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**The Effects of Structure on the Activity, Selectivity, and Stability of
Pt-Sn-DeAlBEA for Propane Dehydrogenation**

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Abstract

Recent research has found that dealuminated zeolite BEA (DeAlBEA) is an attractive support for the dispersion of Pt and PtSn species that serve as catalysts for propane dehydrogenation (PDH). In this study, we report the preparation, structural characterization, and PDH activities of Pt-Sn-DeAlBEA catalysts as a function of the Pt/Al ratio (here Al represents the amount of Al present in the parent zeolite H-BEA). The support Sn-DeAlBEA was prepared by introduction of Sn to DeAlBEA. Characterization of this material by XAS and UV-Vis spectroscopy revealed that the Sn incorporates into BEA the framework as Sn(IV) cations. Pt-Sn-DeAlBEA catalysts were prepared with Pt/Al ratios (0.001-0.026) and were characterized with IR of adsorbed probe molecules and XAS to understand the effect of changing Pt loading on the structure of Pt in Pt-Sn-DeAlBEA. Pt dispersion on DeAlBEA (i.e., Pt-DeAlBEA) produces Pt nanoparticles with an average Pt-Pt coordination number of 9 (~ 25 Å) for Pt/Al ratios of 0.001 and above. By contrast, dispersion of Pt on Sn-DeAlBEA (Sn/Al = 0.15) produces Pt oligomers with an average Pt-Pt coordination number of 3 for Pt/Al = 0.001, but for Pt/Al ratios > 0.013 Pt nanoparticles form which have a Pt-Pt coordination number of 9. Pt-Sn-DeAlBEA exhibits high selectivity to propene (> 97%) and high dehydrogenation rates. Forward rate constants were calculated and compared with values determined for various Pt and PtSn catalysts reported in the literature. The Pt-Sn-DeAlBEA catalysts prepared in this study exhibit significantly higher forward rate constants than those previously reported for Pt and PtSn catalysts. The kinetics of PDH were measured for Pt-Sn-DeAlBEA catalysts with different Pt/Al ratios but identical Sn/Al ratios. In all cases, the kinetics are described by a Langmuir-Hinshelwood rate expression, which is first-order in propane and is inhibited by propane adsorption. The similarity of the apparent activation energies and enthalpies of propane adsorption for all three catalysts suggests that the active species are very small Pt₃Sn clusters strongly bound to the framework of DeAlBEA.

Keywords: Pt-Sn-DeAlBEA, zeolite, propane dehydrogenation, catalyst characterization, kinetics.

Introduction

Recent interest in the direct dehydrogenation of propane to propene has been motivated by the growing industrial demand for propene and the realization that it cannot be met by catalytic cracking of petroleum and steam cracking to naphtha.^{1,2} At the same time, propane has become increasingly available from shale gas. Hence, propane dehydrogenation (PDH) offers a way to close the gap between propene demand and its availability from petroleum.³ The most extensively investigated catalysts for PDH are supported Pt and bimetallic PtSn.^{1,4} Previous studies have found that Pt is quite active for PDH but suffers from deactivation and poor selectivity.⁵⁻⁷ However, the activity, propene selectivity, and stability of Pt improve with decreasing particle size and are best for isolated Pt atoms.^{8,9} Both experimental and theoretical studies have shown that the addition of Sn increases the dispersion of Pt, enhances the rates of PDH, and reduces the rate of coke formation.¹⁰⁻¹⁴ PtSn catalysts contain a variety of structures and Pt/Sn ratios, e.g., Pt particles, PtSn bimetallic alloys (e.g., Pt₃Sn, PtSn), small, supported PtSn bimetallic particles, and isolated Pt atoms interacting with Sn,² the nature of these structures depending on the catalyst preparation procedure, Pt/Sn ratios, and support composition.¹⁵⁻¹⁹ Pt₃Sn is often cited as the most active bulk alloy,¹¹ although PtSn has also been shown to be active.²⁰ The addition of hydrogen to the feed propane has been reported to enhance the rate of PDH by up to 4-fold, with an optimum propane-to-hydrogen ratio of 1:1.^{10,21} Hydrogen addition also decreases the deactivation of PtSn catalysts due to coking by removal of coke precursors through reaction with atomically adsorbed hydrogen,¹⁰ an interpretation supported by theoretical studies.^{22,23} Hydrogen addition has also been found to cause restructuring of PtSn particles and increase Pt-Sn interactions.²⁴⁻²⁶

The resistance of Pt and PtSn clusters and nanoparticles to sintering can be improved by encapsulating them within the pores of a zeolite. Of particular interest has been the idea of using dealuminated Beta zeolite (DeAlBEA) containing non-noble metal sites (Zn, Sn,...). DeAlBEA is formed by removal of framework aluminum atoms to create silanol nests that can then be used to host non-noble metals in the form of $(\equiv\text{SiO})_{n-m}\text{M}^{n+}(\text{OH})_m$ (n is the oxidation state of M ranging from 1+ to 4+ and $0 \leq m \leq n$). These groups then serve as anchors for Pt and facilitate the achievement of a high dispersion of Pt.^{1,4,18,27} A further advantage of using a siliceous/non-acidic support is elimination (or at least reduction) of Brønsted acid sites that can promote coking and, hence, reduce propene selectivity and catalyst stability. In the absence of supported Pt, Sn-DeAlBEA is not very active for PDH.²⁸⁻³⁰ However, dispersion of Pt on Sn-DeAlBEA produces a highly active, selective, and stable catalyst for PDH.^{18,31-33} The active site in Pt-Sn-DeAlBEA has been proposed to be single Pt atoms¹⁸ or small clusters of Pt atoms stabilized by Sn in the zeolite framework.^{18,31,33} Different methods of Pt-Sn-DeAlBEA preparation and pretreatment have been reported. Previous investigations that varied Sn and Pt loadings found that the optimum PDH activity is achieved for Sn/Pt = 3, Sn/Pt = 1, or Sn/Si = 80 (Sn/Pt = 9.9).^{18,31} An important finding is that direct reduction of Pt-Sn-DeAlBEA results in a more stable and active catalyst than calcination followed by reduction due to the formation of smaller Pt domains upon direct reduction.¹⁸

Despite substantial previous work on Pt-Sn-DeAlBEA as a catalyst for PDH, the details of how Pt interacts with Sn in these materials are not fully clear. We also note that most previous studies of Pt-Sn-DeAlBEA have not investigated the effects of catalyst composition and structure on the reaction kinetics. Moreover, comparison of the activities of catalysts reported by different investigators is difficult because most report the net rate of propene production without considering the effects of propane conversion and the approach to equilibrium of this intrinsically reversible

reaction. While some reports have isolated the apparent, first-order rate coefficient for propane dehydrogenation, most do not.^{27,34,35} Therefore, it is not possible to define how catalyst composition and structure affect catalyst activity for propane dehydrogenation.

Here, we describe the preparation and characterization of Sn-DeAlBEA and Pt-Sn-DeAlBEA with the aim of establishing how Sn is anchored to DeAlBEA and how the environment of Pt changes with Sn/Pt ratio at a fixed Sn content. We then investigate how the dispersion of Pt and its interactions with Sn affects the PDH activity and kinetics of Pt-Sn-DeAlBEA. The forward rate constant for PDH ($k_{f,app}$) is calculated from measurements of the net rate of propene formation to properly account for the effects of reaction conditions (T , $P_{C_3H_8}$, weight-hourly space velocity (WSHV), etc.), which affect the propane conversion and the approach to thermodynamics equilibrium. We find that Sn interacts with the silanol nests of DeAlBEA to form Sn(IV) cations that are four-fold coordinated as $(\equiv Si-O)_4Sn$ structures within the zeolite framework, that Pt-Sn-DeAlBEA contains multiple types of Pt sites, and that the interactions of Pt with Sn change with Sn/Pt ratio. We also find that the value of $k_{f,app}$ decreases as the Pt/Al ratio increases (at a fixed Sn/Al ratio), suggesting that highly dispersed Pt structures are the most active for PDH. Our EXAFS data suggest that the most active form of Pt is a Pt_3 cluster interacting with Sn(IV) in the framework of BEA. Compared to previously reported PtSn catalysts, the Pt-Sn-DeAlBEA catalysts reported here exhibit exceptionally high values of $k_{f,app}$.

Methods:

Catalyst preparation

H-BEA was prepared by heating NH_4 -BEA (Alfa Aesar, Si/Al = 12.5) in a quartz boat placed in a quartz tube at 5K/min to 773 K and maintained at this temperature for 4 h in dry synthetic air (Praxair, ultra-zero, 100 mL/min). H-BEA was dealuminated in 13 M HNO_3 for 20 h at 373K with stirring. The solution was filtered and washed extensively with deionized water. The filter cake was dried at 393 K overnight to yield dealuminated BEA (DeAlBEA). This technique has been shown by ^{27}Al NMR to remove framework and extra-framework Al completely.²⁷

Sn and Pt were introduced sequentially to DeAlBEA via wetness impregnation. $SnCl_2 \cdot 2H_2O$ (98.0-103.0%, from Alfa Aesar) was dissolved in ethanol and stirred for 30 min prior to impregnation. The amount of metal was determined by the desired weight loading, while the amount of liquid was kept constant for the weight of DeAlBEA (5.6 mL liquid per gram of DeAlBEA). The solution was added to the siliceous support, and the mixture was ground until all the liquid evaporated (~30 min). The samples were then dried overnight in air at 393 K, followed by calcination in air at 873 K for 2 h. Pt was introduced to both Sn-DeAlBEA and DeAlBEA. To do so, $Pt(NO_3)_4(NH_4)_2$ was dissolved in water and stirred for 30 min prior to impregnation. The amount of metal was determined by the desired weight loading, while the amount of liquid was kept constant relative to the weight of Sn-DeAlBEA (2.8 mL liquid per gram of Sn-DeAlBEA). The solution was added to the siliceous support, and the mixture was ground until all the liquid evaporated (~60 min). Samples were then dried at 393 K for 2 h in static air, followed by heating to 623 K for 2 h in air. These samples are designated as Pt-Sn-DeAlBEA-XX, where XX indicates the Pt/Al ratio. Samples of Sn-DeAlBEA are designated as Sn-DeAlBEA-XX, where XX indicates the Sn/Al. In all instances, Al refers to the amount of Al in the parent H-BEA prior to dealumination.

