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Effects of Cofeeding Hydrogen on Propane Dehydrogenation Catalyzed by Isolated Iron Sites Incorporated into Dealuminated BEA

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Abstract

Propene, used on a large scale to manufacture polypropylene and several commodity chemicals, is increasingly produced by catalytic propane dehydrogenation (PDH). Atomically dispersed Pt has emerged as a promising candidate catalyst for PDH; however, stabilizing atomically dispersed Pt at high temperatures is challenging. Here, we demonstrate the use of dealuminated zeolite Beta with a high Fe content as a host for stabilizing isolated Pt, which is anchored strongly to the zeolite support by Pt–Fe bonds. The isolated Pt–Fe sites exhibit promising PDH performance, including a high apparent forward rate coefficient for propene formation (404.8–26.4 mol propene/mol Pt·bar·s) and a high selectivity ($\geq 96\%$) at 823 K in the presence of H₂. Kinetics data characterizing the rate of PDH with a range of Pt loadings show that atomically dispersed Pt catalyzes propene formation at rates independent of H₂ partial pressure, whereas metallic Pt clusters, formed at high Pt loadings, catalyze the reaction with a slightly negative dependence on H₂ partial pressure. The shift in Pt speciation with Pt loading, confirmed by infrared spectroscopy of adsorbed CO, X-ray absorption spectroscopy, and high-angle angular dark field scanning transmission electron microscopy, suggests that the observed change in kinetics with Pt dispersion is a consequence of a change in the reaction mechanism.

Introduction

Propene, a precursor for products^{1,2} including polypropylene, propylene oxide, and acrylonitrile, has traditionally been produced as a byproduct of naphtha steam cracking³ and petroleum fluid catalytic cracking.^{4,5} However, the decline of naphtha steam cracking, coupled with growing demand for propene, has necessitated the development of on-purpose technologies for propene.⁶ Propane dehydrogenation (PDH) has thus emerged as a leading technology, leveraging abundant, low-cost propane present in shale gas.^{7,8} Supported platinum-containing catalysts are employed extensively in industry as hydrogenation/dehydrogenation catalysts, owing to their exceptional ability to activate H–H and C–H bonds.² However, structure-sensitive side reactions involving C–C bond cleavage, such as hydrogenolysis,⁹ often occur at low-coordination Pt sites, including corner, step, and edge atoms¹⁰ on clusters or nanoparticles, resulting in the formation of low-molecular-weight products and coke. The loss of dehydrogenation selectivity caused by coke can be mitigated by dispersing Pt atomically on supports, which also leads to improved Pt atom utilization.^{2,11}

Stabilizing atomically dispersed Pt at the high temperatures required for PDH (823–873 K) remains a significant challenge because of the tendency of this noble metal to agglomerate, forming Pt clusters/nanoparticles that compromise catalytic performance. Efforts to address this limitation have been explored, but examples illustrating the stabilization of atomically dispersed Pt remain limited. A potentially effective strategy involves introduction of non-noble metal sites on a support that can form strong bonds with Pt, and increasing the loading of the anchoring metal has been shown to enhance the stability of the dispersed Pt. For example, we have shown that Pt–Zn structures on dealuminated Beta zeolites stabilize atomically dispersed Pt, with Pt atoms being bonded to Zn by ca. six strong bonds.¹² Cu,¹³ Sn,^{14–16} Ga,^{17,18} and Fe^{19,20} have also been reported to be effective anchoring elements, with Fe standing out because of its earth abundance, low cost, and ability to enhance catalytic performance. Supported Pt–Fe catalysts, including Pt–Fe–Silicalite-1¹⁹ and Pt0.0015@Fe50-MWW,²⁰ have been reported to be active PDH catalysts. Open questions are how H₂ reduction of such PtFe sites alters their structure and how the addition of H₂ to the propane feed affects the activity and stability of such sites for PDH. Therefore, data are needed to characterize atomically dispersed Pt through various stages of treatment and use to advance the understanding of how well the anchoring metal stabilizes the Pt dispersion.

Previous investigations have shown different effects of H₂ on the PDH activity of Pt, depending on catalyst structure. Co-feeding H₂ has been found to inhibit propene formation on zerovalent Pt (nanoparticles) supported on Mg(Al)O, with the reaction order in H₂ becoming increasingly negative as the Pt particle diameter increased from 3.1 nm to 9.1 nm.²¹ Conversely, the addition of H₂ to a catalyst comprising Pt particles (2.2–1.4 nm) supported on Mg(Ga)(Al)O,^{22,23} has been reported to enhance the rate of propene formation, the optimal H₂/C₃H₈ ratio being 1.25. This enhancement was attributed to reduced formation of coke precursors and enhanced desorption of propene from the catalyst, helping to maintain the active sites.²⁴ However, the influence of co-feeding H₂ on the selectivity of atomically dispersed Pt catalysts stabilized by non-noble metals on the support remains to be determined and is central to possible applications of such catalysts.

The goal of this study was to establish the role of Fe in controlling the dispersion of Pt and the interaction of Pt with Fe, and their influence on the rate of PDH. The catalyst support was

dealuminated zeolite Beta containing Fe (Fe-DeAlBEA),²⁵ which was selected for its high surface area and thermal stability. Dealumination of BEA minimizes its Brønsted acidity and, hence, the rate of propane cracking, and generates silanol nests that serve as anchoring sites for Fe, which, in turn, serve to disperse Pt. The Pt-Fe sites in the zeolite were characterized spectroscopically, before and after exposure to H₂, to provide evidence of how H₂ affects the oxidation state of Pt and structure of the Pt-containing species. We also explored the role of H₂ cofed with propane on catalyst activity, selectivity, and stability for PDH, comparing the atomically dispersed Pt with aggregated Pt. The results demonstrate that the rate of propene formation on atomically dispersed Pt stabilized by Fe nests in the zeolite is independent of H₂ partial pressure, whereas H₂ significantly inhibits the reaction when the Pt is reduced and present as clusters/nanoparticles. We also found that the mechanism and kinetics of PDH depend on the state of Pt dispersion on Fe-DeAlBEA. These findings provide valuable insights for optimizing Pt catalysts for PDH.

Results and Discussion

The xPt0.24Fe-DeAlBEA catalysts were synthesized by adding Pt to Fe supported on dealuminated Beta zeolite, following procedures described previously for PtZn-DeAlBEA.¹² Detailed synthesis information is provided in Section S.1.1 of the Supporting Information (SI). The variable x represents the molar ratio of Pt to Al in the original H-BEA zeolite (Pt/Al₀). Similarly, the number 0.24 represents the ratio of Fe to Al in the original H-BEA zeolite (Fe/Al₀). Catalysts with a range of Pt/Al₀ ratios were prepared: 0.001 (0.02 wt% Pt), 0.0025 (0.05 wt% Pt), 0.005 (0.1 wt% Pt), 0.01 (0.2 wt% Pt), and 0.04 (0.7 wt% Pt), as determined by inductively coupled plasma optical emission spectrometry (ICP) (Table S2 in the SI). The structure of Fe-DeAlBEA before and after Pt addition was characterized using X-ray diffraction (XRD) crystallography, ultraviolet-visible (UV-vis) spectroscopy, X-ray photoelectron spectroscopy (XPS), and infrared (IR) spectroscopy of adsorbed pyridine (details of pyridine-IR experiments are provided in Section S.2.4 in the SI). The addition of small amounts of Pt did not result in new diffraction features, as shown in Figure S1 in the SI, indicating that Pt atoms were well-dispersed, likely as isolated atoms or small clusters. Diffuse reflectance UV-vis spectra of 0.24Fe-DeAlBEA and xPt0.24Fe-DeAlBEA after H₂ pretreatment at 823 K are shown in Figure 1a. The spectrum of 0.24Fe-DeAlBEA exhibits two prominent absorption bands, at 247 nm and 221 nm, attributed to ligand-to-metal charge transfer (LMCT) from oxygen atoms to isolated tetrahedral Fe species.²⁶ Moreover, a shoulder at 270 nm corresponds to charge transfer from oxygen ligands to Fe in octahedral coordination.²⁷ Broad bands extending beyond 300 nm, particularly between 300–460 nm and > 460 nm, are associated with small oligomeric Fe_yO_x clusters and Fe₂O₃ phases,²⁸ attributed to d-d transitions based on crystal field theory.^{26,28} The results indicate that the Fe-DeAlBEA contains predominately framework sites and small amounts of extraframework sites. After Pt addition, the bands at < 300 nm remained largely unchanged, whereas the broad band around 300–400 nm increased slightly in intensity, with the most notable increase observed for the 0.04Pt0.24Fe-DeAlBEA. This comparison suggests that Pt incorporation may lead to slight clustering of Fe species in the catalyst with the highest Pt loading. Also, Fe²⁺ typically exhibits d-d transitions at 700–1000 nm, owing to octahedral distortions.^{29,30} The absence of these bands in the spectra of H₂ pre-treated 0.24Fe-DeAlBEA and xPt0.36Fe-DeAlBEA indicates the absence of detectable Fe²⁺.

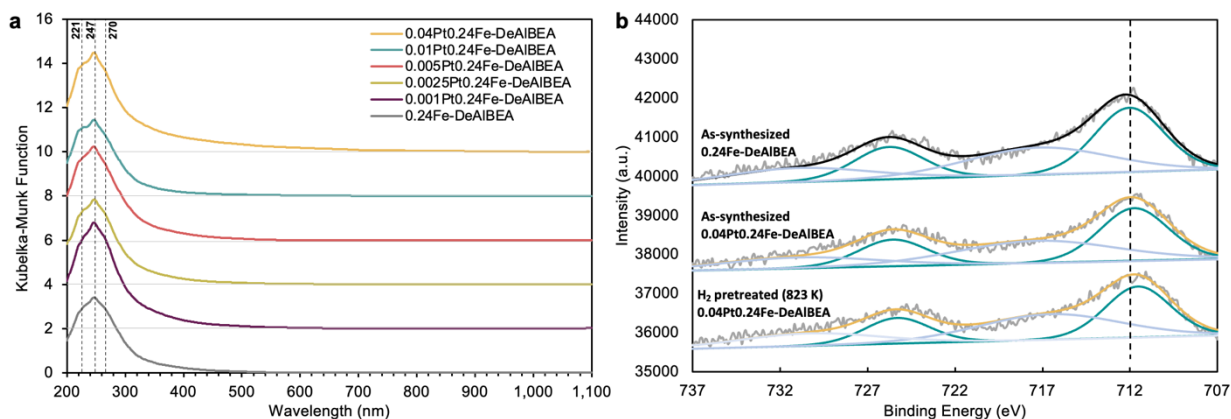


Figure 1. Diffuse reflectance UV-vis spectra of 0.24FeDeAlBEA and xPt0.24Fe-DeAlBEA ($x = 0.04, 0.01, 0.005, 0.0025$, and 0.001) recorded at room temperature after in-situ H_2 treatment at 823 K for 1 h, and (b) XPS data characterizing 0.24Fe-DeAlBEA and 0.04Pt0.24Fe-DeAlBEA, with deconvolution into two peaks. The bold curves represent the fitted data.

