

# Supplementary Materials for

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

**Authors:** Zhikang Xu<sup>1,2†</sup>, Mingbin Gao<sup>3†</sup>, Haibo Zhu<sup>1\*†</sup>, Yuanyuan Yue<sup>1,2</sup>, Zhengshuai Bai<sup>1,2</sup>, Pei Yuan<sup>1,2</sup>, Mao Ye<sup>3\*</sup>, Paolo Fornasiero<sup>4</sup>, Jean-Marie Basset<sup>5</sup>, Xiaojun Bao<sup>2\*</sup>

†The authors contributed equally to the work.

\*Corresponding author. Email:

haibo.zhu@fzu.edu.cn

maoye@dicp.ac.cn

baoxj@fzu.edu.cn

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## Materials and methods

### Materials

Tetraethylorthosilicate (TEOS, 99.99%, Aladdin reagent (Shanghai) Co., Ltd., CAS: 78-10-4); tetrapropylammonium hydroxide solution (TPAOH, 40 wt.%, Aladdin reagent (Shanghai) Co., Ltd., CAS: 4499-86-9); stannous chloride dihydrate ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , 98%, Sahn Chemical Technology (Shanghai) Co., Ltd., CAS: 10025-69-1); chloroplatinic acid hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , >37.5 wt.% Pt, Aladdin reagent (Shanghai) Co., Ltd., CAS: 18497-13-7); ethylenediamine ( $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ , >99%, Sinopharm Chemical Reagent Co., Ltd., CAS: 107-15-3); hydrofluoric acid (HF, 40%, Aladdin reagent (Shanghai) Co., Ltd., CAS: 7664-39-3). Deionized water was supplied from water purification system ( $18.2 \text{ M}\Omega \text{ cm}^{-1}$ ).  $\text{N}_2$  (99.9999%),  $\text{H}_2$  (99.9999%), Ar (99.9999%), 0.5% $\text{H}_2$ -99.5%Ar (99.999%), 10%CO-90%Ar (99.999%),  $\text{C}_3\text{H}_6$  (99.99%) and 5% CO-95%  $\text{N}_2$  (99.999%) were purchased from Fujian Jiuce Gas Co., Ltd.  $\text{C}_3\text{H}_8$  (99.9%) was supplied by Henan Xinshengyuan Chemical Co., Ltd. All the above materials were used directly as received without further purification.

### Synthesis of Pt-Sn@S-1

The Pt-Sn@S-1 samples with different lengths of *b*-axis (defined as  $L_b$ ) were synthesized via one-pot hydrothermal crystallization in fluoride media. Typically, 8.24 g of TEOS, 8.12 g of TPAOH and 3.82 g of deionized water were mixed in a glass beaker at room temperature. Under continuous stirring for 5 hours, 17.0 mg of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  was added into the above solution under stirring until  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  was completely dissolved. The obtained homogeneous mixture was denoted as solution A. Subsequently, in another glass beaker, a Pt solution was prepared by dissolving 2.00 g of an aqueous solution containing 20.0 mg of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  into 0.50 mL of ethylenediamine under stirring at room temperature and denoted as solution B. Then, the solutions A and B were mixed to obtain a synthesis gel under stirring continuously for 1 hour at room temperature, and the molar composition of the synthesis gel was 1.0 TEOS: 0.4 TPAOH: 15  $\text{H}_2\text{O}$ . Afterwards, a certain amount of HF (the molar ratio F/Si = 0.00~0.51) was added slowly and the resulting solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave. The crystallization was conducted in an oven at 170 °C for 24 hours under static conditions. The obtained solid product was collected by filtration, washed with deionized water for several times, and dried at 120 °C overnight. Finally, 2.37 g of powder product was reduced from 30 to 600 °C at a heating rate of 2 °C  $\text{min}^{-1}$ , and then held at 600 °C for 1 hour in high purity hydrogen flowing at 10 mL  $\text{min}^{-1}$ . The obtained Pt-Sn@S-1 samples after reduction are named as Pt-Sn@S-1(0.10  $\mu\text{m}$ ), Pt-Sn@S-1(0.15  $\mu\text{m}$ ), Pt-Sn@S-1(0.50  $\mu\text{m}$ ), Pt-Sn@S-1(3.00  $\mu\text{m}$ ) and Pt-Sn@S-1(4.00  $\mu\text{m}$ ), and the numbers in brackets denote the length of *b*-axis of the S-1 crystals in  $\mu\text{m}$ .

## Characterizations

### Inductively coupled plasma atomic emission spectrometry (ICP-AES)

The actual Pt and Sn loadings of the Pt-Sn@S-1 samples after reduction were measured on a Thermo IRIS Intrepid II XSP atomic emission spectrometer equipped with inductively coupled plasma atomic emission spectrometry (ICP-AES). The samples were fully dissolved in aqua regia and then diluted before the measurements. The concentration of Pt (Sn) in the test samples were obtained by referring to the standard solution of Pt (Sn).

### Scanning electron microscopy (SEM)

To measure the morphology of the Pt-Sn@S-1 samples after reduction, SEM images were recorded on a Nova Nano SEM 230 instrument. Prior to the measurement, the samples were dispersed into fine powder and pre-treated at 120 °C for 2 hours. The SEM samples were prepared by drop-casting the samples on clean silicon wafers and then spraying with gold.

### Powder X-ray diffraction (PXRD)

The PXRD patterns of the Pt-Sn@S-1 samples after reduction were collected on a Rigaku Ultimate III diffractometer (X-ray source: Cu K $\alpha$  ( $\gamma = 1.5406 \text{ \AA}$ ) radiation) in the  $2\theta$  range of 5 to 60°. The dried Pt-Sn@S-1 samples were pressed and placed on the XRD tester for testing. The material composition and crystal structure information on the catalysts were identified by comparing the collected diffraction patterns with the reference patterns in the PDF database.

### High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM)

To know the location distribution of the PtSn species in the zeolite framework, HAADF-STEM images of the Pt-Sn@S-1 samples after reduction were collected on a Thermo Fisher Scientific X-CFEG Spectra 300 instrument operated at 300 kV. The Pt-Sn@S-1(0.10  $\mu\text{m}$ ) sample powder was dispersed in ethanol by ultrasonic wave and deposited on a copper grid coated with an ultra-thin porous carbon film.

### Dual-beam focused ion beam/scanning electron microscopy (FIB/SEM)

The Pt-Sn@S-1(4.00  $\mu\text{m}$ ) sample after reduction for STEM analysis was prepared on copper microcolumn array with a FEI Helios G4 CX double-beam FIB/SEM. Firstly, a layer of C protective cap was coated on the single crystal of the sample. Secondly, it was cut into pieces with 30 kV gallium ion beam, and slowly transferred and fixed to a copper microcolumn display. Finally, most of the remaining C caps were removed with a low 2 kV beam, and the sample was thinned to a thickness of about 50 nm on the copper microcolumn array.

### Synchrotron radiation-based single crystal X-ray diffraction (SR-XRD)

The SR-XRD data of the fresh and spent Pt-Sn@S-1 (4.00  $\mu\text{m}$ ) were collected at the BL17B beamline of Shanghai Synchrotron Radiation Facility (SSRF, Shanghai, China).

Prior to measurement, the powder sample was dried in vacuum. The powder sample was analyzed in the CaF<sub>2</sub> window, and the background of CaF<sub>2</sub> spots was deducted and the two-dimensional X-ray image collection was carried out.

#### Pair distribution function (PDF)

The PDF measurements and analysis of X-ray total scattering data were measured at beamline the BL17B of the National Facility for Protein Science (NFPS), Shanghai Synchrotron Radiation Facility (SSRF) operated at an energy of 20 keV (0.6199 Å). The two-dimensional (2D) XRD image was first integrated to obtain a one-dimensional (1D) total scattering intensity  $I(Q)$  calibration by CeO<sub>2</sub> celebrant by Dioptas 0.5.2 package. Additional scattering measurements with samples held in a Kapton capillary were performed under the same conditions for background subtraction. Then the reduced pair distribution function  $G(r)$  was obtained through Fourier transform of the total scattering structure function  $S(Q)$  derived from  $I(Q)$  by PDFgetX. The following  $G(r)$  equation was used:

$$G(r) = \frac{2}{\pi} \int_0^{\infty} Q[S(Q) - 1] \sin(Qr) dQ \quad (S1)$$

The PDF Rietveld refinement was conducted by PDFgui. The initial structural model was built based on the powder XRD Rietveld refinement structural model. The following parameters including scaling factor, cell parameters, atomic positions except particular positions, isotropic atomic displacement parameters (Biso), and dynamic correlation factor (delta2) were refined.

#### X-ray absorption fine structure (XAFS) spectra

The XAFS spectra of Pt L<sub>3</sub>-edge of the fresh and spent Pt-Sn@S-1 (4.00 μm) and H<sub>2</sub>PtCl<sub>6</sub>·2SnCl<sub>2</sub>@S-1(4.00 μm) samples were collected at the 1W1B beamline of the Beijing Synchrotron Radiation Facility (BSRF, Beijing, China) to investigate how Pt interacts with Sn. The spectra of the reference samples (Pt, PtO<sub>2</sub>, H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O) were acquired in transmission mode, and the spectra of the the fresh and spent Pt-Sn@S-1 (4.00 μm) and H<sub>2</sub>PtCl<sub>6</sub>·2SnCl<sub>2</sub>@S-1(4.00 μm) samples were collected in fluorescence mode. Prior to measurement, the dried powder samples were evenly distributed on special adhesive tapes. All obtained EXAFS data were calibrated by referring to the standard spectra of Pt foil using the Demeter software packages. According to the quality of data ranges ( $k = 3-14 \text{ Å}^{-1}$ ,  $R = 1.5-3.5 \text{ Å}$ ), the Pt L<sub>3</sub>-edge EXAFS spectra were obtained by subtracting the postage appropriate background, and the  $\chi(k)$  data of Pt-Sn@S-1 were Fourier transformed to real ( $R$ ) space using hanging windows.

#### X-ray photoelectron spectroscopy (XPS)

To know the chemical states of Pt and Sn in the samples, the XPS of the Pt-Sn@S-1 samples after reduction were collected on a Kratos Axis Ultra DLD spectrometer (X-ray source: Al K $\alpha$  ( $h\nu = 1486.6 \text{ eV}$ )). The peak fitting of Pt4f and Sn3d was made by using the Thermo Advantage software, and the C1s peak binding energy of contaminated carbon was calibrated to 284.6 eV.

#### Fourier-transform infrared spectroscopy of CO adsorption (CO-FTIR)

CO-FTIR spectra were taken on a Thermo Scientific Nicolet IS50 FTIR spectrometer equipped with an *in-situ* cell. Before measurement, the Pt-Sn@S-1 sample (~10 mg) disk was carefully transferred into the cell. The samples were reduced in H<sub>2</sub> flow of 20 mL min<sup>-1</sup> at 600 °C for 1 hour. Afterward, the cell was cooled down to room temperature in a N<sub>2</sub> flow, and then 5%CO in N<sub>2</sub> was introduced into the cell. Subsequently, the cell was purged with a N<sub>2</sub> flow to remove physically adsorbed CO. The frequency of CO chemisorbed was obtained after the subtraction of the spectra recorded at room temperature before CO chemisorption.

