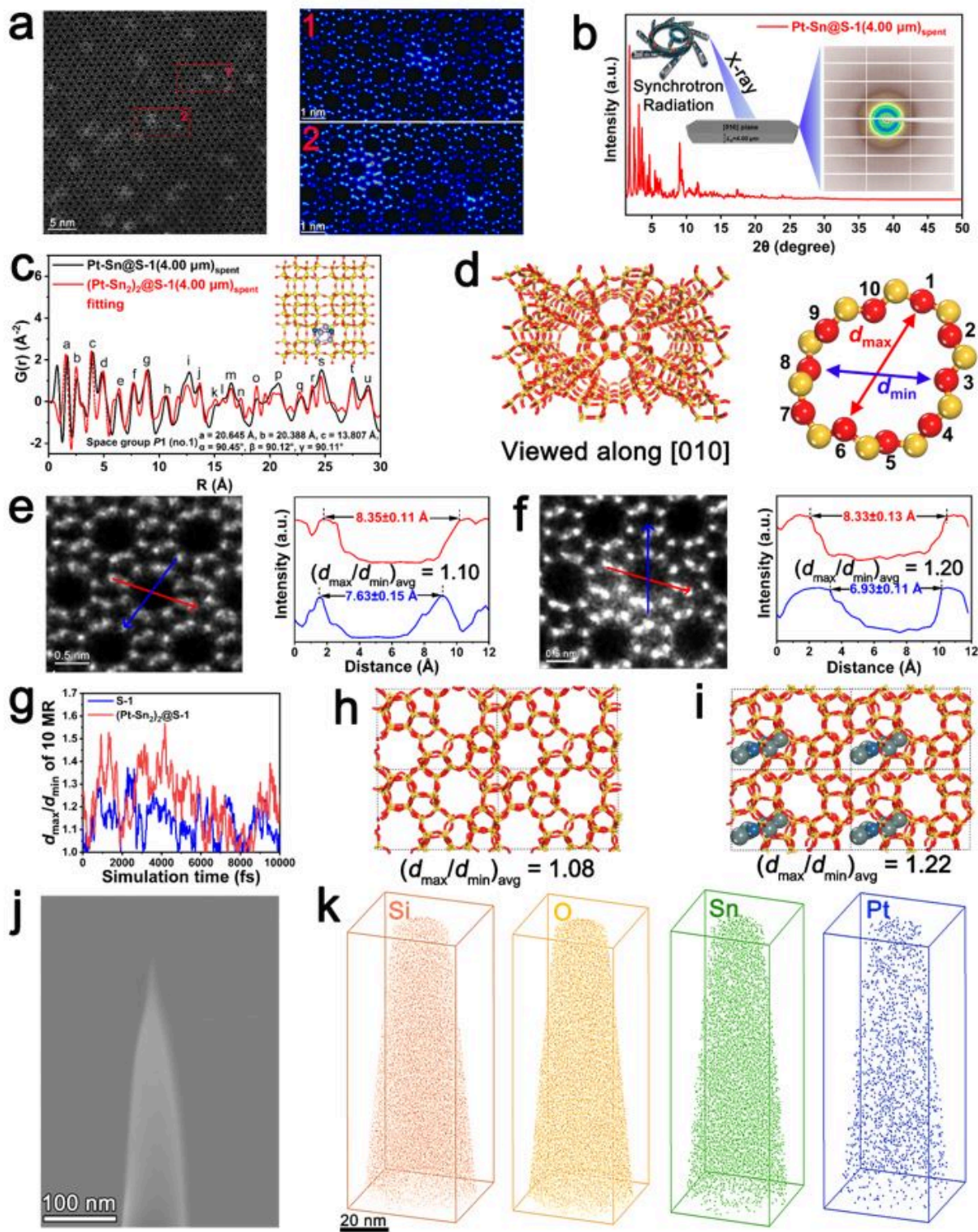


Figure 3

Atomic-level characterization of Pt-Sn@S-1(4.00 μm) after PDH. **a**, STEM images of Pt-Sn@S-1(4.00 μm)_{spent}. **b**, SR-XRD pattern and 2D XRD image of Pt-Sn@S-1(4.00 μm)_{spent}. **c**, Full-range synchrotron PDF analysis for Pt-Sn@S-1(4.00 μm) modelling and corresponding Rietveld refinement of Pt-Sn@S-1(4.00 μm) (inset: cell unit of the optimized theoretical model). **d**, Viewed along the [010] direction of MFI framework and the values of d_{max} and d_{min} in the 10-membered ring. **e**, Profile analysis of 10-membered

ring in S-1 from the [010] projection. **f**, Profile analysis of 10-membered ring from the [010] projection in Pt-Sn@S-1(4.00 μm)_{spent}. **g-i**, Simulated structures for empty MFI framework and MFI framework loaded with (Pt-Sn₂)₂ clusters, and corresponding values of $d_{\text{max}}/d_{\text{min}}$. **j**, Final specimen morphology of (Pt-Sn₂)₂@S-1(4.00 μm) after treatment at 800 °C for APT analysis; and **k**, 3D atom distribution map of Si, O, Sn and Pt within Pt-Sn@S-1(4.00 μm) after treatment at 800 °C. Bounding box dimensions: 30 × 40 × 110 nm³.