The Fe 2p XPS data of the as-synthesized 0.24Fe-DeAlBEA (Figure 1b) display a doublet corresponding to Fe 2p_{3/2} and Fe 2p_{1/2}, which arises from spin-orbit coupling. Each component is further accompanied by a shake-up satellite peak, a feature commonly observed in the spectra of Fe-containing oxides.^{31–33} The spectra were analyzed on the basis of two doublets, with the Fe 2p_{3/2} binding energy determined to be 712.03 eV, with its corresponding satellite at 717.22 eV, with Fe 2p_{1/2} appearing at 725.78 eV and its satellite at 731.02 eV (Table S4 in the SI). This binding energy is higher than those observed for bulk α -Fe₂O₃ (710.8 eV) and γ -Fe₂O₃ (711 eV),^{31–33} indicating that Fe in 0.24Fe-DeAlBEA is present as Fe³⁺. The elevated binding energies, compared with that of bulk iron oxide, are attributed to highly dispersed Fe sites interacting with the zeolite framework, in line with previous investigations of Fe-DeAlBEA.^{34–38} With the addition of Pt to Fe-DeAlBEA, the binding energy decreased only slightly, to 711.75 eV, in the as-synthesized 0.04Pt0.24Fe-DeAlBEA, and further decreased by 0.22 eV after H_2 treatment at 823 K. This small shift in binding energy may indicate a partial reduction of Fe³⁺ to Fe²⁺ or subtle changes in Fe³⁺ coordination with the support. Additional discussion and characterization of DeAlBEA and 0.24Fe-DeAlBEA are available in Ref.²⁵ Here, the focus is on characterizing the electronic and structural properties of Pt in xPt0.24Fe-DeAlBEA.

Figure 2 shows aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of ex-situ H_2 -pretreated xPt0.24Fe-DeAlBEA. The images were acquired to investigate the evolution of Pt particle size and dispersion as a function of Pt loading. The images of the sample with the highest Pt loading, 0.04Pt0.24Fe-DeAlBEA, show distinct Pt nanoparticles, with a broad size distribution, with diameters ranging from 0.8 to 3.2 nm and an average of 1.6 nm. A sample with a lower Pt loading, 0.01Pt0.24Fe-DeAlBEA, is characterized by Pt particles having a narrower size distribution, ranging from 0.6 to 1.9 nm, with the average particle diameter being 1.25 nm. Further decreases in the Pt loading to 0.005Pt0.24Fe-DeAlBEA resulted in a higher Pt dispersion, with the average particle diameter reduced to 0.94 nm. The images of 0.0025Pt0.24Fe-DeAlBEA include faint features that may correspond to individual Pt atoms or small clusters dispersed on the Fe sites. The structures were observed to be unstable under the influence of the electron beam during imaging, as expected. The beam likely caused slight clustering and/or introduced artifacts, making the observed structural features less than conclusive. In the images of the catalyst with the lowest Pt loading, 0.001Pt0.24Fe-

DeAlBEA, no Pt particles are visible, suggesting that Pt is likely atomically dispersed. Additional HAADF-STEM images are presented in the SI (Section S.2.5). To provide further information about the Pt dispersion and Pt-Fe interactions, X-ray absorption spectroscopy (XAS) and IR spectroscopy of adsorbed CO were employed.

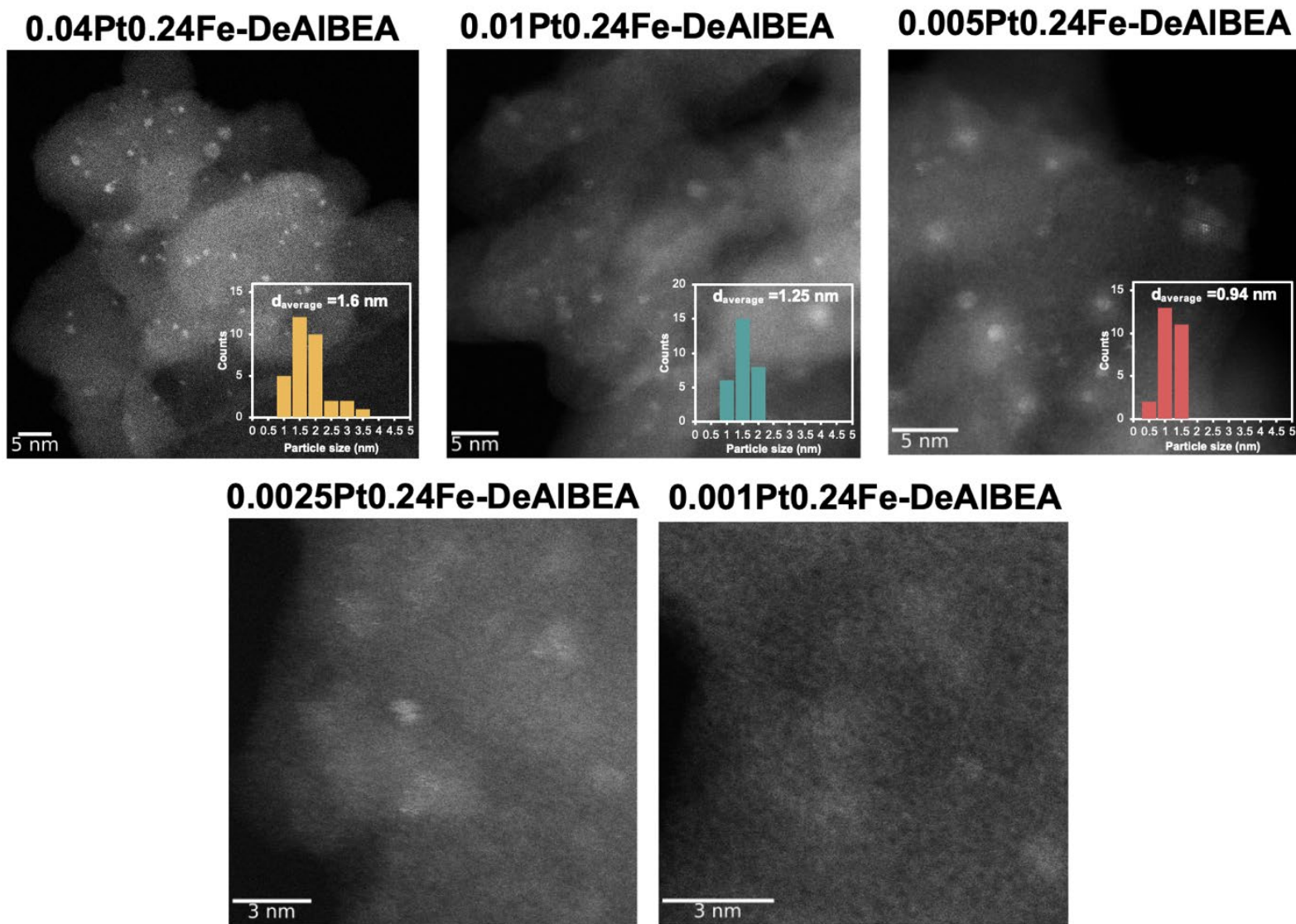


Figure 2. HAADF-STEM images of xPt0.24Fe-DeAlBEA catalysts after ex-situ H₂ treatment at 823 K.

Pt L_{III} edge XAS was used to characterize the oxidation state and local coordination environment of Pt in xPt0.24Fe-DeAlBEA, both before and after H₂ treatment. Pt L_{III} edge X-ray absorption near edge structure (XANES) spectra were collected for the reference standards Na₂Pt(OH)₆ (Pt⁴⁺), Pt(NH₃)₄(NO₃)₂ (Pt²⁺), and Pt foil (Pt⁰), as well as for the as-synthesized catalysts: 0.001Pt-DeAlBEA and xPt0.24Fe-DeAlBEA, with Pt/Al₀ ratios of 0.001, 0.0025, and 0.04 (Figure 3a). The white line intensity, which reflects the density of unoccupied 5d states, is often used as an indicator of Pt oxidation state. High oxidation states are typically associated with a high white line intensity associated with the number of unoccupied 5d orbitals.^{39–41} The white line intensity (Table

S5 in the SI) was observed to decrease in the following order: $\text{Na}_2\text{Pt}(\text{OH})_6 > 0.04\text{Pt}0.24\text{Fe-DeAlBEA} > 0.001\text{Pt}0.24\text{Fe-DeAlBEA} \geq 0.0025\text{Pt}0.24\text{Fe-DeAlBEA} \approx \text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2 > 0.001\text{Pt-DeAlBEA} > \text{Pt foil}$. This trend is consistent with the inference that the catalyst with the highest Pt loading ($0.04\text{Pt}0.24\text{Fe-DeAlBEA}$) incorporated Pt^{2+} and Pt^{4+} , with the Pt^{2+} being dominant. The data indicate that the two catalysts with the lowest Pt loadings ($0.001\text{Pt}0.24\text{Fe-DeAlBEA}$ and $0.0025\text{Pt}0.24\text{Fe-DeAlBEA}$) contained Pt predominantly as Pt^{2+} .

