Coking-Resistant Sub-Nano Dehydrogenation Catalysts:

\[ \text{Pt}_n\text{Sn}_x/\text{SiO}_2 \ (n = 4, 7) \]

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ABSTRACT

We present a combined experimental/theoretical study of Pt\textsubscript{n}/SiO\textsubscript{2} and Pt\textsubscript{n}Sn\textsubscript{x}/SiO\textsubscript{2} (n = 4, 7) model catalysts for the endothermic dehydrogenation of hydrocarbons, using the ethylene intermediate as a model reactant. Mass-selected Pt\textsubscript{n} clusters were deposited onto amorphous SiO\textsubscript{2}/Si(100) to make the Pt\textsubscript{n}SiO\textsubscript{2} model catalysts. To produce Pt\textsubscript{n}Sn\textsubscript{x} clusters, size-selected Pt\textsubscript{n} were used to seed selective deposition of Sn on Pt via a self-limiting H\textsubscript{2}/SnCl\textsubscript{4}/H\textsubscript{2} reaction sequence. Model catalysts were analyzed using C\textsubscript{2}D\textsubscript{4} and CO temperature programmed desorption (TPD), low energy ion scattering (ISS), X-ray photoelectron spectroscopy (XPS), plane wave density functional theory (DFT) global optimization combined with a statistical mechanical description of the catalytic interface, and a DFT mechanistic study. Supported pure Pt\textsubscript{n} clusters are found to be highly active toward dehydrogenation of C\textsubscript{2}D\textsubscript{4}, quickly deactivating due to a combination of carbon deposition and sintering, resulting in loss of accessible Pt sites. Addition of Sn to Pt\textsubscript{n} clusters results in the complete suppression of C\textsubscript{2}D\textsubscript{4} dehydrogenation and carbon deposition, and also stabilizes the clusters against thermal sintering. Theory shows that both systems have thermal access to a multitude of cluster structures and adsorbate configurations that form a statistical ensemble. While Pt\textsubscript{4}/SiO\textsubscript{2} clusters bind ethylene in both di-\(\sigma\)- and \(\pi\)-bonded configurations, Pt\textsubscript{4}Sn\textsubscript{3}/SiO\textsubscript{2} binds C\textsubscript{2}H\textsubscript{4} only in the \(\pi\)-mode, with di-\(\sigma\) bonding suppressed by a combination of electronic and geometric features of the PtSn clusters. Dehydrogenation reaction profiles on the accessible cluster isomers were calculated using the climbing image nudged elastic band (CI-NEB) method. Dehydrogenation of di-\(\sigma\) bound ethylene is computed to dominant, and suppressed by Sn addition, in agreement with the experiments. DFT indicates that after Sn alloying, the barrier for ethane-to-ethylene conversion is lower than that for unwanted ethylene dehydrogenation.

KEYWORDS: dehydrogenation, cluster catalysis, fluxionality, coking, PtSn
INTRODUCTION

Carbon deposition ("coking") in high temperature reactions under hydrocarbon-rich conditions is a serious catalyst deactivation mechanism, thus understanding the mechanism and developing approaches to suppress carbon deposition are interesting. One reaction of this type is endothermic alkane dehydrogenation, and we have been examining carbon deposition over sub-nano Pt\(^1\) and Pt alloy cluster catalysts,\(^2-4\) with the goal of stabilizing the clusters against both coking and sintering, which is a serious problem for clusters at high temperatures. In addition to maximizing the accessibility of precious metal atoms in the surface layer, sub-nano clusters often have size-dependent properties that provide additional opportunities for catalyst tuning.\(^5-15\) Small clusters are also relatively tractable theoretically, thus these systems allow detailed modeling of the effects of cluster physical and chemical properties on reaction mechanisms.\(^9,16-22\) Even for a single cluster size, however, cluster reactions can be quite complex, with multiple structural isomers contributing and evolving during reactions due to thermal and adsorbate effects.

Because reducing coking on Pt-based catalysts is important in many applications, there have been many studies of mitigation strategies. Here we focus on use of Pt-Sn alloy catalysts for dehydrogenation and other reactions where coking is problematic. For example, coke formation has been studied on practical Pt catalysts\(^23-24\) and has been addressed by passivating specific metal sites with Sn, ranging from trace to stoichiometric amounts.\(^25-30\) Though successful, the complex nature of practical catalysts makes detailed understanding of the mechanistic origins of the Pt-Sn relationship and its beneficial effects on catalytic dehydrogenation difficult. It is useful, therefore, to consider model catalysts, including ordered surface alloys and planar supported cluster catalysts. Koel and co-workers studied the branching between alkene desorption and decomposition/dehydrogenation (leading to carbon deposition) on a series of ordered Pt-Sn surface
alloys, ranging from pure Pt(111) to an alloy with 2:1 Pt:Sn stoichiometry. With increasing Sn content, the desorption temperature for the alkenes decreased substantially, without any reduction in the saturation coverage. By decreasing the binding energy, desorption of intact alkenes becomes favored over further dehydrogenation. (i.e., coking is suppressed). It was found that the di-σ ethylene binding geometry was preferred for all the alloys, as well as for Pt (111). In a comparable study using DFT methods, ethane adsorption to extended Pt and PtSn surfaces was explored by Hook et al., who also found that ethylene binds in a di-σ fashion to both Pt and PtSn extended surfaces. As in the experiments, the ethylene adsorption energy decreased below the barrier for dehydrogenation of ethylene, resulting in suppression of dehydrogenation and carbon deposition. This was rationalized as being due to a combination of binding geometry and electronic effects.

For small PtSn supported nanoparticles, some differences have been noted. For example, Shen et al. and Natal-Santiago et al. studied adsorption geometries and energies of ethylene to silica-supported Pt and PtSn catalyst particles (diam. = 2-5 nm) using microcalorimetry and IR spectroscopy. The nano Pt catalyst supported both di-σ and π-bound ethylene, and incorporation of Sn resulted in a decrease in the heat of adsorption and an increase in the fraction of π-bound ethylene with increasing Sn content. The appearance of substantial π-bonding for small PtSn nanoparticles differs from the observation of purely di-σ bonding for extended PtSn surface alloys, suggesting significant effects of particle size. Sub-nanometer, or “ultra-dispersed” catalysts would therefore be expected to have additional differences in catalytic behavior. For example, in a study of propane dehydrogenation, Datye et al., examined 0.6 ± 0.2 nm Pt and PtSn particles on Al2O3. From a thermal stability perspective, it was proposed that Sn helped maintain the dispersion of Pt
particles under reaction and oxidative regeneration conditions, and that this was the major contributor to the prolonged activity for PtSn vs. pure Pt catalysts.

In another study with sub-nanometer particles, Ha and Baxter et al.\textsuperscript{14} added boron to size-selected Pt\textsubscript{n}/Al\textsubscript{2}O\textsubscript{3} model catalysts to suppress dehydrogenation/coking during ethylene temperature-programmed desorption/reaction (TPD/R). The model catalyst was well-defined enough to allow an accurate DFT model to be built and used to examine changes in energetics and mechanisms for ethylene binding/desorption from Pt\textsubscript{n}/Al\textsubscript{2}O\textsubscript{3}\textsuperscript{1} and Pt\textsubscript{n}B\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3}\textsuperscript{3}. Addition of boron suppressed di-\textsigma binding of ethylene, and substantially lowered the desorption energy, such that ethylene desorbed rather than undergoing dehydrogenation leading to carbon deposition.

Here we apply size-selection methods to study PtSn/SiO\textsubscript{2} model catalysts. Size- and composition-selected clusters were prepared by using mass-selected Pt\textsubscript{n} deposition to prepare planar SiO\textsubscript{2} supports decorated by a precisely controlled coverage of size-selected clusters. These were then used to seed highly selective Sn deposition on the clusters via a self-limiting reaction process. The composition and morphology were probed using X-ray photoelectron and low-energy ion scattering spectroscopies (XPS, ISS). Pt\textsubscript{n}/SiO\textsubscript{2} was chosen as the system, because the process used to deposit Sn is quite selective, depositing Sn almost exclusively on the Pt clusters, rather than on the SiO\textsubscript{2} support. We initially examined Sn modification of Pt\textsubscript{n}/alumina/NiAl(110) and Pt\textsubscript{n}/alumina/Ta(110), but found considerable non-selective Sn deposition on the alumina supports. Those systems have interesting catalytic activity,\textsuperscript{35} but for the purpose of studying Pt\textsubscript{n}Sn\textsubscript{x} clusters with well-defined composition, the SiO\textsubscript{2} support is better. Additional detail on catalyst preparation is available below in the Methods section, and a complete characterization of stoichiometry, size, and composition has been previously published.\textsuperscript{2} Here, we compare catalytic properties of Pt\textsubscript{4}/SiO\textsubscript{2} and Pt\textsubscript{7}/SiO\textsubscript{2} to these size- and composition-controlled Pt\textsubscript{4}Sn\textsubscript{3.3}/SiO\textsubscript{2} and
Pt$_7$Sn$_{6.3}$/SiO$_2$ bimetallic cluster catalysts. DFT calculations are used to examine structure and binding properties of the clusters for thermally populated cluster isomer ensembles for Pt$_4$/SiO$_2$ and Pt$_4$Sn$_3$/SiO$_2$. Note that the amorphous structure of the SiO$_2$ native oxide requires a large slab in the calculations. This factor, together with the need to consider the thermally accessible isomer ensembles, makes the DFT calculations quite expensive even for small PtnSn$_x$/SiO$_2$, and infeasible for larger clusters.