Characterization

Specific surface areas of samples were determined by N_2 -adsorption using a Micrometrics Gemini VII instrument. 40-45 mg of catalysts were dehydrated overnight in vacuum at 453 K.

Then, nitrogen (Praxair, UHP) was adsorbed at 77 K to measure an adsorption isotherm. Calculations of the Brunauer–Emmett–Teller (BET) surface area are included in the supplemental information (SI S.1). Metal content was measured with inductively coupled plasma-optical emission spectrometry (ICP-OES).

Infrared (IR) spectra were collected in transmission mode using a Nicolet 6700 Fourier transform spectrometer. Samples (~35 mg) were pressed into thin pellets and loaded into an infrared cell equipped with CaF₂ windows. Helium (Praxair, ultra-zero, 100mL/min) was used as a carrier gas. The sample was then dehydrated at 573 K for 2 h to acquire spectra. Spectra were collected by averaging 64 scans at a resolution of 1 cm⁻¹ at 473 K and 293 K. For IR studies of adsorbed pyridine, 2 μL of adsorbate was injected into the helium feed stream heated to 373 K with heating tape. Spectra were recorded at 10, 20, and 30 min after injection. To obtain IR spectra of adsorbed CO, 1% CO/He (Praxair, CSG) was flowed over the sample for 20 min. Then, the IR cell was flushed with He, and spectra were recorded. Spectra were baseline corrected with a spline function and normalized to the intensity of Si–O–Si framework overtone bands occurring between 1700 and 2000 cm⁻¹. The IR spectra of the adsorbed probe molecule presented were corrected by subtracting the initial spectrum of the sample taken at the adsorption temperature.

Powder X-ray diffraction (XRD) patterns were collected with a D8 Discover GADDS Powder XRD instrument, which uses Cu-Kα radiation. XRD patterns were collected at room temperature, scanning between 7.5° and 80° with 5 frames. Depending on the noise and crystallinity of the samples, 60 or 300 s of contact of the adsorbate with the solid was used to achieve equilibrium.

X-ray absorption spectroscopy (XAS) was performed at the Stanford Synchrotron Radiation Laboratory (SSRL). XAS measurements were performed in fluorescence mode. The monochromator energy was calibrated with Pt foil. The Pt L₃ edge was probed at beamline 9-3 using the 3 mm capillary sample holder. The flow rate of gases to the sample holder was regulated with digital mass flow controllers. The outlet gas was monitored with an in-line mass spectrometer. Ambient samples were measured in flowing He (Praxair, ultra-zero); samples were then heated to 823 K in flowing He and held for 30 min. Samples were then cooled to room temperature, and XAS spectra were collected. XAS data analysis was performed with the Athena/Artemis software using the FEFF routine.

Catalyst Activity

Studies of propane dehydrogenation were carried out using 5 mg of catalyst loaded into a quartz tube reactor (4 mm inner diameter). Quartz wool was used to support the catalyst bed. Tests were performed at atmospheric pressure and 823 K. Catalysts were heated to 823 K at 15 K/min in air and held in He (Praxair, ultra-zero) at 823 K for 30 min. Then, 20.2% C₃H₈/He (Praxair, CSG) diluted with He (Praxair, ultra-zero) to achieve a desired C₃H₈ composition was fed to the reactor. A total flow rate of 200 mL/min (0.7 kPa propane) was used as a reference condition. Reaction products were analyzed with an in-line 7890A Agilent Gas Chromatograph equipped with a 25 m HP-PLOT Q column and a flame ionizing detector (FID). Conversion and selectivity are reported on a molar basis. Net Site-Time Yield (STY) of propylene is reported as moles of propylene per hour per mole Pt. Equations for calculating conversion, selectivity, and STY are given in the SI.

Results and Discussion

Metal weight loading, XRD patterns, and BET areas for all materials

The metal weight loading and metal atom distribution for each catalyst are reported in Table 1. The BET surface area of all samples is essentially the same ($498.2 \pm 19.6 \text{ m}^2/\text{g}$) and does not change notably upon the introduction of Sn and Pt. Powder XRD patterns presented in Figure 1 show that all of the samples are identical to that of the parent H-BEA, confirming the maintenance of the BEA crystal structure through dealumination and introduction of metals. No peaks indicative of bulk Pt or PtSn nanoparticles are observed. Since XRD can only detect nanoparticles greater than 2.5-2 nm in size and $\sim 1\%$ by volume,^{36–39} the absence of diffraction peaks does not eliminate the presence of these particles but only means that their particle size is below the XRD detection limit. These XRD results suggest that adding Pt at high loadings (Pt/Al = 0.02) does not change bulk structures in these Pt-Sn-DeAlBEA catalysts. The absence of peaks for Pt or PtSn nanoparticles is also true for lower loadings of Pt in Pt-Sn-DeAlBEA.

Table 1. Characteristics of HBEA, DeAlBEA, Sn-DeAlBEA, Pt-DeAlBEA, and Pt-Sn-DeAlBEA.

Sample Name	Pt wt.%	Sn wt.%	Pt/Al	Sn/Pt	Sn/Al	BET area (m^2/g)
HBEA	0	0	0	-	-	469.7
DeAlBEA	0	0	0	-	-	515.6
Pt-DeAlBEA-0.001	0.03	0	0.001	-	-	495.5
Pt-DeAlBEA-0.026	0.62	0	0.026	-	-	490.4
Sn-DeAlBEA	0	1.9	0	-	0.15	499.8
Pt-Sn-DeAlBEA-0.001	0.03	1.9	0.0014	96.7	0.13	454.4
Pt-Sn-DeAlBEA-0.002	0.05	1.8	0.0021	59.2	0.13	477.0
Pt-Sn-DeAlBEA-0.003	0.06	1.8	0.0026	47.8	0.13	522.9
Pt-Sn-DeAlBEA-0.013	0.32	2.4	0.013	12.6	0.17	509.9
Pt-Sn-DeAlBEA-0.015	0.36	2.4	0.0150	10.8	0.16	497.0
Pt-Sn-DeAlBEA-0.020	0.48	2.2	0.0199	7.674	0.15	502.7
Pt-Sn-DeAlBEA-0.026	0.62	2.5	0.0258	6.63	0.17	517.0

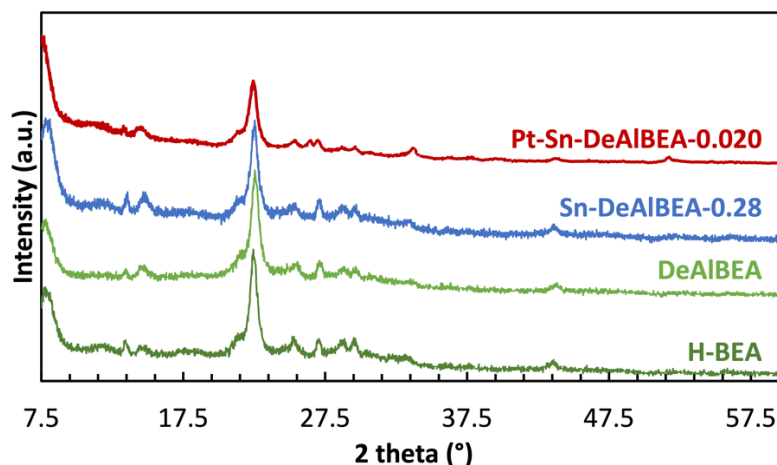


Figure 1. XRD patterns of HBEA, DeAlBEA, Sn-DeAlBEA, and Pt-Sn-DeAlBEA.

IR Spectra of perdeuterated acetonitrile adsorbed on Sn-DeAlBEA

The IR spectrum of CD₃CN adsorbed on Sn-DeAlBEA, shown in Figure 2, was used to identify open and closed Sn sites and silanol nests in Sn-DeAlBEA. Peaks are clearly seen for closed Sn sites (2308 cm⁻¹) and silanol nests (2275-2285 cm⁻¹),^{32,40,41} but there is no evident shoulder or other evidence for open Sn sites (2316 cm⁻¹).^{40,42,43} The intensity of the peaks for CD₃CN adsorbed on silanol groups does not change when Sn is introduced into DeAlBEA at the level of Sn/Al = 0.16, but the peak for CD₃CN interacting with Sn(IV) Lewis acid sites is clearly visible. This means that Sn-DeAlBEA contains ~ 80% of the silanol groups originally present on DeAlBEA, assuming that four silanol groups are consumed with the introduction of one Sn atom.

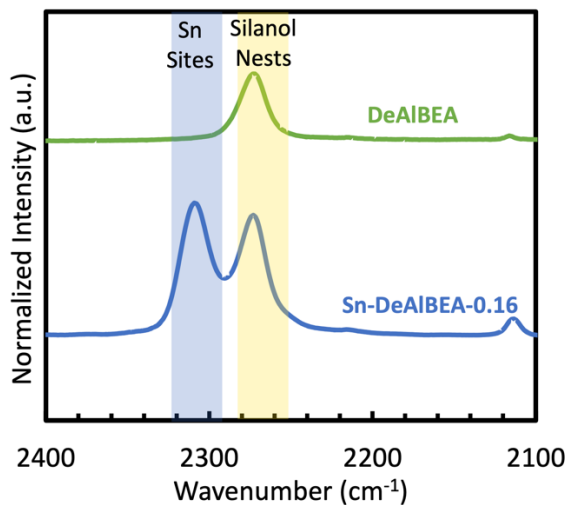


Figure 2. FTIR spectra of CD₃CN adsorbed on DeAlBEA and Sn-DeAlBEA.

