Electronic Supporting Information

Propane dehydrogenation over extra-framework In(I) in chabazite zeolites

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S1. Experimental section

1.1 Catalyst Preparation

Commercial H-CHA samples were obtained by calcining NH$_4$-CHA (ACS Material: SSZ-13 Zeolite, Type A) at 550 °C for 8 h in flowing air with a ramp rate of 2 °C·min$^{-1}$. The Si/Al ratio of commercial H-CHA zeolite was determined to be 10.7 ± 1.1 by X-ray fluorescence (XRF, Rigaku WDXRF), which was referred to as H-CHA(11). The CHA zeolites with varying Si/Al ratios were synthesized using N,N,N-trimethyl-1-adamantanammonium ion (TMAda$^+$) as the structure-directing agent (SDA) based on protocols described in previous reports.$^{1,2}$ To prepare CHA zeolite with Si/Al ratio of 5, 20 g sodium silicate solution (Sigma-Aldrich, 26.5%) and 0.64 g sodium hydroxide (NaOH, Sigma-Aldrich, 99.99%) were added to 48 g de-ionized (DI) H$_2$O at room temperature and stirred for 15 min, followed by the addition of 2 g NH$_4$-Y zeolite (Zeolyst, CBV 500) and stirring for 30 min. Then, 8.4 g of TMAdaOH (SACHEM Inc., 25% aqueous solution) was added to the solution and stirred for another 30 min. The hydrothermal synthesis was carried out at 140 °C for 6 days under rotation. The zeolite samples were centrifuged at 4500 rpm for 10 min, washed with DI water 5 times, and dried at 80 °C overnight. The as-made zeolites were calcined in flowing air at 580 °C for 8 h with a ramp rate of 2 °C·min$^{-1}$ to remove the occluded TMAda$^+$. The calcined sample was referred to as Na-CHA(5).

Afterward, Na-CHA(5) was ion-exchanged with 1M ammonium nitrate aqueous solution (NH$_4$NO$_3$, 99%, Sigma-Aldrich) at 80 °C for 3 h (1 g zeolite corresponds to 150 mL solution) and then centrifugated to remove the supernatant. This process was repeated three times, and then NH$_4$-CHA(5) was dried at 80 °C overnight and treated at 550 °C for 8 h in flowing air with a ramp rate of 2 °C·min$^{-1}$ to obtain H-CHA(5) samples. For the preparation of H-CHA(12), 13 g tetraethyl orthosilicate (TEOS, Sigma-Aldrich) was mixed with 26.4 g TMAdaOH and 2.264 g DI water at room temperature and stirred for 1 h, followed by the addition of 0.7 g aluminum ethoxide (Al(OCH$_3$)$_3$, Sigma-Aldrich) and stirred for an additional 1 h. The resulting solution was then hydrothermally at 150 °C for 6 days under static conditions. The produced crystals were centrifuged, washed, dried and calcined with the same procedure as the CHA(5) samples. The CHA zeolite with a Si/Al ratio of 25 was prepared using the same method as the H-CHA(12) except that the aluminum ethoxide content was decreased to 0.35 g. The Si/Al ratios of H-CHA(5), H-CHA(12), H-CHA(25) were measured by XRF and were determined to be 4.7 ± 0.3, 12.0 ± 1.3, and 24.8 ± 3.0, respectively.

Incipient wetness impregnation with an aqueous solution of indium (III) nitrate hydrate (Sigma-Aldrich) was used to prepare In-CHA samples with varying In/Al ratios. For example, for the preparation of In-CHA(11, 1.0) with In/Al ratio of 1.0, 0.58 g indium(III) nitrate hydrate was dissolved in 1.26 mL DI water. The prepared aqueous indium solution was added dropwise to 1 g H-CHA(11), followed by drying at 80 °C before calcining at 600 °C in flowing air for 2 h with a ramp rate of 5 °C·min$^{-1}$. The calcined In-CHA catalysts were denoted as In-CHA(x, y), where x and y represent the Si/Al ratio and In/Al ratio, respectively. 10In/SiO$_2$ (10 wt% In), 10In/Al$_2$O$_3$ (10 wt% In) were prepared by the same method with SiO$_2$ (Sigma-Aldrich, silica gel davisil, grade 646) and γ-Al$_2$O$_3$ (Alfa Aesar, 99.97% metals basis), respectively. In$_2$O$_3$ was purchased from Sigma-Aldrich (99.99%
trace metals basis) and used as received. We prepared PtSn/Al₂O₃ catalyst (1%Pt and 2.6%Sn) using incipient wetness impregnation with an aqueous solution of H₂PtCl₆·6H₂O (Sigma-Aldrich) and SnCl₂·2H₂O (Sigma-Aldrich) on γ-Al₂O₃.