RESULTS AND DISCUSSION

In the following, we present experiments comparing Ptn/SiO$_2$ and PtnSn$_x$/SiO$_2$, for four clusters: Pt$_4$, Pt$_7$, Pt$_4$Sn$_{3.3}$, and Pt$_7$Sn$_{6.3}$. The theory results are focused on Pt$_4$/SiO$_2$ and Pt$_4$Sn$_3$/SiO$_2$, however, the experiments for Pt$_4$ and Pt$_7$ suggest that similar considerations should apply to the Pt$_7$ and Pt$_7$Sn$_{6.3}$ experiments. The two Ptn cluster sizes were selected because Pt$_4$ and Pt$_7$ had been studied previously on Al$_2$O$_3$ supports, with Pt$_4$ found to have all atoms exposed in the surface layer and Pt$_7$ having both single layer and prismatic 3D isomers, the latter of which was found to isomerize to a single layer structure upon adsorption of multiple ethylene molecules.$^1$ In addition, the low energy structures for Pt$_4$Sn$_3$/SiO$_2$ were already available from our paper describing the method for producing size- and composition-selected PtnSn$_x$/SiO$_2$ model catalysts.$^2$
Ethylene Desorption vs. Dehydrogenation. C$_2$D$_4$ and D$_2$ desorption from Pt$_4$/SiO$_2$ and Pt$_7$/SiO$_2$ are shown in Fig. 1. To examine the effects of repeated C$_2$D$_4$ exposure and heating, a total of four TPD/R runs were carried out, but the figure shows results only for the 1$^{st}$ (black) and 4$^{th}$ (blue) runs. The data for all four runs are shown in Fig. S1. Most experiments were done with C$_2$D$_4$ to avoid interference with H$_2$ detection from high background at mass 2, however, the background is also high at mass 28, corresponding to C$_2$D$_2$. Therefore, some experiments were done using C$_2$H$_4$ to look for acetylene desorption. None was observed. We also looked for ethane signal from possible hydrogenation processes, but the signals were negligible. Because cracking
of C$_2$D$_4$ to D$_2^+$ in the mass spectrometer is weak, this contribution to the D$_2$ signal has not been subtracted in the figure.

The figures also show the C$_2$D$_4$ desorption observed from a Pt-free SiO$_2$ substrate (green), indicating that for the 180 K C$_2$D$_4$ exposure temperature chosen, only a small amount of C$_2$D$_4$ desorbs from the SiO$_2$ substrate, and that SiO$_2$ does not support D$_2$ desorption. We tested the effect of lowering the dose temperature from 180 K to 150 K, observing a large increase in the desorption intensity from the SiO$_2$ support. The integrated C$_2$D$_4$ TPD signal after 180 K dosing on SiO$_2$ corresponds to $\sim 3.5 \times 10^{12}$ molecules/cm$^2$ – well below 1% of a monolayer.

For Pt$_n$/SiO$_2$ samples, C$_2$D$_4$ desorption also begins at 180 K, initially matching the desorption from SiO$_2$, but then continuing with much higher intensities before eventually declining and disappearing by $\sim$500 K. The signal between 180 K and $\sim$220 K is, therefore, attributed to desorption mostly from SiO$_2$ sites, while the signal at higher temperatures is attributed to desorption from sites associated with the Pt$_n$ clusters.

The temperature dependence for desorption of intact C$_2$D$_4$ is different for the two cluster sizes. For Pt$_4$, during the 1$^\text{st}$ TPD/R run, the desorption appears bimodal, with a strong and relatively sharp peak near 250 K, followed by a shoulder in the 350-400 K range, with a rapid intensity drop above 400 K. For Pt$_7$, C$_2$D$_4$ desorption grows more slowly at low temperatures, peaking broadly around 300 K, and declining gradually above 400 K. According to the DFT calculations, the ethylene binding energy of the C$_2$H$_4$/Pt$_4$/SiO$_2$ global minimum structure, where the ethylene is bound in the di-$\sigma$ mode, is roughly 0.14 eV stronger than in the second local minimum structure (23% population at 700 K), where ethylene is $\pi$-bonded. More detailed discussion can be found in the DFT analysis section.
For the 1st run on both Pt4 and Pt7, significant D2 desorption starts just below 300 K and peaks broadly around 440 K, declining to baseline above 600 K. The D2 signal is significantly larger for Pt7 than Pt4. In one experiment, the heat ramp was extended to 1000 K to check for additional C2D4 or D2 desorption above 700 K. None was observed, suggesting that dehydrogenation and desorption go to completion by 700 K. The behavior observed here for Pt4/SiO2 and Pt7/SiO2 is similar to that observed for Ptn/Al2O3 (n =4, 7), with intact C2D4 desorption peaking near 300 K, and D2 desorption in the ~300 – 600 K range.¹

The integrated numbers of C2D4 and D2 molecules desorbing from each sample are listed in Table 1, and because we know the Pt coverage precisely (1.5 x 10¹⁴ atoms/cm²), the integrated desorption numbers are given as molecules per Pt atom. To correct the numbers for the contribution of desorption from the SiO2 substrate, ~0.02 C2D4 molecules/Pt atom should be subtracted. With this correction, we find that ~1.4 and ~2.1 intact C2D4 molecules desorb per Pt4 and Pt7 cluster, respectively, with the corresponding D2 desorption being ~0.33 and ~0.77 D2 molecules per cluster. Given that D2 desorption goes to completion before termination of the heat ramp, the total number of C2D4 adsorbed per cluster can be estimated as #C2D4 desorbing + 0.5 #D2 desorbing, giving ~1.6 and ~2.5 C2D4 adsorbed per Pt4 and Pt7, respectively. In theoretical modeling of Pt4/SiO2, we therefore considered coverages of one and two ethylene molecules per cluster. As expected, the number of adsorbed ethylene per cluster increases with cluster size, however, on a per Pt atom basis, slightly more ethylene adsorbs on Pt4. This effect is consistent with the observation by ISS,² that Pt7/SiO2 has a smaller fraction of its Pt atoms in the surface layer, and thus presents fewer ethylene binding sites.
Fig. 1 also shows the 4th TPD/R run for each sample. Two significant changes are observed: the amount of ethylene desorbing is lower than in the 1st run, and the desorption occurs at lower temperatures. In addition, D₂ desorption is substantially weaker, compared to the 1st TPD/R run. The changes are qualitatively similar for the two cluster sizes, but more dramatic for Pt₇, where more dehydrogenation occurred in the 1st run. These changes imply that substantially less ethylene adsorbs at 180 K, and that the decrease primarily affects the more stable binding sites responsible for desorption at higher temperatures. As will be shown shortly, stronger binding typically corresponds to the di-σ mode of ethylene attachment, which is a precursor for dehydrogenation, which then poisons those sites by carbon deposits. As shown in Fig. S1, the 2nd, 3rd, and 4th TPD/R runs are quite similar, implying that most of the changes to the binding site distribution occur in the 1st TPD/R run. In the 4th TPD run, the differences between Pt₄/SiO₂ and Pt₇/SiO₂ are weaker than in the first, but the Pt₄ sample still had significantly more ethylene desorbing, and with sharper temperature dependence, compared to the Pt₇ sample. Given that both samples had the same total number of Pt atoms, the samples clearly retained at least some memory of the deposited cluster size after repeated TPD/R runs.

**Table 1.** Numbers of C₂D₄ and D₂ molecules desorbing per Pt atom from Fig. 1.

| TPD Run | Pt₄/SiO₂          | Pt₇/SiO₂          |
|---------|-------------------|-------------------|
| 1st     | 0.350 C₂D₄/Pt     | 0.303 C₂D₄/Pt     |
|         | 0.083 D₂/Pt       | 0.110 D₂/Pt       |
| 2nd     | 0.340 C₂D₄/Pt     | 0.282 C₂D₄/Pt     |
|         | 0.076 D₂/Pt       | 0.066 D₂/Pt       |
| 3rd     | 0.270 C₂D₄/Pt     | 0.226 C₂D₄/Pt     |
|         | 0.046 D₂/Pt       | 0.050 D₂/Pt       |
| 4th     | 0.270 C₂D₄/Pt     | 0.187 C₂D₄/Pt     |
|         | 0.024 D₂/Pt       | 0.028 D₂/Pt       |
Run-to-run losses in the number of C$_2$D$_4$-Pt sites selectively affects the most-strongly bound C$_2$D$_4$-Pt sites, and because these are most likely to catalyze dehydrogenation, a run-to-run reduction in D$_2$ desorption is expected, and observed. Given the observation of D$_2$ desorption, the loss of C$_2$D$_4$ binding sites in repeated C$_2$D$_4$ TPD runs is at least partially attributable to poisoning by carbon deposition. We show below using XPS that repeated ethylene TPD runs lead to carbon deposition, although the precise amount was difficult to measure because the sensitivity for carbon is relatively low, and the Pt coverage (where C is depositing) is also very low.\textsuperscript{1} DFT calculations on Pt$_8$/Al$_2$O$_3$ and Pt$_8$/Al$_2$O$_3$ with a carbon atom deposited were done to examine changes in cluster morphology and energetics, showing that deposition of electrophilic C causes some rearrangement in cluster geometry.\textsuperscript{1} Note, however, that supported Pt$_n$ clusters are expected to be quite dynamic under reaction conditions, sintering is also likely.