IR Spectra of pyridine adsorbed on Sn-DeAlBEA, Pt-DeAlBEA, and Pt-Sn-DeAlBEA

IR spectra of adsorbed pyridine can be used to identify the relative amounts and strengths of Brønsted and Lewis acid sites. IR spectra of adsorbed pyridine on DeAlBEA, Sn-DeAlBEA, Pt-DeAlBEA, and Pt-Sn-DeAlBEA are shown in Figure 3. Distinct peaks are evident corresponding to pyridine interacting with silanol nests (1592 cm⁻¹ and 1445 cm⁻¹) and Lewis acid sites (1600-1612 and 1450 cm⁻¹), and pyridinium ions formed via interaction of pyridine with Brønsted acid sites (1544 cm⁻¹).^{40,44-46} Blue shifts in the frequency of the pyridine peak above 1600 cm⁻¹ indicate increasing Lewis acid strength.^{31,47} The peak at 1490 cm⁻¹ corresponds to pyridine interactions with both Lewis and Brønsted acid sites. Dealuminated BEA exhibits peaks at 1592 and 1445 cm⁻¹ ascribed to the interaction of pyridine with H atoms of the Si-OH groups in the silanol nests of DeAlBEA,⁴⁸ but no peaks are present corresponding to Brønsted acid sites (1544 cm⁻¹). It is notable that the spectrum of pyridine adsorbed on Pt-DeAlBEA is very similar to that of DeAlBEA. The absence of a change in the intensity of the peaks for pyridine interaction with silanol groups suggests that the introduction of Pt does not perturb or consume these groups. When pyridine is adsorbed on Sn-DeAlBEA, the presence of Lewis acid sites is clearly evident, and a significant reduction occurs in the intensity of the bands at 1592 and 1445 cm⁻¹ for pyridine interacting with silanol groups. Introduction of Pt to Sn-DeAlBEA results in a reduction in the peaks for pyridine interacting with Sn Lewis acid sites (1600-1612 and 1450 cm⁻¹), suggesting this is due to the interaction of Pt with Sn cations. In summary, the IR spectra of adsorbed pyridine

confirm the presence of Sn Lewis acid sites in Sn-DeAlBEA and show a decrease in these Sn-pyridine interactions upon Pt introduction to form Pt-Sn-DeAlBEA.

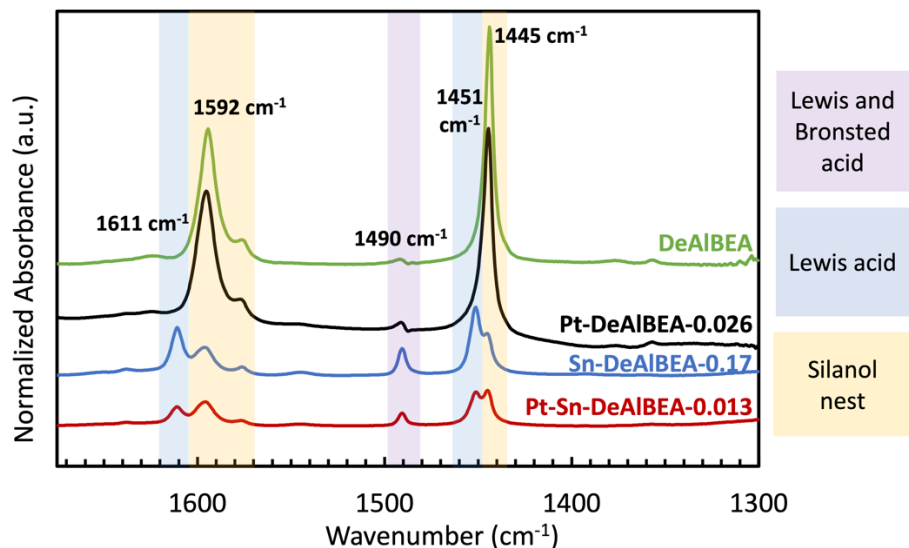


Figure 3. IR spectra of pyridine adsorbed on DeAlBEA, Sn-DeAlBEA-0.13, Pt-DeAlBEA, and Pt-Sn-DeAlBEA-0.013.

IR of CO Adsorbed on Pt-DeAlBEA and Pt-Sn-DeAlBEA

The IR spectra of CO adsorbed on Pt-DeAlBEA and Pt-Sn-DeAlBEA are shown in Figure 4. For Pt-Sn-DeAlBEA-0.001, the IR spectrum of adsorbed CO exhibits peaks at 2068 cm^{-1} and 2136 cm^{-1} . As the Pt/Al ratio increases, a peak at 2097 cm^{-1} appears for Pt-Sn-DeAlBEA-0.003 and is maintained until the Pt/Al ratio reaches 0.02. At an intermediate Pt/Al ratio (0.013), the spectrum also displays a peak at 2089 cm^{-1} . This peak is maintained at higher Pt/Al ratios as well. At the highest Pt/Al ratio (0.026), the IR spectrum of adsorbed CO exhibits peaks at 2092 cm^{-1} and 2127 cm^{-1} . The IR spectra of CO adsorbed on Pt-DeAlBEA with low and high Pt/Al ratios (0.001 and 0.026) are also shown for comparison. The IR spectrum of CO adsorbed on Pt-DeAlBEA-0.001 displays one broad peak at 2092 cm^{-1} , whereas the spectrum for Pt-DeAlBEA-0.026 exhibits two peaks at 2090 cm^{-1} and 2112 cm^{-1} .

All samples of Pt-Sn-DeAlBEA also exhibit a peak above 2120 cm^{-1} ; as the Pt/Al ratio increases, this peak becomes broader, and the area below 2130 cm^{-1} increases. At higher Pt/Al ratios (> 0.013), the IR spectrum of adsorbed CO shows a broad peak centered between $2085\text{--}2095\text{ cm}^{-1}$. At low Pt/Al ratios (0.001–0.003), a peak at 2068 cm^{-1} is also present. The IR spectrum for Pt-Sn-DeAlBEA-0.026 resembles that for Pt-DeAlBEA-0.026, but the peak above 2120 cm^{-1} is blue-shifted relative to that for Pt-DeAlBEA-0.026. For Pt-DeAlBEA-0.001, a blue shift in the frequency of the IR band of adsorbed CO is seen relative to the major peak for Pt-DeAlBEA-0.026.

After PDH, a decrease occurs in the intensity of the CO peaks appearing above 2120 cm^{-1} for both Pt-Sn-DeAlBEA and Pt-DeAlBEA catalysts relative to those for the dehydrated catalysts (Figure S1). At Pt/Al ratios less than or equal to 0.020, a small peak above 2120 cm^{-1} persists for Pt-Sn-DeAlBEA; this high-frequency CO IR peak disappears completely for Pt-Sn-DeAlBEA-0.026 and Pt-DeAlBEA-0.026 after reaction. After the PDH, Pt-Sn-DeAlBEA with Pt/Al ratios from 0.001 to 0.020 also exhibit peaks at 2089 cm^{-1} and 2068 cm^{-1} .

The IR frequency of CO adsorbed on Pt is influenced by the CO coverage and the electronic state of the Pt (i.e., oxidation state, support composition, neighboring elements, and dispersion).^{26,49–57} IR peaks for linearly adsorbed CO on Pt can be grouped into those for CO interacting with positively charged Pt (2110–2300 cm⁻¹) and zero-valent Pt (2050–2100 cm⁻¹).^{50,58–60} Therefore, the peaks observed between 2140 and 2120 cm⁻¹ in Figure 4 are consistent with CO adsorbed on positively charged Pt.^{59,61–63} This assignment is supported by the observed decrease in the areas of these peaks after exposure of Pt-Sn-DeAlBEA to reducing conditions during PDH. (Figure S1). Molecular orbital theory also supports this assignment; more positively charged Pt species will have less significant back-donation of electrons to adsorbed CO and, in turn, a stronger C-O bond and a higher stretching frequency.^{64–66} The increase in the frequency of the band < 2100 cm⁻¹ for CO adsorbed on Pt-Sn-DeAlBEA relative to Pt-DeAlBEA suggests that Pt is more electron-deficient when supported on Sn-DeAlBEA than DeAlBEA.

The IR peak for adsorbed CO observed at 2097 cm⁻¹ is consistent with Pt interacting with framework Sn or oxygen.¹⁸ Similar shifts in $\nu(\text{CO})$ (~10 cm⁻¹) relative to Pt-DeAlBEA have also been reported for Pt-Sn-DeAlBEA prepared by other investigators.³³ Additional studies have observed blue-shifted CO peaks when Pt interacts with Sn due to electron-withdrawing interactions of Pt with Sn.^{53,67,68} This assignment suggests that Pt interacting with a framework Sn or O species has a lower electron density than large Pt clusters. The absence of a peak at 2097 cm⁻¹ for CO adsorbed on Pt-DeAlBEA, even at low Pt/Al ratios, suggests that Sn is necessary to create positively charged Pt, narrowing the potential species to Pt-Sn or Pt-O-Sn interactions. Either way, the peak at 2097 cm⁻¹ can be assigned to Pt interacting closely with electron-withdrawing species in the BEA framework.

The peaks for adsorbed CO appearing at 2080–2095 cm⁻¹ correspond to CO linearly adsorbed on metallic Pt clusters.^{55,61,69–71} This region accounts for the majority of the spectral peak area for Pt-DeAlBEA and Pt-Sn-DeAlBEA at high Pt/Al ratios (0.026). The growth of the area of this peak after reaction (Figure S1) also supports this assignment. For Pt-DeAlBEA-0.001, the blue shift in this peak position relative to that for Pt-DeAlBEA-0.026 is inconsistent with a decrease in Pt particle size and increasingly undercoordinated Pt sites but can also be attributed to a stronger support interaction at low Pt/Al ratios.⁵¹ The observed IR frequency for CO adsorbed on Pt-DeAlBEA-0.001 is still lower than that for CO adsorbed on Pt interacting with Sn or fully isolated Pt.^{18,33,72–77} Notably, these C-O stretching frequencies are slightly red-shifted relative to those observed for Pt-Sn-DeAlBEA, consistent with electron withdrawal and increased Pt dispersion due to the interaction of Pt with Sn.