#### Fourier-transform infrared spectroscopy of C<sub>3</sub>H<sub>6</sub> adsorption (C<sub>3</sub>H<sub>6</sub>-FTIR)

The dynamic adsorption experiment with C<sub>3</sub>H<sub>6</sub> was carried out on the Thermo Scientific Nicolet iS50 FTIR spectrometer with an *in-situ* cell. The dried samples were reduced at 600 °C for 1 hour, purged with N<sub>2</sub>, and cooled to room temperature, followed by adsorption of C<sub>3</sub>H<sub>6</sub> for 20 minutes. The real-time C<sub>3</sub>H<sub>6</sub> desorbed FTIR-spectra were collected in a flow of N<sub>2</sub> (20 mL min<sup>-1</sup>) until the peak of C<sub>3</sub>H<sub>6</sub> (absorbance @ 2800-3000 cm<sup>-1</sup>) disappeared.

#### Intelligent gravitation analysis (IGA)

Dynamic adsorption curves of C<sub>3</sub>H<sub>8</sub> were measured on an intelligent gravimetric analyzer (IGA-100B-DSMS) at 298 K. Prior to the measurement, the sample to be tested was loaded into the sample chamber and activated for 12 hours under high vacuum at 200 °C. After cooling to the adsorption temperature (25 °C), the pressure was increased to 1 bar with a ramp rate of 200 mbar min<sup>-1</sup> and maintained for 200 min.

#### CO chemisorption

The Pt dispersion in Pt-Sn@S-1(4.00 μm) was measured by CO chemisorption using a BELSORB-max apparatus (Japan) at room temperature. Prior to the CO chemisorption, the dried sample was pretreated in a flow of Ar (20 mL min<sup>-1</sup>) for 1 hour at 150 °C, and then reduced in a flow of 0.5%H<sub>2</sub>/Ar (20 mL min<sup>-1</sup>) for 1 hour at 600 °C. Subsequently, the sample was cooled to room temperature in Ar (20 mL min<sup>-1</sup>), and a 10%CO/Ar mixture was introduced into the cell until no more CO was adsorbed. Finally, the Pt metal dispersion was calculated by measuring the amount of chemisorbed CO.

#### Atom probe tomography (APT)

Needle-shaped specimens for atom probe tomography (APT) analysis were prepared by a standard electropolishing technique. APT characterization of the same needle sample was conducted on a Cameca LEAP 4000X SI instrument, at a specimen base temperature of 50 K, under UV laser pulsing at a pulse laser energy of 250 pJ, a pulse frequency of 200 kHz and a target evaporation rate of 0.5% per pulse. APT datum reconstruction and statistical analysis were performed by using a commercial software (Cameca IVAS3.6.12).

#### Thermogravimetric analysis (TGA)

To determine the total amounts of coke in the catalysts, thermogravimetric analyses

(TGA) of the deactivated Pt-Sn@S-1 samples were conducted on a Mettler-Toledo thermobalance in a flow of dry air ( $10 \text{ mL min}^{-1}$ ) from 50 to 800 °C at a heating rate of  $10 \text{ °C min}^{-1}$ . The coking contents were calculated from the weight losses above 373 K by considering that the samples had been dried at 373 K before measurement.

#### Structural illumination imaging (SIM)

The spatiotemporal distribution of the aromatic hydrocarbons deposited in Pt-Sn@S-1(4.00  $\mu\text{m}$ ) crystals was obtained by SIM. The super-resolution image was collected by a Nikon N-SIM super-resolution microscope system equipped with a motorized inverted microscope ECLIPSE Ti2-E, a  $\times 100/\text{NA } 1.49$  oil immersion TIRF objective lens (CFI HP) and an ORCA-Flash 4.0 sCMOS camera (Hamamatsu Photonics K. K.). The imaging of Pt-Sn@S-1(4.00  $\mu\text{m}$ ) crystals with four photomultiplier tubes was conducted in the ranges of 435-485, 500-545, 570-640, 663-738 nm for the four lasers on emission detection of SIM. The wavelengths of multilaser light sources were 405, 488, 561, and 640 nm, respectively. In a typical experiment, the Pt-Sn@S-1(4.00  $\mu\text{m}$ ) crystals after different reaction times were dispersed on glass-bottomed culture dishes (35 mm dish with 20 mm well) and placed close to the objective lens. Subsequently, the images of the samples were obtained in the middle of zeolitic crystals at room temperature. Finally, the software NIS-Elements Ar and N-SIM Analysis were used to study the obtained images and computationally reconstruct the super-resolution images of the Pt-Sn@S-1(4.00  $\mu\text{m}$ ) crystals.

## Catalytic reaction

### Propane dehydrogenation experiments

The propane dehydrogenation experiments over Pt-Sn@S-1 were performed in a fixed-bed reactor at atmospheric pressure. Typically, 0.5 g of a Pt-Sn@S-1 sample diluted with 2.0 g of quartz sand was pretreated in a flow of H<sub>2</sub> at 600 °C at a ramp rate of 5 °C min<sup>-1</sup> from 30 up to 600 °C and then held at 600 °C for 1 hour, followed by feeding pure propane at different WHSVs (kg<sub>C<sub>3</sub>H<sub>8</sub></sub> kg<sub>cat.</sub><sup>-1</sup> h<sup>-1</sup>). The temperature of the catalytic reaction was measured by a thermocouple fixed in the catalyst bed layer. The analysis of reaction products was made using an on-line GC (Panna A-91) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID).

### H<sub>2</sub>S, H<sub>2</sub>O and O<sub>2</sub> resistance experiments

The H<sub>2</sub>S and H<sub>2</sub>O resistance tests were carried out by introducing H<sub>2</sub>S (25 ppm) or H<sub>2</sub>O (37.8 v%) into the propane stream, and the reaction was performed at 600 °C. The O<sub>2</sub> resistance test was carried out by calcinating the spent catalyst in a flow of O<sub>2</sub> at 500 °C for 12 hours, followed by reduction in H<sub>2</sub> at 600 °C for 1 hour. Finally, the treated sample was used in propane dehydrogenation reaction under the conditions WHSV 5.3 h<sup>-1</sup> and 600 °C. The analysis of reaction products was made using an on-line GC (A-91) equipped with a TCD and a FID.

### Catalytic performance calculations

Propane conversion, propylene selectivity and carbon balance (> 98%) were calculated on the carbon basis by Equations S2 to S4, respectively.

$$\text{Propane conversion (\%)} = ([F_{C_3H_8}]_{\text{inlet}} - [F_{C_3H_8}]_{\text{outlet}}) / [F_{C_3H_8}]_{\text{inlet}} \quad (\text{S2})$$

$$\text{Propylene selectivity (\%)} = [F_{C_3H_6}]_{\text{outlet}} / ([F_{C_3H_8}]_{\text{inlet}} - [F_{C_3H_8}]_{\text{outlet}}) \quad (\text{S3})$$

$$\text{Carbon balance (\%)} =$$

$$(1/3[F_{CH_4}]_{\text{outlet}} + 2/3[F_{C_2H_6}]_{\text{outlet}} + 2/3[F_{C_2H_4}]_{\text{outlet}} + [F_{C_3H_6}]_{\text{outlet}} + [F_{C_3H_8}]_{\text{outlet}}) / [F_{C_3H_8}]_{\text{inlet}} \quad (\text{S4})$$

### Mass transfer effects

The Mears' criterion and Thiele modulus were used to examine the effects of external and internal mass transfer on propane dehydrogenation over Pt-Sn@S-1 (4.00 μm), respectively.

The external mass transfer effect can be neglected if the following Mears' criterion is met.

$$\frac{-r_A \rho_b R_{\text{cat}}^n}{k_c C_{Ab}} < 0.15 \quad (\text{S5})$$

where:

$-r_A$  = reaction rate, kmol kg<sup>-1</sup> s<sup>-1</sup>;

$n$  = reaction order;

$R_{\text{cat}}$  = catalyst pellet radius, m;

$\rho_b$  = catalyst bed density, kg m<sup>-3</sup>;

$k_c$  = mass transfer coefficient, m s<sup>-1</sup>;

$C_{Ab}$  = bulk gas concentration of A, kmol m<sup>-3</sup>.

The internal mass transfer effect can be neglected if the following Thiele modulus is met.

$$\frac{-r_A \rho_c R_{\text{cat}}^2}{D_e C_{As}} < 1 \quad (\text{S6})$$

where:

$-r_A$  = reaction rate, kmol kg<sup>-1</sup> s<sup>-1</sup>;

$R_{\text{cat}}$  = catalyst pellet radius, m;

$\rho_c$  = solid catalyst density, kg m<sup>-3</sup>;

$D_e$  = effective gas-phase diffusivity, m<sup>2</sup> s<sup>-1</sup>;

$C_{As}$  = gas concentration of A at the catalyst surface, kmol m<sup>-3</sup>.

## Periodic density functional theory (DFT) computations

### Periodic *ab initio* static simulations

Theoretical computations on the stability of individual  $(\text{Pt-Sn}_2)_x$  ( $x = 1, 2, 3$  and  $4$ ) clusters encaged at different locations of the MFI framework were performed by periodic DFT. Based on the analysis of stability of  $(\text{Pt-Sn}_2)_x$  ( $x = 1, 2, 3$  and  $4$ ) clusters (**Extended Data Fig. 6a-h**), the energy barriers of the elemental PDH reaction steps catalyzed by  $(\text{Pt-Sn}_2)_x$  ( $x = 1$  and  $2$ ) clusters encaged in the MFI framework were performed by periodic DFT. All the periodic DFT computations were performed using the plane-wave pseudopotential method and the generalized gradient approximation (GGA), implemented with the CASTEP code. The plane-wave basis set was converged at a cutoff energy of 400 eV for each model. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation function was used to describe the exchange-correlation effects. Interaction between the valence electrons and the ion core was substituted by an ultrasoft pseudopotential. The self-consistent convergence accuracy was set at  $2 \times 10^{-5}$  eV per atom, the maximum force was 0.08 eV per Å, the maximum stress was 0.1 GPa, and the maximum displacement was  $5 \times 10^{-3}$  Å<sup>1,2</sup>. Here, a single unit cell was employed to simulate  $(\text{Pt-Sn}_2)_x\text{@S-1}$ . A Monkhorst-Pack grid of  $1 \times 1 \times 1$  ( $k$ -point) was used to sample the Brillouin zone for geometry optimization and for calculating the energy of  $(\text{Pt-Sn}_2)_x\text{@S-1}$  including intermediates of the PDH reaction. The complete LST/QST method was implemented for transition search of the elemental PDH reactions.

### Periodic *ab initio* dynamic simulations

To investigate the mobility of  $(\text{Pt-Sn}_2)_x$  ( $x = 1$  and  $2$ ) clusters within S-1, *ab initio* molecular dynamics (AIMD) simulations were performed using the CP2K software package (version 7.1)<sup>3,4</sup>. The *rev*PBE-D3 level of theory<sup>5</sup> was used in combination with Gaussian DZVP (double-zeta valence polarized) basis set<sup>6</sup>, a plane-wave basis set with a cut-off of 350 Ry and a relative cut-off of 60 Ry, and Goedecker-Teter-Hutter (GTH) pseudopotentials<sup>7</sup> for AIMD simulations. The self-consistent field convergence criterion was set at  $10^{-6}$ . All simulations were performed in a periodic zeolite unit cell that represents the MFI topology containing 96 T sites and  $\text{Pt-Sn}_2$  and  $(\text{Pt-Sn}_2)_2$  clusters, respectively. For each simulation case, the cell parameters were obtained by computing time-averaged values from a 20 ps  $NpT$  (amount  $N$ , pressure  $p$  and temperature  $T$ ) molecular dynamics simulation at 600 °C and atmospheric pressure (**Supplementary Tables 11,12**). The temperature and pressure were controlled by a chain of five Nosé-Hoover thermostats<sup>8-11</sup> with a time constant of 1000 wavenumbers and a Martyna-Tobias-Klein (MTK) barostat<sup>12,13</sup>, respectively. A time step of 1 fs was employed for integrating the equations of motion. Production  $NpT$  molecular dynamics runs that were used as input for the metadynamics (MTD) simulations were carried out in the  $NVT$  (amount  $N$ , volume  $V$  and temperature  $T$ ) ensemble at 600 °C<sup>14,15</sup>.