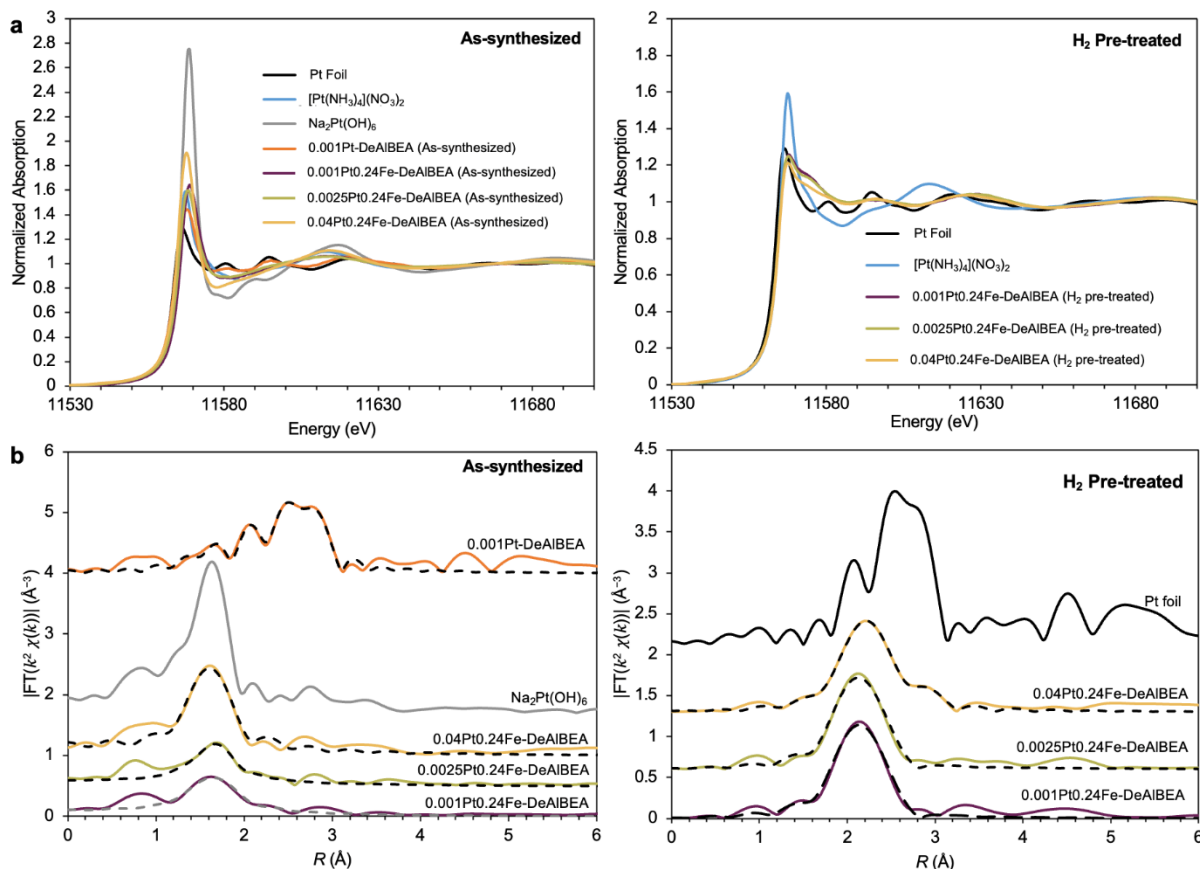


Figure 3. (a) Normalized Pt L_{III}-edge XANES data, and (b) magnitude of the Fourier-transformed k^2 -weighted EXAFS spectra of as-synthesized 0.001Pt-DeAlBEA, xPt0.24Fe-DeAlBEA, and Pt standards. Data characterizing xPt0.24Fe-DeAlBEA ($x = 0.04, 0.0025$, and 0.001) collected at 303 K before and after H₂ treatment at 823 K. The standards were characterized under ambient conditions without any treatment. The fits of the spectra are shown as black dashed lines. The range in k was 3.0–10.0 $\text{\AA}^{-1}$, and the fit range in radial distance was 1.0–3.3 $\text{\AA}$ (k^2 weighting was used in the EXAFS data fitting).

The local coordination environment around Pt in the as-synthesized catalysts was examined using extended X-ray absorption fine structure (EXAFS) spectroscopy. The magnitude of the Fourier-transformed k^2 -weighted EXAFS spectra (k is the wave vector) is compared with those of $\text{Na}_2\text{Pt}(\text{OH})_6$ and Pt foil. The spectra characterizing xPt0.24Fe-DeAlBEA ($x = 0.04, 0.0025$, and 0.001) exhibit a dominant peak between 1–2 $\text{\AA}$, corresponding to a first-shell Pt–O scattering path (Figure 3). Notably, the absence of a significant peak near 2.7 $\text{\AA}$, corresponding to a Pt–Pt scattering path in Pt foil, is consistent with the absence of a substantial proportion of Pt clusters/nanoparticles in the as-synthesized materials, but EXAFS data are not sufficient to rule out the presence of some Pt clusters.⁴² Further, these results do not rule out the presence of small

platinum oxide clusters. (Evidence of Pt–O coordination based on IR spectroscopy of adsorbed CO is discussed below.)

Fitting of the EXAFS data (Table 1) indicates that the average Pt–O coordination number is 4.8 ± 0.6 characterizing the catalyst with the highest Pt loading (0.04Pt0.24Fe-DeAlBEA), suggesting a coordination environment consistent with oxidized Pt species. In contrast, the two catalysts with the lowest Pt loadings (with Pt/Al₀ values of 0.0025 and 0.001) are characterized by average Pt–O coordination numbers of 3.7. We caution that the coordination numbers may have been influenced by the presence of water, as these samples were measured at room temperature without dehydration after exposure to air. Water adsorption could also explain the slightly elevated R-factor (Table 1), as well as the ΔE_0 values (11.5–12.8 eV, Table 1), which exceed the typical range of -10 to 10 eV⁴³. The presence of surface hydroxyl species can affect the local Pt environment, leading to small shifts in both the energy reference and the EXAFS fit quality. Notwithstanding these points, the fit parameters are physically meaningful.

A comparison of the data characterizing 0.001Pt-DeAlBEA and 0.001Pt0.24Fe-DeAlBEA highlights the role of Fe in stabilizing the Pt dispersion. In the absence of Fe (0.001Pt-DeAlBEA), both Pt–O (coordination number 1.5 ± 0.8) and Pt–Pt (coordination number 8.4 ± 0.9) scattering paths are observed, indicating significant Pt aggregation, with an average Pt oxidation state between 2+ and 0. However, when Fe is present (in 0.001Pt0.24Fe-DeAlBEA), no Pt–Pt scattering path was determined in the data fitting, consistent with the inference that Pt remained atomically dispersed in the presence of Fe.

Table 1. Fitted EXAFS parameters characterizing as-synthesized and H₂-pre-treated (823 K) samples; data were acquired at 303 K.

Pre-treatment	Catalyst	Scattering path	CN	ΔE_0 (eV)	$\Delta\sigma^2 \times 10^3$ (Å ²)	R (Å)	R factor
None (as-synthesized sample)	0.001Pt-DeAlBEA	Pt–O	1.5 ± 0.8	6.8 ± 1.0	12.1 ± 9.4	1.92 ± 0.02	0.015
		Pt–Pt	8.4 ± 0.9		5.3 ± 0.6	2.795 ± 0.004	
	0.04Pt0.24Fe-DeAlBEA	Pt–O	4.8 ± 0.6	11.5 ± 1.4	3.7 ± 2.0	2.00 ± 0.01	0.027
	0.0025Pt0.24Fe-DeAlBEA	Pt–O	3.7 ± 0.5	12.8 ± 1.4	11.1 ± 2.6	2.05 ± 0.01	0.06
	0.001Pt0.24Fe-DeAlBEA	Pt–O	3.7 ± 0.6	12.2 ± 1.6	11.2 ± 3.1	2.05 ± 0.01	0.04
H ₂	0.04Pt0.24Fe-DeAlBEA	Pt–Fe	3.3 ± 0.5	5.6 ± 0.7	8.6 ± 1.4	2.607 ± 0.006	0.0009
		Pt–Pt	6.8 ± 1.1		9.9 ± 1.4	2.723 ± 0.009	
	0.0025Pt0.24Fe-DeAlBEA	Pt–Fe	6.5 ± 1.2	0.2 ± 2.0	10.6 ± 2.0	2.56 ± 0.01	0.022
	0.001Pt0.24Fe-DeAlBEA	Pt–Fe	6.8 ± 1.2	1.0 ± 1.8	10.7 ± 1.8	2.57 ± 0.01	0.019

Notation: CN, coordination number; R , scattering path length between the absorber (Pt) and scattering atom; $\Delta\sigma^2$, change in mean square relative displacement, indicating differences in structural disorder; ΔE_0 , energy shift (inner potential correction, also referred to as effective energy origin correction); R-factor, a measure of the goodness of fit in EXAFS analysis.

After H₂ treatment of xPt0.24Fe-DeAlBEA ($x = 0.04, 0.0025$, and 0.001), significant changes were observed in both the oxidation state and local coordination environment of Pt. The white line intensities of each sample decreased after treatment, now resembling the intensity observed for Pt

foil (Figure 3a). This decrease demonstrates a reduction in the oxidation state of Pt towards that characteristic of metallic Pt. The EXAFS spectra of the catalyst with the highest Pt loading, 0.04Pt0.24Fe-DeAlBEA, exhibit a dominant peak between 1.5 and 3.5 Å, accompanied by a small shoulder at higher radial distances. Fitting of the data reveals two primary contributions: a prominent Pt–Fe scattering path at a bonding distance of 2.6 Å with a coordination number of 3.3 ± 0.5 , and a Pt–Pt scattering path at a bonding distance of 2.7 Å, with a coordination number of 6.8 ± 1.1 (Table 1). The Pt–Pt scattering paths, as shown in Figure S18 in the SI, are indicated by two peaks, one centered around 2.5 Å and another around 3.0 Å, with the latter contributing to the observed shoulder. This finding suggests some Pt reduction and clustering in 0.04Pt0.24Fe-DeAlBEA, with some metallic Pt–Pt bonds and some Pt bonding with Fe sites.

In contrast, the EXAFS spectra characterizing the two catalysts with the lowest Pt loadings, 0.0025Pt0.24Fe-DeAlBEA and 0.001Pt0.24Fe-DeAlBEA, do not exhibit the shoulder at 3.0 Å observed in the spectra of the sample with the higher Pt loading. This absence is consistent with a lack of Pt–Pt bonds, confirming the inference that Pt clustering does not occur in these samples. Fitting of the data characterizing the catalysts with low Pt loadings shows that the spectra can be modeled satisfactorily with only a Pt–Fe scattering path. The magnitude and imaginary parts of the FT-EXAFS spectra are shown in Figures S19 and S21 in the SI. The average Pt–Fe coordination number is in the range of 6.5–6.8. This high coordination number is attributed to the high Fe/Pt ratios (240 and 96), corresponding to the relatively high Fe content ($\text{Fe}/\text{Al}_0 = 0.24$) and the low Pt loading. In this sample, Pt atoms are evidently highly dispersed and surrounded by abundant Fe sites, maximizing Pt–Fe interactions, which we infer limit the formation of Pt clusters. These results are consistent with results of a previous investigation of atomically dispersed Pt in 0.36Zn-DeAlBEA ($\text{Pt}/\text{Al}_0 = 0.04$), for which the average Pt–Zn coordination number was estimated to be six, with no EXAFS evidence of Pt–Pt contributions.¹² Thus, in both of these catalysts, the Pt was highly dispersed and stabilized by the non-noble metals in the zeolite pores.