1.2 Materials Characterization

Micropore volumes of the zeolite samples (Table S1) were determined by N₂ adsorption at -196 °C on a Micromeritics 3Flex system using the t-plot method. The specific surface area of SiO₂ and Al₂O₃ supported catalyst (Table S2) was determined by the BET method. All samples were degassed overnight at 350 °C before the adsorption measurements. Powder XRD measurements were conducted on a Bruker D8 diffractometer with Cu Kα radiation (40 kV, 40 mA) in the range of 2θ = 4–50° with a step size of 0.04° and 0.5 s per step. The morphology of the samples was obtained using a scanning electron microscope (SEM, Auriga-60, ZEISS) after coating with a gold/palladium alloy. The bright-field transmission electron microscopy (TEM) images were obtained with a JEOL (JEM-2010F) transmission electron microscope equipped with a field emission gun emitter at 200 kV. The samples were ultrasonically dispersed in methanol, and then the suspension was dropped onto a carbon-coated copper grid. ²⁷Al and ²⁹Si solid-state magic angle spinning nuclear magnetic resonance (MAS-NMR) spectra were acquired on an 11.7 T Bruker Avance III NMR spectrometer with a 4 mm HX probe at spinning speeds of 12 and 10 kHz for ²⁷Al and ²⁹Si respectively. Direct excitation of ²⁷Al and ²⁹Si were performed with pulses of 1.0 (²⁷Al) or 3.5 (²⁹Si) μs. 75 kHz ¹H decoupling was applied during the acquisition.

Reduced catalysts for characterizations were obtained by reducing the calcined samples in a tube furnace with 10 vol% H₂ at 600 °C for 30 min with a ramp rate of 10 °C·min⁻¹ and then cooling to room temperature before removing for storage. H₂ temperature-programmed reduction (H₂-TPR) profiles of the calcined catalysts were obtained using a Micromeritics AutoChem II 2920 equipped with a TCD detector. A sample of about 100 mg of the catalyst was pretreated in He flow (50 mL·min⁻¹) at 200 °C for 1 h and then cooled to 60 °C. The TPR measurement was conducted by heating the sample to 800 °C with a ramp rate of 10 °C·min⁻¹ in a flow of 10 vol% H₂/Ar (50 mL·min⁻¹). The H₂ consumption was determined after calibration using CuO as standard. TGA was performed on a Discovery TGA instrument under air flow (100 mL·min⁻¹) with temperature ramping (10 °C·min⁻¹) to 800 °C.

Ethylamine temperature-programmed desorption (TPD) using the inhouse-built pulse reactor (described later) to determine the Brensted acid sites (BASs) density of CHA zeolites. Typically, 50 mg of the catalyst with a particle size range of 20–40 mesh was loaded into a quartz tube, and dehydrated at 550 °C for 30 min in the flow of 45 mL·min⁻¹ N₂. Subsequently, samples were cooled to 150 °C, followed by the introduction of ethylamine (99%, Sigma-Aldrich), which was achieved by vaporization of liquid ethylamine through a 50 μm capillary tube into the N₂ stream (45 mL·min⁻¹). The ethylamine signal monitored via online mass spectrometry returns to the initial stage, indicating that the adsorption is saturated. Then the sample was purged with He at the same temperature (150 °C, 400 mL·min⁻¹) for 1 h and subsequently heated to 550 °C (10 °C·min⁻¹), during which effluent was monitored using the mass spectrometry. The following AMUs were used for analysis: 27 (C₂H₄), 28 (N₂), 30 (C₂H₅NH₂). The ethylene
concentration was calibrated by pulsing a fixed volume (0.67 mL) of ethylene into the reactor under He flow.

1.3 Transmission Fourier Transformed Infrared Studies
In situ Fourier transform infrared (FTIR) spectra were collected on an Agilent CARY 660 spectrometer equipped with an MCT detector. Catalysts are pressed into self-supporting wafers of about 20 mg and loaded into a custom-made sample holder for vertical alignment in the infrared beam using a customized in situ transmission cell equipped with KBr windows. Typical spectra are the result of 128 coadded scans per spectrum at a spectral resolution of 2 cm$^{-1}$. Vacuum levels of <0.01 mTorr in the transmission cell were achieved by connecting to a vacuum manifold equipped with a mechanical pump and a diffusion pump. The transmission cell was heated by heating tapes controlled by a PID controller with the thermocouple close to the sample wafer. Before all experiments, the samples were dehydrated at 550 °C for 30 min under a vacuum to remove all adsorbed molecules. Chemicals such as H$_2$, D$_2$, D$_2$O, dry air were introduced into the transmission cell and corresponding pressure was controlled via the vacuum manifold.