In MTD simulations<sup>16,17</sup>, the bias potential is constructed on the fly by gradually adding Gaussian shaped hills. The bias potential  $V_G(q, t)$  becomes then the sum of all Gaussian hills by following equation

$$V_G(q, t) = h \sum_{\substack{t'=\tau_G, 2\tau_G, \dots \\ t' < t}} \exp\left(-\frac{(q-q(t'))^2}{2w^2}\right) \quad (S7)$$

where  $q$  is the reaction or diffusion coordinate,  $h$  and  $w$  are the amplitude and width of the Gaussian hill contributions, which are added to the system after each time interval  $\tau_G$  and are systematically updated during the simulation to allow for an accurate and fast convergence, and  $t'$  is the simulation time. After a sufficiently long simulation time, the bias potential is related to the free energy  $F(q)$  via

$$\lim_{t \rightarrow \infty} V_G(q, t) \sim -F(q) \quad (S8)$$

The free energy surface (FES) of the system can be reconstructed based on an inversion of the time dependent bias potential.

All MTD simulations were performed with the CP2K software interfaced with PLUMED<sup>18,19</sup>. Computational details of the MTD technique applied in this work can be found in the literatures<sup>20-22</sup>. A 1D free energy surface for the mobility of Pt-Sn<sub>2</sub> and (Pt-Sn<sub>2</sub>)<sub>2</sub> clusters and agglomeration of Pt-Sn<sub>2</sub> clusters within the MFI framework was constructed by selecting a 1D reaction or diffusion coordinate. As shown in **Extended Data Fig. 8g, h**, the collective variables (CVs) for the migration of (Pt-Sn<sub>2</sub>)<sub>x</sub> ( $x = 1$  and  $2$ ) clusters along the straight and sinusoidal channels of the MFI framework were defined as  $\xi_x$  and  $\xi_y$ , respectively, and the initial locations of (Pt-Sn<sub>2</sub>)<sub>x</sub> clusters were at the intersection sites of the MFI framework. The CVs for the agglomeration between two Pt-Sn<sub>2</sub> clusters were defined by the distance between Pt and Pt. For the simulations of mobility of Pt-Sn<sub>2</sub> and (Pt-Sn<sub>2</sub>)<sub>2</sub> clusters within the MFI framework, the initial height of the Gaussian potentials was set at 5 kJ mol<sup>-1</sup> and after each recrossing of the transition point, the height of the added Gaussian hills was halved to enhance the FES convergence, until a value of 2.5 kJ mol<sup>-1</sup> was obtained. The width of all Gaussians was set to 0.5. For the simulations of dimerization of Pt-Sn<sub>2</sub> to (Pt-Sn<sub>2</sub>)<sub>2</sub> within the MFI framework, the initial height of the Gaussian potentials was set to 5 kJ mol<sup>-1</sup> and after each recrossing of the transition point, the height of the added Gaussian hills was halved to enhance the FES convergence, until a value of 1.25 kJ mol<sup>-1</sup> was obtained. The width of all Gaussians was set to 0.04. A new hill was spawned every 100 time steps and the integration time step was set at 1 fs for all MTD simulations. Furthermore, quadratic walls were used to restrict the simulation to an area of interest on the FES, by limiting the mobility of (Pt-Sn<sub>2</sub>)<sub>x</sub> clusters along the straight or sinusoidal channels of the MFI framework and the locations of two Pt-Sn<sub>2</sub> clusters at intersection sites of the MFI framework. The force constant of the quadratic walls was set to 2000 kJ mol<sup>-1</sup> Å<sup>-2</sup>.

From the obtained FES, the mobility  $D_{yy}$  and  $D_{xx}$  of Pt-Sn<sub>2</sub> and (Pt-Sn<sub>2</sub>)<sub>2</sub> along the straight or sinusoidal channels, respectively, of the MFI framework can be estimated from transition state theory<sup>23,24</sup>. The hopping rate  $k$  from location A to location B is given by

$$k_{A \rightarrow B} = \sqrt{\frac{1}{2\beta\pi m}} \frac{e^{-\beta F(q^*)}}{\int_A^B e^{-\beta F(q)} dq} \quad (S9)$$

where  $\beta = 1/(k_B T)$ ,  $k_B$  is the Boltzmann constant,  $T$  is the temperature,  $m$  is the mass, and the superscript  $*$  is the top energy barrier of the reaction coordinate. The hopping

rate is then easily converted to mobility  $D$  by

$$D = \frac{1}{6} k_{A \rightarrow B} \lambda^2 \quad (\text{S10})$$

where  $\lambda$  is the lattice hop distance.

The forward transition-state reaction kinetic constant  $k_r$  can be written as

$$k_r = A \frac{e^{-\beta F(q^*)}}{\int_R^* e^{-\beta F(q)} dq} \quad (\text{S11})$$

where the prefactor  $A = \left(\frac{1}{2\beta\pi}\right)^{1/2} \langle Z^{1/2} \rangle_{q=q^*}$  can be calculated by the method introduced by Bailleul et al.<sup>25</sup>.

### Agglomeration-migration modelling

Denoting a Pt-Sn<sub>2</sub> cluster as reactant R and a (Pt-Sn<sub>2</sub>)<sub>2</sub> cluster as product P, the agglomeration of R into P can be presented as  $2R \rightarrow P$ , whose reaction kinetics constant  $k_r$  at 600 °C is obtained by AIMD simulations ( $k_r = 4.1 \times 10^6 \text{ s}^{-1}$ ). The mobility  $D_{yy}$  of R and P along the straight channel of the MFI framework is estimated by AIMD simulations ( $D_{yy} = 1.1 \times 10^{-17} \text{ s}^{-1}$ ). Here, as shown in Fig. 4b, P within the MFI framework can be assumed to be approximatively immobile. Thus, the partial differential equations (PDEs) of reaction-mobility of P and R within the zeolite are

$$\frac{\partial C_R}{\partial t} = D_{yy,R} \frac{d^2 C_R}{dy^2} - 2r \quad (\text{S12})$$

$$\frac{\partial C_P}{\partial t} = r \quad (\text{S13})$$

where reaction rate  $r = k_r C_R^2$ ,  $C$  is the intracrystalline content of clusters,  $t$  the time, and  $y$  the Cartesian coordinate. Transforming Equation S12 into the dimensionless form by introducing dimensionless variables  $y_R = C_R/C_R^0$ ,  $R = r/r^0$ ,  $\xi_y = y/l_b$ ,  $\tau = D_{yy,R} \cdot t/l_b^2$  and  $\Phi^2 = r^0 \cdot l_b^2 / (D_{yy,R} \cdot C_R^0)$ , where  $C_R^0$  is the initial content of R within the zeolite,  $r^0$  the reaction rate at the initial content, and  $l_b$  the half length of  $b$ -axis of (Pt-Sn<sub>2</sub>)<sub>x</sub>@S-1. Equations 12 and 13 can be rewritten as

$$\frac{\partial y_R}{\partial \tau} = \frac{d^2 y_R}{d\xi_y^2} - 2\Phi^2 R \quad (\text{S14})$$

$$\frac{\partial y_P}{\partial \tau} = \Phi^2 R \quad (\text{S15})$$

The initial and boundary conditions can be described by

$$\text{I. C. } \tau = 0, 0 \leq \xi_y \leq 1, y_R = 1 \text{ and } y_P = 0 \quad (\text{S16})$$

$$\text{B. C. 1 } \xi_y = 1, y_R = 0 \text{ and } y_P = 0 \quad (\text{S17})$$

$$\text{B. C. 2 } \xi_y = 0, \frac{\partial y_R}{\partial \tau} = 0 \text{ and } \frac{\partial y_P}{\partial \tau} = 0 \quad (\text{S18})$$

Numerical method was implemented to solve the 1D dynamic PDEs by *in-house* developed code. The dynamic evolutions of intracrystalline contents of Pt-Sn<sub>2</sub> and (Pt-Sn<sub>2</sub>)<sub>2</sub> clusters within (Pt-Sn<sub>2</sub>)<sub>x</sub>@S-1 can be visualized.

**Supplementary Table 1.**

Parameters used and estimated for assessing internal and external mass transfer limitations for propane dehydrogenation over Pt-Sn@S-1(4.00  $\mu\text{m}$ ).

| Parameters                                                                            | Pt-Sn@S-1(4.00 $\mu\text{m}$ ) |
|---------------------------------------------------------------------------------------|--------------------------------|
| Catalyst mass, $g_{\text{cat}}$                                                       | 0.50                           |
| Reaction temperature $T$ , $^{\circ}\text{C}$                                         | 600 $^{\circ}\text{C}$         |
| Reaction pressure $p$ , Mbar                                                          | 0.10                           |
| Solid catalyst density $\rho_c$ , $\text{kg m}^{-3}$                                  | 2200                           |
| Catalyst bed density $\rho_b$ , $\text{kg m}^{-3}$                                    | 880                            |
| Catalyst pellet radius $R_{\text{cat}}$ , m                                           | $1.50 \times 10^{-5}$          |
| Reaction rate $-r_A$ , $\text{kmol kg}^{-1} \text{s}^{-1}$                            | $1.05 \times 10^{-5}$          |
| Reaction order $n$                                                                    | 1.00                           |
| Mass transfer coefficient $k_c$ , $\text{m s}^{-1}$                                   | $8.46 \times 10^{-3}$          |
| Bulk gas concentration of A $C_{\text{Ab}}$ , $\text{kmol m}^{-3}$                    | $1.39 \times 10^{-2}$          |
| Effective gas-phase diffusivity $D_e$ , $\text{m}^2 \text{s}^{-1}$                    | $6.12 \times 10^{-8}$          |
| Gas concentration of A at the catalyst surface $C_{\text{As}}$ , $\text{kmol m}^{-3}$ | $1.39 \times 10^{-2}$          |
| Thiele modulus (internal mass transfer)                                               | $6.10 \times 10^{-3} \ll 1$    |
| Mears' criterion (external mass transfer)                                             | $1.18 \times 10^{-3} \ll 0.15$ |

As can be seen from Supplementary Table 1, internal and external mass transfer effects can be negligible under the reaction conditions.

