

Colloidal Synthesis of Well-Defined Bimetallic Nanoparticles for Nonoxidative Alkane Dehydrogenation

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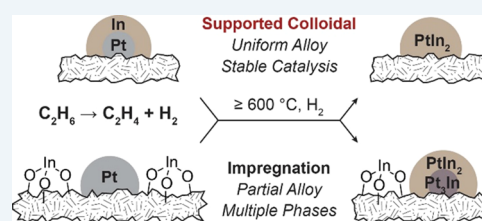
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ABSTRACT: Precise synthesis and characterization of bimetallic nanoparticles are critical toward understanding structure–activity relationships in alkane dehydrogenation catalysis. Traditional synthetic methods for Pt alloy catalysts involve impregnation of two metal salts onto high surface area supports followed by thermal reduction to form an alloy, which frequently results in inhomogeneous alloying and phase segregation of excess metal oxides in the material. In this work, we utilize colloidal methods to synthesize supported Pt–In and Pt–Ga nanoparticles with controlled bimetallic composition. The supported colloidal nanoparticles display phase uniformity while eliminating large excesses of In and Ga oxides, which allows us to ascertain the role that the bimetallic phase and composition play in tuning the reactivity, selectivity, and stability of the catalyst in both ethane and propane dehydrogenation. Indeed, the promoter-rich PtIn₂ phase shows the highest turnover rate for ethane dehydrogenation, which we attribute to both the strong electronic perturbation to Pt sites observed in Pt L_{III}-edge X-ray absorption spectroscopy and the major geometric change at the surface upon formation of the CaF₂ crystal structure adopted by PtIn₂. Finally, we show that the promoter-rich colloidal nanoparticles are more thermally robust than incipient wetness impregnation catalysts of the same composition because they eliminate two deactivation pathways—reduction and vaporization of unalloyed promoter atoms—that only occur on the structurally nonuniform impregnated catalyst.

KEYWORDS: heterogeneous catalysis, colloidal synthesis, dehydrogenation, intermetallic phases, nanoparticles



INTRODUCTION

The recent growth in the production of natural gas from shale deposits presents an opportunity to develop new technologies that efficiently convert C₂ and C₃ alkanes to chemicals and fuels via catalytic dehydrogenation.¹ Ethane and propane dehydrogenation processes are highly endothermic processes that require reaction temperatures ranging from 800 to 1100 K, conditions that present major challenges for catalyst stability and selectivity.^{2,3} Supported bimetallic nanoparticles comprising Pt and a post-transition metal promoter element are among the best catalysts for these reactions but nonetheless require frequent regeneration steps due to catalyst deactivation during operation.^{4–11}

To improve catalyst thermal stability and to better understand structure–activity relationships in alkane dehydrogenation, precise and tunable synthetic methods for supported bimetallic Pt nanoparticles are required. Conventional synthetic methods for generating supported Pt–M catalysts involve sequential impregnation of oxide supports with metal salts followed by a reduction step to alloy the two metals and generate the active catalytic species.^{7,12,13} While impregnation is operationally quite simple, it rarely forms the expected alloy composition for any given ratio of impregnated precursors and instead results in nonuniform alloying and phase segregation of excess metal oxides.^{14–16} Due to the inhomogeneity of phases in the catalyst, clear elucidation of the role that the bimetallic

phase and composition play in the catalytic reaction remains challenging, and catalyst structures evolve more rapidly at elevated temperature due to over-reduction or evaporation of the excess promoter.^{12,17,18} Numerous alternatives to sequential impregnation have been demonstrated in the literature to improve the homogeneity of supported Pt alloy catalysts, including strong electrostatic adsorption, atomic layer deposition, and surface organometallic chemistry, but these methods still rely primarily upon manipulation of the precursor interaction with the support material.^{19–24}

In this work, we develop a colloidal synthetic method to pre-synthesize well-defined Pt–In and Pt–Ga bimetallic nanoparticles prior to supporting on SiO₂ for use as alkane dehydrogenation catalysts. Colloidal synthesis is a powerful strategy that enables access to bimetallic nanoparticles with controlled composition, morphology, and surface capping.²⁵ We chose In and Ga as the alloying elements in this study because they have been shown via incipient wetness impregnation (IWI) to be excellent promoters for selective

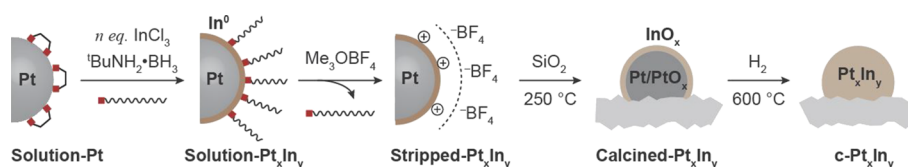
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Scheme 1. Multistep Synthetic Process to Generate Colloidal Pt–In Nanoparticles of Varying Composition Supported on SiO₂ for Catalysis



propane and ethane dehydrogenation.^{4,26,27} Using a multistep colloidal deposition, we can directly synthesize Pt–In and Pt–Ga nanoparticles with good uniformity as well as well-defined size and composition. These nanoparticles are then stripped of organic ligands and deposited onto SiO₂ supports, generating a homogeneous population of supported alloy nanoparticles without large excesses of In or Ga oxides. All of the colloiddally synthesized Pt–In and Pt–Ga nanoparticles are highly active and selective for ethane and propane dehydrogenation with olefin selectivities of >95% at up to 50% alkane conversion. Under kinetic conditions, the colloidal catalysts show significant differences in turnover rates and activation barriers as a function of the surface alloy phase.

Finally, the promoter-rich colloidal catalysts show improved thermal and structural stability when stress-tested at 800 °C, compared to an analogous bimetallic catalyst prepared via IWL, illustrating that pre-synthesis of uniform nanoparticles and elimination of excess promoter oxides remove a key route toward catalyst deactivation under strongly reducing and high temperature conditions.

RESULTS AND DISCUSSION

Synthesis of Pt–M (M = In, Ga) Nanoparticles. The multistep process for the synthesis of colloidal Pt₃In, PtIn₂, and Pt₃Ga nanoparticles supported on SiO₂ for alkane dehydrogenation is illustrated in Scheme 1. The first step in the process, colloidal Pt synthesis and promoter shell deposition, is adapted from a literature synthesis of Pt–Sn bimetallic nanoparticles.²⁸ We first synthesize pure Pt nanoparticles (Solution-Pt) with a diameter of 2.2 nm stabilized by sodium hydroxide and ethylene glycol (Figure 1a; Figure S6).^{29,30} The desired ratio of the InCl₃ precursor is then added to the cleaned colloidal Pt

solution and permitted to passively adsorb to the Pt surface. Two different In loadings were utilized in order to generate a Pt-rich bimetallic phase (Solution-Pt₃In) and an In-rich phase (Solution-PtIn₂). A separate toluene solution containing the reductant tert-butylamine borane, phase-transfer reagent didodecyldimethylammonium bromide, and ligand oleic acid is heated up to 100 °C. Upon injection of the Pt@InCl₃ ethylene glycol layer into the preheated toluene layer, immediate phase transfer of the Pt nanoparticles from the polar layer to the nonpolar layer is observed. Importantly, this phase transfer is not observed when the InCl₃ precursor is omitted from the solution, indicating that the layer of preadsorbed InCl₃ on the Pt surface is responsible for binding of oleic acid and stabilization in the nonpolar solvent. The solution is then stirred at 100 °C for 20 min, allowing the remainder of the In precursor to phase-transfer and deposit onto the Pt surface. The final Pt–In core–shell nanoparticles for both the Pt-rich and In-rich PtIn phases are 2–3 nm in diameter and well-dispersed in nonpolar solvents (Figure 1b; Figures S1a and S6). No nanoparticle ripening or secondary nucleation of In metal or In oxides is observed.