In situ transmission FTIR with d$_3$-acetonitrile (CD$_3$CN) as probe molecule was employed to monitor the presence of BASs and Lewis acid sites (LASs). The self-supporting wafer (~20 mg) was dehydrated at 550 °C for 30 min and then treated with H$_2$ (1 atm) at the same temperature. Introducing H$_2$ into the transmission cell three times for 10 min each time to ensure that the catalyst was completely reduced. The sample was then cooled to 50 °C under vacuum and then the excess of d$_3$-acetonitrile was introduced into the transmission cell followed by evacuation. The dosing procedure was repeated three times to ensure the complete saturation of the sample with d$_3$-acetonitrile. Next, the transmission cell was evacuated for 15 min to remove the physisorbed d$_3$-acetonitrile before collecting the spectrum.

1.4 Pulse Reactor Studies
An inhouse-built pulse reactor was used to determine the H$_2$/O$_2$ consumption of the catalyst at reaction temperature (Fig. S1). Typically, two concurrent gas flows are controlled by calibrated mass flow controllers. An automatic 6-way valve (Vici) connected with a 0.67 mL loop and a 4-way valve are connected to provide pulses or continuous flow. A catalyst sample of 150 mg loaded into a silica glass tube (1/4 inch in diameter) is heated up to 600 °C at a ramp rate of 10 °C·min$^{-1}$ in N$_2$ flow (45 mL·min$^{-1}$). A second gas stream, consisting of pure H$_2$ or pure O$_2$, flows through the loop. Once the sample temperature reaches the target temperature, the loop gas is pulsed via the bypass (Fig. S1) until a stable peak area is achieved, before introducing the periodic pulses into the reactor tube. The in-house instrument has a fast response time in that the pulse signal is detected in less than 10 seconds after switching the 6-way valve. The time interval between pulses is 30 min for H$_2$ pulses and 2 min for O$_2$ pulses. The catalyst can be reduced by 10 vol% H$_2$/N$_2$ or 10 vol% D$_2$/N$_2$ flow by switching the 4-way valve. The feed composition and product are analyzed by online mass spectrometry (Pfeiffer Omnistar). The following AMUs were used for analysis: 2 (H$_2$), 3 (HD), 4 (D$_2$), 18 (H$_2$O), 28(N$_2$), 32 (O$_2$). The quantification of
formed H\textsubscript{2}O is determined by the calibration using CuO as standard (one mole CuO consumes one mole of H\textsubscript{2} and forms one mole of H\textsubscript{2}O).

1.5 Catalytic Reaction Rate Measurements
Catalytic reaction rates were measured using a fixed bed plug flow reactor, consisting of a quartz glass tube (\(\frac{1}{4}\) inch in diameter). The catalyst bed typically contained 15—300 mg of the catalyst with a particle size range of 20—40 mesh. A thermocouple was placed close to the catalyst bed to ensure accurate temperature measurement. Before the rate measurements, the catalyst was heated to 600 °C for 30 min with a ramp rate of 10 °C·min\(^{-1}\) in 10 vol% H\textsubscript{2} with balancing N\textsubscript{2} (20 mL·min\(^{-1}\)), followed by purging with N\textsubscript{2} at the same temperature for another 30 min. The reduced sample was then exposed to 2.5 vol% C\textsubscript{3}H\textsubscript{8} with balancing N\textsubscript{2} (total flow rate: 20 mL·min\(^{-1}\)) with the total pressure maintained at 101.32 kPa. The reactor effluent was periodically injected into an online gas chromatograph (GC) (Agilent 7890), using a heated gas line. The GC was equipped with an RT-Q-BOND column and flame ionization detector (FID) used for product analysis. FID response factors for CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{3}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8} were calibrated before the product analysis. The conversion of C\textsubscript{3}H\textsubscript{8} was calculated using Eq. S1, the selectivity and yield of CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{3}H\textsubscript{6} were determined using Eqs. S2-S3.