**Supplementary Table 2.**

Summary of detailed catalytic performance parameters of some representative Pt-based PDH catalysts reported.

| No. | Catalyst                                          | $T$<br>[°C] | Pt<br>[wt.%] | C <sub>3</sub> H <sub>8</sub> Feed<br>composition<br>[vol%] | WHSV<br>[h <sup>-1</sup> ] <sup>a</sup> | Conv.<br>[%] <sup>b</sup> | Sel.<br>[%] <sup>c</sup> | Specific<br>activity<br>[s <sup>-1</sup> ] <sup>d</sup> | TOF <sup>e</sup> | $k_d$<br>[h <sup>-1</sup> ] <sup>f</sup> | $\tau$<br>[h] <sup>g</sup> | Operat<br>ion<br>time<br>[h] <sup>h</sup> | Ref.                  |
|-----|---------------------------------------------------|-------------|--------------|-------------------------------------------------------------|-----------------------------------------|---------------------------|--------------------------|---------------------------------------------------------|------------------|------------------------------------------|----------------------------|-------------------------------------------|-----------------------|
| 1   | Pt-Sn@S-1(4.00 $\mu$ m)                           | 600         | 0.25         | 100                                                         | 5.30                                    | 44.5-43.4                 | 97.0                     | 1.00                                                    | 1.05             | 0.000<br>223                             | 4478                       | 200                                       | <b>This<br/>study</b> |
| 2   | PtZn/SiO <sub>2</sub> IMA                         | 600         | 0.10         | 67                                                          | 11.0                                    | 34.7-28.2                 | 96.0                     | 4.04                                                    | 8.10             | 0.002                                    | 500                        | 160                                       | (1)                   |
| 3   | PtGa/SiO <sub>2</sub>                             | 600         | 3.00         | 8                                                           | 30.7                                    | 44.7-24.5                 | 98.8                     | 0.56                                                    | 1.69             | 0.018                                    | 54.1                       | 50                                        | (26)                  |
| 4   | PtGa-Pb<br>/SiO <sub>2</sub> (Pt/Pb = 2)          | 600         | 3.00         | 8                                                           | 30.7                                    | 30.3-28.4                 | 99.6                     | 0.38                                                    | 1.15             | 0.001                                    | 1159                       | 96                                        | (26)                  |
| 5   | Pt/Mg(Sn)(Al)O                                    | 600         | 0.50         | 29                                                          | 14.0                                    | 48.3-43.0                 | 86.4                     | 1.05                                                    | 1.07             | 0.002                                    | 561                        | 48                                        | (27)                  |
| 6   | Pt <sub>3</sub> In/SiO <sub>2</sub>               | 600         | 0.30         | 26                                                          | 3.00                                    | 17.5-17.0                 | 92.0                     | 0.08                                                    | -                | 0.018                                    | 57.1                       | 2.5                                       | (28)                  |
| 7   | Pt <sub>3</sub> Ga/CeAl                           | 600         | 1.00         | 26                                                          | 10.0                                    | 41.1-32.2                 | 99.6                     | 0.52                                                    | 1.17             | 0.026                                    | 39.0                       | 15                                        | (29)                  |
| 8   | Pt <sub>3</sub> Ga/Al <sub>2</sub> O <sub>3</sub> | 600         | 1.00         | 26                                                          | 10.0                                    | 39.4-28.1                 | 99.5                     | 0.50                                                    | 1.63             | 0.034                                    | 29.5                       | 15                                        | (29)                  |
| 9   | Pt/CeAl                                           | 600         | 1.00         | 26                                                          | 10.0                                    | 47.1-22.1                 | 62.0                     | 0.59                                                    | 0.89             | 0.076                                    | 13.2                       | 15                                        | (29)                  |
| 10  | PtSn/TS-1                                         | 600         | 0.50         | 16                                                          | 3.00                                    | 53.5-47.7                 | 92.5                     | 0.41                                                    | 1.64             | 0.033                                    | 30.1                       | 7.0                                       | (30)                  |
| 11  | Pt/TA0                                            | 600         | 1.00         | 26                                                          | 10.0                                    | 50.5-21.0                 | 60.0                     | 0.64                                                    | 1.52             | 0.135                                    | 7.4                        | 10                                        | (31)                  |
| 12  | Pt/TA10                                           | 600         | 1.00         | 26                                                          | 10.0                                    | 47.3-25.9                 | 77.0                     | 0.60                                                    | 1.31             | 0.094                                    | 10.6                       | 10                                        | (31)                  |
| 13  | Pt/TA20                                           | 600         | 1.00         | 26                                                          | 10.0                                    | 45.5-17.8                 | 89.0                     | 0.57                                                    | 1.29             | 0.135                                    | 7.4                        | 10                                        | (31)                  |
| 14  | PtSnIn/08Zr-Al                                    | 600         | 0.30         | 16                                                          | 3.30                                    | 57.7-51.7                 | 98.0                     | 0.74                                                    | 4.00             | 0.097                                    | 10.3                       | 2.5                                       | (32)                  |
| 15  | PtCu/Al <sub>2</sub> O <sub>3</sub>               | 600         | 0.10         | 16                                                          | 4.00                                    | 40.0-22.0                 | 90.0                     | 1.97                                                    | 1.97             | 0.213                                    | 4.7                        | 4.0                                       | (33)                  |
| 16  | K-PtSn@MFI-600-<br>22h                            | 600         | 0.40         | 24                                                          | 29.5                                    | 38.7-31.9                 | 97.0                     | 3.50                                                    | 3.50             | 0.012                                    | 83.3                       | 25                                        | (34)                  |
| 17  | PtSn@MFI-600                                      | 600         | 0.42         | 24                                                          | 1.80                                    | 71.0-42.0                 | 88.0-                    | 0.34                                                    | 0.34             | 0.014                                    | 71.4                       | 65                                        | (35)                  |

|    |                                                    |     |      |    |      |           |               |       |       |            |      |     |      |
|----|----------------------------------------------------|-----|------|----|------|-----------|---------------|-------|-------|------------|------|-----|------|
|    |                                                    |     |      |    |      |           | 95.0          |       |       |            |      |     |      |
| 18 | PtFe/SBA-15                                        | 600 | 0.75 | 26 | 3.43 | 34.0-30.0 | 85.0          | 0.16  | 0.97  | 0.108      | 9.2  | 1.7 | (36) |
| 19 | PtFeSn-SBA-15                                      | 600 | 1.00 | 25 | 4.05 | 56.8-44.0 | 89.0          | 0.25  | 0.058 | 0.016      | 62.5 | 7.0 | (37) |
| 20 | PtSn/Al <sub>2</sub> O <sub>3</sub>                | 600 | 0.50 | 60 | 26.5 | 28.8-25.5 | 91.0          | 1.71  | 6.84  | 0.033      | 30.3 | 15  | (38) |
| 21 | Pt/HT-10Ga                                         | 600 | 3.00 | 20 | 8.80 | 8.00-6.00 | 99.0          | 0.26  | 1.22  | 0.169      | 5.9  | 1.8 | (39) |
| 22 | Pt/Mg(Ga)(Al)O                                     | 600 | 0.90 | 20 | 2.60 | 16.0-11.4 | 99.2          | 0.056 | 0.05  | 0.196      | 5.1  | 2.0 | (40) |
| 23 | Commercial<br>PtSnK/Al <sub>2</sub> O <sub>3</sub> | 600 | 0.60 | 56 | 4.00 | 46.5-43.5 | 87.0-<br>85.0 | 0.33  | -     | 0.022      | 45.4 | 6.0 | (41) |
| 24 | PtSnK/ $\theta$ -Al <sub>2</sub> O <sub>3</sub>    | 600 | 0.30 | 67 | 4.00 | 39.9-38.2 | 92.0-<br>95.0 | 0.60  | 1.50  | 0.002<br>9 | 349  | 25  | (42) |
| 25 | PtZn@S-1                                           | 600 | 0.41 | 25 | 5.90 | 45.0-40.0 | 98.0          | 0.81  | 8.13  | 0.003      | 324  | 90  | (43) |
| 26 | RE-PtSn/SBA-15                                     | 600 | 0.75 | 50 | 5.90 | 37.0-20.0 | 90.0          | 0.99  | 4.95  | 0.080      | 12.5 | 8.0 | (44) |
| 27 | PtGa@MFI                                           | 600 | 0.47 | 25 | 5.90 | 22.0-15.0 | 97.0          | 0.31  | 0.81  | 0.023      | 42.6 | 20  | (45) |
| 28 | PtSn<br>/SAPO-34-500                               | 595 | 0.50 | 80 | 5.60 | 34.6-43.9 | 66.0          | 0.48  | 1.60  | 0.149      | 6.7  | 8.0 | (46) |
| 29 | PtSn/MgAl <sub>2</sub> O <sub>4</sub> -rod         | 590 | 0.30 | 10 | 3.20 | 43.2-40.9 | 95.0          | 3.54  | 13.9  | 0.005      | 200  | 20  | (47) |
| 30 | PtSn/MgAl <sub>2</sub> O <sub>4</sub> -sheet       | 590 | 0.30 | 10 | 3.20 | 42.8-39.5 | 95.0          | 3.43  | 12.9  | 0.009      | 111  | 20  | (47) |
| 31 | PtSn/MgAl <sub>2</sub> O <sub>4</sub> -sphere      | 590 | 0.30 | 10 | 3.20 | 43.8-38.5 | 92.9          | 3.33  | 12.3  | 0.011      | 91   | 20  | (47) |
| 32 | PtSn/Al <sub>2</sub> O <sub>3</sub>                | 590 | 0.30 | 10 | 3.20 | 41.6-35.5 | 91.9          | 3.04  | 10.8  | 0.013      | 77   | 20  | (47) |
| 33 | Pt/Al <sub>2</sub> O <sub>3</sub> sheet            | 590 | 0.36 | 16 | 9.40 | 42.7-15.9 | 93.0          | 1.38  | -     | 0.058      | 17.1 | 24  | (48) |
| 34 | PtSn/Al <sub>2</sub> O <sub>3</sub> sheet          | 590 | 0.35 | 16 | 9.40 | 48.7-44.6 | 98.0          | 1.62  | 2.49  | 0.007      | 143  | 24  | (48) |
| 35 | Pt-Sn-Na<br>/Al-SBA-15                             | 590 | 0.50 | 75 | 3.00 | 27.5-12.6 | 94.0          | 0.20  | 0.63  | 0.024      | 41.3 | 40  | (49) |
| 36 | Pt-Na/Sn-ZSM-5                                     | 590 | 0.50 | 75 | 3.00 | 41.7-39.1 | 95.3          | 0.30  | -     | 0.011      | 92.6 | 9.0 | (50) |
| 37 | PtNa<br>/Zn(1.0%)-ZSM-5                            | 590 | 0.50 | 80 | 3.00 | 40.6-37.8 | 93.0          | 0.29  | 0.81  | 0.012      | 85.1 | 9.0 | (51) |
| 38 | PtSn<br>/mesoporous Al <sub>2</sub> O <sub>3</sub> | 590 | 0.50 | 80 | 3.00 | 29.8-24.6 | 92.0          | 0.22  | 3.14  | 0.044      | 22.8 | 6.0 | (52) |
| 39 | PtSn/ZSM-5                                         | 590 | 0.50 | 80 | 3.00 | 33.1-26.3 | 47.7          | 0.24  | 2.61  | 0.054      | 18.4 | 6.0 | (52) |