The peak at 2068 cm⁻¹ can also be attributed to CO interacting with Pt-Sn species. The red shift of this peak relative to other observed CO frequencies is consistent with more electron-rich Pt species. Several studies have observed similar peak positions for PtSn and Pt₃Sn alloys.^{53–55,70,78,79} We note that there is no evidence for the formation of PtSn alloys in the samples of Pt-Sn-DeAlBEA prepared for this study.

To summarize, the IR spectra of adsorbed CO suggest that, at low Pt/Al ratios, Pt-Sn-DeAlBEA contain both positively charged Pt species ($\nu_{\text{CO}} = 2136 \text{ cm}^{-1}$) and Pt interacting with Sn ($\nu_{\text{CO}} = 2068 \text{ cm}^{-1}$). Pt clusters ($\nu_{\text{CO}} = 2089 \text{ cm}^{-1}$) are formed as the Pt/Al ratio increases (≥ 0.013). At the highest Pt/Al ratio (0.026), CO adsorbed on Pt-Sn-DeAlBEA only exhibits IR peaks corresponding to positively charged Pt ($\nu_{\text{CO}} = 2136 \text{ cm}^{-1}$) and metallic Pt clusters ($\nu_{\text{CO}} = 2089 \text{ cm}^{-1}$). Pt-DeAlBEA exhibits CO IR peaks characteristic of metallic Pt clusters at high and low Pt/Al ratios (0.026 and 0.001). Thus, IR spectroscopy of adsorbed CO confirms the importance of Sn in the dispersion of Pt supported on DeAlBEA.

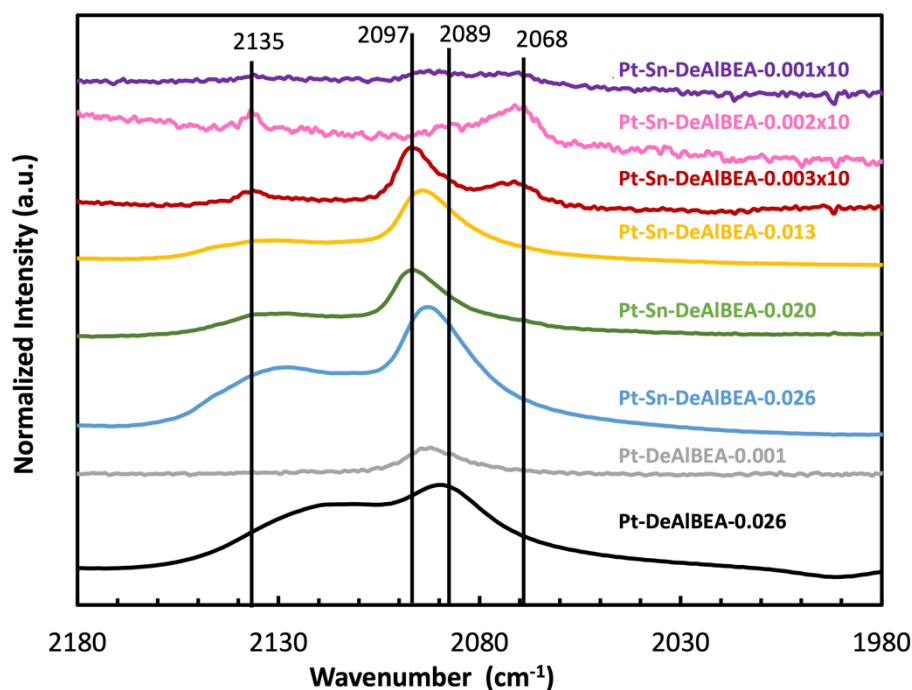


Figure 4. Infrared spectra of CO adsorbed on Pt-DeAlBEA and Pt-Sn-DeAlBEA at 303 K under flowing He. Spectra are offset for clarity.

IR spectra were also collected during CO desorption from Pt-Sn-DeAlBEA and Pt-DeAlBEA, as shown in Figure S2. The spectra of CO desorbing from Pt-DeAlBEA-0.026, Pt-Sn-DeAlBEA-0.026, and Pt-Sn-DeAlBEA-0.013 all exhibit shifts in peak position for the peak corresponding to CO linearly adsorbed to Pt⁰ (2080-2095 cm⁻¹) both with desorption of CO at 303 K as a function of time and upon heating. By contrast, the spectra of CO adsorbed on Pt-Sn-DeAlBEA-0.001 do not exhibit a shift in the position of the IR peaks for adsorbed CO during CO desorption. Shifts in the IR frequency of adsorbed CO with CO coverage are characteristic of CO desorption from Pt clusters.^{72,80–82} If neighboring Pt sites adsorb CO, the neighboring CO molecules experience dipole-dipole interactions, causing a blue shift in the observed frequency. As the CO desorbs, a red-shift in the CO frequency is observed as these dipole-dipole interactions diminish. As CO desorbs from Pt-Sn-DeAlBEA-0.013, a new peak appears at 2110 cm⁻¹ between the broad peaks at 2135 cm⁻¹ and 2090 cm⁻¹. This peak can be attributed to CO linearly adsorbed on isolated Pt atoms.⁸³ These CO desorption experiments indicate Pt nanoparticles exist on Pt-DeAlBEA and Pt-Sn-DeAlBEA samples with Pt/Al ratios ≥ 0.013 . For Pt-Sn-DeAlBEA-0.001, the IR spectra of adsorbed CO do not show evidence of a shift in peak position with changes in CO coverage, indicating that Pt is atomically dispersed either as single atoms or very small Pt_x clusters.

XAS characterization of Sn-DeAlBEA, Pt-DeAlBEA, and Pt-Sn-DeAlBEA

XAS was used to probe the oxidation state and environment of Sn in Sn-DeAlBEA. Figure 5 shows the XAS spectra for Sn-DeAlBEA and tin reference materials. A fit of the EXAFS data is presented in Figure 5B and the relevant fitting parameters are given in the table in Figure 5C. In Figure 5A, the XANES edge position and white line height of Sn-DeAlBEA closely resemble

those of SnO_2 , indicating that Sn is present as Sn(IV) with four oxygen nearest neighbors. The EXAFS fitting results indicated that Sn is connected to four Sn-O bonds having a value of $R_{\text{Sn-O}} = 1.92 \text{ \AA}$, consistent with framework Sn(IV) .^{84,85} Additional fits, including Sn-Sn, were attempted, but these paths do not improve the level of fit. Sn metal (Sn foil) and SnCl_2 are included as reference materials for comparison, but the EXAFS spectra for these materials are quite different from that of Sn-DeAlBEA. Evidence for isolated Sn cations is also supported by UV-Vis spectroscopy. As shown in Figure S3, Sn-DeAlBEA exhibits a well-defined peak at 191 nm and a band edge energy of 5.97 eV. In Sn-DeAlBEA-0.15, Sn is present as framework Sn(IV) cations, consistent with previous studies of Sn-DeAlBEA.^{85,86}

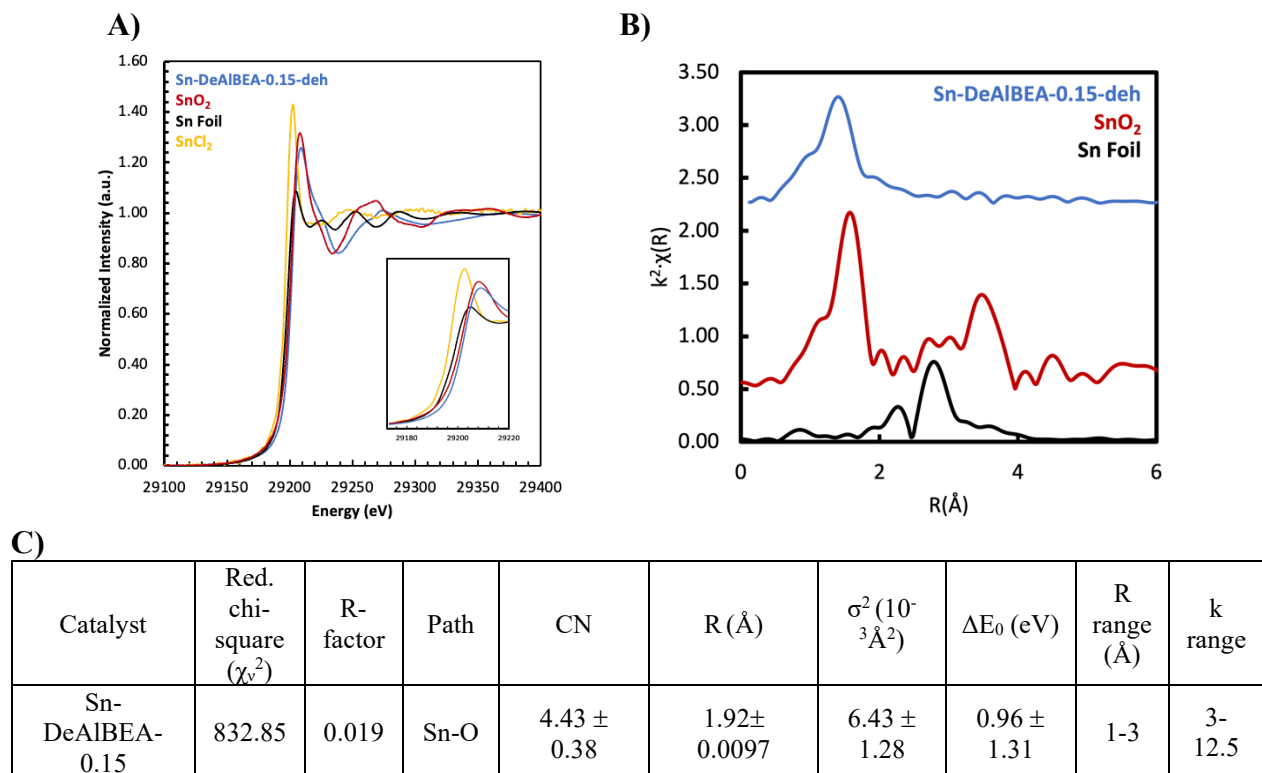


Figure 5. A) XANES spectra and B) EXAFS of dehydrated Sn-DeAlBEA-0.15 and tin reference materials. C) Fitting parameters for dehydrated Sn-DeAlBEA-0.15. The amplitude reduction factor was determined from SnO_2 and fixed in the fitting of Sn-DeAlBEA to 0.770.