The IR spectra of CO adsorbed on as-synthesized xPt0.24Fe-DeAlBEA with Pt/ Al_0 ratios ranging from 0.04 to 0.001 are shown in Figure 4a. Within the 2000–2200 cm^{-1} region, three main bands are observed and assigned to linearly adsorbed CO on Pt sites. The bands observed at 2164 cm^{-1} and 2146 cm^{-1} are attributed to linearly adsorbed CO on isolated Pt sites with Pt in a positive oxidation state, sometimes represented as $\text{Pt}^{\delta+}$. Such isolated Pt sites have been reported on supports such as HZSM-5,⁴⁴ Y zeolite,⁴⁵ TiO_2 ,^{39,46} and $\text{CeO}_2\text{-Al}_2\text{O}_3$ ⁴⁷ (details in Table S15 in the SI). Importantly, the positions of these high-frequency peaks remained unchanged with variations in CO desorption temperature or time, as shown in Figure 4b and 4c for the catalysts with the highest and lowest Pt/ Al_0 ratios (0.04 and 0.001). This invariance suggests the absence of CO–CO dipole interactions resulting from close packing of adsorbed CO molecules, which are commonly observed in the spectra of Pt single crystals^{48–50} and Pt nanoparticles.⁵¹

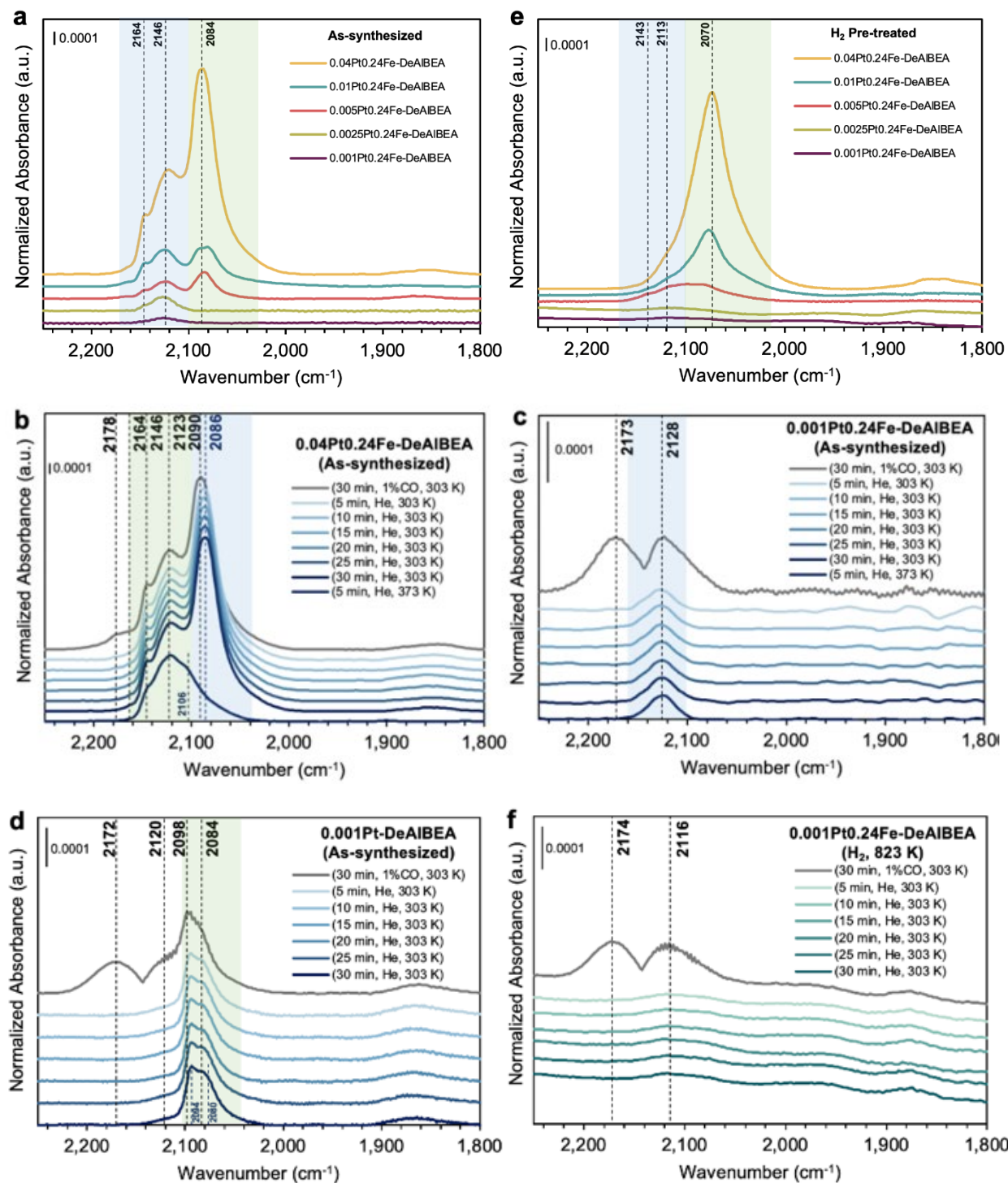


Figure 4. (a) IR spectra of adsorbed CO adsorbed on as-synthesized xPt0.24Fe-DeAlBEA ($x = 0.04, 0.01, 0.005, 0.0025$, and 0.001) after CO desorption for 30 min at 303 K. CO desorption spectra as a function of time and temperature for as-synthesized (b) 0.04Pt0.24Fe-DeAlBEA, (c) 0.001Pt0.24Fe-DeAlBEA, (d) 0.001Pt-DeAlBEA, and (e) IR spectra of CO adsorbed on H₂-pretreated xPt0.24Fe-DeAlBEA catalysts after CO desorption for 30 min at 303 K, (f) CO desorption spectra as a function of time and temperature for H₂-pretreated 0.001Pt0.24Fe-DeAlBEA. The catalysts were calcined in air and then pre-treated in helium at 623 K to remove residues and moisture before

characterization by IR spectroscopy, and the H₂ pre-treatments were performed at 823 K with pure H₂ at 1 atm. All results characterizing the remaining CO desorption experiments are represented in Figure S23 in the SI.

A third band, observed at 2084 cm⁻¹, is attributed to CO adsorbed on Pt clusters. This band appears for 0.04Pt0.24Fe-DeAlBEA and shifts by 4 cm⁻¹ with desorption time (0 to 30 min at 303 K) and upon heating to 373 K. This shift suggests changes in CO dipole-dipole interactions on Pt clusters. The assignment of this band is debated in the literature, with one group associating it with platinum oxide clusters⁵² and another with metallic Pt clusters on HZSM-5⁴⁴; we assign it here to platinum oxide clusters, as supported by XANES evidence indicating the presence of Pt²⁺ and Pt⁴⁺ in the as-synthesized sample. Furthermore, a broad absorption centered at 1850 cm⁻¹, attributed to bridging CO adsorbed on two adjacent Pt sites,⁴⁹ is particularly prominent in the spectrum of 0.04Pt0.24Fe-DeAlBEA. This feature confirms the presence of Pt clusters and further supports the evidence stated above of their formation in catalysts with higher Pt loadings.

As the Pt/Al₀ ratio decreases from 0.04 to 0.0025, the broad band 2084 cm⁻¹ band disappears, indicating that Pt sites are increasingly isolated, no longer forming clusters in the catalysts with the lowest Pt/Al₀ ratios of 0.001 and 0.0025. Comparing the catalysts with the lowest Pt loading (0.001Pt), with and without Fe (0.001Pt0.24Fe vs. 0.001Pt), reveals a key difference: in the absence of Fe, two bands, at 2098 cm⁻¹ and 2084 cm⁻¹, are observed, which shift with CO desorption time, confirming the formation of Pt clusters, as shown in Figure 4d. These clusters likely consist of a mixture of platinum oxide clusters and metallic Pt species, consistent with the Pt–O and Pt–Pt scattering paths observed by EXAFS spectroscopy. In contrast, when Fe is present, these bands are absent (Figure 4c), suggesting that Pt remains atomically dispersed. This observation confirms that oxidized Pt sites dominate in the two catalysts with the lowest Pt loadings prior to reduction and that Fe plays a crucial role in preventing Pt clustering.

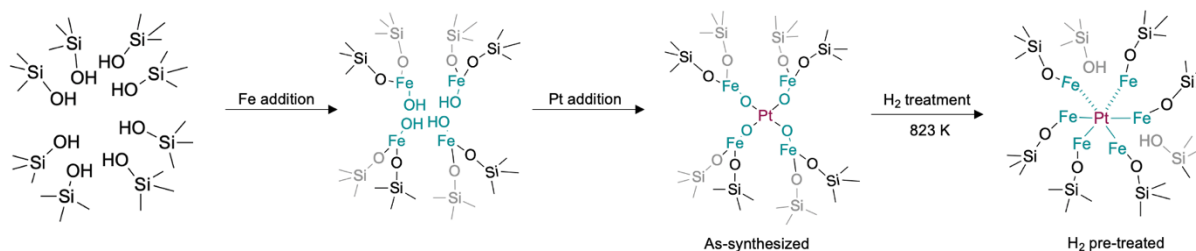
After H₂ treatment at 823 K, significant changes were observed in the CO bands characterizing adsorbed CO, highlighting variations in the Pt coordination and oxidation state, as shown in Figure 4e. For catalysts with high Pt/Al₀ ratios, such as 0.04Pt0.24Fe-DeAlBEA, the intensities of bands at frequencies > 2100 cm⁻¹ decreased significantly, whereas the other peaks grew in intensity. Specifically, the band at 2164 cm⁻¹ disappeared, leaving only weak bands at 2146 cm⁻¹ and 2113 cm⁻¹. Moreover, the band corresponding to linearly adsorbed CO on Pt clusters shifted from 2084 cm⁻¹ to 2070 cm⁻¹. This redshift suggests that Pt was reduced during the H₂ treatment, consistent with the XANES data. The reduction of Pt, combined with strong Fe–Pt interactions, enhances the electron density on Pt atoms, leading to stronger electron donation to adsorbed CO. However, it is challenging to deconvolute the effects of Pt–Pt bonding and Fe–Pt interactions, as reduced Pt-Fe catalysts exhibit a wide range of peaks characterizing adsorbed CO (2095–2030 cm⁻¹).^{19,53–60} Further, Pt single crystals display varying CO peaks depending on their crystallographic planes and CO coverages (2100–2060 cm⁻¹).^{49,50,61} Tables S14 and S16 in the SI provide more details about CO adsorption on Pt single crystals and PtFe catalysts.

The catalysts with the lowest Pt/Al₀ ratios (0.0025 and 0.001) exhibit no detectable CO IR peaks after purging (Figure 4f). The absence of CO adsorption suggests that CO binds too weakly to be detected under these conditions. Two factors contribute to this limitation: (1) the extremely low Pt loadings, which minimize the overall number of adsorption sites, and (2) Fe-induced electronic effects that alter the interaction of Pt with CO. The XANES data indicate that the charge on Pt is zero after hydrogen treatment, consistent with electron donation from neighboring Fe atoms. This

donation increases electron density on Pt, which strengthens π back-donation to CO's antibonding orbitals, thereby weakening the Pt–CO bond and making adsorbed CO less stable.

This effect can be explained in terms of the Blyholder-Nilsson-Peterson (BNP) model,^{62–65} which ascribes CO binding to Pt to a combination of σ -donation from lone-pair CO and π back-donation from Pt d-electrons. In metallic Pt, strong back-donation weakens the C–O bond and shifts CO vibrational frequencies to lower wavenumbers, whereas in oxidized Pt, weaker back-donation strengthens CO adsorption. In the low-Pt-loading samples, electron donation from Fe makes Pt more electron-rich, enhancing back-donation and further destabilizing CO adsorption. This interpretation is supported by the results of CO desorption experiments characterizing 0.04Pt0.24Fe-DeAlBEA (Figure S23 in the SI)—the data show that the band characterizing CO on metallic Pt declined markedly in intensity as the temperature increased from 303 K to 373 K, reinforcing the inference that CO binds weakly to neutral Pt sites. This interpretation is also in line with the observation that CO adsorption signals are absent from the IR spectra of the catalysts with the lowest Pt loadings—Pt is electronically modified by the neighboring Fe, weakening CO binding beyond the detectable limit.

