Supporting Information

Isolated Indium Hydrides in CHA Zeolites: Speciation and Catalysis for Nonoxidative Dehydrogenation of Ethane

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FTIR measurement

Fourier transform infrared spectroscopy (FTIR) measurements were carried out in a home-made *in situ* cell. A self-supported disc comprising mixture of In_2O_3 and proton-type CHA (In_2O_3/CHA, 40 mg) was dehydrated under He flow at 773 K and then treated with H_2 or 10% H_2/He. For measurement of In hydrides, the obtained sample was kept at 773 K under vacuum for 2 h and a background spectrum was obtained below 153 K by cooling the cell using liquid N_2. Next, H_2 flow was introduced to the sample that was kept under H_2 at 773 K for 2 h. Further, the temperature was decreased to below 153 K and the FTIR spectra were recorded (JASCO FT/IR-4600 equipped with a mercury cadmium telluride (MCT) detector). The reaction of In hydrides with ethylene was carried out by treating In-CHA(H_2) with 10% C_2H_4/He at 473 K while the *in situ* formation of In hydrides through the reaction of In-CHA with ethane was examined at 773 K under 100% C_2H_6.

For NH_3 adsorption, temperature was decreased to 373 K after the treatment of the disk of In_2O_3/CHA under 10% H_2/He flow and then the flow was changed from He to purge H_2. A background spectrum under He was obtained followed by introducing NH_3 (1%) to the sample, purging with He, and monitoring the peak derived from adsorbed NH_3 at 373 K.

H−D exchange reaction

For the FTIR measurement, the reactions were carried out using the home-made *in situ* cell described above. Mass spectroscopic observations of a H−D exchange reaction were conducted in a fixed-bed continuous flow system as follows. A powder of In_2O_3/CHA (0.2 g) was treated under 40 mL/min of 5% H_2/N_2 at 773 K to prepare *in situ* In-CHA(H_2). Next, the temperature decreased to 313 K under 40 mL/min of 5% H_2/N_2 flow, and subsequently, the gas was switched to N_2 for at least 1 h to purge H_2 from the gas phase. After the pre-treatment, the H−D exchange reaction of In-CHA(H_2) with D_2 was investigated under 40 mL/min of 5% D_2/N_2 flow with increase in temperature from 313 K to 473 K. The gas-phase products were analyzed by mass spectroscopy (BELmass, MicrotracBEL). The reverse reaction (In-CHA(D_2) with H_2) was examined in a similar way using the *in situ* prepared In-CHA(D_2) and 40 mL/min of 5% H_2/N_2 flow.

XAFS measurement

A In K-edge X-ray absorption fine structure (XAFS) measurement was conducted in transmission mode in a BL14B2 station attached to a Si(311) monochromator at SPring-8 (JASRI), Japan (Proposal Nos. 2019A1614 and 2019B1686). A flow reaction system containing a flow-type cell was used for *in situ* XAFS measurements. A disc of In-CHA was prepared using a self-supported disc of In_2O_3/CHA under 5% H_2/He flow at 773 K in a flow type quartz cell with gas mixture system using mass flow controllers. After the preparation, the temperature was decreased to room temperature (ca. 298 K) followed by the XAFS measurement.