Because we have $\sim$3 x 10$^{-11}$ Torr of CO background in our UHV system, we always monitor CO desorption during TPD/R experiments. Here, $\sim$0.2 CO molecules desorbed \textit{per} Pt atom during the 1\textsuperscript{st} run, with substantially less in subsequent runs. This CO contamination level is $\sim$20 times larger than would be expected if CO sticks only when impinging directly on a Pt site, and shows that for small, well dispersed clusters, substrate-mediated adsorption (reverse spillover) substantially amplifies the contamination rate. Assuming that CO competes with C$_2$D$_4$ for binding sites, there probably would have been additional C$_2$D$_4$ and D$_2$ desorption observed in the 1\textsuperscript{st} TPD/R runs in absences of CO, and the difference between the 1\textsuperscript{st} and subsequent runs would have been larger.
Analogous C$_2$D$_4$ TPD/R experiments for PtSn alloy clusters are shown in Fig. 2, with all four TPDs shown in Fig. S2. In this case, the 1st run was done just after completing the H$_2$/SnCl$_4$/H$_2$ exposure process used to deposit Sn, and prior to any heating. At this point there would have been H as well as a small amount of Cl adsorbed on the clusters. Therefore, it is not surprising that the amount of C$_2$D$_4$ desorbing in this 1st run is substantially smaller than in the 1st run for Pt$_n$/SiO$_2$, because many C$_2$D$_4$ binding sites would have been blocked during the 180 K C$_2$D$_4$ exposure. During this 1st TPD/R run, significant HCl desorption was observed (Fig. S3.), and no Cl was desorbing.

**Figure 2.** Desorption of C$_2$D$_4$ (top) and D$_2$ (bottom) from the first (red), second (black), and fourth (blue) C$_2$D$_4$ TPD/R run. Each spectra was collected after a 10 L dose of C$_2$D$_4$ to Pt$_n$/SiO$_2$ ($n = 4, 7$) at 180 K. C$_2$D$_4$ desorption from bare SiO$_2$ treated with 1 ALD cycle is also plotted (green) – no D$_2$ was observed in that experiment.
detectable by TPD/R, ISS, or XPS after the 1st run. H₂ desorption was not monitored due to large mass 2 background, but 700 K is well above the temperature where hydrogen desorbs from Ptₙ.¹

In the 2nd TPD/R run on each sample, the amount of C₂D₄ desorbing increased substantially, indicating that desorption of HCl and H₂ during the 1st run left more binding sites accessible to C₂D₄. Therefore, we feel that the correct comparison is of the 2nd TPD/R run for PtₙSnₓ/SiO₂, with the 1st run for the Ptₙ/SiO₂ samples. As before, the number of the C₂D₄ molecules desorbing per Pt atom in the 2nd, 3rd, and 4th TPD/R runs is given in Table 2.

**Table 2.** Numbers of C₂D₄ molecules desorbing per Pt atom from Fig. 2 and Fig. S2.

| TPD Run:      | PtₙSn₃.₃/SiO₂       | PtₙSn₆.₃/SiO₂       |
|---------------|---------------------|---------------------|
| 2nd           | 0.190 C₂D₄/Pt       | 0.176 C₂D₄/Pt       |
| 3rd           | 0.210 C₂D₄/Pt       | 0.170 C₂D₄/Pt       |
| 4th           | 0.190 C₂D₄/Pt       | 0.174 C₂D₄/Pt       |

There are several important points of comparison with the results for pure Ptₙ/SiO₂. First, there was no significant D₂ desorption in any run on the PtₙSnₓ/SiO₂ samples, i.e., all ethylene desorbed intact. The absence of D₂ desorption implies that there should be little if any carbon deposition. **Fig. S4** summarizes an XPS experiment that shows substantial carbon deposition in repeated TPD/R runs on Ptₙ/SiO₂, and the complete absence of carbon deposition for PtₙSnₓ/SiO₂ under identical conditions.

Also consistent with the absence of carbon deposition, is the observation that once the H and Cl were desorbed during the 1st run, there was little change in the intensity or temperature dependence of C₂D₄ desorption in TPD runs two through four, compared to the substantial loss of intensity and shifts to lower temperatures observed for pure Ptₙ/SiO₂. Additionally, the number of C₂D₄ molecules adsorbing during the 180 K dose was ~50% smaller for the PtₙSnₓ, compared to the pure
Pt$_n$, presumably due to site blocking by Sn atoms (note difference in vertical scales). Finally, for the Pt$_n$Sn$_x$/SiO$_2$ samples there are cluster size effects on the desorption temperature dependence, weaker than the size effects observed for Pt$_n$/SiO$_2$, but which are quite persistent in repeated runs. From the perspective of improving the stability of sub-nano Pt cluster catalysts under high temperature hydrocarbon rich conditions, the absence of dehydrogenation (i.e., of carbon deposition) and the stability of the samples in repeated TPD/R runs are both important.

The C$_2$D$_4$ thermal desorption spectra were fit to extract desorption energy distributions, $\theta$(E$_{\text{des}}$), as described in the supporting information. An example fit is shown in Fig. S5, and the $\theta$(E$_{\text{des}}$) distributions for the 1st C$_2$D$_4$ TPD on Pt$_4$/SiO$_2$ and the 2nd C$_2$D$_4$ TPD on Pt$_4$Sn$_{3.3}$/SiO$_2$ are compared in Fig. 3. $\theta$(E$_{\text{des}}$) distributions for Pt$_7$/SiO$_2$ and Pt$_7$Sn$_{6.3}$/SiO$_2$ are shown in Fig. S6. Three features were included in the $\theta$(E$_{\text{des}}$) distributions to fit the experimental temperature dependences: a small feature with $E_{\text{des}} < 0.6$ eV attributed to desorption from SiO$_2$ sites, a larger feature with $0.6 < E_{\text{des}} < 1.2$ eV attributed to desorption from cluster sites, and a second feature with $0.8 < E_{\text{des}} < 1.6$ eV also attributed to desorption from cluster sites. Note that there is little difference in the range of $E_{\text{des}}$ observed for Pt$_n$ and Pt$_n$Sn$_x$, consistent with the modest differences in desorption temperatures.
The effects of Sn-alloying on the Pt₁₆/SiO₂ system should be compared to the effects of Sn alloying on ordered PtSn surface alloys studied by Koel and co-workers. In both cases, ethylene dehydrogenation, leading to carbon deposition, is strongly suppressed, compared to pure Pt₁₆/SiO₂ or to Pt(111), but the mechanism appears to be different. For the PtSn surface alloys, the saturation ethylene coverage was Sn-independent, whereas for the clusters, Sn significantly reduced the coverage. For the surface alloys, the ethylene desorption temperature dropped with increasing Sn coverage from ~285 K for pure Pt(111) to 184 K for the \( \sqrt{3} \times \sqrt{3} R30^\circ \) alloy which has 1:2 Sn:Pt ratio in the surface layer. Hook et al. used DFT to examine ethane dehydrogenation over PtSn surface alloys, finding, consistent with the experiments of Koel and co-workers, that Sn depresses the alkene desorption energy below the barrier for dehydrogenation, due to a combination of geometric and electronic effects. Thus in the surface alloys, the suppression of carbon deposition appears to

![Figure 3. Energy desorption \( (E_{\text{des}}) \) profiles for Pt₄/SiO₂ (top) and Pt₄Sn₃.₃/SiO₂ (bottom).](image)
be largely due to the reduction in ethylene binding energy. This was also the conclusion in our study of the effects of boron addition to Ptₙ/ alumina model catalysts,⁴ where boration shifted the ethylene desorption temperatures into the cryogenic range, thereby suppressing dehydrogenation. In contrast, for the Ptₙ vs. PtₙSnₓ clusters here, there is no significant difference between the ethylene desorption temperatures or the extracted Eₜₐₜ distributions, suggesting that suppression of dehydrogenation/carbon deposition must result from a different mechanism.

**ISS probing of the effects of TPD/R.**

ISS experiments were carried out to probe differences in the structure of the Ptₙ and PtₙSnₓ samples, and to provide insight regarding the changes in C₂D₄ and D₂ desorption behavior that occur in multiple TPD runs for Ptₙ/SiO₂. Peaks in ISS data result mostly from events in which He⁺ scatters from a single atom in the surface layer, such that the retained energy, Eₖ/Eₖ₀, depends on the target atom mass.³⁷ Multiple scattering, and scattering from atoms deeper in the surface result in low ion survival probability (ISP), and contribute mostly to the featureless background at low

![Figure 4. Raw ISS spectra for Ptₙ/SiO₂ samples after they have undergone four CO TPDs to 700 K (black) and four C₂D₄ TPDs (red).](image-url)
The usefulness of ISS here is that it is sensitive both to the cluster morphology and to the presence of adsorbates on the cluster surface, due to shadowing, blocking, and ISP effects.\textsuperscript{38-40}

**Fig. 4** summarizes ISS data for Pt\textsubscript{4} and Pt\textsubscript{7} samples after four cycles of C\textsubscript{2}D\textsubscript{4} TPD/R. The results are compared to ISS (on separate samples) after four cycles of CO TPD under identical conditions, to show the effects of TPD with a non-coking adsorbate. Peaks for O, Si, and Pt are observed. For comparison, the intensities of the Pt peak for as-deposited, unheated Pt\textsubscript{n}/SiO\textsubscript{2} samples are indicated in **Fig. 4** by blue stars. The O and Si intensities for the as-deposited samples are not shown because they are essentially identical to the post-TPD/R results in the figure. All the samples were prepared with the same total number of Pt atoms, therefore, if the same fraction of Pt atoms are exposed in the surface layer, the Pt ISS intensities should be identical. It can be seen that the as-deposited Pt intensity is highest for Pt\textsubscript{4}, and \textasciitilde28\% lower for Pt\textsubscript{7}, indicating that some of the Pt atoms in Pt\textsubscript{7}/SiO\textsubscript{2} are not in the surface layer, as would be the case for a 3D cluster structure.