\[
\text{Conversion} = \left(1 - \frac{F_{C_3H_8, \text{outlet}}}{F_{C_3H_8, \text{inlet}}}\right) \times 100\% \tag{S1}
\]

\[
\text{Selectivity} = \frac{n_i \times F_{i, \text{outlet}}}{\sum n_i \times F_{i, \text{outlet}}} \times 100\% \tag{S2}
\]

\[
\text{Yield} = \frac{n_i \times F_{i, \text{outlet}}}{3 \times F_{C_3H_8, \text{inlet}}} \times 100\% \tag{S3}
\]
Carbon balance
\[
\text{Carbon balance} = \frac{3 \times F_{C_3H_8, \text{outlet}} + \sum n_i \times F_i, \text{outlet}}{3 \times F_{C_3H_8, \text{inlet}}} \times 100\%
\]

where \(i\) represents the propane dehydrogenation products \(\text{CH}_4, \text{C}_2\text{H}_4, \text{C}_3\text{H}_6\) in the effluent gas, \(n_i\) is the number of carbon atoms of component \(i\), \(F_i\) is the molar flow rate. The \(C_3H_8\) conversion was measured at differential conversions (< 6%) to avoid secondary reactions. PDH rates were determined from \(C_3H_6\) yield, while \(C_3H_8\) cracking rates were determined from the yields of \(\text{CH}_4\) and \(\text{C}_2\text{H}_4\). Apparent activation energies were determined in the temperature range of 580–620 °C. Carbon balance (Eq. S4) in rates measurement of In-based catalysts was higher than 97%.

The dependence of reaction rates on propane partial pressure for In-CHA(11, 1.0) was determined at 600 °C changing propane flow rate (0.5 – 20 mL·min⁻¹) diluted with \(\text{N}_2\) flow at a constant total flow rate (100 mL·min⁻¹). The \(\text{H}_2\) rate dependence was determined by changing the \(\text{H}_2\) flow rate (1 – 20 mL·min⁻¹) with constant propane flow (5 mL·min⁻¹) and corresponding \(\text{N}_2\) flow rates with total flow rate constant (100 mL·min⁻¹). During the measurements, the reactants were switched to 5 vol% \(C_3H_8/\text{N}_2\) with 100 mL·min⁻¹ total flow rate every 10 h to assess the effect of catalyst deactivation.
S2. Supporting tables and figures

Table S1. Textural properties of H-CHA and In-CHA samples investigated in this work.

| Sample               | Micropore volume$^a$ (cm$^3$·g$^{-1}$) | Micropore volume$^b$ corrected (cm$^3$·g$^{-1}$) |
|----------------------|----------------------------------------|-----------------------------------------------|
| H-CHA(11)            | 0.247                                  | 0.247                                         |
| In-CHA(11, 1.0)      | 0.213                                  | 0.256                                         |
| In-CHA(11, 1.0) reduced | 0.199                                | 0.233                                         |
| H-CHA(5)             | 0.272                                  | 0.272                                         |
| In-CHA(5, 1.0)       | 0.171                                  | 0.242                                         |
| In-CHA(5, 1.0) reduced | 0.110                                | 0.148                                         |
| H-CHA(12)            | 0.292                                  | 0.292                                         |
| In-CHA(12, 1.0)      | 0.224                                  | 0.271                                         |
| In-CHA(12, 1.0) reduced | 0.200                                | 0.234                                         |
| H-CHA(25)            | 0.277                                  | 0.277                                         |
| In-CHA(25, 1.0)      | 0.275                                  | 0.301                                         |
| In-CHA(25, 1.0) reduced | 0.266                                | 0.286                                         |

$^a$Calculated with the $t$-plot method obtained from N$_2$ physisorption isotherms.

$^b$Corrected micropore volume by subtracting the mass of indium species in the In-CHA samples by assuming In$_2$O$_3$ and In$^+$ sites are predominant in the calcined and reduced samples, respectively.
Table S2. Textural properties of In-containing samples and supports investigated in this work.

| Sample               | BET Surface Area (m²·g⁻¹) | BET Surface Area* corrected (m²·g⁻¹) |
|----------------------|---------------------------|-------------------------------------|
| SiO₂                 | 285                       | -                                   |
| 10In/SiO₂            | 250                       | 284                                 |
| 10In/SiO₂ reduced    | 262                       | 291                                 |
| Al₂O₃                | 79                        | -                                   |
| 10In/Al₂O₃           | 60                        | 68                                  |
| 10In/Al₂O₃ reduced   | 51                        | 57                                  |

*Corrected BET surface area is determined by subtracting the mass of indium species by assuming In₂O₃ and In(0) sites are predominant in the calcined and reduced samples, respectively.
Table S3. Composition of the prepared In-based catalysts.

| Sample                  | In/Al ratio<sup>a</sup> | In loading (%)<sup>a</sup> |
|-------------------------|-------------------------|-----------------------------|
| In-CHA(11, 1.0)         | 1.04                    | 14.2                        |
| In-CHA(12, y)           |                         |                             |
|                         | 0.32                    | 4.9                         |
|                         | 0.70                    | 10.8                        |
|                         | 0.98                    | 12.3                        |
|                         | 1.74                    | 19.5                        |
| In-CHA(5, 1.0)          | 0.98                    | 21.3                        |
| In-CHA(25, 1.0)         | 0.95                    | 6.2                         |
| 10In/Al₂O₃              | -                       | 9.6                         |
| 10In/SiO₂               | -                       | 9.9                         |