Computational details

Density functional theory calculations were performed using the Vienna ab initio simulation package (VASP) [1,2] with a periodic boundary condition under a Kohn–Sham formulation [3,4]. All atoms were allowed to fully relax during calculations. Projected augmented wave method [5,6] was applied to describe the core-electron interactions and plane wave basis set was limited to cut-off energy of 450 eV. The forces on atoms were minimized to less than 0.03 eV/Å. An electron-exchange correlation was considered using the generalized gradient approximated Perdew–Burke–Ernzerhof (GGA–PBE) functional [7]. The Γ point was used for Brillouin zone sampling. Van der Waals (vdW) dispersion corrections were included in all calculations by the semi-empirical Grimme's D3 method [8,9]. the lattice constants of CHA zeolite were fixed at values given in the International Zeolite Association database ($a = b = 13.675$ Å, $c = 14.767$ Å, $\alpha = \beta = 90.0°$, and $\gamma = 120°$) [10]. For vibration calculation, all atoms except In hydrides were fixed. The conjugate gradient method was used to optimize intermediate structures during the climbing-image nudge elastic band (CI–NEB) calculations as implemented in VTST-Tools [11]. For CI–NEB calculations, the spring constant between adjacent images was set to 5.0 eV/Å^2; moreover, the calculations were considered converged when the maximum forces on all atoms were less than 0.05 eV Å^{-1}. The Gibbs free energy of each species was calculated using vibrational frequency analysis based on harmonic normal mode approximation by the finite difference method in VASP. A limited set of atoms that are determined as non-zeolite framework atoms (indium, carbon, and hydrogen atoms) in the unit cell, were used to calculate vibrational frequencies. The vibrational contribution to the free energy for each structure at 873.15 K was calculated based on the calculated frequencies. Neglecting the spurious frequencies contributes to the enthalpy and entropy; hence, spurious frequencies under 100 cm^{-1} were replaced with 50 cm^{-1} for all the structures to give consistent results [12]. Ethane, ethylene, and hydrogen in gas phase were calculated using ideal gas approximation at 873.15 K and their transitional and rotational contributions to the free energy were evaluated at partial pressures of 0.02, 2×10^{-4}, and 2×10^{-4} atm, respectively.

Dehydrogenation of ethane

Nonoxidative dehydrogenation of ethane was performed in a fixed-bed continuous-flow system at 933 K. The catalyst was prepared *in situ* by treatment of a 0.1 g of In_2O_3/CHA under 50 mL of 10% H_2/He flow at 773 K for 30 min to promote RRSIE followed by He purge for 1 h before dehydrogenation. Ga- and Zn-exchanged zeolites were prepared through the impregnation of the corresponding nitrate precursors ($Ga(NO_3)_3 \cdot 9H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$) to CHA (Tosoh, NH_4^+-type, $SiO_2/Al_2O_3 = 22.3$) or ZSM5 (Tosoh, NH_4^+-type, $SiO_2/Al_2O_3 = 22$) followed by calcination under air at 773 K. Before the reaction, the catalysts were treated under a H_2/He flow at 993 K for Ga or at 773 K for Zn in the reactor. $PtSn/Al_2O_3$ and $PtGa/Al_2O_3$ were prepared by a conventional impregnation method of H_2PtCl_6

and $(NH_4)_2SnCl_6$ or $Ga(NO_3)_3$ to γ-Al_2O_3 (prepared by calcination of boehmite (γ-AlOOH, SASOL Chemicals) at 1173 K for 3 h) followed by *in situ* reduction of the obtained powder under a H_2/He flow at 973 K for 1 h. For all the dehydrogenation experiments, the gas from the reactor was analyzed by Shimadzu GC-14B with a SHINCARBON ST column and gas sampler (GS5100). The conversion, selectivity, and carbon balance were calculated as follows:

$$\text{Conv.} [\%] = \frac{[ethane]_{init} - [ethane]}{[ethane]_{init}} \times 100$$

$$\text{Selec.} [\%] = \frac{[ethylene]}{[ethylene] + [methane]} \times 100$$

$$\text{Carbon balance} [\%] = \frac{([ethane] + [ethylene] + [methane])}{[ethane]_{init}} \times 100$$

For reuse experiment, the In-CHA after 90 h reaction was treated with 50 mL of 5% O_2/He at 873 K for 90 min in the reactor to calcine the coke and then treated with 50 mL of 10% H_2/He followed by He purge for 1 h. The dehydrogenation was performed in the same reaction conditions for 20 h. To obtain the relationship between conversion and selectivity, the reaction was carried out at 773–893 K for Ga-ZSM-5 and PtSn/Al_2O_3 and at 913–953 K, respectively.