After four CO TPD runs, the Pt intensities for both sizes decrease significantly. This decrease suggests significant sintering of the clusters, although there may also be some contribution from isomerization to structures with fewer atoms in the surface layer.\textsuperscript{1-2, 39, 41-42} To test for the possibility that CO adsorption might affect the sintering/isomerization process, a separate experiment was performed in which a Pt\textsubscript{4}/SiO\textsubscript{2} sample was simply flashed to 700 K four times in the absence of any deliberate adsorbate exposure. The resulting Pt ISS intensities were identical to those observed for clusters having undergone four CO TPDs, i.e., the effects are thermal, with no significant effect of small CO exposures.
The decreases in Pt ISS signal after 4 C\textsubscript{2}D\textsubscript{4} TPD/R experiments are substantially larger. This could be taken as evidence that C\textsubscript{2}D\textsubscript{4} enhances sintering, however, we know from the observation of D\textsubscript{2} desorption and the appearance of carbon in post-TPD/R XPS, that there is carbon deposition on these samples. The ISS results are, therefore, confirmation that this carbon is deposited on, and blocks access to Pt sites, as opposed to depositing on the SiO\textsubscript{2} support. Given that the clusters may also be sintering during TPD/R, it is most useful to compare the carbon deposition on a per Pt atom, rather than a per cluster basis. From the 1\textsuperscript{st} TPD/R run data in (Fig. 1), we can see that Pt\textsubscript{4} has a higher density of C\textsubscript{2}D\textsubscript{4} binding sites (0.43/Pt atom), than Pt\textsubscript{7} (0.36/Pt atom), and a lower D\textsubscript{2}/C\textsubscript{2}D\textsubscript{4} desorption ratio (0.23), compared to 0.36 for Pt\textsubscript{7}. If we assume each D\textsubscript{2} desorption results in deposition on one C atom, then for Pt\textsubscript{4} the 1\textsuperscript{st} TPD/R run deposits ~0.1 C/Pt atom, while for Pt\textsubscript{7}, it should deposit slightly more – 0.13 C/Pt. As can be seen from Fig. S1 the differences are smaller in subsequent TPD/R runs. After four runs, the final Pt ISS intensities are similar for the two clusters.

Analogous ISS experiments for Pt\textsubscript{n}Sn\textsubscript{x}/SiO\textsubscript{2} are shown in Fig. 5. Sets of...

**Figure 5.** Raw ISS Scans for Pt\textsubscript{4}Sn\textsubscript{3.3}/SiO\textsubscript{2} and Pt\textsubscript{7}Sn\textsubscript{6.3}/SiO\textsubscript{2} after four C\textsubscript{2}D\textsubscript{4} TPDs (red) and 4 CO TPDs (black)
PtSn/SiO\textsubscript{2} samples were prepared and exposed to either four C\textsubscript{2}D\textsubscript{4} TPD/R runs, or four CO TPD runs, then examined by ISS. It can be seen that the O and Si peaks are similar to those in the Pt/SiO\textsubscript{2} samples, as expected because Sn deposits primarily on the Pt clusters\textsuperscript{2} but that the Pt peak is substantially less intense, and a peak for Sn is observed.

It is also interesting to compare the post TPD ISS to ISS measured just after the H\textsubscript{2}/SnCl\textsubscript{2}/H\textsubscript{2} treatment (prior to any heating), and after the initial heating to drive off H and Cl. For the treated, unheated sample, the Sn peak is larger and the Pt peak is smaller (Sn:Pt ratio \approx 2) compared to those in Fig. 5, as might be expected for Sn initially deposited on top of the Pt clusters. After initial heating to drive off H and Cl, the spectrum is essentially identical to the post-TPD spectra shown in Fig. 5. i.e., neither of the repeated TPD/R experiments has any

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**Figure 6.** \textsuperscript{13}CO TPD after four CO TPDs (black line) and a \textsuperscript{13}CO TPD after four C\textsubscript{2}D\textsubscript{4} TPDs for Pt\textsubscript{n}/SiO\textsubscript{2} (red). CO desorption from SiO\textsubscript{2} is also shown (green)
significant effect on the ISS. The stability with respect to repeated C\textsubscript{2}D\textsubscript{4} TPD/R runs is a consequence of the absence of carbon deposition on the clusters. Consistent with the TPD/R data in Fig. 2, ISS shows that Sn alloying significantly reduces the number accessible Pt binding sites, but that the sites present are quite stable.

**CO desorption as a probe of accessible Pt sites.** The final approach used to probe the effects of repeated heating and C\textsubscript{2}D\textsubscript{4} exposure on the clusters was to carry out \textsuperscript{13}CO TPD after the C\textsubscript{2}D\textsubscript{4} TPD/R sequence (on different samples than those used for ISS characterization). Fig. 6 compares CO TPD measured for a sample first subjected to four C\textsubscript{2}D\textsubscript{4} TPD/R runs (red) to the CO desorption measured in the 4\textsuperscript{th} in a series of sequential CO TPDs (black). For comparison, CO desorption from the SiO\textsubscript{2}

![Graph](image)

**Figure 7.** CO TPD spectra of Pt\textsubscript{n}Sn\textsubscript{x}/SiO\textsubscript{2} after four CO TPDs (black) and four C\textsubscript{2}D\textsubscript{4} TPDs (red). The 2\textsuperscript{nd} \textsuperscript{13}CO TPD from H\textsubscript{2}/SnCl\textsubscript{4}/H\textsubscript{2} – SiO\textsubscript{2} is also shown (green).
substrate is also shown (green). The ion signals were converted to numbers of CO molecules using the process described above, and the integrated number of CO molecules indicated in the text on each frame of the figure have been corrected for CO desorbing from the SiO$_2$ substrate, i.e., the numbers correspond to the CO desorbing from Pt sites. For Pt$_4$ and Pt$_7$, repeated C$_2$D$_4$ TPD/R results in far larger attenuation of Pt-associated CO binding sites, and particularly of the sites with high $E_{\text{des}}$, compared to repeated CO TPD runs. This mirrors the ISS results, where C$_2$D$_4$ TPD/R caused a much larger Pt intensity attenuation.

**Fig. 7** shows the analogous results for Sn ALD-treated samples. In this case, the desorption shown for the substrate (“H$_2$/SnCl$_4$/H$_2$ – SiO$_2$”) is for SiO$_2$ subjected to the Sn ALD treatment, then heated to drive off any residual Cl or H, before being probed by CO TPD. For the Sn-treated samples, the differences in CO desorption for samples after repeated CO TPDs vs. repeated C$_2$D$_4$ TPD/R runs are much smaller than for the Sn-free Pt$_n$/SiO$_2$ samples. For Pt$_4$Sn$_{3.3}$, repeated C$_2$D$_4$ TPD/R runs resulted in a shift in intensity from the higher to the lower temperature desorption feature, with a ~14% decrease in the integrated number of CO molecules desorbing, compared to the effects of four CO TPD runs. For Pt$_7$Sn$_{6.3}$, similar, but smaller changes in the desorption temperature dependence were observed, and the integrated number of CO molecules desorbing was identical for the samples subjected to multiple CO or C$_2$D$_4$ TPD experiments. It is not clear why the difference between the effects of C$_2$D$_4$ and CO TPD/R was larger for the smaller cluster size, however, for such a small cluster it would not be surprising if the degree of sintering occurring during the TPD heat ramps is affected by whether the clusters are saturated by CO or by C$_2$D$_4$. Note that in the analogous experiments on pure Pt$_4$, both the low and high temperature desorption features decreased significantly more after C$_2$D$_4$ TPD/R, such that the decrease in total number of
CO binding sites was almost 60% bigger than in multiple CO TPDs. Clearly, the carbon deposition occurring during C2D4 TPD on pure Pt₄ has a large effect on the site availability.

**DFT Analysis of the Effects of Sn Alloying on Ethylene Binding and Dehydrogenation.** Supported cluster catalysts can have many structural isomers accessible in the ≤700 K temperature regime of interest here. These isomers can have similar energies, despite having different morphologies, with different morphologies favoring different binding sites and chemical character. It is important to consider these different isomers in the mechanism, because they are expected to be thermally-populated due to high fluxionality of the clusters in this temperature regime. Due to the large amount of sampling needed for the reliable exploration of the potential energy surfaces, we focus the theory on Pt₄/SiO₂ and Pt₄Sn₃/SiO₂.