The coordination and local environment of Pt were also probed with XAS. XANES data for the Pt-L_3 edge are presented in Figure 6A. Pt foil exhibits an edge energy of 11563.2 eV and a modest white line height, consistent with zero-valent Pt with Pt neighbors. XANES spectra of Pt-DeAlBEA show a slight increase in edge energy (11563.7 eV) relative to Pt foil (11563.2 eV), as do the XANES spectra of Pt-Sn-DeAlBEA-0.001 and Pt-Sn-DeAlBEA-0.013, which both exhibit small increases in edge energies relative to Pt foil (11563.5 and 11563.6 eV, respectively). All DeAlBEA samples show higher white line intensities than that seen for Pt foil (1.28). The white line intensity decreases slightly with increasing Pt loading (1.51 for Pt-Sn-DeAlBEA-0.001 vs 1.49 for Pt-Sn-DeAlBEA-0.013) and increases with the addition of Sn (1.44 for Pt-DeAlBEA-0.001 vs. 1.51 for Pt-Sn-DeAlBEA-0.001). The increases in edge energies and white line intensities relative to Pt foil for Pt-DeAlBEA and Pt-Sn-DeAlBEA are consistent with a slight decrease in the electron

density of Pt. Increases in the white line intensity have also been shown to correlate with reductions in Pt nanoparticle size.^{87,88} The XANES data shown in Figure 6A are consistent with positive and zero-valent Pt species identified by IR spectroscopy of adsorbed CO on Pt-DeAlBEA and Pt-Sn-DeAlBEA. The observed decrease in the electron density of Pt with increasing Pt dispersion obtained from XANES data also agrees with the findings deduced from IR spectroscopy of adsorbed CO.^{89,90} The similarity in the value of edge energy observed for Pt-Sn-DeAlBEA to that for Pt foil suggests that most of the Pt in Pt-Sn-DeAlBEA-0.013, PtSn-DeAlBEA-0.001, and Pt-DeAlBEA-0.001 exists as Pt⁰, with only a minority of the Pt present in a higher oxidation state.

EXAFS data for the Pt-L₃ edge are presented in Figure 6B, and the fitting parameters are presented in Table 2. The EXAFS spectra for Pt foil are used to determine the amplitude reduction factor (0.798) and as a reference for metallic Pt-Pt interactions ($R_{\text{Pt-Pt}} = 2.77 \text{ \AA}$, $\text{CN}_{\text{Pt-Pt}} = 12$ (fixed)). The features in the R-space for Pt foil can be attributed conclusively to Pt-Pt interactions. The EXAFS fitting results for Pt-DeAlBEA-0.001 show Pt-Pt scattering paths ($R_{\text{Pt-Pt}} = 2.76 \text{ \AA}$, $\text{CN}_{\text{Pt-Pt}} = 9.05 \pm 1.70$) as well as Pt-O scattering paths ($R_{\text{Pt-O}} = 1.92 \text{ \AA}$, $\text{CN}_{\text{Pt-O}} = 1.03 \pm 0.69$). Pt-Sn-DeAlBEA-0.0013 and Pt-Sn-DeAlBEA-0.001 are best fit with Pt-Pt, Pt-O and Pt-Sn paths. Fits of the EXAFS data for Pt-Sn-DeAlBEA closely resemble those for Pt/DeAlBEA-0.001 with the addition of a Pt-Sn path. On the other hand, PtSn-DeAlBEA-0.001 exhibits fewer Pt-Pt scatterers ($R_{\text{Pt-Pt}} = 2.74 \text{ \AA}$, $\text{CN}_{\text{Pt-Pt}} = 3.90 \pm 1.92$) and more Pt-O scatterers ($R_{\text{Pt-O}} = 2.03 \text{ \AA}$, $\text{CN}_{\text{Pt-O}} = 3.24 \pm 0.60$) relative to Pt-DeAlBEA-0.001 and Pt-Sn-DeAlBEA-0.013. Additionally, there is a slight decrease in the Pt-Pt scattering distance. Decreases in the Pt-Pt distance and coordination number have previously been shown to coincide with decreases in Pt cluster size.^{91,92}

The EXAFS data for all samples exhibit Pt-Pt interactions ($R_{\text{Pt-Pt}} = 2.74\text{-}2.77 \text{ \AA}$, $N_{\text{Pt-Pt}} > 1$), indicating some degree of Pt-Pt clustering. The lowest Pt/Al ratio shows the lowest number of Pt-Pt interactions ($\text{CN}_{\text{Pt-Pt}} = 3$), consistent with higher Pt dispersion for this loading. We note that even at intermediate Pt/Al ratios, the EXAFS pattern of Pt-Sn-DeAlBEA resembles that of Pt foil. Specifically, high Pt-Pt coordination numbers are observed. The trends in Pt-Pt coordination numbers suggest that Pt dispersion increases with a reduction in the Pt/Al ratio and with the inclusion of Sn in the DeAlBEA framework. At all Pt/Al ratios, there are minimal Pt-Sn interactions ($\text{CN}_{\text{Pt-Sn}} \leq 1$), suggesting that Pt and Sn do not form alloys in Pt-Sn-DeAlBEA. Therefore, analysis of the EXAFS data is consistent with the presence of small, metallic Pt clusters that interact with framework Sn sites together with a small number of isolated Pt atoms that are positively charged, and as the Pt/Al ratio increases, small Pt nanoparticles with a $\text{CN}_{\text{Pt-Pt}} = 9$, which corresponds to a particle size of $\sim 25 \text{ \AA}$.

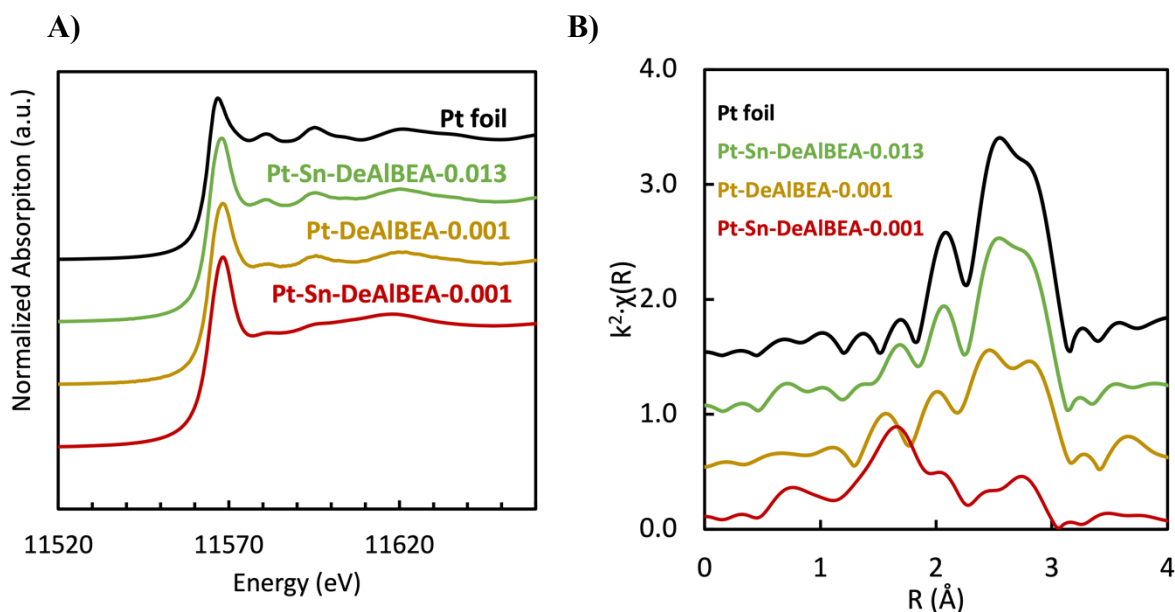


Figure 6. A) Normalized Pt L₃-edge XANES spectra and B) the magnitude of the Fourier-transformed k²-weighted EXAFS spectra of PtSn-DeAlBEA and Pt-DeAlBEA Catalysts at ambient conditions. Spectra are offset for clarity.

Table 2. EXAFS Fitting Parameters for Pt L₃-edge spectra of Pt-DeAlBEA and Pt-Sn-DeAlBEA Catalysts.