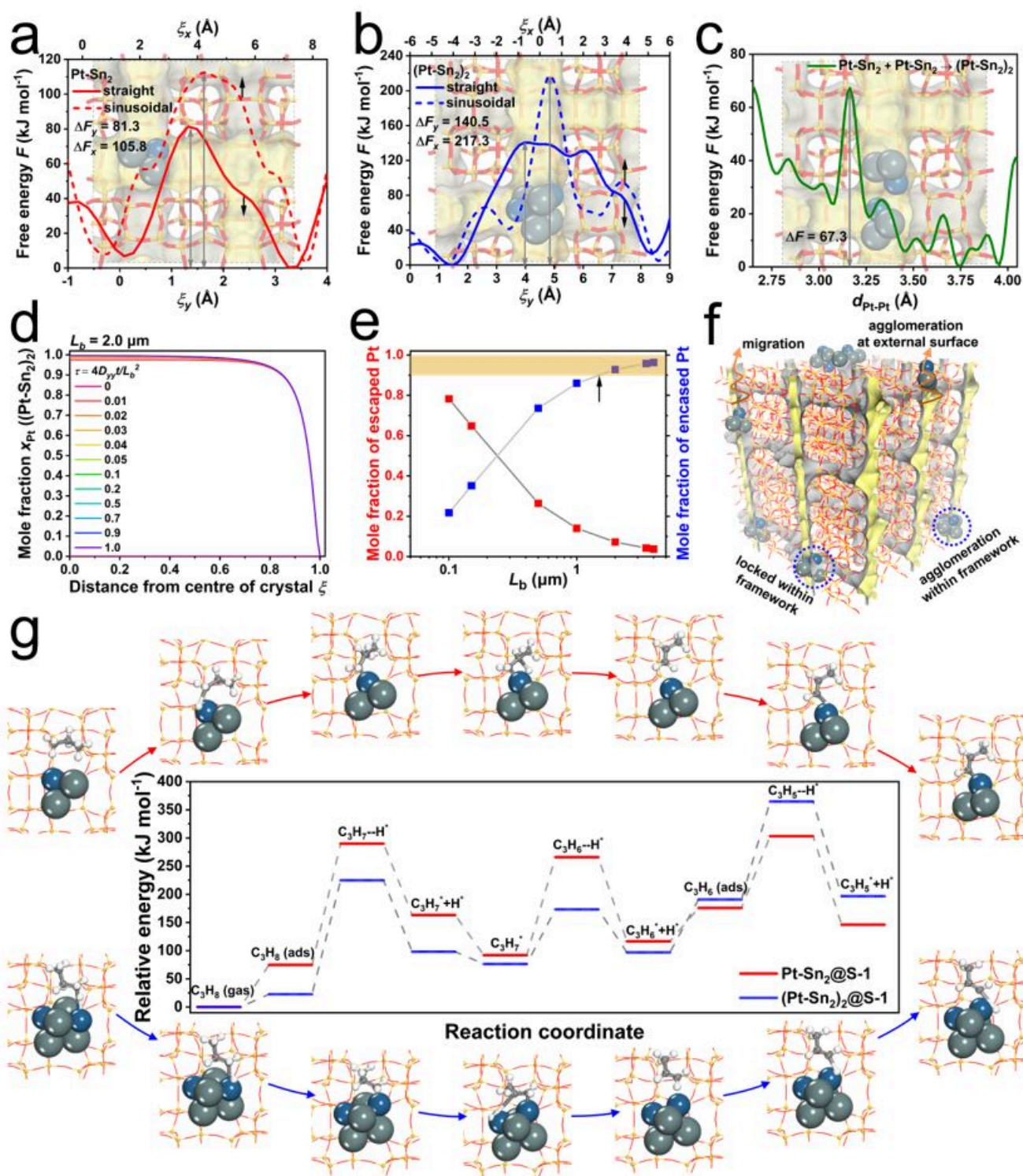


Figure 4

DFT computations for PDH reaction steps and migration-agglomeration modelling for Pt-Sn@S-1 catalysts. Free energy profiles for the mobility of **(a)** Pt-Sn₂ and **(b)** (Pt-Sn₂)₂ clusters along the straight and sinusoidal channels and **(c)** the agglomeration of Pt-Sn₂ clusters into (Pt-Sn₂)₂ clusters within the MFI framework at 600 °C. **d**, Dynamic evolutions of ratios of intracrystalline Pt content of (Pt-Sn₂)₂ clusters to initial Pt content in (Pt-Sn₂)_x@S-1 with the critical *b*-axis length of 2 μm. **e**, Mole fraction of escaped Pt from zeolite channels (left) and mole fraction of encapsulated Pt in zeolite channels (right) versus the *b*-axis length of (Pt-Sn₂)₂@S-1 obtained by migration-agglomeration modelling. **f**, Scheme of Pt-Sn₂ cluster migration-agglomeration in zeolite channel for the formation of locked (Pt-Sn₂)₂ and Pt-Sn nanoparticle. **g**, Energy profiles for dehydrogenation of propane to propylene and coke precursor on Pt-Sn₂ and (Pt-Sn₂)₂ clusters within the MFI framework. All the intermediates marked with * indicate that they are adsorbed on the surfaces of clusters.

Supplementary Files

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