From the experiments, an average of ~1.4 C₂D₄ molecules are adsorbed per Pt₄ cluster; therefore, each isomer has also been optimized with either one or two C₂H₄ molecules adsorbed. Structures obtained from the global optimization are shown in Figs. 8 and S7. Note that C₂H₄ is able to bind in several configurations depending on the isomer. For instance, C₂H₄ in the global minimum structure of C₂H₄/Pt₄/SiO₂ preferentially binds in the di-σ binding mode, whereas in the global minimum of (C₂H₄)₂/Pt₄/SiO₂ there is one di-σ bound ethylene, and one π-bound ethylene. Note that other higher energy isomers, which are thermally accessible at higher temperatures, can have different C₂H₄ binding preferences than the global minimum, as shown in Fig. 8. Previously, it was shown that the stronger di-σ interaction favors dehydrogenation.¹
Referencing the literature augments our interpretations, as ethylene dehydrogenation has been thoroughly studied via DFT and various surface analysis methods over extended Pt surfaces. For example, for temperatures around 100 K, LEED showed ethylene adsorption having a clear preference for di-σ adsorption to Pt(100)\(^{48}\) and Pt(111).\(^{49}\) In contrast, EELS analysis of stepped/lower-coordinated Pt sites (Pt(210) and Pt(110)) showed π-binding of ethylene.\(^{50}\) The di-σ binding was probed using TPD of mixed C\(_2\)D\(_4\) and C\(_2\)H\(_4\) adsorbed on Pt(111) by Janssens \textit{et al.}, who reported recombinative desorption of isotope-scrambled ethylene at ~285 K, indicating dissociative adsorption.\(^{51}\) Just above the 285 K desorption peak, hydrogen evolution begins, with the first H loss resulting in a surface-bound ethylidyne, although this is largely considered to be a

\[\text{Figure 8. Thermally-accessible geometries of C}_2\text{H}_4/Pt_4/\text{SiO}_2 \text{ obtained from global optimization calculations. The geometries of (C}_2\text{H}_4)_2/Pt_4/\text{SiO}_2 \text{ are shown in Fig. S7.}\]
spectator between the first and remaining H dissociation events. As the sample temperature continues to increase, additional dehydrogenation occurs, indicated by additional H\textsubscript{2} desorption until 700 K. Results for the π-bound molecules on low-coordinated stepped surfaces were quite different. For example Yagasaki et al. studied C\textsubscript{2}H\textsubscript{4} decomposition on Pt(210) and reported that some desorbs intact around 250 K, but the residual π-adsorbed C\textsubscript{2}H\textsubscript{4} undergoes dehydrogenation around 300 K, as shown by desorption of H\textsubscript{2} and detection of surface ethylidyne with both C atoms coordinated to the surface. Further heating the Pt(210) surface to 700 K drives dehydrogenation to completion.

Pt(110) showed different behavior, as reported by Yagasaki et al. Here, the some of the π-adsorbed ethylene is isomerized to the di-σ mode by 160 K. From 270 K–330 K, it undergoes decomposition to both C atoms and ethylidyne surface species, while evolving methane and hydrogen. The strongly bound ethylidyne then completes dehydrogenation by 450 K. For comparison, an IR absorption study was done on Al\textsubscript{2}O\textsubscript{3}-supported Pt nanoparticles around 180 K that resulted three ethylene adsorption modes: π-adsorption, di-σ adsorption, and spontaneous ethylidyne formation. Interestingly, all π-adsorbed ethylene was found to desorb intact by room temperature, while the di-σ bound ethylene is converted to ethylidyne and hydrogen.

Interpretation of our DFT and experimental results in light of these results allows conclusions to be made about the mechanism in our Pt\textsubscript{tn}/SiO\textsubscript{2} experiments. The three structures I, II, and III shown in Fig. 8 and structure I in Fig. S7 each have significant contributions to the cluster ensemble and we thus expect surface-bound ethylene species to adsorb in both the π and di-σ modes. We consider the comment by Mohsin et al., that ethylidyne can spontaneously form at this temperature (as a result of dissociation of surface ethylene). In a D\textsubscript{2} thermal desorption study for Pt(100), Pasteur et al. showed recombinative desorption between 250 K and 500 K. Spontaneous D\textsubscript{2}
desorption is therefore not expected; rather we would expect these species to exist as surface-bound.

The calculated structures for ethylene on bare Pt$_4$/SiO$_2$ offer some explanation for the ISS experiments, which were conducted at 150 K, where only the lowest energy isomers are accessible, and all Pt atoms are in the surface layer. This results in the highest scattering intensity for as-deposited Pt$_4$ clusters, when compared to larger, multilayered clusters.$^1$ At higher temperatures, the catalytic activity observed experimentally is a result of a linear combination of the populated structures and the mechanisms they individually promote. With a combination of binding modes, diverse chemical behavior is expected, where both intact desorption of ethylene and dehydrogenation of ethylene would be expected, as observed.

In bulk, calorimetric experiments by Anres et al. showed that PtSn has a highly negative enthalpy of formation.$^{57}$ Similarly, Liu and Ascencio reported DFT simulations for clusters of a few hundred atoms that found PtSn clusters to be energetically favorable compared to pure Pt clusters.$^{58}$ For sub-nano clusters, DFT shows that Sn incorporation to size-selected Pt clusters results in substantial electron transfer from Sn to Pt atoms, and reduces the fluxionality of the clusters, such that one isomer dominates the ensemble.$^2$ The dominant isomer is an intermixed Pt$_4$Sn$_3$ structure, with each atom showing a relatively high degree of coordination. From the chemistry perspective, one important result was that adding Sn quenches all unpaired spins on Pt, while in the pure Pt$_4$/SiO$_2$ system there are low energy isomers with unpaired electrons available for adsorbate binding.

To examine the effects of ethylene adsorption on PtSn clusters, DFT calculations were performed for ethylene adsorbed on both the global minimum Pt$_4$Sn$_3$/SiO$_2$ structure, and on several of the lowest energy isomers. The lowest energy isomer changes when ethylene is adsorbed, thus
we expect the isomer ensemble to change as the clusters are heated with adsorbed ethylene. The most stable isomers for C₂H₄/Pt₄Sn₃/SiO₂ are shown in Fig. 9, along with Boltzmann population and Bader charge data. Structures with two adsorbed ethylene molecules are shown in Fig. S8. As shown in Fig. 9, the most stable isomers for a single ethylene have it π-bonded to Pt atoms in the cluster, however, as shown Fig. S8, one isomer was found for (C₂D₄)₂/Pt₄Sn₃ in which one of ethylene molecules is bound with one C atom bound to Sn, and one to an adjacent Pt atom. Note that for a single ethylene, di-σ binding has been completely eliminated by incorporation of Sn into

**Figure 9.** Thermally-accessible geometries of C₂H₄/Pt₄Sn₃/SiO₂ obtained from global optimization calculations. Note that the ensemble is dominated by C₂H₄ π-binding mode. The geometries of (C₂H₄)₂/Pt₄Sn₃/SiO₂ are shown in Fig. S8.
the Pt₄ clusters. Structure I is the preferred C₂H₄/Pt₄Sn₃/SiO₂ isomer, with greater than 69% of the population at 700 K. The only structure with di-σ C₂H₄ is structure II for adsorption of two ethylene molecules (Fig. S8). While there is still some diversity in the lowest energy isomer distribution, C₂H₄ is only able to adsorb via π interaction, which is expected to limit the catalytic branching toward the products of deeper dehydrogenation on the Pt₄Sn₃.₃/SiO₂ catalyst.

In order to compare the barriers of C₂H₄ dehydrogenation on Pt₄/SiO₂ vs. Pt₄Sn₃/SiO₂, CI-NEB calculations were done on the three structures of Pt₄/SiO₂ and Pt₄Sn₃/SiO₂ that are most populated at 700 K. For every structure, the barrier to break each of the four C-H bonds is considered. The minimum energy pathway for each isomer along with the structures of reactants, transition states, and products are shown in Fig. 10. Additional CI-NEB reaction paths for other isomers and ethylene binding sites, along with the structures involved, are summarized in Figs S9 - S13.

The lowest reaction barrier of the most populated C₂H₄/Pt₄/SiO₂ structure is 0.95 eV, whereas this value for C₂H₄/Pt₄Sn₃/SiO₂ is 1.29 eV. Isomer II of C₂H₄/Pt₄Sn₃/SiO₂ has a more accessible low-energy path (1.00 eV) which makes it the most active of the three lowest-energy isomers of the system. This confirms our working hypothesis that the less stable isomers tend to be more reactive, and they must be considered in order to accurately describe the catalytic properties of dynamic catalysts. Of course, the contributions of the isomers II and III to the reaction is smaller because of their smaller presence in the ensemble (see Figs. 8 and 9).