A similar biphasic solution is utilized for the Pt₃Ga nanoparticles, but instead of preforming the Pt nanoparticles, the Pt and Ga precursors are co-reduced at room temperature as they phase-transfer from the ethylene glycol layer to the toluene layer. Compared to InCl₃, the passive adsorption of GaCl₃ to the surface of preformed Pt nanoparticles is too weak to drive the phase transfer. The room-temperature co-reduction strategy forms homogeneous nanoparticles at the lower Ga loading (Solution-Pt₃Ga) but is difficult to extend to the Ga-rich phases due to the propensity for GaCl₃ to secondary nucleate as amorphous Ga₂O₃ (Figure S2a).

In order to perform high-temperature gas phase catalysis, the colloidal nanoparticles must be stripped of capping organic ligands and uniformly deposited onto a support oxide. We utilize a biphasic chemical method to strip the organic ligands off the surface of the Pt–In and Pt–Ga nanoparticles using trimethyloxonium tetrafluoroborate or tetrabutylammonium hydroxide.^{31–33} Importantly, the ligand stripping reagents leave behind a relatively clean and highly charged surface, resulting in good morphology retention and colloidal stability in polar solvents such as *N*-methylformamide (Figure 1c; Figures S1b and S2b). These ligand-stripped nanoparticles are then deposited onto mesoporous SiO₂ and dried at 250 °C (Figure 1d; Figures S1c and S2c). No significant change in particle size or morphology is observed for any of the colloidal nanoparticles after supporting on SiO₂ (Figure 1; Figures S1, S2, and S6). Finally, the supported colloidal nanoparticles are reduced in 5% H₂ to form the bimetallic alloys prior to the catalytic reaction.

To track the fate of the promoter atom during our multistep synthesis process, we utilize X-ray fluorescence (XRF) to characterize the Pt/M atomic percentages (Table S1). We label the solution-phase nanoparticles capped with organic

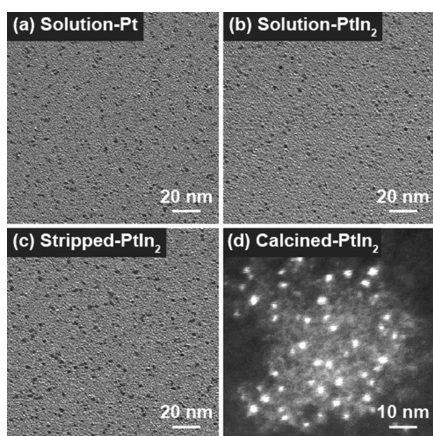


Figure 1. TEM and HAADF-STEM characterization of intermediate stages in the colloidal bimetallic nanoparticle synthesis. (a) Solution-Pt capped with ethylene glycol, (b) Solution-PtIn₂ capped with oleic acid, (c) Stripped-PtIn₂ capped with BF₄[−] in solution, and (d) Calcined-PtIn₂ supported on SiO₂.

ligand as Solution-PtM, the ligand-stripped nanoparticles as Stripped-PtM, the nanoparticles supported on SiO₂ and dried in air as Calcined-PtM, and the reduced, supported nanoparticles as c-PtM (Scheme 1). For all three compositions, 80–90% of the In or Ga precursors introduced in solution are incorporated into the bimetallic nanoparticle during the biphasic deposition step (Table S1, Solution-PtM). The ligand-stripping and SiO₂ supporting step as well as the H₂ reduction step can cause additional promoter atom loss through etching and vaporization, most clearly seen in the Pt₃In composition, which results in promoter/Pt ratios that are slightly lower than required to form the desired Pt₃M and PtM₂ intermetallic phases. Some batch-to-batch variability is observed for the synthetic process, but the trends in promoter loss are consistent. For clarity, all forthcoming spectroscopic and catalytic characterization will refer to the colloidal nanoparticles supported on SiO₂ and reduced in 5% H₂ as c-Pt, c-Pt₃In, c-Pt₃Ga, and c-PtIn₂ based on the intermetallic structure closest to the experimental composition.

X-ray Diffraction. In order to determine if the c-PtM nanoparticles in fact form the desired alloy phases for catalysis after 600 °C reduction, powder X-ray diffraction (XRD) patterns were collected and compared to reference patterns of intermetallic Pt₃In, Pt₃Ga, and PtIn₂ phases (Figure 2; Table

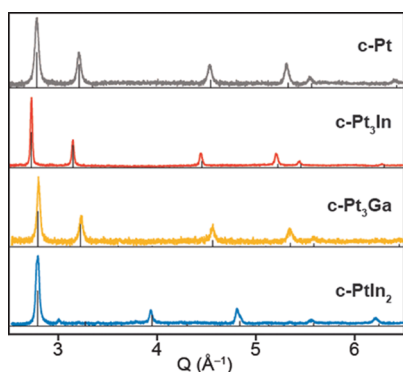


Figure 2. Ex-situ XRD patterns collected at room temperature for c-Pt (gray solid lines), c-Pt₃In (red solid lines), c-Pt₃Ga (yellow solid lines), and c-PtIn₂ (blue solid lines) after reduction in 5% H₂ at 600 °C compared with reference XRD patterns for each phase.

S2). The XRD patterns for c-Pt, c-Pt₃In, and c-Pt₃Ga are characteristic of a face-centered cubic (FCC) structure. The lattice parameters of the Pt₃M alloys are very similar to those of pure Pt, which makes it difficult to definitively assign the phases of c-Pt₃Ga and c-Pt₃In using diffraction alone. Nonetheless, good agreement is observed between the theoretical and experimental patterns. When reduced at higher temperature, weak intermetallic peaks are observed between 3.4–4.4 Å^{−1} for c-Pt₃In, confirming formation of the intermetallic alloy (Figure S9).

In contrast, the XRD pattern of the c-PtIn₂ catalyst is distinctly different from a typical FCC pattern. The observed pattern corresponds to a calcium fluoride (CaF₂) fluorite crystal structure, and no peaks from the Pt-rich FCC phases remain. The fluorite PtIn₂ unit cell comprises an expanded FCC Pt sublattice with eight In atoms occupying the tetrahedral holes (Figure S13). Interestingly, some of the expected reflections for fluorite PtIn₂ are suppressed, and closer examination of the Miller indices show that the even-numbered (h k l) reflections tend to diffract more strongly,

while the odd-numbered reflections are suppressed (Figure S10). Combined with the slight shift in the XRD peaks toward lower Q, these data suggest that c-PtIn₂ may contain vacancy or antisite defects due to the <2:1 ratio of In/Pt in the sample. In addition, several impurity peaks between 2.9 and 3.5 Å^{−1} and at 5.3 Å^{−1} suggest the presence of a small amount of the Pt₃In₂ phase (Figure S10; Table S3).