Thus, Scheme 1 is a summary of our interpretation of the interaction of Pt with Fe-DeAlBEA in both as-prepared PtFe-DeAlBEA and after its H₂ reduction at 823 K. This scheme is built upon the data accumulated for Fe-DeAlBEA²⁵ and PtFe-DeAlBEA. To emphasize the plausibility of the structural model, we note that BEA zeolite has a three-dimensional, interconnected pore system consisting of 4-, 5-, 6-, and 12-membered rings than can accommodate the proposed structure.⁶⁶ Further, aluminum can exist as isolated Al atoms in two rings or as Al pairs (Al–O–(Si–O)₂–Al sequences) in single rings. The latter were demonstrated by the results of experiments performed with ion-exchanged Co²⁺ to probe the Al pair sites that each bear a negative charge—showing that 40–65% of the framework Al atoms in BEA zeolite (for Si/Al < 18) exist as Al pairs, with the remaining Al atoms being isolated.^{67,68}



Scheme 1. Schematic Representation of the Formation of Atomically Dispersed Pt Sites in the zeolite Beta-supported catalyst.

In the first step of Scheme 1, dealumination of BEA removes framework Al, leading to the formation of silanol nests ($\equiv\text{Si-OH}$ groups). The removal of a single Al atom generates a silanol nest with four $\equiv\text{Si-OH}$ groups, whereas the removal of Al pairs (common in BEA) results in the formation of larger pockets—consisting of two adjacent silanol nests containing up to eight $\equiv\text{Si-OH}$ groups. Upon Fe addition, approximately four $(\equiv\text{SiO})_2\text{Fe-OH}$ groups are incorporated into these nests.²⁵ Subsequent Pt incorporation into Fe-DeAlBEA leads to a structure in which Pt ^{$\delta+$} is coordinated to four oxygen atoms, as shown by the EXAFS data ($\text{CN}_{\text{Pt-O}} = 3.7 \pm 0.6$). A structure

consistent with these findings includes $\text{Pt}^{\delta+}$ ($\delta = 2-4$) bonded to four Fe^{3+} ions via Pt–O–Fe bonds in adjacent silanol nests

Deducing the structure of Pt in the nests in PtFe-DeAlBEA following H_2 reduction at 823 K is challenging. XANES spectra show that Pt is reduced to Pt^0 , and analysis of the EXAFS data gives a best-fit $\text{CN}_{\text{Pt-Fe}} = 6.8 \pm 1.2$. This value of $\text{CN}_{\text{Pt-Fe}}$ is high, pointing to the larger nests. There is no precedent for such a structure in the literature of organometallic complexes (but in crystalline $\text{PtFe}_4(\text{CO})_{12}(\text{PMe}_2\text{Ph})_2(\mu_5\text{-C})$ (Me is methyl; Ph is phenyl), Pt bonds to four Fe atoms in a square pyramidal structure, stabilized by a central carbido carbon ligand⁶⁹). Thus, to test our inference that a Pt–Fe coordination number > 6 is plausible, we refitted the EXAFS data using fixed values of $\text{CN}_{\text{Pt-Fe}} = 4$ and 5 (Table S13 and Figure S21). These lower values of $\text{CN}_{\text{Pt-Fe}}$ provided acceptable fits with the same average Pt–Fe distance as found with $\text{CN}_{\text{Pt-Fe}} = 6.8 \pm 1.2$. However, they did not provide the lowest R-factor and value of reduced χ^2 [reduced Chi-Square] and do not represent the data as well as the optimized fit with the latter CN value.

Therefore, for consistency with the EXAFS data, we hypothesize that during the reduction of PtFe-DeAlBEA, the Fe^{3+} ions in the sample undergo reduction to Fe^{2+} , leading to the formation $\equiv\text{SiO-Fe-Pt}$ bonds (Scheme 1). Accumulation of additional Fe atoms near Pt may result from the reduction of $(\equiv\text{SiO})_2\text{Fe-OH}$ groups and followed by Fe migration resulting in the incorporation of 6 Fe^{2+} ions around each Pt atom in the larger nests mentioned above, as shown in Scheme 1. Supporting this interpretation, the XPS data collected after reduction of Fe-DeAlBEA (Figure 1b) show a primary Fe^{3+} peak at 711.1 eV along with a broad feature spanning 708–716 eV, suggesting the presence of a small fraction of Fe present as Fe^{2+} . Because Fe^{2+} typically appears in the spectra between 708–710 eV, the data thus support the hypothesis of partial Fe reduction. However, as XPS provides an ensemble-averaged Fe oxidation state, it cannot distinguish Fe species specifically coordinated to Pt. Given that only 6 of 240 Fe atoms are expected to be near Pt, their contribution to the overall XPS signal is likely too small to be distinctly detected. Thus, to summarize, these observations lead to the structure shown Scheme 1 to represents our best model for the bonding of Pt in H_2 reduced PtFe-DeAlBEA, Pt remains atomically dispersed.

Kinetics of propane dehydrogenation catalysis

Influence of Pt loading on propane dehydrogenation activity of xPt0.24Fe-DeAlBEA

The effect of Pt loading on PDH activity of xPt0.24Fe-DeAlBEA was investigated for $x = \text{Pt}/\text{Al}_0$ ranging from 0.04 to 0.001. Experiments were conducted with a once-through flow reactor operated at 823 K and atmospheric pressure with partial pressures of $P_{\text{C}_3\text{H}_8} = P_{\text{H}_2} = 14.68$ kPa. The propane conversion and propene selectivity are shown in Figure 5a. As the Pt/Al_0 ratio increases, the propane conversion increases from 19.6% to 28.1% at a fixed weight hourly space velocity of 37 h^{-1} , whereas the selectivity to propene decreases from 99.5% to 95.8%. The trends in propane conversion and propene selectivity over time on stream are shown in Figure S36 in the SI. Notably, the propane conversion catalyzed by the base support, 0.24Fe-DeAlBEA, is $< 2\%$ under the same conditions, as displayed in Figure S26 in the SI, confirming that the contribution of 0.24Fe-DeAlBEA to the activity reported in Figure 5a is negligible. The measured rate of propene formation was corrected by dividing by the approach to equilibrium to obtain the forward rate of propene formation (Section S.1.3 of the SI). The forward rate shown in Figure 5b, normalized by

the number of moles of Pt in the catalyst, increases significantly with decreasing Pt loading, rising from 7 C₃H₆/(mol Pt·s) at a Pt/Al₀ ratio of 0.04 to approximately 59–63 C₃H₆/(mol Pt·s) at a Pt/Al₀ ratio of 0.001. This trend is partly a result of a fraction of Pt atoms not being exposed at the surfaces of Pt nanoparticles in 0.04Pt0.24Fe-DeAlBEA, as evidenced by HAADF-STEM particle size analysis, resulting in reduced activity per mole of total Pt. With an average Pt cluster diameter of approximately 1.6 nm (Figure 2), about 70% of the Pt atoms in these clusters are exposed at the surface. After correcting for Pt dispersion, the forward rate of propene formation per surface Pt atom for 0.04Pt0.24FeDeAlBEA increases to 10 mol C₃H₆/(mol·Pt·s). However, this rate remains approximately six times lower than that for 0.001Pt0.24DeAlBEA. Each of the catalysts was found to be quite stable: for example, 0.001Pt0.24Fe-DeAlBEA maintains activity over 33 h of continuous operation (Figure 5c), exhibiting a first-order deactivation rate constant, k_d , of 0.008 h⁻¹. This stability, along with the higher forward rate of propene formation per Pt atom at lower loadings, indicates more effective Pt utilization and higher PDH activity for atomically dispersed Pt compared with catalysts incorporating larger Pt ensembles.

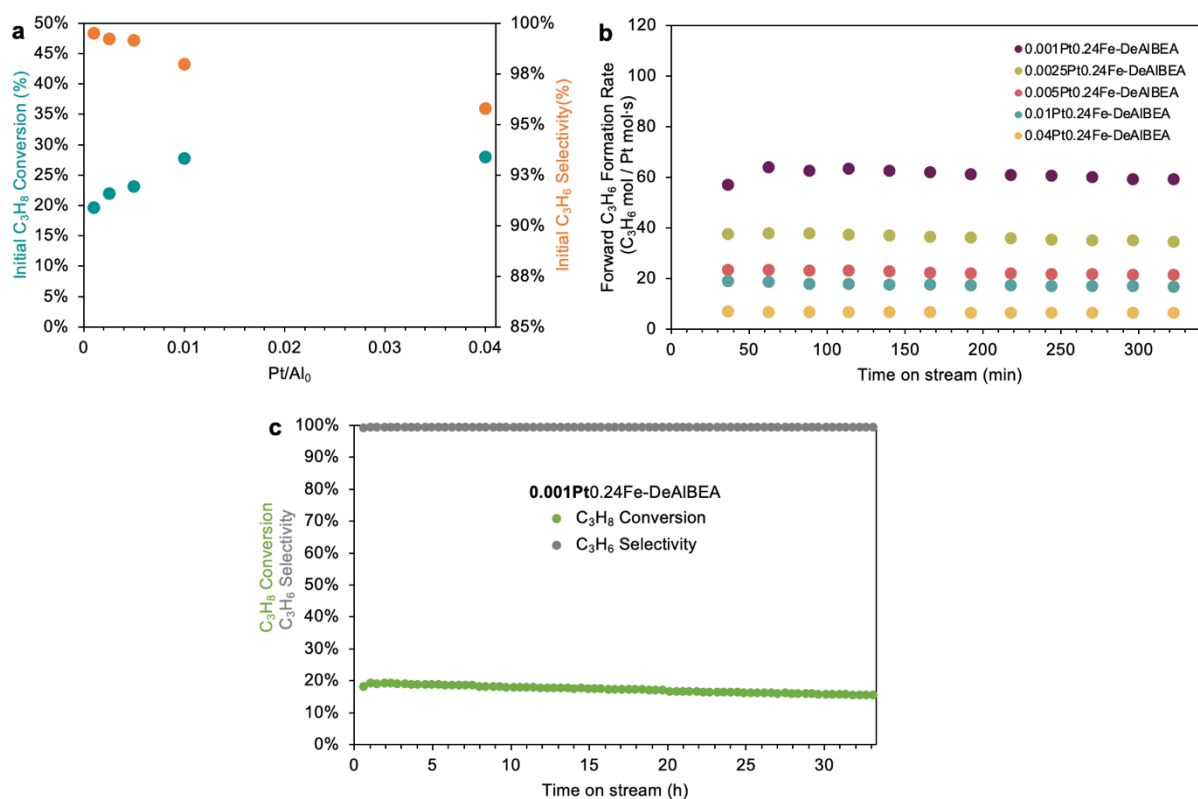


Figure 5. (a) Comparison of propane conversion and propene selectivity as a function of Pt/Al₀ of xPt0.24Fe-DeAlBEA catalysts, (b) forward propene formation rate as a function of time on stream, and (c) long-term stability data for 0.001Pt0.24Fe-DeAlBEA. (Reaction conditions: $P_{C_3H_8} = P_{H_2} = 14.68$ kPa, 823 K, feed rate 48 mL(NTP)/min, and catalyst mass 20 mg; the catalyst was H₂ pretreated at 823 K).