The kinetic studies were carried out under the following conditions.

•TOF dependency on $p(H_2)$ for In-CHA (In/Al = 0.8)

$p(H_2)$ = 0.02–0.08, $p(C_2H_6)$ = 0.02, balanced with He (total flow rate: 50 mL/min), 933 K

•TOF dependency on $p(C_2H_6)$ for In-CHA (In/Al = 0.8)

$p(H_2)$ = 0.02, $p(C_2H_6)$ = 0.02–0.08, balanced with He (total flow rate: 50 mL/min), 933 K

•TOF dependency on $p(H_2)$ for Ga-CHA (Ga/Al = 0.8)

$p(H_2)$ = 0.02–0.08, $p(C_2H_6)$ = 0.04, balanced with He (total flow rate: 50 mL/min), 913 K

•TOF dependency on $p(C_2H_6)$ for Ga-CHA (Ga/Al = 0.8)

$p(H_2)$ = 0.04, $p(C_2H_6)$ = 0.02−0.08, balanced with He (total flow rate: 50 mL/min), 913 K

•M/Al effect on formation rate for In-CHA

$p(C_2H_6)$ = 0.02, balanced with He (total flow rate: 50 mL/min), 933 K

•M/Al effect on formation rate for Ga-CHA

$p(C_2H_6)$ = 0.04, balanced with He (total flow rate: 50 mL/min), 913 K

•Eyring plot for In-CHA (In/Al = 0.8)

$p(C_2H_6)$ = 0.02, balanced with He (total flow rate: 50 mL/min), 873–933 K

•Eyring plot for Ga-CHA (Ga/Al = 0.8)

$p(C_2H_6)$ = 0.04, balanced with He (total flow rate: 50 mL/min), 873–933 K

Temperature-programmed oxidation (TPO) measurement

TPO measurement was performed using BELCAT II (MicrotracBEL). After the 2 h reaction, 40 mg of catalyst was used for the TPO experiment. The catalyst was pretreated at 423 K for 30 min under He atmosphere. The gas flow was switched to 50% O_2/He (40 mLmin^{-1}) and then the temperature was increased to 1073 K at 5 K/min. During the reaction, the CO_2 generated through coke oxidation (m/e = 44) was measured by mass spectroscopy (BELmass, MicrotracBEL).

Figures
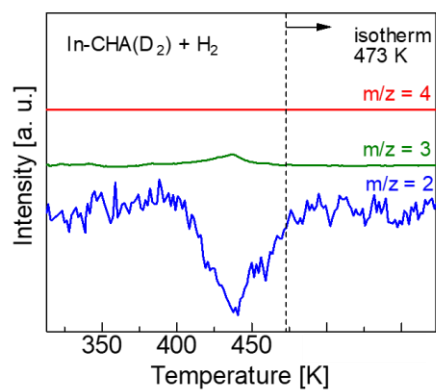
Figure S1. Mass profiles for m/z = 2, 3, and 4 during the reaction between In-CHA(D_2) and H_2
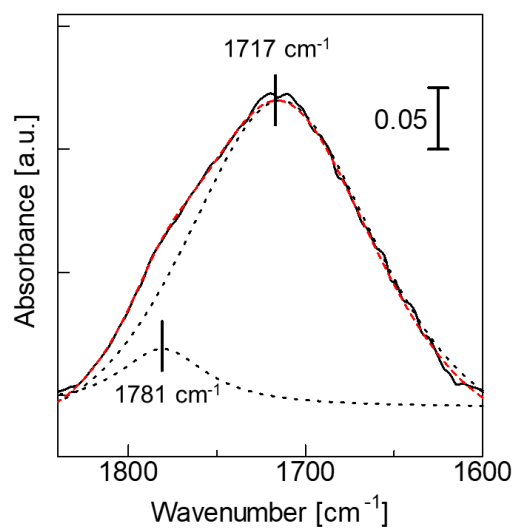