X-ray Absorption Spectroscopy. Because of the ambiguity of the XRD patterns for the Pt₃M phases, we turned to X-ray absorption spectroscopy (XAS) measurements at the Pt L_{III} (11.564 keV), In K (27.940 keV), and Ga K (10.367 keV) edges to more clearly elucidate the degree of alloying and local coordination environment of the colloidal PtM nanoparticles. Prior to reduction at 600 °C, all of the Calcined-PtM samples are partially oxidized at the Pt and promoter edges due to the air calcination step used to dry the samples after adsorption onto the SiO₂ support (Figure S11; Table S5). Once the samples are reduced in 5% H₂ at 600 °C, the X-ray absorption near edge (XANES) region for both the Pt and promoter edges clearly show electronic perturbations due to alloy formation. The Pt L_{III}-edge XANES spectra for c-Pt₃In, c-PtIn₂, and c-Pt₃Ga show slightly suppressed white line intensities and significant shifts in edge energy to higher values compared to monometallic c-Pt (Figure 3a). The increase in XANES edge energy is indicative of an upward shift in unfilled valence states of Pt, which is typically coupled to a downward shift in the filled d-band states of Pt.^{34–36} Both c-Pt₃In and c-Pt₃Ga show moderate shifts of 0.2 and 0.4 eV in the edge energy, while c-PtIn₂ is shifted by 1.4 eV. The latter indicates

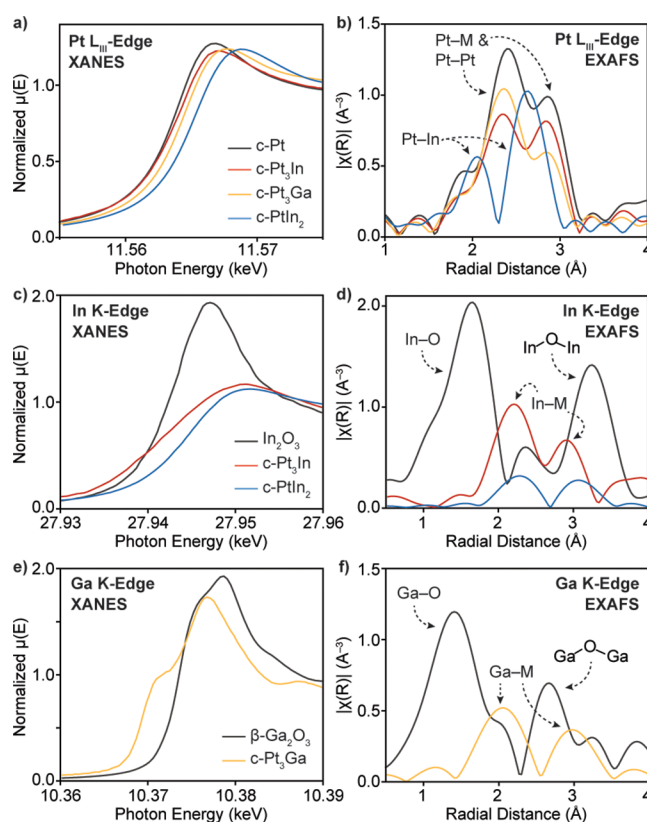


Figure 3. XAS spectra collected on the supported colloidal catalysts after reduction at 600 °C with 5% H₂. (a) Pt L_{III}-edge XANES, (b) Pt L_{III}-edge EXAFS, (c) In K-edge XANES, (d) In K-edge EXAFS, (e) Ga K-edge XANES, and (f) Ga K-edge EXAFS.

that the change in the energy of the Pt valence orbitals increases with an increasing number of promoter bonds, e.g., PtIn₂ has a greater XANES edge energy than Pt₃In. The magnitudes of Pt edge energy shift are consistent with those observed for other PtM bimetallic nanoparticles and reflect the strength of orbital hybridization between Pt and promoter atoms due to the extent of alloy formation and the promoter identity.^{16,20,36–38} At the K-edge for In and Ga, the XANES data are consistent with reduction of In and Ga species, exhibiting lower white line intensities and a shift to lower edge energy compared to the In₂O₃ and β -Ga₂O₃ reference samples (Figure 3c,e).^{18,39,40} X-ray photoelectron spectroscopy (XPS) of the Pt 4f, In 3d, and Ga 2p regions for all c-PtM samples corroborates the fact that metal atoms are reduced in the catalyst compared to the In₂O₃ and Ga₂O₃ references (Figures S25–S30; Table S9). However, both the XANES and XPS of c-Pt₃Ga suggest that a fraction of oxidized Ga remains in the sample.^{40,41}

The X-ray absorption fine structure (EXAFS) region of the spectra provides clear evidence of bimetallic alloy formation in all PtM samples (Figure 3b,d,f). Local structures, coordination numbers (CNs), and bond distances (Rs) at the Pt, In, and Ga edges were determined from k^2 -weighted first shell fitting of the EXAFS spectra, utilizing scattering pathways derived from crystal structures of the expected intermetallic compounds (Table 1; Figures S13–S16). In all samples, the total Pt

Table 1. Pt L_{III}, In K, and Ga K-Edge Fitting Parameters for Supported Colloidal Catalysts after Reduction at 600 °C with 5% H₂/He and Reference Samples at Each Edge

sample	edge	XANES edge energy (keV)	scattering pair	CN	R (Å)	σ^2 (Å ²)
Pt Foil Ref.	Pt	11.5640	Pt–Pt	12	2.77	0.004
In ₂ O ₃ Ref	In	27.9438	In–O	4	2.18	0.007
β -Ga ₂ O ₃ Ref.	Ga	10.3737	Ga–O	4	1.88	0.007
c-Pt	Pt	11.5640	Pt–Pt	11.3	2.77	0.007
c-Pt ₃ In	Pt	11.5642	Pt–Pt	7.6	2.77	0.007
			Pt–In	2.7	2.82	0.007
			In–Pt	11.6	2.80	0.008
c-Pt ₃ Ga	Pt	11.5646	Pt–Pt	8.3	2.74	0.007
			Pt–Ga	1.4	2.69	0.007
			Ga–Pt	4.8	2.69	0.008
c-PtIn ₂	Pt	11.5654	Pt–In	7.8	2.75	0.010
			In–Pt	3.9	2.82	0.008
			In–In	2.0	3.20	0.008

coordination number is lower than the value expected for bulk FCC (CN = 12) and CaF₂ (CN = 8) crystal structures, which reflects the ~2–3 nm diameter of the supported colloidal nanoparticles.^{42,43}

In the monometallic c-Pt sample, a Pt–Pt CN of 11.3 at a bond distance of 2.77 Å is structurally analogous to Pt foil (Figure 3b; Figure S14). For c-PtIn₂, the fitted EXAFS data indicate that each Pt atom is surrounded by 7.8 In atoms at a bond distance of 2.75 Å, consistent with the theoretical PtIn₂ intermetallic structure where only In first nearest neighbors are present. No Pt–Pt scattering density is observed, further confirming the complete formation of the PtIn₂ alloy. In contrast, both the c-Pt₃In and c-Pt₃Ga samples show evidence of incomplete alloying. The Pt–Pt CN is ~8 in both cases, and the Pt–M CN is 2.7 for In and 1.4 for Ga. In the theoretical Pt₃M structure, we anticipate CNs of 8 and 4 for Pt–Pt and

Pt–M, respectively. Based on the ratio of the Pt–M CN to Pt–Pt CN, we estimate that ~75% of Pt atoms in Pt₃In and ~40% in Pt₃Ga are present in the alloy form, while the remainder of the Pt atoms remains in a Pt-rich environment. While the EXAFS data are an average measurement, we postulate based on our colloidal synthetic method that each nanoparticle forms an incompletely alloyed structure as opposed to forming a heterogeneous mixture of pure Pt and pure Pt₃M nanoparticles. The catalytic data in the next section also corroborate this hypothesis.