The effect of cofeeding H₂ on PDH

The effect of cofeeding H₂ on PDH was investigated using the catalyst with the highest Pt loading (0.04Pt0.24Fe-DeAlBEA), as shown in Figure S26 in the SI. Co-feeding H₂ reduced initial propane

conversion from 43.5% to 28.1% and slightly decreased propene selectivity, from 97.1% to 95.8%. However, the forward propene formation rate increased from 5.08 to 6.81 mol C₃H₆/(mol Pt·s). More importantly, H₂ co-feeding significantly improved catalyst stability, as the deactivation rate coefficient decreased from 0.66 h⁻¹ (without H₂) to 0.008 h⁻¹ (with H₂) after 4 h of reaction.

Coke formation was indicated by the appearance of major IR bands at 1580 cm⁻¹, 1449 cm⁻¹, 1357 cm⁻¹, and a shoulder at 1608 cm⁻¹ after reaction without H₂, as shown in Figure S28 in the SI. These peaks correspond to conjugated aromatic coke C=C (1580 cm⁻¹)^{70–76} and likely a different type of conjugated aromatics (1608 cm⁻¹). The broad peak at 1449 cm⁻¹ corresponds to asymmetric CH₃ and symmetric =CH₂ deformations,⁷² and the peak at 1357 cm⁻¹ corresponds to symmetric CH₃ deformations,⁷³ characterizing aliphatic C–H bonds in hydrocarbons such as propene and reaction intermediates. When H₂ was cofed with propane, the peaks at 1449 and 1357 cm⁻¹ disappeared completely, and the coke band at 1580 cm⁻¹ decreased in intensity by 82%. These results suggest that cofed H₂ reduces the coverage of the catalyst surface with propene and coke precursors, consistent with a DFT investigation of Pt(111).²⁴ The catalyst with the lowest Pt loading (0.001Pt0.24Fe-DeAlBEA) was characterized by significantly smaller coke-related peaks in the IR spectra (Figure S29 in the SI) after the PDH reaction with cofed H₂.

Kinetics of PDH in the presence of H₂

The influence of reaction temperature and the partial pressures of propane and H₂ on the rate of PDH was investigated for xPt0.24Fe-DeAlBEA. Two sets of experiments were performed under differential conversion conditions at 753 K and lower temperatures, at which deactivation is not a concern. The first set of experiments determined the effect of varying propane partial pressure (1.7–13.3 kPa) and temperature (693–753 K) at a fixed H₂ partial pressure (13.3 kPa), as shown in Figure 6 for xPt0.24Fe-DeAlBEA, where x = 0.04, 0.005, and 0.001 (plots of the data for 0.01Pt0.24Fe and 0.0025Pt0.24Fe-DeAlBEA are shown in Figure S39 in the SI). The rate of propene formation is observed to increase with both propane partial pressure and temperature.

To facilitate the identification of the effects of catalyst Pt content, Figure 7a shows the order of reaction in propane partial pressure as a function of the reaction temperature. Notable in this figure is the evidence that the trends in the order in propane partial pressure with temperature differ depending on the Pt loading. Catalysts with high Pt loadings (Pt/Al₀ = 0.04, 0.01, 0.005) are characterized by data showing that the reaction order decreases with increasing temperature, suggesting stronger reactant inhibition at higher temperature. By contrast, data characterizing the catalysts with lower Pt loadings (Pt/Al₀ = 0.0025, 0.001), show that the reaction order increases with temperature. However, at 753 K, all catalysts exhibit similar reaction orders (~0.61–0.64). A shift in the propane reaction order suggests a change in the reaction mechanism as the Pt transitions from nanoparticles to atomically dispersed species, consistent with trends observed in the CO-IR and XAS data.

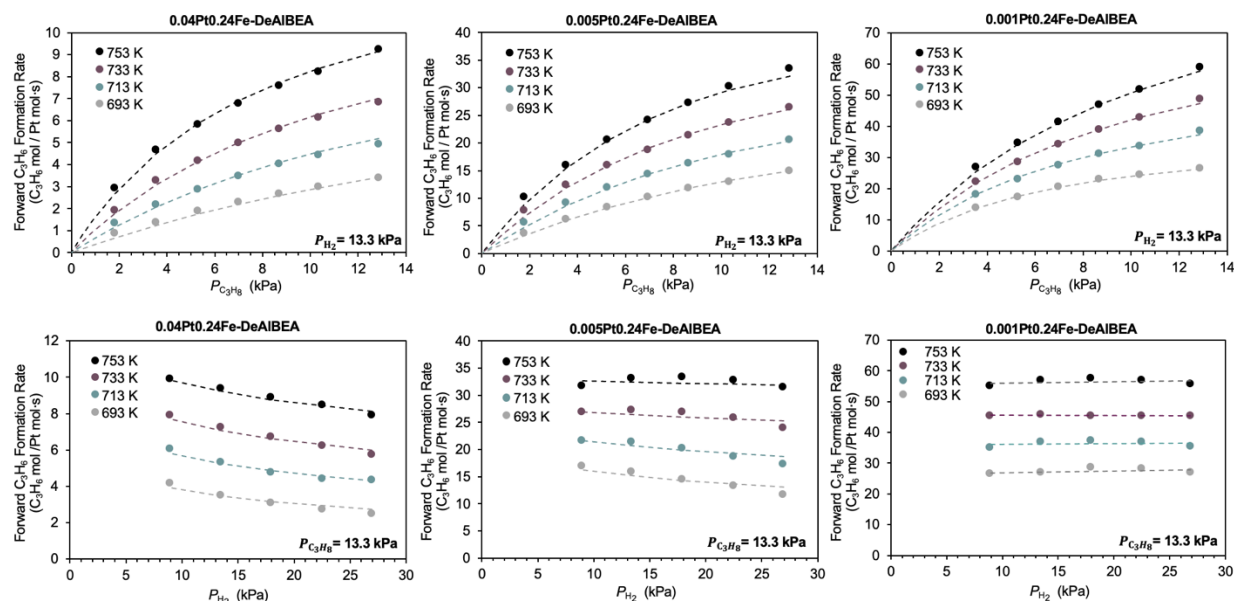


Figure 6. Forward propene formation rate as a function of propane and H_2 partial pressures characterizing $xPt0.24Fe$ -DeAlBEA catalysts, where $x = 0.04, 0.005, 0.001$ (Reaction conditions: $P_{C_3H_8} = 1.7\text{--}13.3$ kPa (fixed $P_{H_2} = 13.3$ kPa) and $P_{H_2} = 9\text{--}27$ kPa (fixed $P_{C_3H_8} = 13.3$ kPa), 693–753 K, catalyst pre-treated in H_2 at 832 K, feed rate 233 mL(NTP)/min, catalyst mass 5 mg, C_3H_6 selectivity > 98.5%, and C_3H_8 conversion $\leq 6\%$). Model fit is represented by dashed lines. Details in SI.

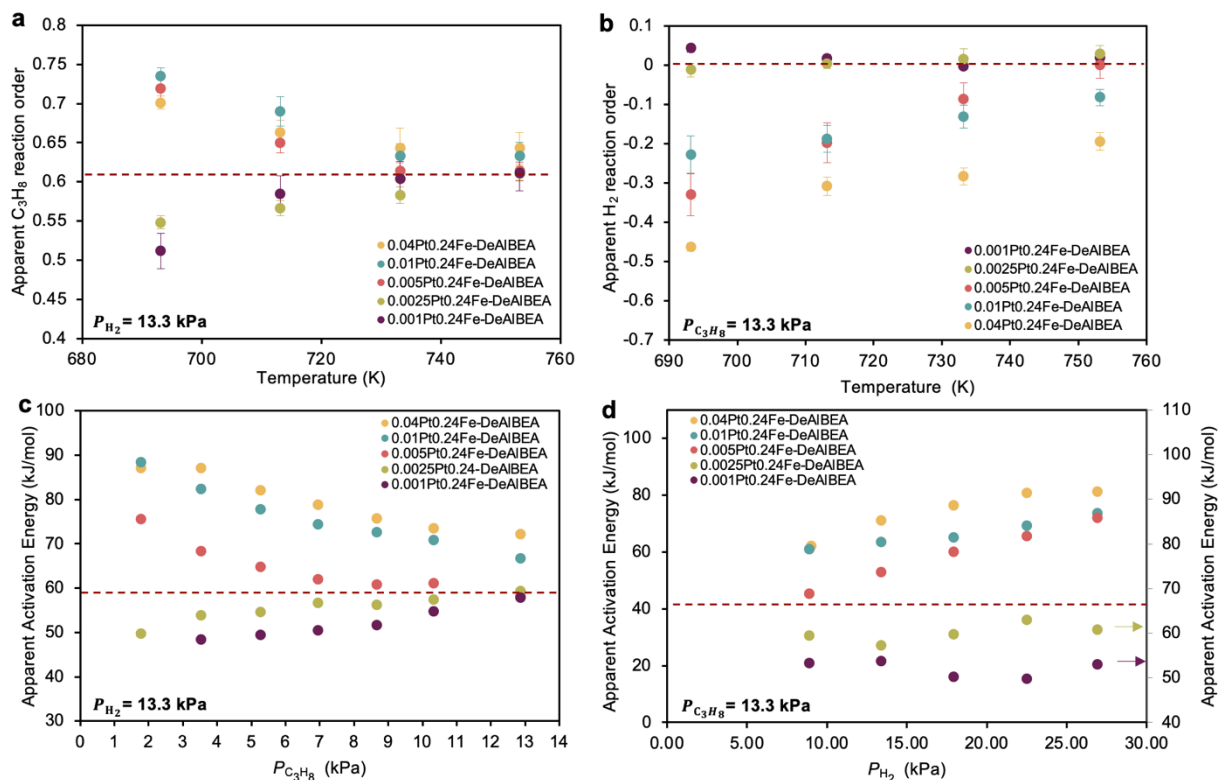
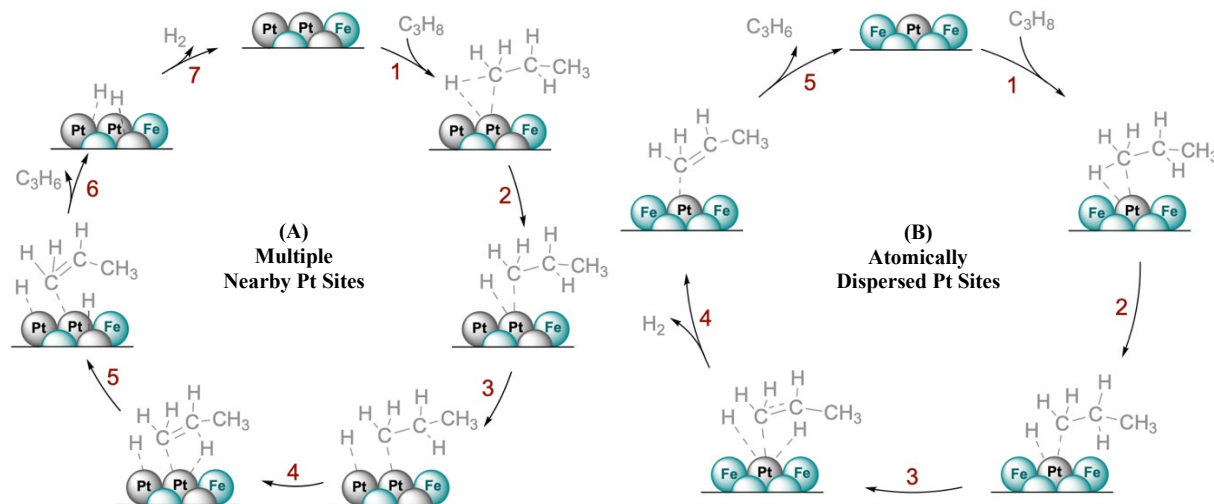


Figure 7. Reaction order with respect to (a) C_3H_8 and (b) H_2 as a function of temperature. Apparent activation energy as a function of (c) C_3H_8 partial pressure and (d) H_2 partial pressure characterizing $xPt0.24Fe$ -DeAlBEA catalysts

(Reaction conditions: $P_{C_3H_8}$ = 1.7–13.3 kPa (fixed P_{H_2} = 13.3 kPa) and P_{H_2} = 9–27 kPa (fixed $P_{C_3H_8}$ = 13.3 kPa), temperature 693–753 K, catalyst H_2 -pre-treated at 832 K, feed flow rate 233 mL(NTP)/min, catalyst mass 5 mg, C_3H_6 selectivity > 98.5%, and C_3H_8 conversion $\leq$ 6%).