Sample	Red. χ^2 (χ_v^2)	R-factor	Path	CN	R (Å)	σ^2 (10^{-3}Å^2)	ΔE_0 (eV)
Pt foil	1031.9	0.0021	Pt-Pt	12 (fixed)	2.77 ± 0.005	4.2 ± 2.6	7.36 ± 0.36
Pt-DeAlBEA-0.001	71.3	0.021	Pt-Pt	9.05 ± 1.70	2.76 ± 0.01	5.18 ± 1.28	6.60 ± 1.64
			Pt-O	1.03 ± 0.69	1.92 ± 0.04	5.41 ± 9.29	
			Pt-Pt	3.90 ± 1.92	2.74 ± 0.03	6.51 ± 4.48	7.56 ± 5.27
Pt-Sn-DeAlBEA-0.001	291.7	0.015	Pt-Sn	1.07 ± 0.80	2.92 ± 0.05	6.14 ± 2.78	13.94 ± 2.01
			Pt-O	3.24 ± 0.60	2.03 ± 0.02	6.14 ± 2.78	13.94 ± 2.01
			Pt-Pt	9.98 ± 1.45	2.77 ± 0.001	4.63 ± 1.32	6.34 ± 3.09
Pt-Sn-DeAlBEA-0.013	53.2	0.0014	Pt-Sn	0.74 ± 0.58	2.89 ± 0.07	8.41 ± 6.21	17.32 ± 3.49
			Pt-O	1.81 ± 0.72	2.07 ± 0.04	8.41 ± 6.21	17.32 ± 3.49
			Pt-Pt	9.98 ± 1.45	2.77 ± 0.001	4.63 ± 1.32	6.34 ± 3.09

$$S_0^2 = 0.798$$

The XAS results reported here for Pt foil agree closely with those reported previously for the Pt L₃ edge.^{26,72,93,94} We also note that the Pt-Pt and Pt-O distances identified in this study (2.69-2.74 Å) are similar to those reported in other studies of Pt-Sn-DeAlBEA. The observation of large Pt clusters and evidence of Pt-Sn interactions have been reported previously for Pt-Sn-DeAlBEA.⁹⁵

Previous XAS studies of Pt-Sn-DeAlBEA-0.014 have also reported evidence for isolated Pt in the as-prepared material ($CN_{Pt-Pt} = 0$) and small Pt clusters ($CN_{Pt-Pt} = 3$) following reduction.¹⁸ However, this study did not report Pt-Sn interactions but suggested that Pt interacts with Sn via Pt-O-Sn linkages. Attempts to fit Pt-O-Sn paths in our work resulted in non-sensical coordination numbers or worse fits than those obtained only using Pt-Sn paths. The differences in Pt coordination may be due to different pretreatment conditions; the samples in earlier work were reduced (in H₂) at 773 K, while samples in the present study were treated in air at 623 K - a procedure chosen because it resulted in better Pt dispersion in Pt-Zn-DeAlBEA.²⁷ Additionally, the Sn-DeAlBEA used in the earlier study was synthesized through hydrothermal structural reconstruction (dealumination, followed by hydrothermal introduction of Sn) rather than sequential dealumination and impregnation, as was done here. While XAS data for Pt-DeAlBEA at low Pt/Al ratios have not been reported previously, such data are available for isolated Pt sites and Pt clusters on other supports. Evidence for significant Pt clustering ($CN_{Pt-Pt} = 8$) has also been reported previously for Pt-DeAlBEA (Pt/Al=0.014).¹⁸ These XAS results are similar to those presented here for Pt-DeAlBEA-0.001. XAS studies of isolated Pt on other supports (Pt₁/CeO₂ and Pt/SiO₂) have shown that the EXAFS pattern of isolated Pt often resembles PtO₂.^{89,96} These observations are consistent with the increases in edge energy and white line intensity for PtSn-DeAlBEA-0.001. In summary, the XAS results for Pt-Sn-DeAlBEA-0.013 resemble those reported previously for Pt-Sn-DeAlBEA, but these results exhibit unique Pt-Sn interactions (i.e., absence of alloying or bonding to oxygen).

To summarize, evidence from characterization of Pt-DeAlBEA and Pt-Sn-DeAlBEA by UV-Vis spectroscopy, IR spectroscopy of adsorbed pyridine and CO, and XAS suggests that these materials contain two types of Pt, as illustrated in Figure 7. The first is atomically dispersed Pt atoms interacting with either Sn(IV) contained in the zeolites framework or with O atoms associated with ≡SiOH groups in silanol nests. Such Pt atoms are partially charged due to electron transfer from the Pt atom to either framework Sn(IV) cations or the O atoms of silanol groups. The second form of Pt is small to medium-sized clusters in which one of the Pt atoms of the cluster interacts with framework Sn(IV) cations or the O atoms of silanol groups. When Pt is added to Sn-DeAlBEA, the Sn(IV) cations in the zeolite framework facilitate the dispersion of Pt into isolated Pt atoms and small Pt clusters. High Pt dispersion is achieved for Pt/Al < 0.020 at a constant Sn/Al ratio of 0.15. Small nanoparticles are formed in PtSn-DeAlBEA at higher Pt/Al ratios and in Pt-DeAlBEA for all Pt/Al ratios down to Pt/Al = 0.001.

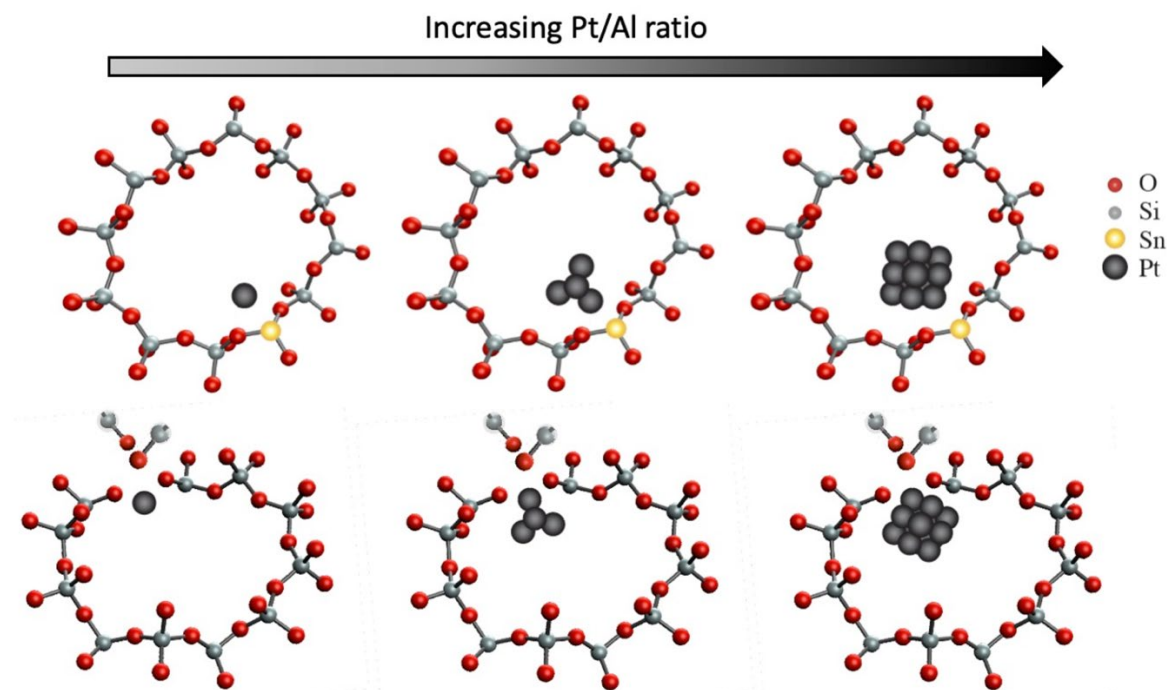


Figure 7. Potential Pt Structures in Pt-Sn-DeAlBEA and Pt-DeAlBEA as a function of Pt/Al ratio. Hydrogen atoms are omitted for clarity.

Propane Dehydrogenation on Pt-DeAlBEA, Sn-DeAlBEA, and Pt-Sn-DeAlBEA

The PDH activity and selectivity of Pt-DeAlBEA and Pt-Sn-DeAlBEA catalysts are shown in Figure 8. The activities of both DeAlBEA and Sn-DeAlBEA are negligible compared to those of Pt-DeAlBEA and Pt-Sn-DeAlBEA (Figure S4A). Time on stream data for PDH over Pt-Sn-DeAlBEA are presented in Figure S4. All Pt-Sn-DeAlBEA catalysts exhibit high selectivity to propene ($> 97\%$). Additionally, Pt-Sn-DeAlBEA exhibits better stability ($k_d = 0.002 \text{ h}^{-1}$ for Pt/Al = 0.002 to $k_d = 0.071 \text{ h}^{-1}$ for Pt/Al = 0.026) than Pt-DeAlBEA ($k_d = 0.19 \text{ h}^{-1}$ for Pt/Al = 0.026) (Table S3). The PDH activity per total Pt atoms is highest at the lowest Pt/Al ratio, decreases with increasing Pt/Al ratio, and then plateaus at high Pt/Al ratios. This trend indicates that the most active Pt sites in Pt-Sn-DeAlBEA are formed at the lowest Pt/Al ratios. The data shown in Figure 8A are adjusted for the dispersion of Pt using the integrated intensity of the IR spectrum of adsorbed CO to estimate the fraction of accessible Pt sites (Figure 4, Table S1; Additional details of dispersion estimations are presented in S.6). As seen in Figure 8B, differences in Pt dispersion do not fully account for the significant decrease in dehydrogenation rate at high Pt/Al ratios. This figure also shows that even after adjustment for Pt dispersion, the activity of Pt-DeAlBEA-0.026 is significantly lower than that of Pt-Sn-DeAlBEA, suggesting that a major part of the activity in the latter catalyst is attributable to small Pt clusters containing three or so atoms that interact with a Sn(IV) cation in the framework of Sn-DeAlBEA. The similarity in the dehydrogenation rates for Pt-Sn-DeAlBEA with Pt/Al between 0.001 and 0.013 after correction for Pt dispersion shown in Figure 8B indicates that all accessible Pt atoms in these catalysts have the same activity.