At the In edge, both c-Pt₃In and c-PtIn₂ show a set of peaks between 2 and 4 Å typical of In–metal scattering and no discernable scattering intensity at the In–O distance (Figure 3d; Figure S15). For c-Pt₃In, the In–Pt CN is 11.6 at a bond distance of 2.80 Å, which matches closely with the fitted values at the Pt edge and indicates complete incorporation of In into the bimetallic structure. The c-PtIn₂ sample was found to have an In–Pt CN of 3.9 with a bond distance of 2.82 Å, slightly longer than the bond distance at the Pt edge but still fairly consistent with the ideal crystal structure of PtIn₂. Similar results are obtained at the Ga edge for the c-Pt₃Ga catalyst with no clear Ga–O scattering that would indicate the presence of excess promoter oxides (Figure 3f; Figure S16). A lower than expected Ga–Pt CN of 4.8, however, could be due to Ga species that are not fully incorporated into the bimetallic structure. To quantify the quality of the fits, we analyzed the relationship between the mole fraction (χ) for Pt and the promoter obtained using XRF and the fitted coordination numbers for Pt–M compared to M–Pt at both the Pt and promoter edges. We expect the following relationship to hold for the colloidal nanoparticles because all atoms are fully reduced and incorporated into the alloy nanoparticles:

$$\chi(\text{Pt}) \times \text{CN}(\text{Pt} - \text{M}) = \chi(\text{M}) \times \text{CN}(\text{M} - \text{Pt})$$

All three c-PtM samples adhere closely to the expected relationship, indicating that the EXAFS fits at the Pt and promoter edges are accurate and consistent with the average composition of the sample (Table S7). Together with XRD, the XANES and EXAFS data provide a clear picture of the bimetallic phases formed upon reduction of the supported colloidal nanoparticles. Complete alloying is observed in the c-PtIn₂ sample, while partial alloying is observed in c-Pt₃In and c-Pt₃Ga. In all three cases, all of the In and Ga in the catalyst are fully incorporated into the bimetallic nanoparticle with no clear evidence of In₂O₃ or Ga₂O₃ remaining on the support.

Alkane Dehydrogenation. The catalytic performances of c-Pt₃Ga, c-Pt₃In, and c-PtIn₂ for propane and ethane dehydrogenation were evaluated and compared to that of monometallic c-Pt. Conversion and selectivity for propane dehydrogenation (PDH) were determined using a gas mixture of 2.5% C₃H₈ and 2.5% H₂ with balance N₂ at 550 °C after the catalysts were reduced at 550 °C. Analogously, ethane dehydrogenation (EDH) was evaluated in a gas mixture of 2.5% C₂H₆ and 2.5% H₂ with balance N₂ at 600 °C after the catalysts were reduced at 600 °C. Catalyst evaluation was carried out in the presence of H₂ since an increase in the hydrogen-to-hydrocarbon ratio accelerates hydrogenolysis and slows catalyst coking, allowing us to more rigorously test catalyst selectivity toward dehydrogenation. In both propane and ethane dehydrogenation, monometallic c-Pt shows low initial selectivity toward the alkane dehydrogenation product with significant formation of the C–C hydrogenolysis products methane, ethane, and ethylene for PDH and methane for EDH

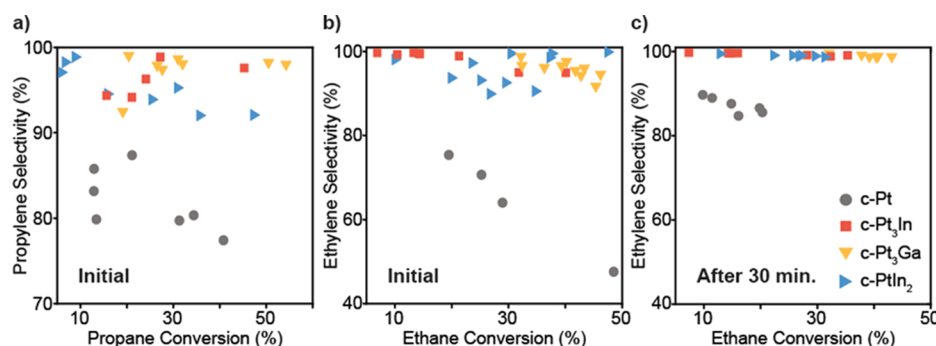


Figure 4. Catalytic results for alkane dehydrogenation on c-Pt (gray solid sphere), c-Pt₃In (red solid square), c-Pt₃Ga (yellow solid triangle), and c-PtIn₂ (blue solid triangle). (a) Initial selectivity and conversion for propane dehydrogenation at 550 °C with a feed of 2.5% C₃H₈, 2.5% H₂, and N₂ balance. (b) Initial selectivity and conversion for ethane dehydrogenation at 600 °C with a feed of 2.5% C₂H₆, 2.5% H₂, and N₂ balance. Catalysts were evaluated at a total flow rate of 100 cm³ min⁻¹. (c) Selectivity and conversion after 30 min of EDH.

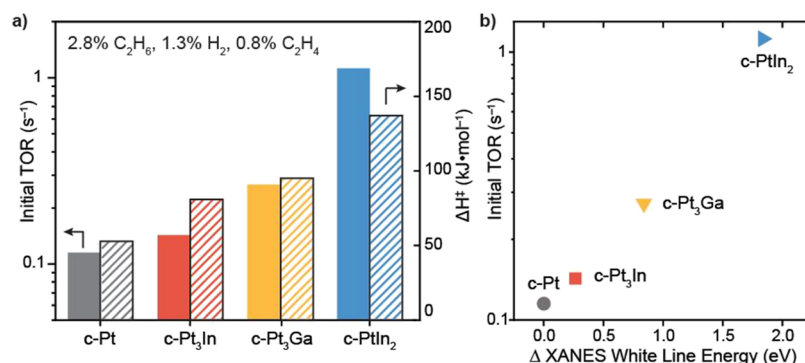


Figure 5. (a) Initial TOR at 600 °C (solid, left) and enthalpy of activation (shaded, right) for supported colloidal nanoparticles in ethane dehydrogenation. Measurements were performed with a feed of 2.83% C₂H₆, 1.33% H₂, and 0.83% C₂H₄ at a total flow rate of 150 cm³ cm⁻¹. (b) Initial TOR vs. shift in XANES white line energy relative to monometallic Pt.