The second set of experiments was performed to assess the influence of H_2 partial pressure (9–27 kPa) at a fixed propane partial pressure (13.3 kPa) for reaction at temperatures of 693–753 K. The results of these experiments are shown in Figure 6. The catalysts with high Pt loadings (Pt/Al_0 = 0.04, 0.01) are characterized by propene formation rates that decrease with increasing H_2 partial pressure, suggesting inhibition by H_2 . The catalyst with the intermediate Pt loading (Pt/Al_0 = 0.005) is characterized by rates showing a slight decrease with respect to H_2 partial pressure at lower temperatures (Figure 6). At 753 K, the dependence of rate on H_2 partial pressure showed a behavior similar to that of the catalysts with the lowest Pt loadings, increasing slightly from 31 to 33 C_3H_6 /(mol Pt·s), peaking at 17.9 kPa of H_2 partial pressure before decreasing slightly. Data characterizing the catalysts with the low Pt loadings (Pt/Al_0 = 0.0025, 0.001) show that the propene formation rate increases slightly with respect to H_2 partial pressure, reaching a maximum at 17.9 kPa, with an increase of less than 4%, indicating that the rate of PDH is nearly independent of H_2 partial pressure. The data determining reaction orders show a negative dependence on H_2 partial pressure for catalysts with high Pt loadings, and the order became less negative with increasing temperature, as shown in Figure 7b. Conversely, catalysts with low Pt loadings (Pt/Al_0 = 0.0025, 0.001) are characterized by near-zero reaction orders with respect to H_2 , reflecting its limited influence. These results again suggest a shift in reaction mechanisms with a change in the Pt dispersion—catalysts with high Pt loadings, containing clusters, are more affected by H_2 and propane partial pressures, whereas the catalysts incorporating atomically dispersed Pt exhibit minimal sensitivity to the partial pressures of these components.

We propose that PDH on Pt clusters containing Pt or Pt and Fe atoms proceeds via the pathway shown in Scheme 1A. The choice of this mechanism is motivated by our prior analysis of it using density functional theory (DFT).⁷⁷ This prior investigation confirmed that the reaction begins with propane physisorption on a single Pt site, followed by α -hydride abstraction on the same Pt atom to form a propyl group and a hydrogen atom. The hydrogen atom then migrates to a nearby Pt site, minimizing the system energy. Next, β -hydride elimination from the propyl group forms propene, followed by further hydrogen migration and propene desorption. The cycle is completed with the recombination of two hydrogen atoms on adjacent Pt sites and the subsequent desorption of H_2 .



Scheme 2. Proposed reaction mechanisms for propane dehydrogenation (A) on multiple nearby Pt sites and (B) on atomically dispersed Pt sites. The accurate structure of atomically dispersed Pt is shown in Scheme 1.

The rate expression for propene formation, based on a Langmuir–Hinshelwood mechanism with uniform catalytic sites and assuming that the first C–H bond cleavage is the rate-determining step, is shown in Scheme 2A. This expression, normalized by the number of active sites, is provided in Table 2, with the fitted data presented as dashed lines in Figure 6. The parameters determined in the data fitting, including the intrinsic activation energy (E_2), propane adsorption energy (ΔH_1), and hydrogen desorption energy (ΔH_7), were obtained from Arrhenius and van't Hoff plots (refer to Tables S26–30 in the SI for more details). As shown in Table 2, the intrinsic activation energy for propane dehydrogenation is nearly the same for the three catalysts with Pt/Al₀ ratios of 0.04, 0.01, and 0.005, ranging from 28 to 29.1 kJ/mol. The heat of propane adsorption increases slightly in magnitude from -40 kJ/mol for Pt/Al = 0.04 to -42 kJ/mol for Pt/Al = 0.01. Attempts to fit the data for Pt/Al₀ = 0.005, as shown in Figure 6, led to unphysical values of E_2 and ΔH_1 . For this reason, we chose to fit the rate data for this catalyst with a rate equation that interpolates between the rates characterizing catalysts with the highest and lowest Pt/Al ratios (0.04 and 0.001, respectively). This approach resulted in a very good representation of the kinetics for 0.005Pt0.24Fe-DeAlBEA, taking the fraction of active Pt sites associated with 0.04Pt0.24Fe-DeAlBEA to be 0.52 and the fraction of active Pt sites associated with 0.001Pt0.24Fe-DeAlBEA to be 0.48 (Figure S40 in the SI).

Table 2 shows that ΔH_7 and ΔS_7 values decrease with Pt loading, a trend consistent with theoretical predictions.⁷⁸ At lower Pt loadings, Pt atoms are surrounded by Fe, which donates electron density, shifting the Pt d-band center downward and weakening the Pt–H bond. This result aligns with DFT studies showing a reduced enthalpy of hydrogen adsorption as the Fe content increases from that in Pt₃ to that in Pt₂Fe and then PtFe₃, explaining the observed trend.⁷⁸ Notwithstanding this alignment with theoretical predictions, the measured ΔH_7 value (255 kJ/mol) (and ΔS_7 (0.288 kJ/mol·K)) for 0.04Pt0.24Fe-DeAlBEA is higher than the typical literature range for the heat of H₂ desorption/adsorption on Pt single crystals^{79,80} and PtFe alloys⁷⁸, which is between -50 kJ/mol and -90 kJ/mol. Likewise, the entropy of adsorption is not expected to be lower than that associated with complete loss of all entropy for gas-phase H₂ (-0.160 kJ/mol·K).⁸¹

To address this discrepancy, alternative mechanisms were explored, as shown in Table S21. For instance, a two-site model proposed by Zhu et al.²¹, which involves C–H bond activation through two Pt atoms, was tested. This model yielded a reasonable hydrogen desorption enthalpy (92 kJ/mol). However, this scenario resulted in an unrealistic outcome whereby propane adsorption appeared to be endothermic (52 kJ/mol), implying stronger adsorption at higher temperatures. But such behavior could occur in the presence of strong competitive adsorption between propane and hydrogen, whereby hydrogen adsorbs preferentially at lower temperatures. According to this interpretation, as the temperature increases, hydrogen coverage decreases significantly, freeing up sites for propane adsorption, thereby increasing propane coverage at higher temperatures. However, this explanation remains speculative, as endothermic adsorption of propane contradicts thermodynamics expectations. Therefore, although the mechanism we propose provides ΔH_7 values that deviate from typical literature ranges, it remains the most reasonable framework for capturing the observed propane adsorption energy and intrinsic activation energy trends. Notably, intrinsic activation energy values for supported Pt catalysts range from 34–90 kJ/mol (Table S39), based on various mechanisms and in the absence of H₂.

Table 2. Kinetics fitting parameters for xPt0.24Fe-DeAlBEA catalysts.

Catalyst	Rate expression	E_2 (kJ/mol)	ΔH_1 (kJ/mol)	ΔH_7 (kJ/mol)	ΔS_1 (kJ/mol·K)	ΔS_7 (kJ/mol·K)
0.04Pt0.24Fe-DeAlBEA	$r_f = \frac{k_2 K_1 P_{C_3H_8}}{(1 + K_1 P_{C_3H_8} + K_7^{-0.5} P_{H_2}^{0.5})}$	29.1 ± 3.5	-40.6 ± 5.4	255 ± 22	-0.014 ± 0.007	0.288 ± 0.030
0.01Pt0.24Fe-DeAlBEA		28.7 ± 0.9	-42.0 ± 4.5	378 ± 7	-0.031 ± 0.006	0.498 ± 0.105
0.0025Pt0.24Fe-DeAlBEA	$r_f = \frac{k_2 K_1 P_{C_3H_8}}{(1 + K_1 P_{C_3H_8})}$	73 ± 3	-34.6 ± 1.9	-	-0.026 ± 0.002	-
0.001Pt0.24Fe-DeAlBEA		72.2 ± 9.5	-38.8 ± 4.1	-	-0.033 ± 0.005	-

The behavior of atomically dispersed Pt sites in the two catalysts with the lowest Pt loadings can be explained by a similar mechanism, as displayed in Scheme 2B. In this mechanism, propane physisorbs on an isolated Pt atom surrounded by Fe atoms and then undergoes α -hydride abstraction followed by β -hydride elimination. The two hydrogen atoms combine on the same Pt atom and desorb as H₂, followed by propene desorption. The rate expression in Table 2 is independent of H₂ partial pressure, consistent with the results shown in Figure 6. The slightly higher adsorption strength for 0.001Pt0.24Fe-DeAlBEA compared with 0.0025Pt0.24Fe-DeAlBEA is subtle and falls within the range of heats of adsorption observed for the highest Pt loading. Despite the higher activation energy, the reaction rate can still be higher if the pre-exponential factor is sufficiently large. For the 0.001Pt0.24Fe-DeAlBEA catalyst at 753 K, the intrinsic activation energy is 72 kJ/mol, with a pre-exponential factor of 1.1×10^7 mol C₃H₆/(mol Pt·s·bar), resulting in a forward rate constant (k_2) of 110 mol C₃H₆/(mol Pt·s·bar). In contrast, for the catalyst with the highest Pt loading (0.04Pt0.24Fe-DeAlBEA), the pre-exponential factor is 1.5×10^3 mol C₃H₆/(mol Pt·s·bar), and k_2 is 14.8 C₃H₆/(mol Pt·s·bar). This comparison indicates that the system compensates for the higher activation energy by significantly increasing the frequency of successful reactions, as reflected by the large pre-exponential factor in the atomically dispersed Pt catalysts.