<sup>a</sup>Determined by XRF.
Fig. S2 Solid-state MAS-NMR spectra of the H-CHA and In-CHA with calcined and reduced conditions: (a, b) $^{29}\text{Si}$ NMR and $^{27}\text{Al}$ NMR of H-CHA(11) and In-CHA(11, 1.0); (c, d) $^{29}\text{Si}$ NMR and $^{27}\text{Al}$ NMR of H-CHA(5) and In-CHA(5, 1.0); (e, f) $^{29}\text{Si}$ NMR and $^{27}\text{Al}$ NMR of H-CHA(12) and In-CHA(12, 1.0); (g, h) $^{29}\text{Si}$ NMR and $^{27}\text{Al}$ NMR of H-CHA(25) and In-CHA(25, 1.0).
Fig. S3 SEM images of (a) H-CHA(11), (b) In-CHA(11, 1.0), (c) In-CHA(11, 1.0) reduced, (d) H-CHA(5), (e) In-CHA(5, 1.0), (f) In-CHA(5, 1.0) reduced, (g) H-CHA(12), (h) In-CHA(12, 1.0), (i) In-CHA(12, 1.0) reduced, (j) H-CHA(25), (k) In-CHA(25, 1.0), (l) In-CHA(25, 1.0) reduced samples.
Fig. S4 XRD patterns of H-CHA(x) and In-CHA(x, 1.0) samples investigated after calcination and reduction: (a) x=5; (b) x=12; (c) = 25. The diffraction peaks at 2θ values of 30.6°, 35.5° marked with asterisks are readily assignable to In$_2$O$_3$ (JCPDS 060416) on these catalysts.
**Fig. S5** TEM images of (a) H-CHA(11), (b) In-CHA(11, 1.0), (c) reduced In-CHA(11, 1.0), and (d) H_2-O_2 treated In-CHA(11, 1.0).
Fig. S6 XRD patterns of the In-CHA(12, y) samples with varying In/Al ratios from 0.3 to 1.7 (calcined and reduced conditions). The diffraction peaks at 2θ values of 30.6°, 35.5° marked with asterisks are assigned to In$_2$O$_3$ (JCPDS 060416), and diffraction peaks at 2θ values of 33.0°, 36.3° and 39.2° marked with # symbol are assigned to metallic In(0) (JCPDS 05-0642).
**Fig. S7** O₂ pulses results on the In-CHA(11, 1.0) catalyst at 600 °C: (a) reduced by H₂ pulses on the calcined sample; (b) reduced by H₂ pulses on H₂-O₂ treated sample; (c) reduced by 10 vol% H₂ flow for 30 min.
Fig. S8 O$_2$ pulses results on the In-based catalyst (reduced via H$_2$ pulses) at 600 °C: (a) In$_2$O$_3$; (b) 10In/SiO$_2$; (c) 10In/Al$_2$O$_3$; (d) In-CHA(11, 1.0).
**Fig. S9** H\textsubscript{2} pulses results of CuO catalyst for calibration of H\textsubscript{2}O formation amounts. Test condition: 50 mg CuO, 600 °C. Cu: 625 μmol, consumed H\textsubscript{2}: 655 μmol, formed H\textsubscript{2}O: 640 μmol. H\textsubscript{2}/Cu = 1.05 and H\textsubscript{2}O/H\textsubscript{2} = 0.98.
Fig. S10 (a) H₂-TPR profiles, (b) results of H₂ pulses experiments and (c) subsequent O₂ pulses at 600 °C on In-CHA(12, y) with varying In/Al ratios (as indicated in the figure legends).
Fig. S11 (a) H$_2$-TPR profiles, (b) results of H$_2$ pulse experiments and (c) subsequent O$_2$ pulse at 600 °C on In-CHA(x, 1.0) with varying Si/Al ratios (as indicated in the figure legends).
Fig. S12 Determination of formed H$_2$O/consumed H$_2$ ratio from H$_2$ pulses as a function of pulse number on varying catalysts: (a) In-CHA(12, y) with varying In/Al ratios and (b) In-CHA(x, 1.0) with varying Si/Al ratios.
**Fig. S13** Results of H₂ pulse experiments on In-CHA(12, 1.0) at different temperatures (as indicated in the figure). The number in parentheses represents the ratio of formed H₂O to consumed H₂ at a specific pulse.
Fig. S14 FTIR spectra of In-CHA(11, 1.0) catalyst and H-CHA(11) catalyst collected during the H₂ reduction process at 550 °C (indicated in the figure legends). Black and red traces represent spectra before and after reduction by H₂ (1 atm) at 550 °C, respectively. The background spectrum was collected in the spectral cell without a sample pellet at room temperature under vacuum.
Fig. S15 FTIR spectra of reduced In-CHA(11, 1, 0) catalyst at 550 °C in (a) high and (b, c) low wavenumber ranges: (i) after H₂ treatment; (ii) after D₂ treatment for 10 min; (iii) (i) subtracted from spectrum (ii). The background spectrum was collected in the spectral cell without a sample pellet at room temperature under vacuum.
**Fig. S16** FTIR spectra of H-CHA(11) catalyst at 550 °C in (a) high and (b) low wavenumber ranges: (i) after dehydration; (ii) after H₂ treatment for 10 min; (iii) after D₂ treatment for 10 min; (iv) after H₂ treatment for 10 min again. The background spectrum was collected in the spectral cell without a sample pellet at room temperature under vacuum.
**Fig. S17** FTIR spectra of D₂ reduced (a) In-CHA(12, y) with varying In/Al ratios ranging from 0 to 1.7 and (b) H-CHA(x, 1.0) with varying Si/Al ratios ranging from 5 to 25 catalysts at 550 °C (indicated in the figure legends). The background spectrum was collected in the spectral cell without a sample pellet at room temperature under vacuum.
**Fig. S18** FTIR spectra of reduced In-CHA(5, 1.0) catalyst at 550 °C in (a) high and (b, c) low wavenumber ranges: (i) after H₂ treatment; (ii) after D₂ treatment for 10 min; (iii) (i) subtracted from spectrum (ii). The background spectrum was collected in the spectral cell without a sample pellet at room temperature under vacuum.
Fig. S19 FTIR spectra of reduced In-CHA(12, 0.3) catalyst at 550 °C in (a) high and (b, c) low wavenumber ranges: (i) after H₂ treatment; (ii) after D₂ treatment for 10 min; (iii) (i) subtracted from spectrum (ii). The background spectrum was collected in the spectral cell without a sample pellet at room temperature under vacuum.