|    |                                                      |     |      |     |      |           |               |       |       |            |      |     |      |
|----|------------------------------------------------------|-----|------|-----|------|-----------|---------------|-------|-------|------------|------|-----|------|
| 40 | Pt-Sn/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>      | 590 | 0.50 | 80  | 3.00 | 29.4-22.7 | 76.0          | 0.21  | 3.28  | 0.058      | 17.2 | 6.0 | (52) |
| 41 | PtSn/SBA-15                                          | 590 | 0.50 | 80  | 3.00 | 11.0-6.00 | 80.0          | 0.08  | 2.00  | 0.110      | 9.1  | 6.0 | (52) |
| 42 | PtCu/MgAl <sub>2</sub> O <sub>4</sub>                | 590 | 1.00 | 48  | 6.80 | 25.7-21.0 | 87.5          | 0.24  | 6.41  | 0.011      | 89.2 | 24  | (53) |
| 43 | PtAg/MgAl <sub>2</sub> O <sub>4</sub>                | 590 | 1.00 | 48  | 6.80 | 30.6-16.7 | 95.1          | 0.28  | 0.4   | 0.034      | 29.8 | 24  | (53) |
| 44 | PtAu/MgAl <sub>2</sub> O <sub>4</sub>                | 590 | 1.00 | 48  | 6.80 | 33.7-16.6 | 60.0          | 0.31  | 0.44  | 0.040      | 25.1 | 24  | (53) |
| 45 | PtSn-K/ZSM-5                                         | 590 | 0.46 | 80  | 3.00 | 34.4-32.0 | 92.0          | 0.25  | 2.61  | 0.015      | 66.7 | 8.0 | (54) |
| 46 | PtSn/Al <sub>2</sub> O <sub>3</sub>                  | 590 | 0.50 | 16  | 5.20 | ~58.0     | 97.0          | 0.61  | 0.61  | 0.012      | 83.3 | 20  | (55) |
| 47 | PtSn<br>/Al <sub>2</sub> O <sub>3</sub> fiber        | 590 | 0.46 | 80  | 3.00 | 24.7-23.5 | 92.5          | 0.18  | 0.26  | 0.009<br>4 | 106  | 7.0 | (56) |
| 48 | PtSnNa/CeZSM-5                                       | 590 | 0.50 | 80  | 3.00 | 43.5-40.7 | 84.0-<br>96.0 | 0.29  | 0.81  | 0.017      | 60.2 | 6.9 | (57) |
| 49 | PtSnNa/SUZ-4                                         | 590 | 0.50 | 25  | 3.00 | 24.7-20.2 | 90.0-<br>94.0 | 0.16  | -     | 0.029      | 34.7 | 9.0 | (58) |
| 50 | Pt-Sn <sub>2</sub> /MgAl <sub>2</sub> O <sub>4</sub> | 580 | 0.55 | 10  | 2.4  | 44.0-18.7 | 92.0          | 0.23  | 0.42  | 0.014      | 73.3 | 90  | (59) |
| 51 | Pt-Sn <sub>3</sub> /MgAl <sub>2</sub> O <sub>4</sub> | 580 | 0.53 | 10  | 2.40 | 42.0-18.7 | 97.0          | 0.23  | 0.42  | 0.013      | 78.5 | 90  | (59) |
| 52 | Pt-Sn <sub>4</sub> /MgAl <sub>2</sub> O <sub>4</sub> | 580 | 0.50 | 10  | 2.40 | 50.0-31.5 | 98.0          | 0.29  | 0.53  | 0.009      | 116  | 90  | (59) |
| 53 | Pt-Sn <sub>5</sub> /MgAl <sub>2</sub> O <sub>4</sub> | 580 | 0.42 | 10  | 2.40 | 45.0-37.5 | 98.0          | 0.31  | 0.58  | 0.003      | 294  | 90  | (59) |
| 54 | Pt-Sn <sub>6</sub> /MgAl <sub>2</sub> O <sub>4</sub> | 580 | 0.39 | 10  | 2.40 | 44.0-38.9 | 99.0          | 0.33  | 0.61  | 0.002      | 428  | 90  | (59) |
| 55 | Pt/0.5Sn-SBA-15                                      | 580 | 0.72 | 70  | 8.30 | 43.8-38.3 | 98.5          | 0.62  | 3.10  | 0.038      | 26.4 | 6.0 | (60) |
| 56 | PtSn/SiO <sub>2</sub>                                | 580 | 1.00 | 16  | 4.70 | 47.0-44.0 | 99.0          | 0.26  | 0.43  | 0.015      | 66.1 | 8.0 | (61) |
| 57 | PtSn/Al <sub>2</sub> O <sub>3</sub>                  | 580 | 1.00 | 16  | 4.70 | 45.0-35.0 | 98.0          | 0.23  | 0.38  | 0.050      | 19.1 | 8.0 | (61) |
| 58 | PtGa-Ca-Pb/SiO <sub>2</sub>                          | 580 | 3.00 | 100 | 5.90 | 36.6-25.2 | 98.0-<br>97.0 | 0.087 | 0.174 | 0.002      | 500  | 252 | (62) |
| 59 | PtLa/mz-deGa                                         | 580 | 1.00 | 100 | 11.0 | 42.5-16.1 | 96.0-<br>93.0 | 0.55  | 1.10  | 0.003      | 356  | 480 | (63) |
| 60 | PtGa-R                                               | 575 | 0.51 | 10  | 5.40 | 38.0-29.0 | 97.0          | 0.48  | 0.60  | 0.143      | 6.98 | 2.8 | (64) |
| 61 | PtSn<br>/MgAl <sub>2</sub> O <sub>4</sub> -ALT       | 575 | 1.00 | 16  | 14.7 | 33.0-29.0 | 99.0          | 0.59  | 1.18  | 0.057      | 17.6 | 3.3 | (65) |
| 62 | PtSn/Al <sub>2</sub> O <sub>3</sub>                  | 575 | 1.00 | 27  | 14.7 | 21.1-16.6 | 99.0          | 0.38  | 0.41  | 0.330      | 3.1  | 4.0 | (66) |

|    |                                                         |     |      |     |      |           |               |      |      |              |            |       |                       |
|----|---------------------------------------------------------|-----|------|-----|------|-----------|---------------|------|------|--------------|------------|-------|-----------------------|
| 63 | Pt-Sn <sub>2</sub> /meso-Al <sub>2</sub> O <sub>3</sub> | 570 | 0.50 | 10  | 2.90 | 42.4-40.8 | 99.0          | 0.31 | 0.45 | 0.003<br>3   | 303        | 20    | (67)                  |
| 64 | PtZn <sub>4</sub> @S-1-H                                | 550 | 0.72 | 25  | 3.60 | 47.4-40.4 | 93.2-<br>99.2 | 0.25 | 0.25 | 0.001        | 1000       | 216.7 | (68)                  |
| 65 | PtZn <sub>4</sub> @S-1-H                                | 550 | 0.72 | 25  | 108  | 21.2-11.8 | 98.3-<br>98.6 | 3.55 | 3.55 | 0.072        | 13.9       | 10.3  | (68)                  |
| 66 | 0.3Pt0.5Zn@S-1                                          | 550 | 0.30 | 37  | 6.50 | 45.0-42.0 | 99.5          | 1.20 | 1.20 | 0.002        | 500        | 60    | (69)                  |
| 67 | Pt-Sn@S-1(4.00 μm)                                      | 550 | 0.25 | 100 | 5.30 | 28.6-28.4 | 99.5-<br>97.1 | 1.00 | 1.05 | 0.000<br>002 | 4584<br>92 | 4500  | <b>This<br/>study</b> |
| 68 | Pt <sup>0</sup> Zn <sup>δ+</sup> /SiO <sub>2</sub>      | 550 | 3.05 | 20  | 75.0 | 30.2-16.1 | 98.1          | 0.96 | 0.96 | 0.027        | 36.8       | 30    | (70)                  |
| 69 | Ga <sup>δ+</sup> Pt <sup>0</sup> /SiO <sub>2</sub>      | 550 | 4.37 | 20  | 98.3 | 31.9-18.2 | 99.0          | 1.36 | 1.36 | 0.038        | 26.5       | 20    | (71)                  |
| 70 | Ga <sup>δ+</sup> Pt <sup>0</sup> /SiO <sub>2</sub>      | 550 | 4.37 | 20  | 43.3 | 36.5-26.9 | 90.9          | 0.76 | 0.76 | 0.023        | 44.2       | 20    | (71)                  |
| 71 | Ga <sup>δ+</sup> Pt <sup>0</sup> /SiO <sub>2</sub>      | 550 | 4.37 | 20  | 2.00 | 40.7-38.5 | 63.5          | 0.04 | 0.04 | 0.005        | 214        | 20    | (71)                  |
| 72 | PtSn/MgAl <sub>2</sub> O <sub>4</sub>                   | 550 | 0.50 | 50  | 36.6 | 12.0-11.0 | 92.0-<br>95.0 | 0.50 | -    | 0.280        | 3.5        | 3.0   | (72)                  |
| 73 | 2Pt-0.6Sn/γ-Al <sub>2</sub> O <sub>3</sub>              | 540 | 2.00 | 12  | 3.50 | 42.9-39.2 | 93.7          | 0.09 | 0.60 | 0.020        | 49.0       | 6.0   | (73)                  |
| 74 | 2Pt-1.2Sn/γ-Al <sub>2</sub> O <sub>3</sub>              | 540 | 2.00 | 12  | 3.50 | 43.5-41.4 | 96.9          | 0.09 | 0.60 | 0.011        | 87.2       | 6.0   | (73)                  |
| 75 | 2Pt-2.4Sn/γ-Al <sub>2</sub> O <sub>3</sub>              | 540 | 2.00 | 12  | 3.50 | 42.8-41.7 | 98.3          | 0.09 | 0.60 | 0.006        | 166        | 6.0   | (73)                  |
| 76 | 2Pt-3.6Sn/γ-Al <sub>2</sub> O <sub>3</sub>              | 540 | 2.00 | 12  | 3.50 | 42.8-41.8 | 98.6          | 0.09 | 0.60 | 0.005        | 183        | 6.0   | (73)                  |
| 77 | Pt/BN                                                   | 540 | 0.50 | 12  | 3.53 | 28.0-18.0 | 97.0          | 0.22 | 0.48 | 0.090        | 11.1       | 8.0   | (74)                  |
| 78 | PtSn/Al <sub>2</sub> O <sub>3</sub>                     | 519 | 0.35 | 30  | 3.50 | 31.0-20.0 | 95.0-<br>98.0 | 0.11 | 0.39 | 0.290        | 3.4        | 4.9   | (75)                  |
| 79 | Pt/SiO <sub>2</sub>                                     | 500 | 3.90 | 20  | 43.2 | 21.3-12.5 | 92.0-<br>94.4 | 0.15 | 0.32 | 0.213        | 4.7        | 3.0   | (76)                  |

$$[a] \text{ WHSV (h}^{-1}\text{)} = \frac{F_{\text{C}_3\text{H}_8} \times 44}{22414 W_c}, \text{ where } F_{\text{C}_3\text{H}_8} \text{ is the flow rate of C}_3\text{H}_8 \text{ (mL), and } W_c \text{ is the weight of the catalyst (g).}$$

[b] The first and last values of propane conversion are obtained throughout the reaction.

[c] The first and last values of propene selectivity are obtained throughout the reaction.

[d] *Specific activity* ( $s^{-1}$ ): the moles of  $C_3H_8$  formation per mole Pt atoms per second to reflect the apparent activity.

*Specific activity* ( $s^{-1}$ ) =  $\frac{F_{C_3H_8} \times X_{C_3H_8}}{\frac{W_C \times W_{Pt}}{M_W}}$ , where  $F_{C_3H_8}$  is the flow rate of  $C_3H_8$  (mL),  $X_{C_3H_8}$  is the conversion of propane,  $W_C$  is the weight of catalyst (g),  $M_W$  is the Pt atomic weight ( $g\ mol^{-1}$ ),  $W_{Pt}$  is the weight of supported Pt on the catalysts (g).

[e] *TOF* ( $s^{-1}$ ): the turnover frequency.

*TOF* ( $s^{-1}$ ) =  $\frac{F_{C_3H_8} \times X_{C_3H_8}}{\frac{W_C \times W_{Pt}}{M_W} \times D}$ , where  $F_{C_3H_8}$  is the flow rate of  $C_3H_8$  (mL),  $X_{C_3H_8}$  is the conversion of propane,  $W_C$  is the weight of catalyst (g),  $M_W$  is the Pt atomic weight ( $g\ mol^{-1}$ ),  $W_{Pt}$  is the weight of supported Pt on the catalysts (g), and D is dispersion of Pt ( $Pt_{surface}/Pt_{total}$ ).