Additionally, Fig. 11 gives the values for the 700 K ensemble-average rate constants (kₚₑₑ) for C₂H₄/Pt₄/SiO₂ and C₂H₄/Pt₄Sn₃/SiO₂ along with the rate constant calculated for each isomer, and the contribution of that isomer to the ensemble. The results show that the Pt₄/SiO₂ ensemble is more active at 700 K toward ethylene dehydrogenation than the Pt₄Sn₃/SiO₂ ensemble. At lower temperatures, such as the ~300 K onset temperature for dehydrogenation, the difference would be
larger. These results confirm the experimental finding that introducing Sn to the cluster makes it

**Figure 10.** Lowest energy reaction profiles of breaking C-H bond obtained from CI-NEB calculations for each isomer of (a) C2H4/Pt4/SiO2 and (b) C2H4/Pt4Sn3/SiO2 along with the structures of reactants, transition states, and products.
Another interesting result is that on many cluster isomers, two of the hydrogens of ethylene can be removed significantly more easily than the other two. For instance, according to the C\textsubscript{2}H\textsubscript{4}/Pt\textsubscript{4}/SiO\textsubscript{2} isomer I reaction pathways in Fig. S9, the barriers corresponding to breaking C-H\textsubscript{3} and C-H\textsubscript{4}, which are plotted as I-3 and I-4, are almost 2 eV lower than those of C-H\textsubscript{1} and C-H\textsubscript{2} (I-1...
and I-2). This can be understood by structure analysis (Fig. S10): the Pt atoms on the top of the cluster are more undercoordinated and active than the Pt atoms attached to the surface; thus, placing the detached H atoms on the top Pt sites is favorable (on either atop or bridge sites).

Note that all reaction profiles obtained from CI-NEB calculations along with the structures can be found in Figs. S9–13, and the corresponding numerical data is summarized in Table S1. By comparing these structures, we find that on Pt₄Sn₃/SiO₂, in the product state, the Pt-C bonds between C₂H₃ and the catalyst are elongated, compared to those on Pt₄/SiO₂. This suggests that the product might more easily leave Pt₄Sn₃/SiO₂ (or recombine and leave), whereas it is more likely to undergo further dehydrogenation on Pt₄/SiO₂.

Additionally, the properties of the ensemble of clusters with one and two adsorbed C₂H₄ are summarized in Tables S2 and S3. As can be seen, the Pt₄ cluster has negative charge due to electron transfer from the support, while the charge of Pt₄Sn₃ is positive, as expected from the more electropositive nature of Sn. Moreover, the ethylene binding energy of Pt₄Sn₃/SiO₂ is ~0.7–0.8 eV weaker than that of Pt₄/SiO₂ as is clear from Table S3; this makes it easier for ethylene to desorb from the cluster rather than undergo further dehydrogenation.

Next, MD simulations were run for 10 ps at 700 K to allow sampling of the adsorbate and cluster motion. The average C-C bond distance in C₂H₄/Pt₄Sn₃/SiO₂ is 0.1 Å shorter than that in C₂H₄/Pt₄/SiO₂, consistent with its looser binding to the PtSn clusters, and indicating the bond being closer to double in character (Figs. S14 and S15). Furthermore, the average $\angle$PtCC bond angle in C₂H₄/Pt₄/SiO₂ is very close to the tetrahedral angle (104.94 °) showing the $\sigma$-bonding interaction between ethylene and the cluster. On the other hand, the average $\angle$HCC bond angle in C₂H₄/Pt₄Sn₃/SiO₂ is 120.47 ° showing a significant C-C double bond nature and $\pi$ interaction between the adsorbate and the cluster. Note that during the MD simulations of C₂H₄/Pt₄Sn₃/SiO₂,
ethylene becomes partially detached from the cluster at 5.059 ps, which is shown in Fig. S17, whereas on C$_2$H$_4$/Pt$_4$/SiO$_2$ ethylene is always attached to the cluster. This again suggests that ethylene is more likely to desorb from the Pt$_4$Sn$_3$/SiO$_2$ surface, rather than remaining on the surface and undergoing dehydrogenation.

Ethane-to-ethylene conversion is the ultimate target for these catalysts, but in UHV experiments, it is infeasible to probe C$_2$D$_6$ dehydrogenation over Pt$_n$/SiO$_2$ and Pt$_n$Sn$_x$/SiO$_2$, because ethane does not stick at relevant temperatures. However, DFT can be useful to bridge the gap. We performed calculations of C$_2$H$_6$ dehydrogenation on the pure and Sn-alloyed Pt clusters, to show that PtSn clusters can actually dehydrogenate C$_2$H$_6$ and form the desired C$_2$H$_4$ product. Fig. 12 shows the barriers corresponding to ethane dehydrogenation on the Pt$_4$/SiO$_2$ and Pt$_4$Sn$_3$/SiO$_2$ global minimum structures. The reaction barriers are 0.22 eV for Pt$_4$/SiO$_2$, and 0.58 eV for Pt$_4$Sn$_3$/SiO$_2$, i.e. lower than the ones obtained for C$_2$H$_4$ dehydrogenation (0.96 eV and 1.30 eV, for Pt$_4$/SiO$_2$ and Pt$_4$Sn$_3$/SiO$_2$, respectively). The reason PtSn can dehydrogenate ethane relatively easily, but not ethylene, has to do with the type of sites required for the two reactions. Whereas di-$\sigma$ ethylene activation requires the binding to two Pt atoms, ethane binds to a single Pt atom with both the H and the C atoms of the activated C-H bond. Such sites are available on both pure and Sn-alloyed Pt clusters. These results suggest that both catalysts should successfully dehydrogenate alkanes, whereas dehydrogenation of alkenes is harder, and further hindered by alloying of the cluster catalyst with Sn. This justifies the use of C$_2$H$_4$ as a model for selectivity of dehydrogenation catalysis.

In the past, we proposed that Si and Ge as new highly competitive alloying elements for Pt.$^{59-60}$ Both Si and Ge have very similar effect on Pt clusters to the effect of Sn: mixing, Pt site separations, and electronic spin quenching. Both Ge and Si were shown to suppress
Figure 12. Lowest energy reaction profiles of breaking C-H bond obtained from CI-NEB calculations for the global minimum isomer of (a) C₂H₆/Pt₄/SiO₂ and (b) C₂H₆/Pt₄Sn₃/SiO₂ along with the structures of reactants, transition states, and products.
dehydrogenation beyond ethylene. However, for PtGe, the step of ethane dehydrogenation was actually accelerated compared to the process on pure Pt, and that is different from the effect of Sn, which makes ethane dehydrogenation less facile (though still quite accessible).

CONCLUSIONS

We have presented a study comparing the activity and selectivity of Ptₙ/SiO₂ and PtₙSnₓ/SiO₂ for ethylene desorption vs. dehydrogenation and carbon deposition. Alloying of sub-nano Ptₙ clusters with Sn resulted in considerable improvement in selectivity by blocking the di-σ binding mode of ethylene, while preserving the π-mode. The origin of this selectivity is electronic and geometric. Adding Sn quenches all unpaired spins on Pt, which are required for the di-σ ethylene binding. Also, Sn intermixes with Pt and separates Pt atoms from each other, thus again preventing di-σ ethylene binding. This resulted in suppression of the dehydrogenation mechanism, allowing ethylene to desorb from the catalytic surface intact before decomposition into high binding energy coke precursor surface species. The improvement in catalyst selectivity thus results in an improvement in run-to-run stability, suggesting that sub-nano PtSn alloy clusters could be a promising candidate for high temperature dehydrogenation catalysts.

On the mechanistic side, we find that many different pathways can feasibly contribute to the reaction mechanism, due to the co-existence of multiple cluster isomers, multiple binding geometries of ethylene to the clusters, and multiple accessible C-H bond dissociation paths. Metastable cluster isomers with attached ethylene can have lower barriers to C-H dissociation than the corresponding global minima of the same stoichiometry, and thus contribute substantially to the overall ensemble-average rate of the reaction. It is indeed important that the selectivity of the cluster catalyst is an ensemble property. Pure Pt cluster catalysts usually bind ethylene in the di-
σ mode and efficiently dehydrogenate it, but they can also bind ethylene in the π-mode that discourages dehydrogenation and have high reaction barriers that are within thermal reach to the population. PtSn clusters, on the other hand, mostly favor the π-mode of ethylene binding, favoring desorption instead of dehydrogenation, however, to the extent that some higher energy cluster isomers contribute, they may have thermally-accessible dehydrogenation pathways. DFT calculations combined with statistical analysis confirm that adding Sn to Pt clusters significantly slows down ethylene dehydrogenation.

METHODS

Experimental. Experiments were performed using an instrument described in detail elsewhere, which allows sample creation by size-selected cluster deposition in ultra-high vacuum (UHV), with characterization of physical and chemical properties in in situ. The cluster deposition beamline includes a laser vaporization cluster source, ion guides for transport through several differential pumping stages, a quadrupole mass filter for cluster size selection, a valve/lens that isolates the cluster beamline from the UHV system, and a final ion guide that transports ions to the sample, where they are deposited through a 2 mm diameter mask. Samples are mounted via heater wires to a liquid N₂ cryostat that is mounted to a precision manipulator on a rotating “lid” assembly that allows samples to be positioned for sample exchange, cleaning, film growth, cluster deposition, and characterization. Temperature can be controlled in the range from ~120 K to 2100 K.

The UHV section (base pressure 1.0 x 10⁻¹⁰ Torr) includes capabilities for X-ray and UV photoelectron spectroscopy, low energy He⁺ ion scattering spectroscopy, and ion neutralization electron spectroscopy, with analysis area set to 1.1 mm diameter, i.e., smaller than the 2.0 mm
cluster spot. The instrument is also equipped with a differentially pumped mass spectrometer that views the sample through a 2.5 mm diameter aperture in the end of skimmer cone. The cone is surrounded by dosing tubes that are connected to either leak valves or pulsed valves, allowing calibrated continuous or pulsed gas doses with local pressure at the sample position roughly an order of magnitude higher than the increase in background pressure.