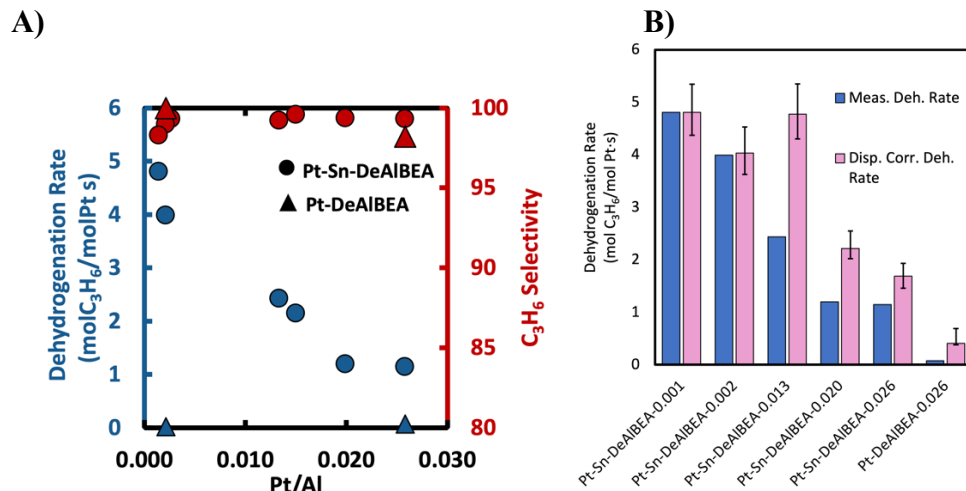


Figure 8. A) Propane Dehydrogenation Activity of Pt-Sn-DeAlBEA as a Function of Pt/Al ratio. Reaction Conditions: 823 K, 0.7 kPa C₃H₈, 200 mL/min total flow. Sn/Al ratios are constant (Sn/Al = 0.2). B) Effect of Dispersion on Propane Dehydrogenation rate. Dispersion estimates derived from IR of adsorbed CO results (Table S1). In all cases, the conversion of propane was less than 15%, and the approach to equilibrium was less than 2.5%. As a consequence, all of the rate data represent the rate of the forward reaction for PDH, and the rate of the reverse reaction can be neglected.

Kinetics of PDH over Pt-Sn-DeAlBEA Catalysts

Figure 9 shows the dependence of the rate of PDH on the propane partial pressure measured at different reaction temperatures for three samples of Pt-Sn-DeAlBEA. As noted in Table 3, all data were collected under conditions where the propane conversion ranged from 2.5% to 26%, but the approach to thermodynamic equilibrium was much less than 2%. Consequently, the measured rates of propene formation can be regarded as the true forward rate of propane dehydrogenation, neglecting the reverse reaction, propene hydrogenation. For the purposes of fitting a rate expression to the data, the reactor was assumed to behave as a plug-flow reactor (PFR). This mode of data treatment is particularly important when the propane conversion is > 5%. As discussed in S.12 of the SI, the basic form of the rate expression assumes that the rate-limiting step for PDH is the dissociation of adsorbed propane and that the only relevant surface intermediates are adsorbed propane. This mechanism has been used successfully to interpret the rate of propane dehydrogenation over Pt-Zn-DeAlBEA.²⁷ Interestingly, a Langmuir-Hinshelwood rate expression considering propene site occupation also fit the data well; however, accounting for propene and propene site occupation simultaneously provided a worse fit (Table S9). IR spectroscopy was performed after the PDH reaction to look for evidence of adsorbed propene with the aim of distinguishing these rate laws (Figure S5). While the resulting spectra displayed C-H vibrational modes at 2950, 2919, and 2838 cm⁻¹ attributable to adsorbed propane or propene, similar to what was observed in studies of PDH on Pt/SiO₂,^{97–99} no evidence was found for C=C vibrational modes at 1650 cm⁻¹ characteristic of molecular propene.^{100,101}

The rate laws and the corresponding rate parameters that give the best fit for each catalyst are shown in Table 3. The apparent activation energy is nearly the same (within error) for all Pt/Al ratios. Previous studies that varied Sn content at constant Pt loading also found that the activation

energy for PDH remains nearly constant (58 - 62.7 kJ/mol for Pt-Sn/NaY).¹⁰² The heat of propane adsorption becomes slightly more negative with increasing Pt/Al, although the significant errors in these values do not allow for definitive determination of this parameter. We note that the magnitude of this error is similar to that reported in previous studies.^{103–106} The similarity in the magnitude of the rate parameters for the three Pt/Al ratios suggests that similar active sites exist at all Pt/Al ratios, which suggests that the observed decrease in overall activity with increasing Pt/Al ratio, seen in Figure 8, is caused by dilution of active sites with much less active Pt species at high Pt/Al ratios. In other words, only the highly dispersed Pt species interacting with Sn are responsible for the observed PDH activity. This hypothesis is consistent with recent theoretical work showing that small Pt clusters interacting with Sn (e.g., Pt₂Sn and Pt₃Sn) are the most active and stable structures for PDH.¹⁰⁷

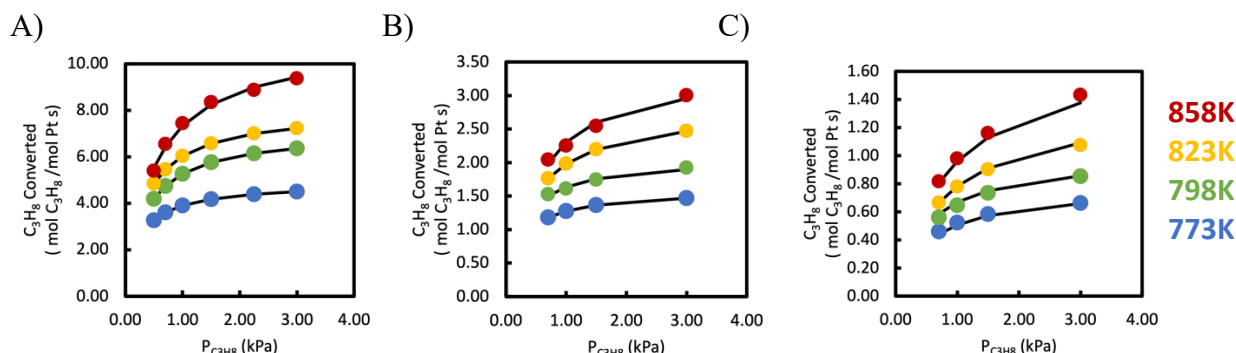


Figure 9. The dependence of the moles of converted C₃H₈ per mol Pt per s with propane partial pressure over Pt-Sn-DeAlBEA was measured at different temperatures and 9.4 moles of propane/s per moles of Al for A) Pt-Sn-DeAlBEA-0.001, B) Pt-Sn-DeAlBEA-0.013, and C) Pt-Sn-DeAlBEA-0.026. Colored circles indicate experimental data collected at various temperatures, and black curves show the calculated value obtained from the fitted kinetic parameters in Table 3.

Table 3. Fitted rate parameters for Pt-Sn-DeAlBEA catalysts.

Catalyst	Conv. (%)	Frac. Appr. to Equil.	Rate law	E ₁ (kJ/mol)	Ln(A ₁)	ΔH (kJ/mol)	ΔS (J/mol K)	E _{app} (kJ/mol)	Ln(A _{app})	R ²
Pt-Sn-DeAlBEA-0.001	2.5 – 6.9	0.0001 – 0.0018	$\frac{k_1 K_{C_3H_8} P_{C_3H_8}}{1 + K_{C_3H_8} P_{C_3H_8}}$	50.68 ± 6.31	9.51 ± 0.94	-40.90 ± 11.43	-3.05 ± 14.09	9.78 ± 17.74	9.14 ± 2.63	0.981
Pt-Sn-DeAlBEA-0.013	7.7 – 24	0.0011 – 0.015	$\frac{k_1 K_{C_3H_8} P_{C_3H_8}}{1 + K_{C_3H_8} P_{C_3H_8}}$	52.53 ± 4.70	8.65 ± 0.70	-51.37 ± 10.68	-15.52 ± 13.16	1.16 ± 15.38	6.78 ± 2.28	0.996
Pt-Sn-DeAlBEA-0.026	7.7 – 26	0.0011 – 0.019	$\frac{k_1 K_{C_3H_8} P_{C_3H_8}}{1 + K_{C_3H_8} P_{C_3H_8}}$	55.06 ± 3.36	8.32 ± 0.50	-33.16 ± 13.12	1.54 ± 16.17	21.90 ± 16.48	8.51 ± 2.44	0.982

Where $k_{app} = k_1 K_{C_3H_8}$

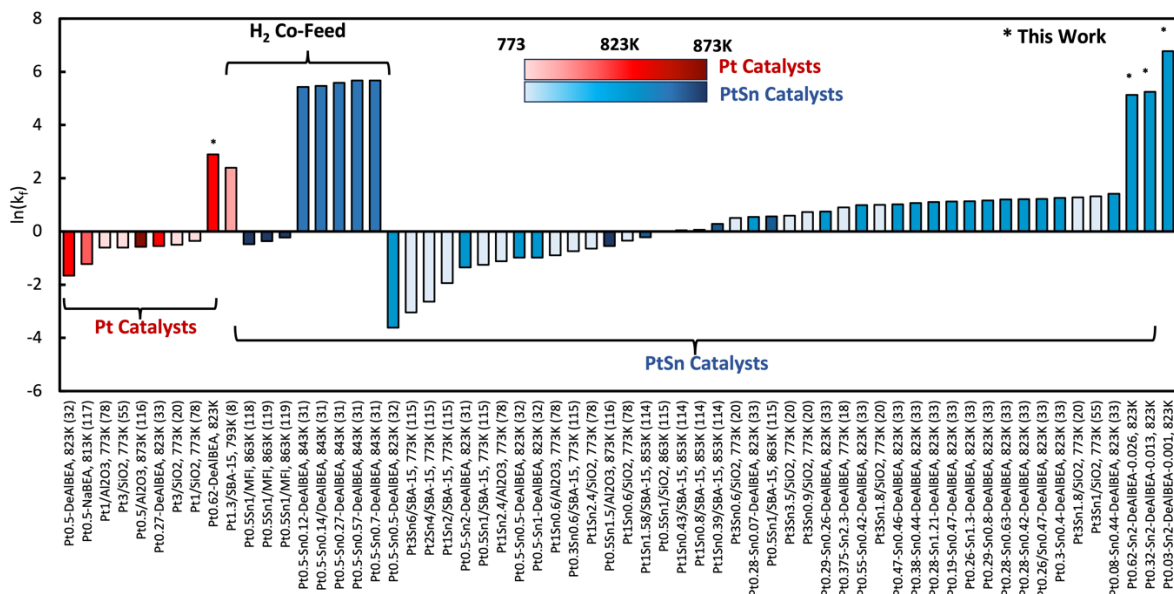
Apparent activation energies for PDH over PtSn catalysts reported in the literature range from 26 to 212 kJ/mol (Table S11).^{103,104,108–111} This wide range has been attributed to differences in the size of Pt particles, dispersion, and Pt surface site accessibility for these different Pt catalysts.¹¹⁰ The apparent activation energies for PtSn/Al₂O₃ (44.7 to 169.7 kJ/mol) and PtSn/Mg(Al)O (34.6 to 81 kJ/mol) are generally higher than those reported here. The fitted enthalpies of propane adsorption for Pt-Sn-DeAlBEA fall within the range previously reported for propane adsorbed on Pt and PtSn catalysts (-7.7 to -85.8 kJ/mol).^{104,109–112,112} It is notable, though,

that the enthalpy for propane adsorption reported for supported Pt and PtSn catalysts is much smaller in magnitude than that for propane adsorption on Pt single crystal surfaces (-247.9 to -283.8 kJ/mol).¹¹³