(Figure 4a,b, gray solid spheres; Figures S17a–c and S19a). Additionally, the selectivity for propylene and ethylene declines rapidly as a function of increasing conversion, consistent with literature reports of monometallic Pt catalysts synthesized using IWI.^{8,44}

For all three colloidal bimetallic nanoparticles supported on SiO₂, the initial olefin selectivity rises above 90% at all conversions and no clear decrease in selectivity is observed with increasing conversion (Figure 4a,b). These data suggest that all catalysts expose primarily alloyed surfaces even when the average structure is only partially alloyed. The Pt–In catalysts tend to increase in both alkane conversion and olefin selectivity over the first 30–60 min of the reaction, which creates significant variability in the initial selectivity vs. conversion data (Figures S18 and S20a,b). If we evaluate, instead, the selectivity vs conversion in EDH after 30 min of reaction, we find that the data are much less noisy and that all colloidal bimetallic catalysts show >98% selectivity toward ethylene between 5 and 45% ethane conversion with almost no decay in selectivity at higher conversions (Figure 4c). The monometallic c-Pt data are more difficult to interpret at this time point because its conversion decreases and selectivity increases dramatically during the first 30 min (Figure S20c). Nonetheless, the bimetallic nanoparticles remain noticeably more selective and are capable of maintaining stable and high alkane conversions over a longer period of time compared to monometallic Pt. The high dehydrogenation selectivity and evolution of catalyst behavior over time have previously been observed on Pt–In and Pt–Ga bimetallic catalysts prepared

using IWI and attributed to changes in ensemble geometry at the surface of the nanoparticle upon formation of alloy phases.^{4,26,27}

While the selectivity vs conversion data for both ethane and propane dehydrogenation look very similar across all three colloidal bimetallic nanoparticles, we anticipate that bimetallic composition, phase, and morphology should have a strong impact on the kinetics of alkane dehydrogenation.^{16,36–38} Initial turnover rates (TORs) were determined for EDH at <10% conversion under differential conditions using a reaction mixture of 2.83% ethane, 1.33% H₂, and 0.83% ethylene at 600 °C, normalized by the amount of surface Pt obtained from CO chemisorption (Table 2; Table S10). The initial TOR varies by an order of magnitude across the colloidal samples with monometallic Pt showing a TOR value of 0.12 s⁻¹, the two Pt₃M nanoparticles showing slightly higher TOR values of 0.14 and 0.27 s⁻¹, and the promoter-rich PtIn₂ showing the highest TOR of 1.1 s⁻¹ (Figure 5a). Both DFT calculations and experimental heat of adsorption measurements have suggested that alloying induces a downward shift in the d-band center, which weakens the binding of adsorbates to Pt surface atoms and facilitates product desorption.^{9,45–49} Using the shift in white line energy in the XANES spectrum as a proxy for the lowering of filled d-band energies, we indeed see a clear correlation between Pt electronics and the initial TOR (Figure 5b).⁵⁰ The c-PtIn₂ sample, whose XANES white line shifts to higher energy by nearly 2 eV compared to monometallic Pt, shows the highest TOR for EDH. The c-Pt₃Ga and c-Pt₃In catalysts, while of similar average ensemble geometry, show

Table 2. Kinetic Parameters for all Supported Colloidal Catalysts and IWI Comparison Samples^a

catalyst	TOR ₆₀₀ (s ⁻¹)	Pt dispersion (%)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)
c-Pt	0.12	32	53	-212
c-Pt ₃ In	0.14	13	81	-177
c-Pt ₃ Ga	0.27	10	95	-156
c-PtIn ₂	1.1	8	137	-96
iwi-PtIn ₂	1.3	9	140	-99
c-PtIn ₂ ^b	0.43	7	176	-59
iwi-PtIn ₂ ^b	0.060	11	70	-196

^aReduction is carried out at 600 °C for 30 min with 5% H₂ unless otherwise indicated. ^bCatalysts reduced at 800 °C for 30 min with 5% H₂.

fairly significant differences in edge energy, with the more energetically perturbed Pt₃Ga showing the higher TOR in EDH.

We also measured the initial TOR at four different temperatures for all colloidal catalysts in order to obtain activation parameters using an Eyring plot (Figure S31). While there may be some error in the extrapolated activation parameters due to the relatively narrow range of temperatures required for this reaction (843–873 K), we observe very significant differences in both the enthalpy and entropy of activation for the colloidal bimetallic phases (Table 2). As the initial TOR increases in the order of c-Pt < c-Pt₃In < c-Pt₃Ga < c-PtIn₂, we observe, somewhat surprisingly, that the enthalpy of activation ($\Delta H^\ddagger$) also increases significantly from 53 to 137 kJ mol⁻¹ (Figure 5a). These trends in the enthalpy of activation are consistent with apparent activation energies from literature examples of IWI Pt/SiO₂ and Pt–In/SiO₂ catalysts for EDH.¹⁶ The increase in the reaction rate, therefore, must instead be driven by more positive entropies of activation (Table 2). Given that the surface ensemble geometry of Pt changes across the Pt, Pt₃M, and PtM₂ phases, we anticipate that changes in the binding geometry of the key transition state structures to the surface will strongly impact the entropic activation parameters.

The catalytic stability of all colloidal catalysts was tested over a 9 h period at a fixed catalyst loading of 100 mg at 600 °C in 2.5% C₂H₆ and 2.5% H₂ with balance N₂. As expected, the monometallic c-Pt catalyst deactivates rapidly in the first hour of the reaction from 35 to <10% conversion and remains at low conversion for the remainder of the reaction (Figure 6a, gray solid sphere). The ethylene selectivity, correspondingly, rises from 68% to 88% in the first hour and decays slowly thereafter (Figure 6b, gray solid sphere). All colloidal bimetallic catalysts

show similar initial conversions ranging from 25 to 48% but much higher ethylene selectivity and greater stability over the 9 h reaction time. The c-Pt₃Ga catalyst still deactivates significantly from 47 to 36% over 9 h, but the ethylene selectivity is essentially constant at 98% from the second hour onward (Figure 6a,b, yellow solid triangle). Both the c-PtIn₂ and c-Pt₃In catalysts also show consistently high ethylene selectivity (>98%) throughout the 9 h reaction but somewhat different conversion behavior. The c-Pt₃In catalyst increases in conversion over the first 60 min but then decays slowly from 36 to 33% over the remaining 8 h (Figure 6a,b, red solid square). In contrast, the c-PtIn₂ catalyst shows a very gradual increase in conversion from 25 to 30% over the entire 9 h reaction (Figure 6a,b, blue solid triangle).

Structural reorganization, nanoparticle sintering, and coking likely contribute to catalyst evolution over time during EDH. Based on STEM images obtained after the 9 h stability test, all supported colloidal catalysts sinter slightly with 2–3 nm increases in the average particle diameter (Figures S4 and S7). To determine the amount of coke deposited on the catalyst over the course of EDH, we performed thermogravimetric analysis (TGA) on the spent catalysts (Figure 6b-inset; Figure S33). The monometallic c-Pt and bimetallic c-Pt₃Ga show very similar amounts of coke deposited during the reaction (0.22–0.24 wt %), which are likely a significant cause of the loss in conversion during the stability test. Both c-Pt₃In and c-PtIn₂ show ~5x lower carbon removed (0.05 wt %), consistent with their higher stability.