[f]  $k_d$  ( $h^{-1}$ ): the deactivation constant.

$k_d$  ( $h^{-1}$ ) =  $\frac{\ln\left(\frac{1-X_f}{X_f}\right) - \ln\left(\frac{1-X_i}{X_i}\right)}{t}$ , where  $X_i$  is the initial conversion of propane,  $X_f$  is the final conversion of propane,  $t$  is the time throughout the reaction.

[g]  $\tau$  (h): the catalyst life,  $\tau = \frac{1}{k_d}$

[h] *Operation time* (h): the total time throughout the reaction in hours for a single run.

**Supplementary Table 3.**

Detailed structural information obtained from the Pt L<sub>3</sub>-edge  $\chi(R)$  space spectrum fitting of H<sub>2</sub>PtCl<sub>6</sub>·2SnCl<sub>2</sub>@S-1(4.00  $\mu\text{m}$ ) and Pt-Sn@S-1(4.00  $\mu\text{m}$ )<sub>fresh</sub>.

| H <sub>2</sub> PtCl <sub>6</sub> ·2SnCl <sub>2</sub><br>@S-1(4.00 $\mu\text{m}$ ) | Reduced Chi-square ( $\chi_v^2$ ) | <i>R</i> -factor (%) | amp/ $S_0^2$    | $N_{(\text{Pt-Cl path})}$   | $R_{(\text{Pt-Cl path})}(\text{\AA})$   | $\sigma_{(\text{Pt-Cl path})}^2(10^{-3}\text{\AA}^2)$   | $\Delta E_0(\text{eV})$ |
|-----------------------------------------------------------------------------------|-----------------------------------|----------------------|-----------------|-----------------------------|-----------------------------------------|---------------------------------------------------------|-------------------------|
|                                                                                   | 394.20                            | 0.0031               | $0.88 \pm 0.15$ | 5                           | $2.32 \pm 0.02$                         | $2.2 \pm 1.1$                                           | $4.58 \pm 1.63$         |
|                                                                                   |                                   |                      | amp/ $S_0^2$    | $N_{(\text{Pt-O path})}$    | $R_{(\text{Pt-O path})}(\text{\AA})$    | $\sigma_{(\text{Pt-O path})}^2(10^{-3}\text{\AA}^2)$    | $\Delta E_0(\text{eV})$ |
|                                                                                   |                                   |                      | $0.80 \pm 0.11$ | 1                           | $1.20 \pm 0.02$                         | $3.8 \pm 1.2$                                           | $2.47 \pm 1.07$         |
| Pt-Sn@S-1(4.00 $\mu\text{m}$ ) <sub>fresh</sub>                                   | Reduced Chi-square ( $\chi_v^2$ ) | <i>R</i> -factor (%) | amp/ $S_0^2$    | $N_{(\text{Pt-O path})}$    | $R_{(\text{Pt-O path})}(\text{\AA})$    | $\sigma_{(\text{Pt-O path})}^2(10^{-3}\text{\AA}^2)$    | $\Delta E_0(\text{eV})$ |
|                                                                                   | 898.89                            | 0.0471               | $0.91 \pm 0.14$ | 6                           | $2.22 \pm 0.13$                         | $3.2 \pm 1.3$                                           | $3.24 \pm 0.88$         |
|                                                                                   |                                   |                      | amp/ $S_0^2$    | $N_{(\text{Pt-O-Sn path})}$ | $R_{(\text{Pt-O-Sn path})}(\text{\AA})$ | $\sigma_{(\text{Pt-O-Sn path})}^2(10^{-3}\text{\AA}^2)$ | $\Delta E_0(\text{eV})$ |
|                                                                                   |                                   |                      | $0.84 \pm 0.16$ | 2                           | $3.50 \pm 0.11$                         | $5.8 \pm 2.2$                                           | $3.20 \pm 0.14$         |

**Supplementary Table 4.**

Crystal structure data from PDF Rietveld refinement for Pt-Sn@S-1(4.00  $\mu\text{m}$ )<sub>fresh</sub>.

|                            |                                                                                                                                               |
|----------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------|
| Space group                | <i>P</i> 1 (no. 1)                                                                                                                            |
| Unit cell parameters       | $a = 20.568 \text{ \AA}, b = 20.439 \text{ \AA}, c = 13.724 \text{ \AA}$<br>$\alpha = 90.43^\circ, \beta = 90.09^\circ, \gamma = 90.02^\circ$ |
| Volume ( $\text{\AA}^3$ )  | 5769.13                                                                                                                                       |
| $\chi_{\text{sq}}$         | 239.86                                                                                                                                        |
| Reduced $\chi_{\text{sq}}$ | 0.0511                                                                                                                                        |
| <i>R</i> <sub>w</sub>      | 0.0578                                                                                                                                        |

**Supplementary Table 5.**Label peak assignments to the atomic pairs in Pt-Sn@S-1(4.00  $\mu\text{m}$ )<sub>fresh</sub>.

| Labels | Atomic pair                                          | Atomic pair distances (Å) |
|--------|------------------------------------------------------|---------------------------|
| a      | O-Si/(Sn)                                            | 1.60                      |
| b      | O-O; Pt-Sn                                           | 2.59                      |
| c      | O-O/(Si)/(Sn); Si-Si/(Sn)/(Pt)                       | 3.96                      |
| d      | O-O/(Si)/(Sn); Si-Si                                 | 5.02                      |
| e      | O-O/(Si)/(Sn); Si-Si/(Sn)                            | 6.47                      |
| f      | O-O/(Si)/(Sn); Si-Si/(Pt)/(Sn)                       | 7.73                      |
| g      | O-O/(Si)/(Pt)/(Sn), Si-Si/(Pt)/(Sn)                  | 8.94                      |
| h      | O-O/(Si)/(Sn); Si-Si/(Pt)/(Sn)                       | 10.75                     |
| i      | O-O/(Si)/(Pt)/(Sn); Si-Si/(Pt)/(Sn)                  | 11.81                     |
| j      | O-O/(Si)/(Pt)/(Sn); Si-Si/(Pt)                       | 12.59                     |
| k      | O-O/(Si)/(Pt); Si-Si; Sn-Sn                          | 13.73                     |
| l      | O-O/(Si)/(Pt)/(Sn); Si-Si/(Pt)/(Sn); Pt-Sn           | 15.14                     |
| m      | O-O/(Si); Si-Si/(Sn)                                 | 16.56                     |
| n      | O-O/(Si)/(Pt)/(Sn); Si-Si/(Pt)/(Sn)                  | 17.46                     |
| o      | O-O/(Si)/(Pt)/(Sn); Si-Si/(Pt)/(Sn)                  | 18.92                     |
| p      | O-O/(Si)/(Pt)/(Sn); Si-Si; Pt-Sn                     | 19.66                     |
| q      | O-O/(Si)/(Pt)/(Sn); Si-Si/(Pt)/(Sn); Pt-Sn           | 22.76                     |
| r      | O-O/(Si)/(Pt)/(Sn); Si-Si/(Pt); Pt-Sn                | 23.94                     |
| s      | O-O/(Si); Si-Si/(Sn); Pt-Sn                          | 24.73                     |
| t      | O-O/(Si)/(Pt); Si-Si/(Pt)/(Sn)                       | 27.51                     |
| u      | O-O/(Si)/(Pt)/(Sn); Si-Si/(Pt)/(Sn); Pt-Sn;<br>Sn-Sn | 29.01                     |

**Supplementary Table 6.**

Crystal structure data from PDF Rietveld refinement for Pt-Sn@S-1(4.00  $\mu\text{m}$ )<sub>spent</sub>.

|                            |                                                                                                                                                           |
|----------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------|
| Space group                | <i>P</i> 1 (no. 1)                                                                                                                                        |
| Unit cell parameters       | $a = 20.645 \text{ \AA}$ , $b = 20.388 \text{ \AA}$ , $c = 13.807 \text{ \AA}$<br>$\alpha = 90.45^\circ$ , $\beta = 90.12^\circ$ , $\gamma = 90.11^\circ$ |
| Volume ( $\text{\AA}^3$ )  | 5811.05                                                                                                                                                   |
| $\chi_{\text{sq}}$         | 306.521                                                                                                                                                   |
| Reduced $\chi_{\text{sq}}$ | 0.0606                                                                                                                                                    |
| <i>R</i> <sub>w</sub>      | 0.0586                                                                                                                                                    |

**Supplementary Table 7.**

Label peak assignments to the atomic pairs in Pt-Sn@S-1(4.00  $\mu\text{m}$ )<sub>spent</sub>.

| Labels | Atomic pair                                                | Atomic pair distances (Å) |
|--------|------------------------------------------------------------|---------------------------|
| a      | O-Si                                                       | 1.61                      |
| b      | O-O; Pt-Sn                                                 | 2.55                      |
| c      | O-O/(Si)/(Sn); Si-Si/(Sn)/(Pt);<br>Pt-Sn; Sn-Sn            | 3.97                      |
| d      | O-O/(Si)/(Sn)/(Pt); Si-Si/(Pt)                             | 4.81                      |
| e      | O-O/(Si)/(Sn)/(Pt); Si-Si/(Sn)                             | 6.32                      |
| f      | O-O/(Si)/(Sn)/(Pt); Si-Si/(Pt)/(Sn)                        | 7.64                      |
| g      | O-O/(Si)/(Pt)/(Sn), Si-Si/(Pt)/(Sn)                        | 8.97                      |
| h      | O-O/(Si)/(Pt)/(Sn); Si-Si/(Pt)/(Sn)                        | 10.75                     |
| i      | O-O/(Si)/(Pt)/(Sn); Si-Si/(Pt)/(Sn)                        | 12.74                     |
| j      | O-O/(Si)/(Pt)/(Sn); Si-Si/(Pt)/(Sn); Pt-Sn                 | 13.56                     |
| k      | O-O/(Si)/(Pt); Si-Si/(Pt)/(Sn); Pt-Sn                      | 15.12                     |
| l      | O-O/(Si)/(Pt)/(Sn); Si-Si/(Pt)/(Sn); Pt-Sn                 | 15.69                     |
| m      | O-O/(Si)/(Pt)/(Sn); Si-Si/(Pt)/(Sn)                        | 16.48                     |
| n      | O-O/(Si)/(Pt)/(Sn); Si-Si/(Pt)/(Sn); Sn-Sn                 | 17.32                     |
| o      | O-O/(Si)/(Pt)/(Sn); Si-Si/(Pt)/(Sn); Pt-Sn                 | 18.78                     |
| p      | O-O/(Si)/(Pt)/(Sn); Si-Si/(Pt)/(Sn); Pt-Sn                 | 20.74                     |
| q      | O-O/(Si)/(Pt)/(Sn); Si-Si/(Pt)/(Sn); Pt-Sn;<br>Sn-Sn       | 22.88                     |
| r      | O-O/(Si)/(Pt)/(Sn); Si-Si/(Pt)/(Sn); Pt-Sn                 | 23.83                     |
| s      | O-O/(Si)/(Pt)/(Sn); Si-Si/(Pt)/(Sn);<br>Pt-Pt/(Sn); Sn-Sn  | 24.67                     |
| t      | O-O/(Si)/(Pt)/(Sn); Si-Si/(Pt)/(Sn); Pt-Sn;<br>Sn-Sn       | 27.53                     |
| u      | O-O/(Si)/(Pt)/(Sn); Si-Si/(Pt)/(Sn); Pt-<br>Pt/(Sn); Sn-Sn | 28.88                     |

**Supplementary Table 8.**

Detailed structural information obtained from the Pt L<sub>3</sub>-edge  $\chi(R)$  space spectrum fitting of Pt-Sn@S-1(4.00  $\mu\text{m}$ )<sub>spent</sub> ( $S_0^2=0.90$ ).