A small UHV-compatible antechamber chamber is attached to the main UHV section, isolated by a gate valve. When the valve is opened, the sample can be inserted into the antechamber, and when in position, the two chambers are isolated by a triple differentially pumped seal that mates to the cryostat. This allows the antechamber to be vented for sample exchange, or used for “gassy” processes such as annealing in O₂ or Sn deposition, without exposing the main UHV system to high gas loads.

Model Ptₙ/SiO₂/Si(100) and PtₙSnₓ/SiO₂/Si(100) catalysts were prepared on substrates consisting of 10 mm x 14 mm pieces of oxidized Si(100), using a fresh substrate for each experiment. The SiO₂/Si(100) substrates are referred to throughout as “SiO₂” substrates. Substrates were cleaned by annealing at 700 K in 5.0 x 10⁻⁶ Torr O₂ for 20 minutes, followed by 2 min of annealing in UHV. After cleaning, the initial adventitious carbon from air exposure was largely removed, but a small C 1s signal remaining, which we roughly estimated to be ~0.1 ML equivalent. We attempted to remove this residual carbon by sputtering, followed by various annealing protocols in both vacuum and O₂ at temperatures up to 1100 K, and while sputtering does remove the carbon, it creates a large number of defect sites that do not completely anneal away. These create large desorption signals during temperature-programmed desorption (TPD) experiments, interfering with detection of species desorbing from the low coverage of clusters, therefore, we opted to use just O₂ annealing for sample cleaning.
The thickness of the oxidized surface layer was estimated to be 1.1 nm, from modeling of the Si\(^{4+}\) and Si\(^0\) relative intensities measured by XPS, with photoemission cross sections and asymmetry parameters taken from work by Yeh and Lindau\(^{62}\) and electron effective attenuation lengths calculated using the NIST EAL database program of Powell and Jablonski.\(^{64}\) Prior to cluster deposition, the sample cryostat was cooled, and then the sample was flashed to 700 K to drive off any adventitious species that might have adsorbed during cooling. As the sample cooled after the 700 K flash, Pt\(_n\) cluster deposition was initiated once the sample reached 300 K and continued as the sample cooled to 180 K. To allow easy exchange of SiO\(_2\) substrates, they are mounted using a tungsten clip to clamp the substrates to a molybdenum backing plate, which is spot welded to Ta heater wires that also act as thermal conductors to the sample cryostat. A type C thermocouple is spot welded to back of the backing plate for temperature measurement.

We chose to study two small clusters, Pt\(_4\) and Pt\(_7\), both deposited at \(\sim 1\) eV/atom, as measured using retarding potential analysis of the ion beam on the substrate. Deposition was monitored by integrating the Pt\(_n^+\) neutralization current, and for all samples here, the coverage was \(1.5 \times 10^{14}\) Pt atoms/cm\(^2\), equivalent to \(\sim 10\%\) of a close-packed Pt monolayer. The absolute coverage of clusters is thus \(1.5 \times 10^{14}/n\) clusters/cm\(^2\), where \(n = 4\) or 7.

The method used to prepare size- and composition-selected PtSn alloy clusters, along with experimental and theoretical characterization of the cluster properties, has been described in detail,\(^2\) and additional information is given in the Supporting Information. Briefly, size-selected Pt\(_n\) (\(n = 4, 7\)) clusters deposited on SiO\(_2\) substrates were used to “seed” selective Sn deposition via a self-limiting reaction sequence, carried out at 300 K. Pt\(_n\)/SiO\(_2\) samples were first exposed to \(\sim 21000\) L of H\(_2\), which saturates the Pt clusters with H atoms, with essentially no effect on the SiO\(_2\) substrate.\(^5\) Next, the samples were exposed to \(\sim 24\) L of SnCl\(_4\) vapor, which reacts with
hydrogenated Pt sites, leading to HCl desorption and binding of SnCl\textsubscript{x}. The samples were then exposed to an additional 21000 L of H\textsubscript{2}, causing additional HCl desorption, such that <10\% of the Cl remained on the cluster surface, along with H and Sn. Finally, the samples were heated briefly to 700 K, desorbing the remaining H and Cl, but with no loss of Sn. ISS showed evidence that heating also allowed the Sn to mix into the Pt cluster, forming an alloy.

Sn deposition was found to be >40 times more efficient on hydrogenated Pt sites than on the SiO\textsubscript{2} support. The cluster Pt:Sn stoichiometry estimated by XPS for the Pt\textsubscript{4} and Pt\textsubscript{7} seed clusters (Pt\textsubscript{4}Sn\textsubscript{3.3}, Pt\textsubscript{7}Sn\textsubscript{6.3}) was close to 1:1. It is important to note that the Pt:Sn stoichiometry is unaffected by increasing the reactant exposures,\textsuperscript{2} i.e., the stoichiometry is controlled by the seed cluster size\textsuperscript{2} and the saturation coverage of the ALD reactants on the clusters. Therefore, we expect that the stoichiometry to be reasonably uniform from cluster to cluster, at least as initially prepared.

Desorption and dehydrogenation of ethylene on Ptn/SiO\textsubscript{2} and PtnSn\textsubscript{x}/SiO\textsubscript{2} was characterized by C\textsubscript{2}D\textsubscript{4} TPD/R. Samples were cooled to 180 K and exposed to 10 L of C\textsubscript{2}D\textsubscript{4}, which is roughly twice the dose needed to saturate cluster-associated binding sites that are stable at this temperature.\textsuperscript{1} 180 K was chosen to minimize adsorption on the amorphous SiO\textsubscript{2} substrate. After the C\textsubscript{2}D\textsubscript{4} exposure, samples were positioned 0.5 mm away from the 2.5 mm diameter aperture that allows desorbing molecules to pass into the ion source of the differentially pumped mass spectrometer (UTI 100C with Extrel electronics). The sample temperature was then ramped at 3 K/sec up to 700 K, while monitoring signal for D\textsubscript{2}\textsuperscript{+}, H\textsubscript{2}O\textsuperscript{+}, \textsuperscript{12}CO\textsuperscript{+}, \textsuperscript{13}CO\textsuperscript{+}, C\textsubscript{2}D\textsubscript{4}\textsuperscript{+}, H\textsuperscript{35}Cl\textsuperscript{+}, \textsuperscript{12}CO\textsubscript{2}\textsuperscript{+}, \textsuperscript{13}CO\textsubscript{2}\textsuperscript{+}, and Cl\textsubscript{2}\textsuperscript{+}.

CO TPD was used to examine changes in the number and properties of accessible Pt sites accompanying the ethylene TPD experiments. As with the C\textsubscript{2}D\textsubscript{4} TPD/R experiments, samples were exposed to 10 L of \textsuperscript{13}CO at 180 K, then positioned 0.5 mm away from the 2.5 mm diameter
skimmer cone aperture, and the sample temperature was ramped at 3 K/s, to 700 K while monitoring the same masses as above.

After completion of each set of TPD/R experiments, the sample was moved away from the aperture, and the mass spectrometer sensitivity was calibrated by leaking $2.0 \times 10^{-8}$ Torr of $\text{C}_2\text{D}_4$, $\text{D}_2$, $^{13}\text{CO}$, and $\text{Ar}$ into the main UHV chamber background. Taking the ionization gauge sensitivity into account, these background pressures create well-defined fluxes of the molecules of interest through the skimmer cone aperture into the mass spectrometer ionization source. Ar was used as a UHV-friendly calibrant for HCl. The masses are similar and should therefore have similar transmission efficiency, and the difference in ionization cross-sections was taken into account using ionization gauge sensitivity factors reported by the gauge manufacturer. This calibration information was used to convert ion signals for $\text{C}_2\text{D}_4^+$, $\text{D}_2^+$, $\text{CO}^+$, and $\text{H}^{35}\text{Cl}^+$ to the corresponding number of desorbing molecules, based on the assumption that detection efficiency should be similar for molecules desorbing from the surface and effusing from the gas phase. We previously compared calibrations obtained by this method to calibration by desorption of well-defined (2x2)-CO layers from Pd single crystals, and obtained very similar results.40, 65 We conservatively estimate that the absolute uncertainty in the calibrated desorption signals to be $\sim \pm 50\%$, with uncertainty for comparing experiment to experiment of $\sim \pm 15\%$.

**Computational.** Global optimization done in this study was performed based on plane wave density functional theory (PW-DFT) calculations with the Vienna Ab initio Simulation Package (VASP)66-69 using projector augmented wave (PAW) potentials70 and the PBE71 functional. Plane waves were chosen based on the kinetic energy cutoff of 400.0 eV. Moreover, the convergence parameters of $10^{-5}$ ($10^{-6}$) eV for geometric(electronic) relaxations and Gaussian
smearing with the sigma value of 0.1 eV were used. In order to model the substrate used in the experiment, the chosen SiO$_2$ slab was previously optimized$^{72}$ elsewhere at the B3LYP/6-31G(d,p)$^{73-76}$ level. The obtained cell parameters used in this study are $a = 12.4$ Å, $b = 13.1$ Å, $c = 32.0$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, and $\gamma = 88^\circ$ which includes the vacuum gap of 10 Å in the z-direction. Note that the lower half of the slab was kept fixed during the global optimization and only the $\Gamma$-point sampling was used to obtain the energy thanks to the fairly large super cell used in this study.