For comparison, we utilize literature IWI methods to synthesize supported bimetallic nanoparticles with compositions approximately matching our c-PtM samples: 1:1.3 Pt/In (iwi-Pt₃In), 1:2.6 Pt/In (iwi-PtIn₂), and 1:1.4 Pt/Ga (iwi-Pt₃Ga) (Table S1; Figure S8b).¹⁶ After reduction at 600 °C, the IWI catalysts behave very similarly to the supported colloidal catalysts in both kinetic activation barriers and catalytic stability for EDH (Table S11; Figure S23). The promoter-rich Pt–In catalysts, regardless of the preparation method, consistently show the highest initial TOR under kinetic conditions and most stable conversion and selectivity under equilibrium-limited conditions (Table 2; Table S8). Based on all of the structural and catalytic data discussed herein, we postulate that the promoter-rich PtIn₂ phase presents an optimal electronic and geometric environment around each Pt active site to enable both high dehydrogenation turnover rates and low catalyst coking rates, resulting in active, selective, and stable EDH reactivity.

High-Temperature Stress Test. Finally, a critical advantage of the promoter-rich catalysts prepared via colloidal synthesis is their ability to tolerate more reducing conditions and temperatures higher than 600 °C, which will be needed in order to drive the endothermic EDH reaction at industrially

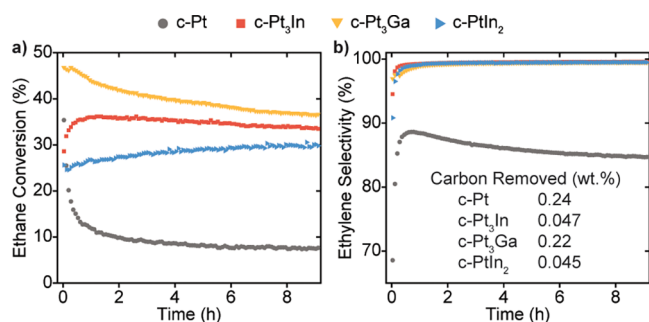


Figure 6. Ethane dehydrogenation stability test for c-Pt (gray solid sphere), c-Pt₃In (red solid square), c-Pt₃Ga (yellow solid triangle), and c-PtIn₂ (blue solid triangle) at 600 °C with a feed of 2.5% C₂H₆, 2.5% H₂, and N₂ balance. (a) Ethane conversion vs time, (b) ethylene selectivity vs time, and (inset) TGA weight loss after 9 h reaction.

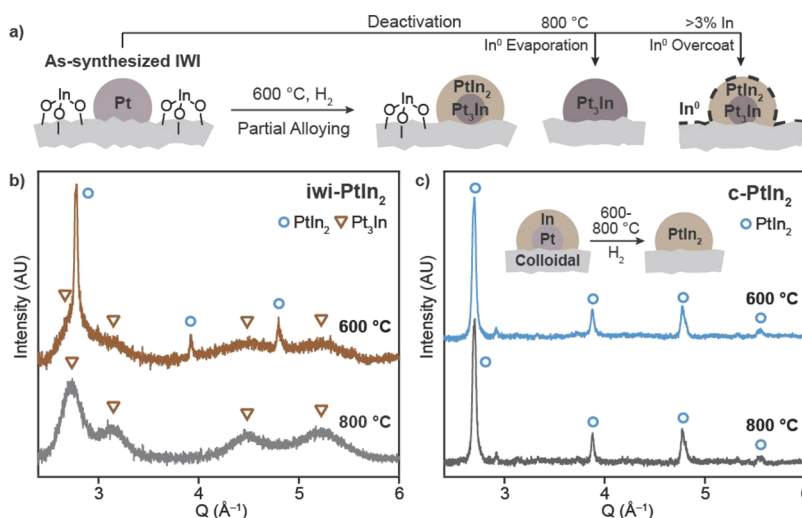


Figure 7. (a) Schematic for the desired partial alloying process and two undesired deactivation pathways in promoter-rich Pt–In catalysts synthesized via IWI. (b) Powder XRD patterns for iwi-PtIn₂ reduced at 600 and 800 °C. (c) Powder XRD patterns for c-PtIn₂ reduced at 600 and 800 °C.

relevant pressures.^{3,51} Bimetallic Pt catalysts prepared via IWI with reducible promoters such as Bi, Sn, In, and Co are known to deactivate as the promoter concentration is increased due to over-reduction of the excess promoter ions on the support surface (Figure 7a).^{18,35,52–55} Additionally, many of the post-transition metal promoters have low heats of vaporization in the metallic form and evaporate from the surface at high temperatures.⁵⁶ Our colloidal method should eliminate both of these deactivating pathways by dialing in the correct ratio of promoter to Pt during the nanoparticle synthesis in order to form the promoter-rich, fully alloyed PtM₂ phase with no excess promoter on the surface. To understand how the precursor structures thermally evolve to form the bimetallic alloy and to stress-test these catalysts under more stringent conditions, we compare IWI and colloidal preparations of the promoter-rich PtIn₂ composition after reduction at 800 °C.

We first characterize the structure of the iwi-PtIn₂ catalyst after the standard 600 °C reduction condition. The XRD pattern shows a mixture of crystalline phases with sharp peaks corresponding to the PtIn₂ phase and broad peaks matching an FCC Pt₃In phase, indicating incomplete formation of the promoter-rich alloy even though an excess of In precursor (2.6 equiv with respect to Pt) is impregnated (Figure 7b). Fitting of the In K-edge EXAFS shows significant unreduced In oxide species remaining on the surface while the Pt L_{III}-edge EXAFS corroborates the presence of mixed Pt–In phases (Figures S12, S14, and S15; Table S6). This iwi-PtIn₂ sample is representative of the challenges associated with traditional IWI synthetic methods in achieving catalyst structure uniformity, particularly in promoter-rich compositions. Nonetheless, the kinetic parameters in EDH, the initial TOR at 600 °C and $\Delta H^\ddagger$, for iwi-PtIn₂ are nearly identical to those observed for c-PtIn₂, confirming that the surface of the nanoparticle forms the PtIn₂ alloy phase, while the nanoparticle core remains in the FCC Pt₃In phase (Table 2; Figure 8).

After a 30 min reduction step at 800 °C in 5% H₂ on both the iwi- and c-PtIn₂ catalysts, we observe major differences in their structure and reactivity in EDH. The c-PtIn₂ catalyst deactivates slightly by a factor of 2 to an initial TOR of 0.43 s^{−1}, most likely due to slight particle sintering that occurs

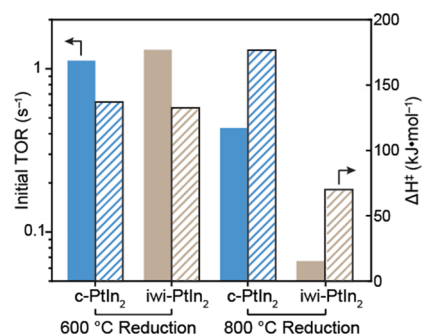


Figure 8. Initial TOR at 600 °C (solid, left) and enthalpy of activation (shaded, right) in ethane dehydrogenation for colloidal and IWI PtIn₂ catalysts after 600 or 800 °C pre-reduction. Measurements were performed with a feed of 2.83% C₂H₆, 1.33% H₂, and 0.83% C₂H₄ at a total flow rate of 150 cm³ cm^{−1}.