Fig. S20  FTIR spectra of reduced In-CHA(12, 0.7) catalyst at 550 °C in (a) high and (b, c) low wavenumber ranges: (i) after H₂ treatment; (ii) after D₂ treatment for 10 min; (iii) (i) subtracted from spectrum (ii). The background spectrum was collected in the spectral cell without a sample pellet at room temperature under vacuum.
Fig. S21 FTIR spectra of reduced In-CHA(12, 1.0) catalyst at 550 °C in (a) high and (b, c) low wavenumber ranges: (i) after H₂ treatment; (ii) after D₂ treatment for 10 min; (iii) (i) subtracted from spectrum (ii). The background spectrum was collected in the spectral cell without a sample pellet at room temperature under vacuum.
Fig. S22 FTIR spectra of reduced In-CHA(25, 1.0) catalyst at 550 °C in (a) high and (b, c) low wavenumber ranges: (i) after H$_2$ treatment; (ii) after D$_2$ treatment for 10 min; (iii) (i) subtracted from spectrum (ii). The background spectrum was collected in the spectral cell without a sample pellet at room temperature under vacuum.
Fig. S23 (a) H₂ (2 amu), HD (3 amu), and D₂ (4 amu) signals as a function of time when switching the N₂ flow to 10 vol% D₂ flow on In-CHA(12, y) with In/Al ratios ranging from 0 to 1.7 (indicated in the figure legends). The samples were reduced via 10 vol% H₂/N₂ flow for 30 min and purged by N₂ flow for another 30 min before switching to 10 vol% D₂ flow. (b, c) Integrated H₂ and HD peak area in (a) and relative BAS densities as a function of (b) In/BAS ratios and (c) In/Al ratios (normalized to the H₂ and HD peak area or BAS density of H-CHA(12)). (d) H₂, HD and D₂ signals as a function of time when switching the N₂ flow to 10 vol% H₂ flow on In-CHA(12, y) with varying In/Al ratios ranging from 0 to 1.7 (indicated in the figure legends). The samples were reduced via 10 vol% D₂/N₂ flow for 30 min and purged by N₂ flow for another 30 min before switching to 10 vol% H₂ flow. (e, f) Integrated D₂ and HD peak area in (d) as a function of (e) In/BAS ratios and (f) In/Al ratios (normalized to the D₂ and HD peak area or BAS density of H-CHA(12)).
**Fig. S24** (a) H₂ pulses results of In-CHA(11, 1.0) catalyst with calcined and H₂-O₂ treated conditions at 600 °C. (b) Determination of formed H₂O/consumed H₂ ratio from H₂ pulses as a function of pulse number on In-CHA(11, 1.0) catalyst with calcined and H₂-O₂ treated conditions.
**Fig. S25** XRD patterns of the H-CHA(11) and In-CHA(11, 1.0) samples with different treatments. The diffraction peaks at 2θ values of 30.6°, 35.5° marked with asterisks (*) are assigned to In$_2$O$_3$ (JCPDS 060416) on these catalysts.
Fig. S26 C₃H₆ yield and C₃H₆ selectivity as a function of time on stream over 10In/Al₂O₃. Reaction conditions: 600 °C, C₃H₈ partial pressure 2.54 kPa with balancing N₂, space time 806400 g_{cat}·s·mol_{C₃H₈}⁻¹. The propane conversions are below 6% in the rate measurements. The dotted line in the figure represents the C₃H₆ yield without catalyst under the same conditions.
**Fig. S27** (a) C$_3$H$_6$ yield and (b) C$_3$H$_6$ selectivity as a function of time on stream over 10In/Al$_2$O$_3$ and bare Al$_2$O$_3$ catalysts. Reaction conditions: 600 °C; C$_3$H$_8$ partial pressure, 2.54 kPa with balancing N$_2$, space time, 806400 g$_{Cat}$.s·mol$_{C_3H_8}^{-1}$.
Fig. S28 (a) C$_3$H$_6$ yield and (b) C$_3$H$_6$ selectivity as a function of time on stream over 10In/SiO$_2$ and bare SiO$_2$ catalysts. Reaction conditions: 600 °C; C$_3$H$_8$ partial pressure, 2.54 kPa with balancing N$_2$, space time, 806400 g$_{\text{Cat}}$·s·mol$_{\text{C}_3\text{H}_8}^{-1}$. 
Note: H2-TPR profile of bulk In2O3 sample (Fig. 1a) shows that a higher reduction temperature is needed to bulk In2O3 sample than other samples such as In-CHA. Considering that H2 pulses cannot reduce the bulk In2O3, we used 10 vol%H2 flow to reduce the sample and monitored the formation of H2O (Fig. S29a). The H2O signal shows that a long time (~4 hours) is needed to completely reduce bulk the In2O3 at 600 °C, and the H2O/In ratio was determined to be 1, suggesting that the In2O3 can be completely reduced to In(0). XRD pattern of reduced In2O3 sample (8 hours of reduction) shows no presence of bulk In2O3, but strong diffraction peaks of In(0), supporting the complete reduction of In2O3 to In(0), shown in Fig. S29b. Propane dehydrogenation tests show that In(0) is almost inactive for propane dehydrogenation (Fig. S29c and d). The gradually decreased reaction rates on the In2O3 sample (reduced 0.5 h) were interpreted as the gradual reduction of remaining In2O3 to In(0).