| Samples                                         | path       | C. N. <sup>[a]</sup> | R ( $\text{\AA}$ ) <sup>[b]</sup> | $\sigma^2 (\times 10^{-3} \text{\AA}^2)$ <sup>[c]</sup> | $\Delta E$ (eV) <sup>[d]</sup> | R factor <sup>[e]</sup> |
|-------------------------------------------------|------------|----------------------|-----------------------------------|---------------------------------------------------------|--------------------------------|-------------------------|
| Pt foil                                         | Pt-Pt      | 12*                  | 2.77*                             | 4.1 $\pm$ 0.8                                           | 6.2 $\pm$ 1.4                  | 0.01                    |
| PtO <sub>2</sub>                                | Pt-O       | 6*                   | 1.98*                             | 2.5 $\pm$ 1.1                                           | 8.3 $\pm$ 1.1                  | 0.01                    |
|                                                 | Pt-Pt      | 2*                   | 3.14*                             | 9.1 $\pm$ 5.7                                           |                                |                         |
| Pt-Sn@S-1(4.00 $\mu\text{m}$ ) <sub>spent</sub> | Pt-O       | 0.6 $\pm$ 0.2        | 1.86 $\pm$ 0.02                   | 9.4 $\pm$ 1.8                                           | 2.2 $\pm$ 1.9                  | 0.02                    |
|                                                 | Pt-Pt      | 1.3 $\pm$ 0.3        | 2.74 $\pm$ 0.02                   | 9.6 $\pm$ 7.2                                           |                                |                         |
|                                                 | Pt-O-Pt/Sn | 2.4 $\pm$ 1.9        | 3.10 $\pm$ 0.02                   | 9.6 $\pm$ 4.8                                           |                                |                         |

<sup>a</sup>C. N.: coordination numbers; <sup>b</sup>R: bond distance; <sup>c</sup> $\sigma^2$ : Debye-Waller factors; <sup>d</sup> $\Delta E_0$ : the inner potential correction. <sup>e</sup>R factor: goodness of fit. \*The experimental EXAFS fit by fixing C. N. as the known crystallographic value.

**Supplementary Table 9.**

Adsorption energies ( $\text{kJ mol}^{-1}$ ) of intermediates on  $\text{Pt-Sn}_2$  and  $(\text{Pt-Sn}_2)_2$  clusters within the MFI framework relative to energy of propane.

| Adsorbate                                          | $\text{Pt-Sn}_2@S-1$ | $(\text{Pt-Sn}_2)_2@S-1$ |
|----------------------------------------------------|----------------------|--------------------------|
| $\text{CH}_3\text{CH}_2\text{CH}_3$ (ads.)         | 74.67                | 22.60                    |
| $\text{CH}_3\text{CH}_2\text{CH}_2^* + \text{H}^*$ | 163.24               | 98.11                    |
| $\text{CH}_3\text{CH}_2\text{CH}_2^*$              | 91.97                | 76.39                    |
| $\text{CH}_3\text{CHCH}_2^* + \text{H}^*$          | 116.50               | 96.99                    |
| $\text{CH}_3\text{CHCH}_2$ (ads.)                  | 175.74               | 190.81                   |
| $\text{CH}_3\text{CHCH}^* + \text{H}^*$            | 146.06               | 196.71                   |

**Supplementary Table 10.**

Energy barriers for elemental PDH reactions on the Pt-Sn<sub>2</sub> and (Pt-Sn<sub>2</sub>)<sub>2</sub> clusters within the MFI framework (kJ mol<sup>-1</sup>).

|        | Reaction                                                                                                        | Pt-Sn <sub>2</sub> @S-1 | (Pt-Sn <sub>2</sub> ) <sub>2</sub> @S-1 |
|--------|-----------------------------------------------------------------------------------------------------------------|-------------------------|-----------------------------------------|
| Step 1 | CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> (ads.) → CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> * + H* | 215.37                  | 202.13                                  |
| Step 2 | CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> * → CH <sub>3</sub> CHCH <sub>2</sub> * + H*                    | 173.93                  | 144.96                                  |
| Step 3 | CH <sub>3</sub> CHCH <sub>2</sub> (ads.) → CH <sub>3</sub> CHCH* + H*                                           | 127.39                  | 173.93                                  |

**Supplementary Table 11.**

Averaged unit cell parameters and volumes of (Pt-Sn<sub>2</sub>)<sub>x</sub> ( $x = 1$  and  $2$ ) clusters located at the intersection sites of MFI framework obtained by AIMD simulations.

| Clusters                           | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\alpha$ (°) | $\beta$ (°) | $\gamma$ (°) | $V$ (Å <sup>3</sup> ) |
|------------------------------------|---------|---------|---------|--------------|-------------|--------------|-----------------------|
| Pt-Sn <sub>2</sub>                 | 20.00   | 19.83   | 13.33   | 89.94        | 89.80       | 90.01        | 5285.54               |
| (Pt-Sn <sub>2</sub> ) <sub>2</sub> | 20.00   | 19.85   | 13.34   | 90.18        | 89.81       | 89.97        | 5296.96               |

**Supplementary Table 12.**

Averaged unit cell parameters and volumes of (Pt-Sn<sub>2</sub>)<sub>x</sub> ( $x = 1, 2$  and  $3$ ) and Pt<sub>4</sub>-Sn<sub>7</sub> clusters located at the intersection sites of MFI framework obtained by period DFT simulations.

| Clusters                           | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\alpha$ (°) | $\beta$ (°) | $\gamma$ (°) | $V$ (Å <sup>3</sup> ) |
|------------------------------------|---------|---------|---------|--------------|-------------|--------------|-----------------------|
| Pt-Sn <sub>2</sub>                 | 20.56   | 20.41   | 13.73   | 89.91        | 90.07       | 90.19        | 5758.41               |
| (Pt-Sn <sub>2</sub> ) <sub>2</sub> | 20.57   | 20.44   | 13.72   | 90.43        | 90.10       | 90.02        | 5769.14               |
| (Pt-Sn <sub>2</sub> ) <sub>3</sub> | 20.61   | 20.44   | 13.73   | 90.09        | 90.11       | 90.08        | 5782.49               |
| Pt <sub>4</sub> -Sn <sub>7</sub>   | 20.58   | 20.45   | 13.76   | 90.14        | 90.21       | 90.05        | 5790.60               |

**Supplementary Movie 1.**

Migration-agglomeration scheme of Pt-Sn<sub>2</sub> clusters in S-1 with  $L_b$  of 0.10  $\mu\text{m}$  for the formation of Pt-Sn particles at S-1 surface.

**Supplementary Movie 2.**

Migration-agglomeration scheme of Pt-Sn<sub>2</sub> clusters in S-1 with  $L_b$  of 4.00  $\mu\text{m}$  for the formation of fully-confined (Pt-Sn<sub>2</sub>)<sub>2</sub> in S-1 channels.

## References

- Chen, S. et al. Propane dehydrogenation on single-site [PtZn<sub>4</sub>] intermetallic catalysts. *Chem* **7**, 387-405 (2020).
- Yang, M., Zhu, Y., Zhou, X., Sui, Z. & Chen, D. First-principles calculations of propane dehydrogenation over PtSn catalysts. *ACS Catal.* **2**, 1247-1258 (2012).
- VandeVondele, J. et al. Quickstep: fast and accurate density functional calculations using a mixed Gaussian and plane waves approach. *Comput. Phys. Commun.* **167**, 103-128 (2005).
- Jürg, H., Marcella, I., Florian, S. & Joost, V. Atomistic simulations of condensed matter systems. *WIREs Comput. Mol. Sci.* **4**, 15-25 (2014).
- Yang, K., Zheng, J., Zhao, Y. & Truhlar, D. G. Tests of the RPBE, revPBE,  $\tau$ -HCTHhyb,  $\omega$ B97X-D, and MOHLYP density functional approximations and 29 others against representative databases for diverse bond energies and barrier heights in catalysis. *J. Chem. Phys.* **132**, 164117 (2010).
- VandeVondele, J. & Hutter, J. Gaussian basis sets for accurate calculations on molecular systems in gas and condensed phases. *J. Chem. Phys.* **127**, 4365-4477 (2007).
- Goedecker, S., Teter, M. & Hutter, J. Separable dual-space Gaussian pseudopotentials. *Phys. Rev. B* **54**, 1703-1710 (1995).
- Shuichi, N. A molecular dynamics method for simulations in the canonical ensemble. *Mol. Phys.* **100**, 191-198 (2002).
- Shuichi, N. A unified formulation of the constant temperature molecular dynamics methods. *J. Chem. Phys.* **81**, 511-519 (1984).
- Hoover, W. G. Canonical dynamics: equilibrium phase-space distributions. *Phys. Rev. A* **31**, 1695-1697 (1985).
- Martyna, G. J., Klein, M. L. & Tuckerman, M. Nosé-Hoover chains: the canonical ensemble via continuous dynamics. *J. Chem. Phys.* **97**, 2635-2643 (1992).
- Martyna, G. J., Tobias, D. J. & Klein, M. L. Constant pressure molecular dynamics algorithms. *J. Chem. Phys.* **101**, 4177-4189 (1994).
- Martyna, G. J., Tuckerman, M. E., Tobias, D. J. & Klein, M. L. Explicit reversible integrators for extended systems dynamics. *Mol. Phys.* **87**, 1117-1157 (1996).
- Sun, Y. et al. High-rate nanofluidic energy absorption in porous zeolitic frameworks. *Nat. Mater.* **20**, 1015-1023 (2021).
- Gonzalez, I. L. et al. Insight into the effects of confined hydrocarbon species on the lifetime of methanol conversion catalysts. *Nat. Mater.* **19**, 1-7 (2020).
- Laio, A. & Parrinello, M. Escaping free-energy minima. *Proc. Natl. Acad. Sci. U.S.A.* **99**, 12562-12566 (2002).
- Iannuzzi, M., Laio, A. & Parrinello, M. Efficient exploration of reactive potential energy surfaces using Car-Parrinello molecular dynamics. *Phys. Rev. Lett.* **90**, 238302 (2003).
- Tribello, G. A., Bonomi, M., Branduardi, D., Camilloni, C. & Bussi, G. PLUMED 2: new feathers for an old bird. *Comput. Phys. Commun.* **185**, 604-613 (2014).
- Bonomi, M., Bussi, G., Camilloni, C., Tribello, G. & Rydzewski, J. Promoting transparency and reproducibility in enhanced molecular simulations. *Nat. Methods* **16**, 670-673 (2019).
- Cnudde, P. et al. Light olefin diffusion during the MTO process on H-SAPO-34: a complex interplay of molecular factors. *J. Am. Chem. Soc.* **142**, 6007-6017 (2020).
- Cnudde, P. et al. Experimental and theoretical evidence for promotional effect of acid sites on the diffusion of alkenes through small-pore zeolites. *Angew. Chem. Int. Ed.* **60**, 10016-10022 (2021).
- Bailleul, S., Cnudde, P., Vanduyfhuys, L., Waroquier, M. & Speybroeck, V. V. Ab initio enhanced sampling kinetic study on MTO ethene methylation reaction. *J. Catal.* **388**, 38-51 (2020).
- Beerdse, E., Smit, B. & Dubbeldam, D. Molecular simulation of loading dependent slow diffusion in confined systems. *Phys. Rev. Lett.* **93**, 248301 (2004).
- Beerdse, E., Dubbeldam, D. & Smit, B. Understanding diffusion in nanoporous materials. *Phys. Rev. Lett.* **96**, 044501 (2006).
- Bailleul, S. et al. Ab initio enhanced sampling kinetic study on MTO ethene methylation reaction. *J. Catal.* **388**, 38-51 (2020).
- Nakaya, Y., Hirayama, J., Yamazoe, S., Shimizu, K. I. & Furukawa, S. Single-atom Pt in intermetallics as an ultrastable and selective catalyst for propane dehydrogenation. *Nat. Commun.* **11**, 2838 (2020).
- Zhu, Y. et al. Lattice-confined Sn (IV/II) stabilizing raft-like Pt clusters: high selectivity and durability in propane dehydrogenation. *ACS Catal.* **7**, 6973-6978 (2017).