during the 800 °C anneal (Figure 8; Figure S5b). In accordance with the particle growth, all of the XRD peaks narrow, but the sample remains in the fluorite PtIn₂ phase (Figure 7c). This is in stark contrast to the iwi-PtIn₂ sample after 800 °C reduction, which exhibits a 20x reduction in the initial TOR for EDH despite only modest nanoparticle sintering (Figure 8; Figure S5a). Intriguingly, the XRD pattern of the iwi-PtIn₂ after 800 °C reduction shows that the CaF₂ phase completely disappears and only broad FCC features remain, which can be assigned to either metallic Pt or Pt₃In (Figure 7b). The $\Delta H^\ddagger$ drops significantly from 140 kJ mol^{−1} in the 600 °C iwi-PtIn₂ phase to 70 kJ mol^{−1} after 800 °C reduction, a value that is similar to an iwi-Pt₃In control sample (Figure 8; Table S11). Furthermore, the elemental analysis using XRF reveals that only 1.7 wt % In remains in the sample, compared to the 3 wt % originally loaded (Table S1). As a result, we postulate that the primary structural evolution pathway during the high temperature stress-test for In-rich catalysts prepared by IWI corresponds to In reduction and evaporation from the catalyst, which occurs because the as-impregnated catalyst comprises highly nonuniform Pt and InO_x regions (Figure 7a). In contrast, the uniform composition of the colloidal PtIn₂ particle ensures that c-PtIn₂ remains fully alloyed even at 800 °C and retains all of the In originally

incorporated during the colloidal synthesis (Table S1). Notably, the thermal phase instability of iwi-PtIn₂ revealed by the high-temperature stress test does not necessarily impact the catalytic stability under equilibrium-limited EDH conditions. All Pt–In phases, prepared using either IWI or colloidal methods, show stable ethane conversion over time during the 9 h EDH stability test at 600 °C (Figures S22 and S24; Table S8).

CONCLUSIONS

In conclusion, we have demonstrated a colloidal synthetic method to obtain tunable bimetallic structures of Pt₃In, PtIn₂, and Pt₃Ga, which are readily stripped of organic ligands and supported onto SiO₂ for high-temperature alkane dehydrogenation catalysis. XRD and XAS characterization after high temperature reduction clearly show the formation of the desired alloy phases in partially alloyed core–shell structures in the cases of Pt₃In and Pt₃Ga and a full alloy in the case of PtIn₂. All three alloy phases show high olefin selectivity across a wide range of conversions in ethane and propane dehydrogenation. However, very different initial turnover rates and activation parameters are observed for each catalyst, which are correlated to both the electronic and geometric properties of each alloy phase. The c-PtIn₂ catalyst, which shows both the largest perturbation in Pt L-edge XANES energy and the largest geometric change compared to the monometallic catalyst, is the most active and stable in EDH at 600 °C. In all cases, the colloidal synthetic method ensures that promoter atoms are fully incorporated into the bimetallic nanoparticle and no excess promoter oxide remains on the surface. As a result, a high-temperature stress test at 800 °C leaves c-PtIn₂ relatively unchanged compared to the standard reduction conditions at 600 °C, while an analogous bimetallic sample prepared by IWI deactivates by over 20x in the EDH turnover rate due to the propensity of the promoter atom to reduce and vaporize from the support at high temperature.

EXPERIMENTAL METHODS

Synthesis of Solution-Pt Nanoparticles. Monometallic Pt nanoparticles were synthesized according to a literature procedure.²⁹ Briefly, an ethylene glycol solution of NaOH (50 mL, 300 mM) was mixed with an ethylene glycol solution of H₂PtCl₆•H₂O (50 mL, 20 mM) at room temperature. The solution was then heated to 160 °C for 3 h under an inert atmosphere. The resulting homogeneous black colloidal solution was precipitated with 2 equiv of HBF₄ with respect to Pt and an equal volume of water relative to ethylene glycol. The solid was collected by centrifugation and redispersed in an appropriate volume of ethylene glycol to obtain a 10 mM solution by Pt mol %.³⁰ The resulting solution has excellent colloidal stability, and no precipitate is observed after standing for several days.

Synthesis of Solution-Pt₃In₂ Nanoparticles. Preparation of Pt–In nanoparticles was achieved by reduction of an In³⁺ precursor in the presence of preformed Pt nanoparticles. The synthesis of Solution-PtIn₂ is provided in detail. A solution of toluene (32 mL) and oleic acid (OAc, 8 mL) was heated to 100 °C in air, and didodecyltrimethylammonium bromide (DDAB, 0.818 mmol) and a tert-butylamine borane complex (tBuNH₂•BH₃, 1.56 mmol) in 8 mL of toluene were added under stirring. Separately, InCl₃ (0.413 mmol) was added to 20 mL of a 10 mM colloidal solution of Pt nanoparticles in

ethylene glycol. The ethylene glycol solution was injected into the toluene solution under N₂ over a period of 10 min, forming a biphasic system. The reaction was further heated at 100 °C for 20 min, upon which transfer of nanoparticles from the ethylene glycol layer to the toluene layer was observed. The resulting nanoparticles were recovered from the toluene layer by precipitation with methanol as the antisolvent, collection by centrifugation, and redissolution in hexanes or chloroform. For Solution-Pt₃In, 16 mL of OAc and 200 μL of oleylamine (OAm) were utilized in the reductant toluene solution, and 0.200 mmol of InCl₃ was added to the Pt ethylene glycol solution.

Synthesis of Solution-Pt₃Ga Nanoparticles. An ethylene glycol solution (5.32 mL) containing GaCl₃ (0.0524 mmol) and H₂PtCl₆ (0.175 mmol) was combined with a toluene solution (4.62 mL) containing OAm (3.7 mmol), and OAc (3.5 mmol) at room temperature under N₂. Subsequently, 0.471 mmol of DDAB and 2.74 mmol of tBuNH₂•BH₃ in 4.62 mL of toluene were added under stirring. The solution was stirred at room temperature for 1 h under N₂. The resulting nanoparticles were recovered following the same procedure described above.

Ligand Stripping and Supporting of Colloidal Nanoparticles. A representative method for Pt–In compositions is provided. A 10 mM solution of Solution-Pt_xIn_y nanoparticles (20 mL) in hexanes was combined with Me₃OBf₄ (0.1 mmol, 1 equiv with respect to Pt) in 10 mL of acetonitrile to form a biphasic solution. For Solution-Pt₃Ga nanoparticles, tetrabutylammonium hydroxide was used as the ligand-stripping agent; additional details are provided in the Supporting Information. In all cases, the solution was stirred at room temperature until the hexane layer fully decolorized, and the particles settled at the interface of the solvent layers. The ligand-stripped nanoparticles were resuspended in N-methylformamide (Stripped-PtM) and could be recovered by precipitation using toluene as the antisolvent. The stripped nanoparticles were deposited on SiO₂ by IWI to give a 2 wt % Pt loading and dried at 250 °C under O₂ for 20 min (Calcined-PtM).