Figure S2. Deconvolution of the bands around 1700–1800 cm^{-1} in the FTIR spectrum of In-CHA(H_2)
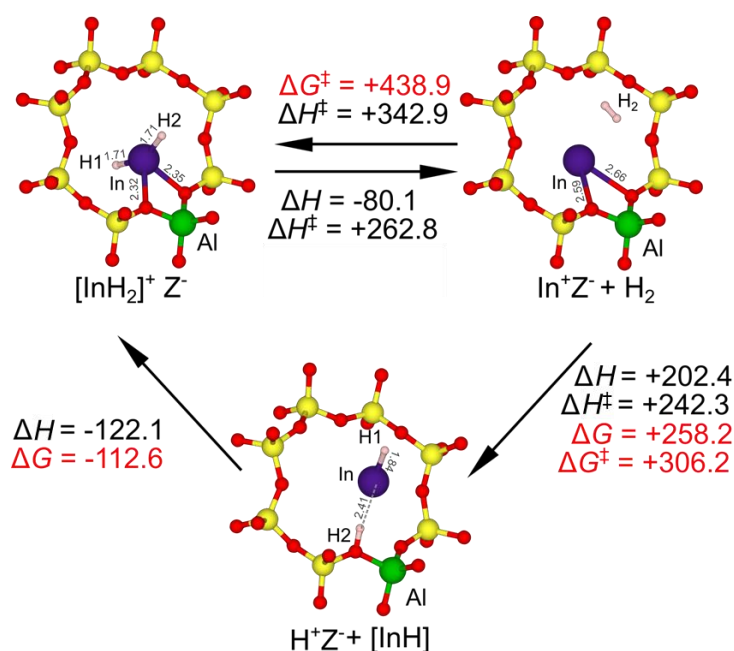
Figure S3. Enthalpy and free energy for interconversion between Z[InH$_2$] and Z[In]
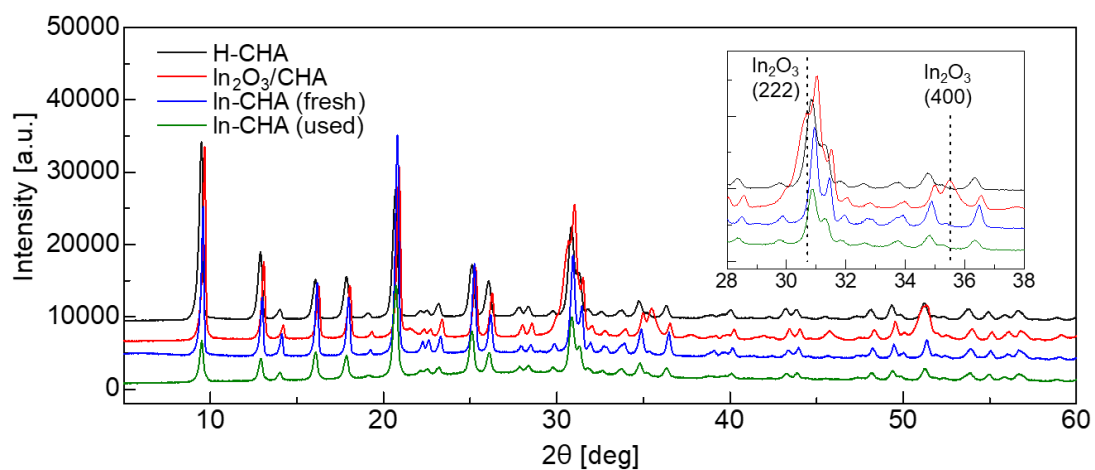