Fig. S29 (a) H2O and H2 signal during the in situ reduction of In2O3 at 600 °C. (b) XRD patterns of bulk In2O3 and reduced In2O3 with varying time. (c) C3H6 yield and (d) C3H6 selectivity as a function of time on stream over In2O3 with different reduction time. Reaction conditions: 600 °C, C3H8 partial pressure 2.54 kPa with balancing N2, space time 806400 gCat·s·molC3H8⁻¹. The dotted line in the figure represents the C3H6 yield (0.39%) and C3H6 selectivity (60%) without catalyst under the same conditions.
Fig. S30  (a) The reaction rates and C$_3$H$_6$ selectivity on the In-based catalyst. (b) The corrected reaction rates and C$_3$H$_6$ selectivity on In-based catalyst by subtracting the reaction rate derived from thermal cracking.
Fig. S31 (a) propane dehydrogenation rate and (b) \( \text{C}_3\text{H}_6 \) selectivity as a function of time on stream over H-CHA(11) and In-CHA(11, 1.0) catalysts. Reaction conditions: 600 °C; \( \text{C}_3\text{H}_8 \) partial pressure, 2.54 kPa with balancing N\(_2\). The propane conversions are below 6% in the rate measurements.
Fig. S32 (a) Propane dehydrogenation rate and (b) C$_3$H$_6$ selectivity as a function of time on stream over In-CHA(12, y) with varying In/Al ratios. Reaction conditions: 600 °C; C$_3$H$_8$ partial pressure, 2.54 kPa with balancing N$_2$. The propane conversion is below 6% in the rate measurements.
Fig. S33 (a) Propane dehydrogenation rate and (b) C$_3$H$_6$ selectivity as a function of time on stream over In-CHA(x, 1.0) with varying Si/Al ratios. Reaction conditions: 600 °C; C$_3$H$_8$ partial pressure, 2.54 kPa with balancing N$_2$. The propane conversion is below 6% in the rate measurements.
Fig. S34 (a) Propane dehydrogenation rate and (b) C₃H₆ selectivity as a function of time on stream over H-CHA(x) with varying Si/Al ratios. Reaction conditions: 600 °C; C₃H₈ partial pressure, 2.54 kPa with balancing N₂. The propane conversion is below 6% in the rate measurements.
Fig. S35 \( \text{C}_3\text{H}_8 \) dehydrogenation rate and \( \text{C}_3\text{H}_6 \) selectivity as a function of Si/Al ratios on H-CHA catalysts investigated. Reaction rates were collected at TOS = 21 min. Reaction conditions: 600 °C; \( \text{C}_3\text{H}_8 \) partial pressure, 2.54 kPa with balancing N\(_2\). The propane conversion is below 6% in the rate measurements.
Fig. S36 C\textsubscript{3}H\textsubscript{6} yield and C\textsubscript{3}H\textsubscript{6} selectivity as a function of time on stream over PtSn/Al\textsubscript{2}O\textsubscript{3}. Reaction conditions: 600 °C, C\textsubscript{3}H\textsubscript{8} partial pressure 2.54 kPa with balancing N\textsubscript{2}, space time 134400 g\textsubscript{Cat}·s·mol\textsubscript{C3H8}\textsuperscript{-1}. The dotted line in the figure represents the C\textsubscript{3}H\textsubscript{6} yield (0.39%) without catalyst under the same conditions.
Table S4. Values of turn-over frequency (TOF) and pre-exponential factor and entropy changes to propane dehydrogenation over In-CHA catalyst at 600 °C.