Comparison of PDH Activity for Pt-Sn-DeAlBEA to Those Reported in the Literature

Comparison of the activities of the Pt-Sn-DeAlBEA catalysts reported in this study to those for Pt and PtSn catalysts reported in the literature is challenging because the temperature, propane partial pressure, hydrogen partial pressure, propane conversion, and approach to equilibrium in each study are different. For this reason, all catalysts are compared on the basis of the apparent forward rate coefficient for PDH ($k_{f,app}$) calculated as described in S.9 of the SI. To compensate for the sublinear dependence of the forward rate of PDH on the propane partial pressure observed in our study, the values of $k_{f,app}$ were calculated for data collected at a low propane partial pressure (0.7 kPa) and a high temperature (823K). A comparison of $k_{f,app}$ to k_1 and $K_{C_3H_8}$ for Pt-Sn-DeAlBEA catalysts is included in Table S10. It is noted that a similar approach could not be used to determine values of $k_{f,app}$ from data reported for other Pt and PtSn catalysts, and hence, the values determined (see Table S4) may be underestimated for the reasons discussed S5.1.

Figure 10 shows values of $k_{f,app}$ for different Pt and PtSn catalysts.^{18,20,32,33,55,78,114–119} The values of $k_{f,app}$ for the Pt-Sn-DeAlBEA catalysts prepared in this study are significantly higher than those previously reported for PtSn and Pt catalysts when compared at the same temperature (823 K) and in the absence of H_2 addition to the feed. It is notable that values of $k_{f,app}$ for PtSn catalysts reported in Ref. 31 in which H_2 was co-fed with propane are comparable to those observed for Pt-Sn-DeAlBEA in the absence of added H_2 . To assess the effect of H_2 addition on the activity of Pt-Sn-DeAlBEA catalysts reported here, PDH was carried out with H_2 co-fed over PtSn-DeAlBEA-0.001 (Figure S4B). The addition of H_2 (1:1 $C_3H_8:H_2$) resulted in a 25% increase in propane conversion, corresponding to a 26-fold increase in the value of $k_{f,app}$ and the selectivity to propene increased slightly from 98 to 100%.



The differences in values of $k_{f,app}$ for Pt-Sn-DeAlBEA found in this study relative to those derived from data presented in the literature may be a consequence of the method used for catalyst preparation and pretreatment. Sequential grafting of Sn and Pt precursors results in the formation of alloyed PtSn nanoparticles coordinated to framework Sn sites.³¹ By contrast, sequential impregnation of Sn and Pt precursors, the method employed here and in other studies, results in framework Sn coordinated with isolated Pt species or small Pt clusters.^{18,32,33} The Pt-Sn-DeAlBEA catalysts reported here were prepared with higher Sn/Pt ratios (Sn/Pt = 97 - 6.6) than those used in earlier studies (Sn/Pt = 0.5 - 10.1).^{18,32,33} Additionally, the Pt loading in the Pt-Sn-DeAlBEA catalysts (0.03 – 0.62 wt.%) reported here is generally lower than that used in previous studies (0.3 – 1 wt.%).^{18,32,33} One study also reports that direct reduction of Pt-Sn-DeAlBEA results in a more stable and active catalyst relative to sequential calcination and reduction steps.¹⁸ This stability is attributed to forming smaller Pt domains (Sn-O-Pt) with direct reduction.¹⁸ By contrast, we found that pre-reduction decreased the stability relative to pretreatment in He.

The characterization data reported here suggests that the most active species in Pt-Sn-DeAlBEA are small Pt clusters containing, on average, three Pt atoms that interact with a Sn(IV) cation contained in the framework of DeAlBEA. This conclusion is also drawn in a recent theoretical investigation of Pt_x ($x = 1, 2, 3, 4$) and Pt_xSn_y ($x = 1, 2, 3$ and $y = 1$ or $x = 2$ and $y = 2$) structures, which reported tradeoffs in PDH activity with increasing Pt nuclearity.¹⁰⁷ Significant differences in rate-limiting steps and adsorbed species were found depending on the structure, but ultimately, Pt_3Sn was identified as the most active and stable species for PDH.

It is also interesting to compare the activity of Pt-Sn-DeAlBEA to that of PtZn/DeAlBEA reported by the present authors.²⁷ The most active Pt-Sn-DeAlBEA catalyst (Pt/Al = 0.001) has a value of $k_{f,app} = 878$ mol C_3H_6 /(mol Pt·s·bar) at 823 K, which is considerably higher than that for PtZn/DeAlBEA, ($k_{f,app} = 37$ mol C_3H_6 /(mol Pt·s·bar)). We note, though, that Pt-Sn-DeAlBEA deactivates more rapidly ($k_d = 0.002$ to 0.071 h⁻¹ for Pt/Al = 0.001 to 0.026) than Pt-Zn-DeAlBEA ($k_d = 0.004$ to 0.014 h⁻¹ for Pt/Al = 0.04 to 0.1). This suggests that Zn is more effective than Sn in suppressing the formation of coke, the primary cause of deactivation. These findings are consistent with previous work that reported higher coking rates on PtSn/Al₂O₃ than PtZn/Al₂O₃ catalysts.¹²⁰ The decrease in coking rate was attributed to the ability of zinc to stabilize more highly dispersed Pt species.¹²⁰ The differences in activity and stability of Pt-Sn-DeAlBEA and Pt-Zn-DeAlBEA may be due to differences in the number of heteroatoms (Zn or Sn) interacting with Pt. For instance, Pt in Pt-Zn-DeAlBEA interacts with 4-6 Zn(II) sites, while Pt in Pt-Sn-DeAlBEA only interacts with one framework Sn(IV) site and possibly a small number of other Pt atoms. This may be the reason for the high activity of Pt-Sn-DeAlBEA, but also its greater susceptibility to deactivation relative to Pt-Zn-DeAlBEA.

Conclusions

Pt-Sn-DeAlBEA catalysts were prepared by adding Pt to Sn-DeAlBEA, a support derived by the reaction of Sn with silanol nests produced by the dealumination of BEA zeolite. Characterization of Sn-DeAlBEA showed that Sn is incorporated in the zeolite framework as Sn(IV) cations, replacing Al and the charge compensating proton in the parent H-BEA. The presence of Sn(IV) cations in Sn-DeAlBEA stabilizes Pt in the form of very small Pt clusters and Pt nanoparticles. By contrast, Pt introduction into DeAlBEA produced predominantly Pt nanoparticles. While Pt could be dispersed largely as small Pt clusters (containing ~ 3 Pt atoms) in Pt-Sn-DeAlBEA for Pt/Al ratios ≤ 0.013 , increased formation of large Pt clusters and nanoparticles occurred at higher Pt/Al ratios.

The specific activity (i.e., per Pt atom) of Pt-Sn-DeAlBEA for PDH, measured under conditions far from thermodynamic equilibrium, shows a decrease with Pt/Al ratio for Pt/Al > 0.013, even after compensation for the dispersion of Pt in catalysts with Pt/Al ratios > 0.02. The kinetics of propane dehydrogenation can be described by a Langmuir-Hinshelwood expression that is first-order in the partial pressure of propane but is inhibited by propane adsorption. The nearly identical rate parameters observed across all Pt/Al ratios suggest that the active site is the same in all cases. The nuclearity of Pt in the lowest loading catalyst (Pt/Al = 0.001) is three based on EXAFS characterization, suggesting that the active sites are Pt₃Sn species closely coupled to the BEA framework. This conclusion is consistent with recent theoretical analyses showing that Pt₃Sn clusters are particularly active for PDH. Therefore, the decline in specific activity observed with increasing Pt/Al ratio is attributed to dilution of Pt₃Sn clusters by increasingly large Pt clusters or nanoparticles that exhibit minimal interaction with Sn cations in the BEA framework.

The PDH activity of Pt-Sn-DeAlBEA was compared with those of supported Pt and PtSn catalysts reported in the literature based on calculated values of the apparent first-order rate coefficient for PDH, $k_{f,app}$. The values of $k_{f,app}$ for Pt-Sn-DeAlBEA are significantly higher than those reported previously for Pt and PtSn catalysts, including those supported on DeAlBEA. The high activity for catalysts reported here is attributed to highly dispersed Pt species interacting with Sn cations introduced into the framework of BEA.

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Authors contributions

N.G. L. conducted the research; N. G. L. and A. T. B contributed equally to writing the manuscript.

Notes

The authors declare no competing financial interest.

Associated Content

Supporting information:

Full sets of data (available in the main text or the Supporting Information), including interpretation of IR spectra; EXAFS data at Pt LIII edge; catalyst characterization by BET, UV-Vis, XRD, and XAS; tables of XAS fitting results; calculations of rate constants; and discussion of kinetic expressions and parameters.

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TOC Graphic