28. Zha, S. et al. Identification of Pt-based catalysts for propane dehydrogenation via a probability analysis. *Chem. Sci.* **9**, 3925-3931 (2018).
29. Wang, T. et al. Effects of Ga doping on Pt/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts for propane dehydrogenation. *AIChE J.* **62**, 4365-4376 (2016).
30. Li, J. et al. Size effect of TS-1 supports on the catalytic performance of PtSn/TS-1 catalysts for propane dehydrogenation. *J. Catal.* **352**, 361-370 (2017).
31. Jiang, F. et al. Propane dehydrogenation over Pt/TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts. *ACS Catal.* **5**, 438-447 (2015).
32. Long, L. et al. The comparison and optimization of zirconia, alumina, and zirconia-alumina supported PtSnIn trimetallic catalysts for propane dehydrogenation reaction. *J. Ind. Eng. Chem.* **51**, 271-280 (2017).
33. Sun, G. et al. Breaking the scaling relationship via thermally stable Pt/Cu single atom alloys for catalytic dehydrogenation. *Nat. Commun.* **9**, 4454 (2018).
34. Liu, L. et al. Structural modulation and direct measurement of subnanometric bimetallic PtSn clusters confined in zeolites. *Nat. Catal.* **3**, 628-638 (2020).
35. Liu, L. et al. Regioselective generation and reactivity control of subnanometric platinum clusters in zeolites for high-temperature catalysis. *Nat. Mater.* **18**, 866-873 (2019).
36. Cai, W. et al. Subsurface catalysis-mediated selectivity of dehydrogenation reaction. *Science Adv.* **4**, 5418 (2018).
37. Qiu, Y. et al. Various metals (Ce, In, La, and Fe) promoted Pt/Sn-SBA-15 as highly stable catalysts for propane dehydrogenation. *Ind. Eng. Chem. Res.* **58**, 10804-10818 (2019).
38. Lee, M. H., Nagaraja, B. M., Lee, K. Y. & Jung, K. D. Dehydrogenation of alkane to light olefin over PtSn/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> catalyst: effects of Sn loading. *Catal. Today* **232**, 53-62 (2014).
39. Redekop, E. A. et al. Delivering a modifying element to metal nanoparticles via support: Pt-Ga alloying during the reduction of Pt/Mg(Al,Ga)Ox catalysts and its effects on propane dehydrogenation. *ACS Catal.* **4**, 1812-1824 (2014).
40. Sun, P., Siddiqi, G., Chi, M. & Bell, A. T. Synthesis and characterization of a new catalyst Pt/Mg(Ga)(Al)O for alkane dehydrogenation. *J. Catal.* **274**, 192-199 (2010).
41. Razavian, M. & Fatemi, S. Synthesis and application of ZSM-5/SAPO-34 and SAPO-34/ZSM-5 composite systems for propylene yield enhancement in propane dehydrogenation process. *Micropor. Mesopor. Mater.* **201**, 176-189 (2015).
42. Shi, Y. et al. Influence of support on the catalytic properties of Pt-Sn-K/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> for propane dehydrogenation. *RSC Adv.* **7**, 19841-19848 (2017).
43. Zhang, B. et al. PtZn intermetallic nanoalloy encapsulated in silicalite-1 for propane dehydrogenation. *AIChE J.* **67**, 1-12 (2021).
44. Wang, J. et al. On the role of Sn segregation of Pt-Sn catalysts for propane dehydrogenation. *ACS Catal.* **11**, 4401-4410 (2021).
45. Zhang, B., Zheng, L., Zhai, Z., Li, G. & Liu, G. Subsurface-regulated PtGa nanoparticles confined in silicalite-1 for propane dehydrogenation. *ACS Appl. Mater. Interfaces* **13**, 16259-16266 (2021).
46. Nawaz, Z., Tang, X., Chu, Y. & Wei, F. Influence of calcination temperature and reaction atmosphere on the catalytic properties of Pt-Sn/SAPO-34 for propane dehydrogenation. *Chin. J. Catal.* **31**, 552-556 (2010).
47. Xie, J. et al. Fine tuning the morphology of spinel as ultra-stable catalyst support in propane dehydrogenation. *Adv. Mater. Interfaces* **8**, 2101325 (2021).
48. Shi, L. et al. Al<sub>2</sub>O<sub>3</sub> nanosheets rich in pentacoordinate Al<sup>3+</sup> ions stabilize Pt-Sn clusters for propane dehydrogenation. *Angew. Chem. Int. Ed.* **54**, 14200-14204 (2015).
49. Duan, Y., Zhou, Y., Zhang, Y., Sheng, X. & Xue, M. Effect of sodium addition to PtSn/AlSBA-15 on the catalytic properties in propane dehydrogenation. *Catal. Lett.* **141**, 120-127 (2011).
50. Zhang, Y., Zhou, Y., Huang, L. Xue, M. & Zhang, S. Sn-modified ZSM-5 as support for platinum catalyst in propane dehydrogenation. *Ind. Eng. Chem. Res.* **50**, 7896-7902 (2011).
51. Zhang, Y. et al. Structure and catalytic properties of the Zn-modified ZSM-5 supported platinum catalyst for propane dehydrogenation. *Chem. Eng. J.* **270**, 352-361 (2015).
52. Zhang, Y. et al. Comparative study of bimetallic Pt-Sn catalysts supported on different supports for propane dehydrogenation. *J. Mol. Catal. A Chem.* **381**, 138-147 (2014).
53. Ren, G. et al. Effect of group IB metals on the dehydrogenation of propane to propylene over anti-sintering Pt/MgAl<sub>2</sub>O<sub>4</sub>. *J. Catal.* **366**, 115-126 (2018).
54. Zhang, Y. et al. Catalytic structure and reaction performance of PtSnK/ZSM-5 catalyst for propane dehydrogenation: influence of impregnation strategy. *J. Mater. Sci.* **50**, 6457-6468 (2015).

55. Jang, E. J., Lee, J., Jeong, H. Y. & Kwak, J. H. Controlling the acid-base properties of alumina for stable PtSn-based propane dehydrogenation catalysts. *Appl. Catal. A Gen.* **572**, 1-8 (2019).
56. Zhang, H. et al. Morphology-controlled fabrication of biomorphic alumina-based hierarchical LDH compounds for propane dehydrogenation reaction. *New J. Chem.* **42**, 103-110 (2018).
57. Zhang, Y. et al. Propane dehydrogenation over Ce-containing ZSM-5 supported platinum-tin catalysts: Ce concentration effect and reaction performance analysis. *RSC Adv.* **6**, 29410-29422 (2016).
58. Zhou, H., Gong, J., Xu, B., Yu, L. & Fan, Y. PtSnNa@SUZ-4-catalyzed propane dehydrogenation. *Appl. Catal. A Gen.* **527**, 30-35 (2016).
59. Zhu, H. et al. Sn surface-enriched Pt-Sn bimetallic nanoparticles as a selective and stable catalyst for propane dehydrogenation. *J. Catal.* **320**, 52-62 (2014).
60. Li, B., Xu, Z., Chu, W., Luo, S. & Jing, F. Ordered mesoporous Sn-SBA-15 as support for Pt catalyst with enhanced performance in propane dehydrogenation. *Chin. J. Catal.* **38**, 726-735 (2017).
61. Motagamwala, A. H., Almallahi, R., Wortman, J., Igenegbai, V. O. & Linic, S. Stable and selective catalysts for propane dehydrogenation operating at thermodynamic limit. *Science* **373**, 217-222 (2021).
62. Nakaya, Y., Xing, F., Ham, H., Shimizu, K. I. & Furukawa, S. Doubly decorated platinum-gallium intermetallics as stable catalysts for propane dehydrogenation. *Angew. Chem. Int. Ed.* **60**, 19715-19719 (2021).
63. Ryoo, R. et al. Rare-earth-platinum alloy nanoparticles in mesoporous zeolite for catalysis. *Nature* **585**, 221-224 (2020).
64. Xu, Y. et al. Sintering-resistant Pt on Ga<sub>2</sub>O<sub>3</sub> rods for propane dehydrogenation: the morphology matters. *Ind. Eng. Chem. Res.* **57**, 13087-13093 (2018).
65. Shan, Y., Wang, T., Sui, Z., Zhu, Y. & Zhou, X. Hierarchical MgAl<sub>2</sub>O<sub>4</sub> supported Pt-Sn as a highly thermostable catalyst for propane dehydrogenation. *Catal. Commun.* **84**, 85-88 (2016).
66. Wang, H. et al. Coke formation on Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst for propane dehydrogenation. *Ind. Eng. Chem. Res.* **57**, 8647-8654 (2018).
67. Zhu, X. et al. Pt-Sn clusters anchored at Al<sup>3+</sup> penta sites as a sinter-resistant and regenerable catalyst for propane dehydrogenation. *J. Energy Chem.* **65**, 293-301 (2021).
68. Sun, Q. et al. Subnanometer bimetallic platinum-zinc clusters in zeolites for propane dehydrogenation. *Angew. Chem. Int. Ed.* **59**, 19450-19459 (2020).
69. Wang, Y., Hu, Z., Lv, X., Chen, L. & Yuan, Z. Ultrasmall PtZn bimetallic nanoclusters encapsulated in silicalite-1 zeolite with superior performance for propane dehydrogenation. *J. Catal.* **385**, 61-69 (2020).
70. Rochlitz, L. et al. Silica-supported, narrowly distributed, subnanometric Pt-Zn particles from single sites with high propane dehydrogenation performance. *Chem. Sci.* **11**, 1549-1555 (2020).
71. Searles, K. et al. Highly productive propane dehydrogenation catalyst using silica-supported Ga-Pt nanoparticles generated from single-sites. *J. Am. Chem. Soc.* **140**, 11674-11679 (2018).
72. Salmones, J., Wang, J., Galicia, J. A. & Aguilar-Rios, G. H<sub>2</sub> reduction behaviors and catalytic performance of bimetallic tin-modified platinum catalysts for propane dehydrogenation. *J. Mol. Catal. A Chem.* **184**, 203-213 (2002).
73. Sun, C. et al. A comparative study on different regeneration processes of Pt-Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts for propane dehydrogenation. *J. Energy Chem.* **27**, 311-318 (2018).
74. Wang, Y. et al. Boosting selectivity and stability on Pt/BN catalysts for propane dehydrogenation via calcination & reduction-mediated strong metal support interaction. *J. Energy Chem.* **67**, 451-457 (2021).
75. Bari s, O. A., Holmen, A. & Blekkan, E. A. Propane dehydrogenation over supported Pt and Pt-Sn catalysts: catalyst preparation, characterization, and activity measurements. *J. Catal.* **158**, 1-12 (1996).
76. Deng, L. et al. Strong metal-support interaction between Pt and SiO<sub>2</sub> following high-temperature reduction: a catalytic interface for propane dehydrogenation. *Chem. Commun.* **53**, 6937-6940 (2017).