Figure S4. XRD pattern of the fresh In-CHA, precursor material In$_2$O$_3$/CHA, In-CHA used for the dehydrogenation, and H-CHA
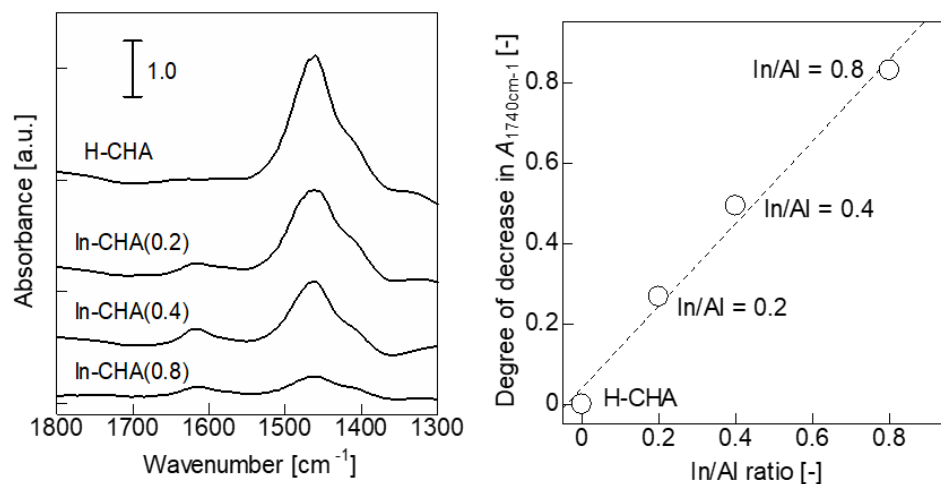
Figure S5. FTIR spectra of NH_3 adsorption experiment for In-CHA with different In/Al ratio (left) and relationship between the degree of decrease in peak area around 1740 cm^{-1} ($A_{1740cm}$$^{-1}$) and In/Al ratio (right)
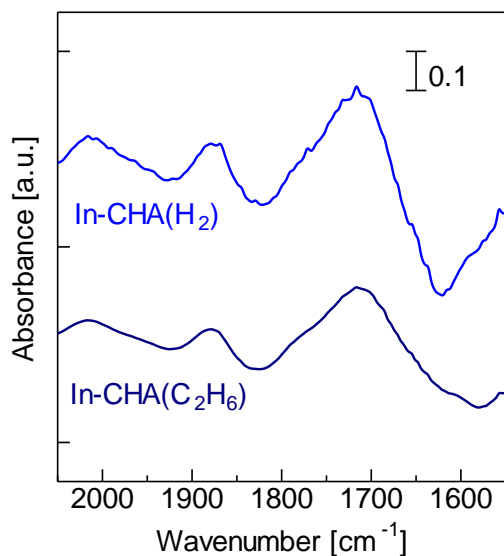

Figure S6. FTIR spectra of the In-CHA after treatment with ethane at 773 K
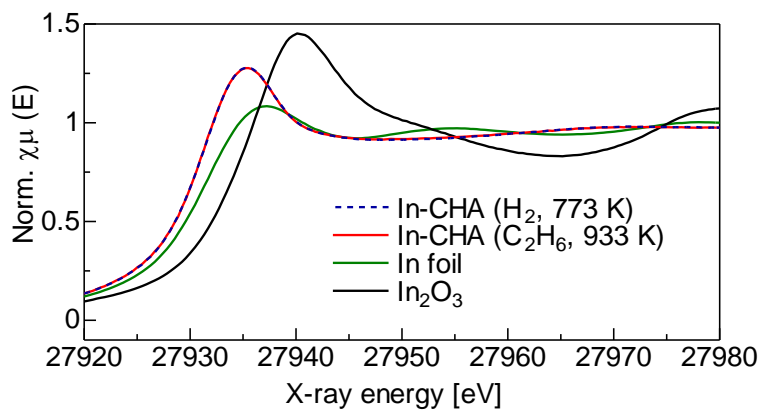

Figure S7. *In situ* XAFS spectra of In-CHA in the presence of H_2 (773 K) or ethane (933 K)

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