Synthesis of iwi-PtIn₂ by IWI. A Pt–In bimetallic catalyst with a target loading of 2 wt % Pt and 3 wt % In was prepared by sequential IWI based on a literature method.¹⁶ First, 560 mg of In(NO₃)₃•x H₂O (1.87 mmol) and 1.07 g of citric acid (3 equiv wrt In, 5.6 mmol) were dissolved in 1.87 mL of nanopure water. The pH of the solution was raised to 11 by adding NH₄OH. The resulting solution was then added dropwise to 7.0 g of SiO₂ under continuous stirring. The resulting powders were dried for 14 h at 125 °C and subsequently calcined at 600 °C for 3 h. Separately, 284 mg of Pt(NH₃)₄(NO₃)₂ (0.733 mmol) was dissolved in 2.5 mL of 30% aqueous NH₄OH and 1.75 mL of water. The resulting solution was added dropwise to the previously synthesized In/SiO₂ material. The obtained catalyst was dried for 14 h at 125 °C and calcined at 225 °C for 3 h. The Pt–In powders were reduced at 250 °C for 30 min and then at 600 °C for 30 min in flowing 5% H₂ at 100 cm³ min^{−1}.

X-ray Diffraction (XRD). Ex-situ XRD measurements were performed at room temperature on a Panalytical Empyrean Powder X-ray diffractometer with a Cu Kα source (1.54 Å) and a high speed PIXcel 3D Medipix detector. Continuous scans were collected between 2θ = 25° – 110° with a step size of 0.013° and a time per step of 20.40 s using a reflection/transmission spinner in Bragg–Brentano mode.

X-ray Absorption Spectroscopy (XAS). In-situ XAS experiments were carried out at the 10-ID-C and 10-BM-B beamlines at the APS at the Pt L_{III} (11.564 keV), In K (27.940 keV), and Ga K (10.367 keV) edges in transmission mode. Silica-supported nanoparticle samples were ground to a fine powder and pressed to form a self-supported wafer and sealed in a gas-tight sample holder. Samples were treated in $100\text{ cm}^3\text{ min}^{-1}$ 5% H_2/He for 30 min at $600\text{ }^\circ\text{C}$. Spectra were obtained after cooling the sample to room temperature under inert gas. Pt foil (11.564 keV), In foil (27.940 keV), and $\beta\text{-Ga}_2\text{O}_3$ powder (10.375 keV) were used for energy calibration and were scanned simultaneously through a third ion chamber as internal energy calibrants during each measurement.

XAS data analysis was performed using the Artemis software, part of the Demeter software package.⁵⁷ Spectra were fit to a variety of crystallographic structures: PtO, Pt, Pt_3In , PtIn_2 , Pt_3Ga , In_2O_3 , and $\beta\text{-Ga}_2\text{O}_3$. Pt foil, In_2O_3 powder, and $\beta\text{-Ga}_2\text{O}_3$ powder were first fit to their known crystallographic structures in order to determine an appropriate amplitude reduction factor (S_0^2) for each elemental edge. Subsequently, the various atomic paths of the samples were fit to determine the following parameters: average coordination number (CN), alignment offset energy (ΔE), path length adjustment (ΔR), and Debye-Waller factor (σ^2). In all cases, a k^2 -weighed Fourier Transform in a k range of 2.7 to $11\text{ \AA}^{-1}$ was used to carry out the fitting. The reported R-factor is a goodness of fit metric based on the statistical χ^2 value.

Dehydrogenation Activity Measurements. Catalyst testing was performed in a fixed-bed reactor with a quartz reactor tube (9.5 mm ID). The mass of the catalyst sample ranged from 50 to 240 mg, depending on the desired conversion. The catalyst was diluted with high purity SiO_2 (Davisil grade 636, $480\text{ m}^2\text{ g}^{-1}$) to maintain a catalyst bed height of 12.7 mm. A thermocouple was positioned at the bottom of the catalyst bed in order to measure the reaction temperature within the bed. Before doing any testing, the catalysts were reduced under $100\text{ cm}^3\text{ min}^{-1}$ of 5% H_2/N_2 at 600 or $800\text{ }^\circ\text{C}$ for 30 min. Following the reduction, a reaction mixture consisting of either 2.5% C_2H_6 or C_3H_8 , 2.5% H_2 , and balance N_2 was introduced at $100\text{ cm}^3\text{ min}^{-1}$ total flow.

Kinetic Measurements. For kinetic measurements, a gas mixture of 2.83% C_2H_6 , 1.33% H_2 , 0.83% C_2H_4 , and balance N_2 was introduced at $150\text{ cm}^3\text{ min}^{-1}$ total flow in order to keep the initial ethane conversion below 10%. Calculations of EDH rates were performed as follows. In order to treat the plug flow reactor as a differential reactor and model it as a continuous stirred-tank reactor, the concentration of reactants and temperature are assumed to be constant throughout the catalyst bed. In order to satisfy these conditions and overcome product inhibition, C_2H_4 was added in the reactor feed in an amount that would result in a differential change ($<10\%$) across the catalyst bed due to dehydrogenation or hydrogenolysis. Thus, the reaction rate can be modeled following the equation below and assumed to be constant throughout the reactor

$$r = \frac{q([\text{C}_2\text{H}_6]_0 - [\text{C}_2\text{H}_6])}{W}$$

Where r corresponds to the observed rate of reaction ($\text{mol C}_2\text{H}_6\text{ g}_{\text{cat}}^{-1}\text{ s}^{-1}$); q is the volumetric flow rate of C_2H_6 (mL min^{-1}); $[\text{C}_2\text{H}_6]_0$ is the initial ethane concentration ($\text{mol C}_2\text{H}_6\text{ mL}^{-1}$); $[\text{C}_2\text{H}_6]$ is the ethane concentration ($\text{mol C}_2\text{H}_6\text{ mL}^{-1}$); and W is the mass of the catalyst (g).

Because EDH is an equilibrium-limited reaction, the forward reaction rate is related to the observed rate of reaction, r , by

$$r_f = \frac{r}{(1 - \eta)}$$

$$\eta = \frac{[\text{C}_2\text{H}_4][\text{H}_2]}{K_{\text{eq}}[\text{C}_2\text{H}_6]}$$

where r_f is the forward rate ($\text{mol C}_2\text{H}_6\text{ g}_{\text{cat}}^{-1}\text{ s}^{-1}$) and η is the approach to the equilibrium parameter. The kinetic measurement conditions are set such that the value of η always remains below 0.17.⁵⁸

To determine activation parameters for each catalyst, the rate of the reaction was measured at four temperatures between 570 and $600\text{ }^\circ\text{C}$. Enthalpies and entropies of activation were extracted from the Eyring equation given below:

$$k = \frac{k_B T}{h} \exp\left(\frac{-\Delta H^\ddagger + T\Delta S^\ddagger}{RT}\right)$$

where k is the rate constant, k_B is Boltzmann's constant, h is Planck's constant, $\Delta H^\ddagger$ is the enthalpy of activation (J mol^{-1}), $\Delta S^\ddagger$ is the entropy of activation ($\text{J mol}^{-1}\text{ K}^{-1}$), R is the gas constant ($\text{J mol}^{-1}\text{ K}^{-1}$), and T is the reaction temperature (K).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.0c01554>.

Additional materials and experimental methods, physical characterization of materials, and catalytic data (PDF)

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Notes

The authors declare no competing financial interest.

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