| Catalyst        | TOF \(\text{mol}_{\text{C}_3\text{H}_8}/\text{mol}_{\text{In}} \cdot \text{s}^{-1}\) | Apparent rate constant \(\text{mol}_{\text{C}_3\text{H}_8}/\text{mol}_{\text{In}} \cdot \text{s}^{-1} \cdot \text{bar}^{-1}\) | Pre-exponential factor \(\text{mol}_{\text{C}_3\text{H}_8}/\text{mol}_{\text{In}} \cdot \text{s}^{-1} \cdot \text{bar}^{-1}\) | \(\Delta S^{\text{app}}\) \(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}\) |
|-----------------|--------------------------------|--------------------------------|-------------------------------|------------------|
| In-CHA(11, 1.0) | \(4.1 \times 10^{-5}\)          | \(1.5 \times 10^{-3}\)           | 716                           | -207             |
| In-CHA(25, 1.0) | \(8.8 \times 10^{-5}\)          | \(3.5 \times 10^{-3}\)           | 11606                         | -184             |
| In-CHA(12, 1.0) | \(5.2 \times 10^{-5}\)          | \(2.1 \times 10^{-3}\)           | 6849                          | -189             |
| In-CHA(5, 1.0)  | \(2.7 \times 10^{-5}\)          | \(3.1 \times 10^{-3}\)           | 47944839                      | -115             |
Fig. S37 TGA data of spent In-based catalyst. The catalysts were tested for 15 h reaction at 600 °C, C₃H₈ partial pressure was 2.54 kPa with balancing N₂.
Fig. S38 (a, b) FTIR spectra of (a) \( \text{C}_3\text{H}_8 \) treatment (1.33 kPa) and (b) \( \text{C}_3\text{H}_6 \) treatment (1.33 kPa) on reduced H-CHA(12) for 2 min, 4 min, 6 min, 8 min, 10 min, respectively and after evacuation. (c, d) FTIR spectra of (a) \( \text{C}_3\text{H}_8 \) treatment (1.33 kPa) and (b) \( \text{C}_3\text{H}_6 \) treatment (1.33 kPa) on reduced In-CHA(12, 1.0) for 2 min, 4 min, 6 min, 8 min, 10 min, respectively and after evacuation. The background spectrum is collected in the spectral cell with a reduced sample pellet at 550 °C under vacuum.
Fig. S39 XRD patterns of the spent catalyst. The diffraction peaks at 2θ values of 30.6°, 35.5° marked with asterisks are readily assignable to In$_2$O$_3$ (JCPDS 060416), and diffraction peaks at 2θ values of 33.0°, 36.3° and 39.2° marked with pound keys are associated with In(0) (JCPDS 05-0642) on these catalysts.
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