The apparent activation energy for PDH also depends on the loading of Pt as well as the partial pressures of propane and H₂. As shown in Figure 7c, at a fixed H₂ partial pressure, the apparent activation energy decreases with increasing propane partial pressure for catalysts with Pt loadings of Pt/Al₀ = 0.04–0.005 but increases with propane partial pressure for catalysts with Pt loadings of Pt/Al₀ = 0.0025 and 0.001. At a fixed propane partial pressure, the apparent activation energy increases with H₂ partial pressure for catalysts with Pt loadings of Pt/Al₀ = 0.04–0.005 but is nearly independent of H₂ partial pressure for catalysts with Pt loadings of Pt/Al₀ = 0.0025 and 0.001. These results again point to a difference in the mechanism of PDH for catalysts with higher and lower loadings of Pt. The three catalysts with the highest Pt loadings are characterized by apparent activation energies, E_{app} , predicted by the models (Table S37) that depend on propane surface coverage ($\theta_{C_3H_8}$) and hydrogen surface coverage (θ_H), expressed as $E_2 + (1 - \theta_{C_3H_8})\Delta H_1 + 0.5\theta_H \Delta H_7$. However, the two catalysts with the lowest Pt loadings are characterized by values of E_{app} that vary only with propane partial pressure, being expressed as $E_2 + (1 - \theta_{C_3H_8})\Delta H_1$. The fitted E_{app} graphs representing the data are presented in Table S38 of the SI. The models, using fitted parameters for intrinsic activation energies and enthalpies of adsorption, accurately capture the observed trends in E_{app} , confirming the reliability of the proposed mechanisms to describe the relationships between Pt loading, reaction kinetics, catalyst surface coverage, and apparent activation energy.

Comparisons of the performance of catalysts with various Pt-containing species reported by various researchers are complicated by differences in the reaction conditions, including temperature, feed composition, and feed space velocity. Because PDH is a reversible reaction, with the rate of the back reaction typically being significant, the net rate of propene formation at a given temperature is an inappropriate metric for comparing different catalysts unless the measurements of propene formation are acquired at differential propane conversions, which is not commonly the case. For these reasons, we have chosen to use the apparent first-order forward rate coefficient characterizing propene formation, k_f , as the appropriate metric of catalyst performance. Details concerning the calculation of k_f are given in Section S.3.11 of the SI. Figure 8 provides a comparison of the values of k_f for 0.001Pt0.24Fe-DeAlBEA with those reported for other PtFe and Pt-containing PDH catalysts. Although k_f may be underestimated for 0.001Pt0.24Fe-DeAlBEA because it neglects inhibition by adsorbed propane, it remains a reliable metric for comparing catalysts at a common temperature. The figure shows that 0.001Pt0.24Fe-DeAlBEA achieves the second-highest reported value of k_f (404 mol C₃H₆/(mol Pt·bar·s)), after PtSn/DeAlBEA-0.00113¹⁴ (813 mol C₃H₆/(mol Pt·bar·s)). However, 0.001Pt0.24Fe-DeAlBEA exhibits a high propene selectivity (99.6%) and a forward formation rate of 63.9 mol C₃H₆/(mol Pt·s). In contrast to PtSn/DeAlBEA-0.001, which contains Pt clusters, 0.001Pt0.24Fe-DeAlBEA does not contain Pt clusters, which means that this new Fe-containing catalyst exhibits a higher utilization of Pt, which is atomically dispersed. The value of k_f for this catalyst in the presence of hydrogen is higher than that of other PtFe catalysts, such as Pt-Fe-Silicalite-1¹⁹ and Pt0.0015@Fe50-MWW,²⁰ which have k_f values of 120.7 and 221 mol C₃H₆/(mol Pt·bar·s), respectively (Table S40).

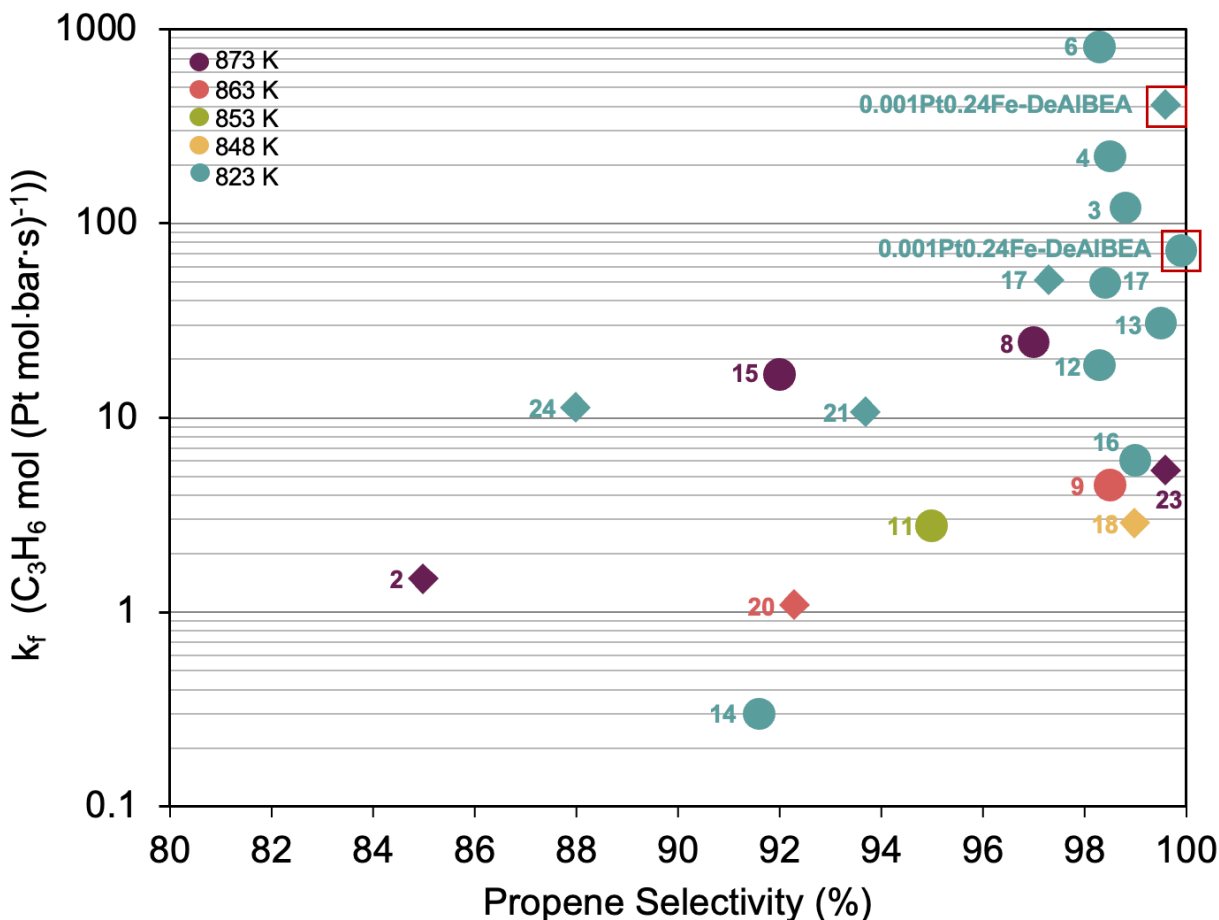


Figure 8. Comparison of forward rate coefficient k_f for PDH for Pt-containing catalysts. The catalysts include: PtFe@Pt/SBA-15⁸²(2), Pt-Fe-Silicalite-1¹⁹(3), Pt0.0015@Fe50-MWW²⁰(4), PtSn-DeAlBEA-0.001¹⁴(6), K-PtSn@MFI¹⁶(8), PtSnAl_{0.2}/SBA-15⁸³(9), PtSn/2Mg-SBA-15⁸⁴(11), PtZn4@S-1-H⁸⁵(12), 0.04Pt-0.36Zn-DeAlBEA¹²(13), Pt-Zn/Na-Y⁸⁶(14), GaPt@S-1¹⁷(15), PtGa/SiO₂¹⁸(16), Pt(0.5)Mn/SiO₂⁸⁷(17), Pt-Sn/Al₂O₃⁸⁸(18), PtSnK/ZSM-5⁸⁹(20), Pt/Mg(Sn)(Al)O@Al₂O₃⁹⁰(21), PtGa/CeO₂-Al₂O₃⁹¹(23), 0.1Pt10Cu/Al₂O₃¹³(24). Except for the data represented by diamonds (◆), all experiments were conducted without cofed H₂. The numbers in the figure correspond to selected catalysts from Table S40 in the SI.

Conclusions

This study examines the effects of Pt dispersion and interactions with Fe in the family of catalysts xPt0.24Fe-DeAlBEA on the PDH activity. In the as-synthesized catalysts, Pt is present predominantly as Pt²⁺ surrounded only by Pt–O bonds. CO-IR spectra show that, in catalysts with low Pt/Al₀ ratios (0.001–0.0025), Pt is atomically dispersed, with no evidence of clustering. After H₂ reduction at 823 K, EXAFS data reveal that, at Pt/Al₀ ratios of 0.0025 and 0.001, Pt is atomically dispersed and exhibits an average Pt–Fe coordination number of 6, whereas, at high Pt/Al₀ ratios (e.g., 0.04), Pt is present as clusters which exhibit Pt–Pt and Pt–Fe bonds. Kinetics data show that the rate of PDH catalyzed by Pt clusters is characterized by a positive order in propane partial pressure that decreases with increasing temperature and a negative order in H₂ partial pressure that becomes less negative with increasing temperature, suggesting a mechanism involving propane adsorption on one site and hydrogen recombination across two nearby sites. In contrast, isolated Pt in Pt-Fe sites demonstrates an increasingly positive order in propane partial

pressure with increasing temperature and a zero-order dependence on H₂ partial pressure, consistent with a single-site mechanism dominated by propane inhibition. The catalyst with the lowest Pt loading shows the highest apparent forward rate constant for PDH, emphasizing the superior efficiency of atomically dispersed Pt in Pt-Fe sites for propane dehydrogenation.

ASSOCIATED CONTENT

Supporting Information

A detailed methods section outlines each experimental procedure, along with additional characterizations and analyses using XRD, BET, XPS, UV-vis, HAADF-STEM, XAS, and IR spectroscopy of adsorbed pyridine and carbon monoxide. It also includes an analysis of propane dehydrogenation kinetics based on various reaction mechanisms for five xPt_{0.24}Fe-DeAlBEA catalysts and a comparison of their PDH performances with those of platinum-containing catalysts reported in the literature.

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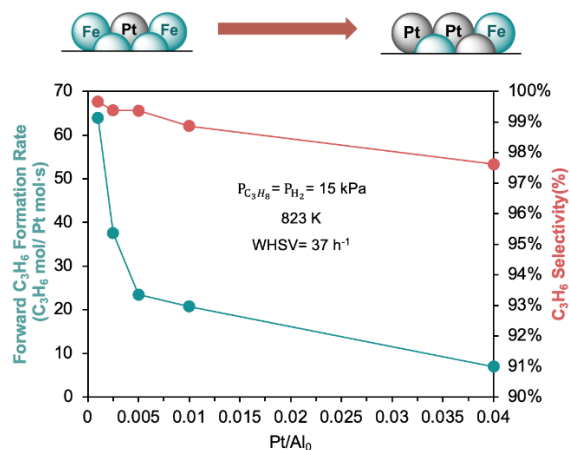
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