The supported Pt$_4$ and Pt$_4$Sn$_3$ clusters, without and with the adsorbed ethylene, were globally optimized. Larger Pt$_7$-based clusters were not considered due to the enormous computational expense, additionally given the need for a larger super cell representing the slab. To produce the initial cluster geometries on the surface, we use our in-house code, parallel global optimization and pathway toolkit PGOPT, that automatically generates structures based on the bond length distribution algorithm (BLDA).$^{43}$ Initial structures for the global optimization calculations should be created, such that they are less prone to encounter Self-Consistent Field (SCF) convergence problems. This can be done by avoiding chemically unfavorable configurations, which results in the reduction of configuration search space and the computational cost of calculation. By constraining the distance of atoms to their closest and second closest neighbors to follow a normal distribution, one can achieve this goal. That is to say, both closest and second closest distances are fitted to normal distribution based on which the initial structures are generated. Subsequently, each generated structure was optimized using DFT and duplicate structures were removed thereafter. The ethylene molecules were placed on the clusters in a multitude of possible orientations and binding sites. Then each structure was optimized using DFT, and duplicates were filtered out. In this study, 200 unique structures were generated and optimized to find the putative global
minimum and the accessible local minima. To take into account the effect of coverage, we also
optimized the clusters with two ethylene adsorbed per cluster. A cut-off energy of 0.4 eV was
used to select the thermodynamically accessible isomers at relevant temperatures. More detailed
discussion about obtaining the vibrational partition functions and corrected Boltzmann population
was published before. The Bader charge analysis was used to obtain partial atomic charges.
Furthermore, Boltzmann populations were calculated with the assumption that the system can
sufficiently equilibrate as

$$P_i = \frac{Z_{\text{elec},i} Z_{\text{trans},i} Z_{\text{vib},i} Z_{\text{rot},i}}{\sum_i Z_i} \approx \frac{g_i e^{-\beta E_i}}{\sum_i g_i e^{-\beta E_i}}$$

where $Z_{\text{elec},i}$, $Z_{\text{trans},i}$, $Z_{\text{vib},i}$, and $Z_{\text{rot},i}$ are electronic, translational, vibrational, and rotational
partition functions, respectively. For the lowest-energy isomers with adsorbed ethylene, which
contributed significantly into the respective thermal ensembles, the reaction profile for ethylene
dehydrogenation were calculated using climbing image nudged elastic band (CI-NEB) method.
Three isomers of each cluster with adsorbed ethylene were chosen and the dissociation of every
C-H bond within every adsorbed configuration was tested. All transition states were confirmed
by phonon calculations. The distance between the structures (images) in CI-NEB calculations
used as reaction coordinate is defined as

$$d_{12} = \sqrt{\frac{1}{N} \sum_i (x_{i,1} - x_{i,2})^2 + (y_{i,1} - y_{i,2})^2 + (z_{i,1} - z_{i,2})^2}$$

Rate constants for each pathway were calculated based on harmonic transition state theory. The
ensemble-average rate constant were calculated based on the contribution of each isomer using its
Boltzmann population at 700 K:
\[ k_{\text{ens}} = k_1 P_1 + k_2 P_2 + k_3 P_3 \]

where \( P_i \) is the Boltzmann population and \( k_i (i = 1–3) \) is the sum over all four pathway rate constants obtained from CI-NEB for isomer \( i \).

Finally, \textit{ab initio} MD simulations ran for 10 ps at 700 K with the time step of 1 fs starting from Pt\(_4\)/SiO\(_2\) and Pt\(_4\)Sn\(_3\)/SiO\(_2\) global minimum structures. Nosé–Hoover thermostat was utilized for equilibration during the MD simulations.\(^8\)

ASSOCIATED CONTENT

Supporting Information Available:

Contains complete sets of C\(_2\)D\(_4\) TPD for Pt\(_n\)/SiO\(_2\) and Pt\(_n\)Sn\(_x\)/SiO\(_2\), HCl desorption during the first C\(_2\)D\(_4\) TPD for Pt\(_n\)Sn\(_x\)/SiO\(_2\), an C 1s XPS regional spectra, the remaining Arrhenius fit plots for Pt\(_7\)/SiO\(_2\) and Pt\(_7\)Sn\(_{6.3}\)/SiO\(_2\), structures of reactants, products, transition states obtained from CI-NEB, Bader charge of all local minima structures along with their Boltzmann populations, Ethylene binding energies obtained from DFT, bond length and bond angle distribution of C\(_2\)H\(_4\)/Pt\(_4\)/SiO\(_2\) and C\(_2\)H\(_4\)/Pt\(_4\)Sn\(_3\)/SiO\(_2\) obtained MD simulations, XYZ coordinates of minimum energy pathways obtained from CI-NEB.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGEMENT
This work was supported by the U.S. Air Force Office of Scientific Research under AFOSR Grants FA9550-19-1-0261 and FA9550-16-1-0141.
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**Pt Catalyst:**
- High spin: di-τ C_D bond
- Coking \(\rightarrow\)

**PtSn Catalyst:**
- Closed shell: \(\pi\) C_D bond
- No Coking \(\rightarrow\)

\[ C_D D_4^{\text{Pt}} \rightarrow C_D D_4^{\text{PtSn}} + D_2^{(0)} \]

\[ C_D D_4^{\text{PtSn}} \rightarrow C_D D_4^{(4+)} \]

Temperature (K)
Coking-Resistant Sub-Nano Dehydrogenation Catalysts: Pt\textsubscript{n}Sn\textsubscript{x}/SiO\textsubscript{2} (n = 4, 7)

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Supporting information

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Fig. S1 shows four sequential C$_2$D$_4$ TPD runs from Pt$_4$/SiO$_2$ (top) and Pt$_7$/SiO$_2$ (bottom). As discussed in the main text and shown in Table 1, the overall number of available C$_2$D$_4$ decreased incrementally with each cycle. Similarly, the amount of liberated D$_2$ incrementally decreases. C$_2$D$_4$ desorption from clean SiO$_2$ is also shown for each cluster size. There are two distinguishable features for Pt$_4$, and less so for Pt$_7$. C$_2$D$_4$ desorption begins at the onset of the heat ramp (180 K), peaking around 260 K, and decreasing to baseline by ~500 K. Incremental loss in the number of desorbed C$_2$D$_4$(intact) and D$_2$ molecules is consistent with coke deposition.

Figure S1. Four sequential C$_2$D$_4$ TPD from Pt$_4$/SiO$_2$. Intact C$_2$D$_4$ is shown as solid lines, and D$_2$ desorption is shown at hollow symbols. Intact C$_2$D$_4$ desorption from clean SiO$_2$ is also shown in each panel as a dashed pink line.
As was done for Fig. S1, four sequential C$_2$D$_4$ TPDs were carried out on the Pt$_4$Sn$_{3.3}$/SiO$_2$ catalyst. Numbers of C$_2$D$_4$ molecules per Pt atom are shown in Table 2 of the manuscript. Results are plotted in Fig. S2 along with C$_2$D$_4$ desorption from a cluster-free SiO$_2$ surface that has been exposed to a H$_2$/SnCl$_4$/H$_2$ treatment. All four spectra are shown for Pt$_4$Sn$_{3.3}$/SiO$_2$ and Pt$_7$Sn$_{6.3}$/SiO$_2$, with the D$_2$ desorption plotted separately on inset plots.

Note the anomalous behavior of the first ethylene TPD (red) in Fig. S2. This is attributed to the surface being covered with residual H and Cl atoms as a result of the Sn deposition process. The removal of these adsorbates has been described in detail previously, and the mass 36 (HCl) desorption during the first C$_2$D$_4$ TPD is shown in Fig. S3 for both cluster sizes.

**Figure S2.** Four sequential desorption spectra of C$_2$D$_4$ (solid lines) and D$_2$ (inset plots) from the first (red) and fourth (blue) C$_2$D$_4$ TPD. Each spectra was collected after a 10 L dose of C$_2$D$_4$ to Pt$_n$Sn$_x$/SiO$_2$ (n = 4, 7). C$_2$D$_4$ desorption from bare SiO$_2$ treated with 1 ALD cycle is also plotted (pink line), no D$_2$ is observed.
Using a method described previously\textsuperscript{1-2}, the C$_2$D$_4$ thermal desorption spectra can be fit to extract desorption energy distributions by using the first order rate equation:

\[ I(t) \propto -\frac{d\theta}{dt} = (\theta(E_{\text{des}}) \cdot \nu) e^{\frac{-E_{\text{des}}}{RT(t)}} \]

with \( I(t) \) being the time-dependent C$_2$D$_4$ desorption signal, \( E_{\text{des}} \) the desorption energy, \( \nu \) the exponential pre-factor, \( T(t) \) is the heat ramp, and \( \theta(E_{\text{des}}) \) is the distribution of occupied binding site energies. For all experiments here, a nominal heat ramp rate of 3 K/s was used, but temperature versus time data is always collected during TPD acquisition in order to account for fluctuations in the heating ramp rate, though no corrections were needed. For the fit, a simulated \( \theta(E_{\text{des}}) \) is calculated for each contributing peak and plotted to match the experimentally measured \( I(t) \). The greatest source of uncertainty here is the pre-exponential factor, \( \nu \). It is not practicable to carry out the series of studies that would be required to estimate \( \nu \) from the TPD data, and we simply assumed a value of \( 10^{14} \text{ s}^{-1} \), which is in the range of values often used for CO TPD\textsuperscript{3-7}. In previous studies\textsuperscript{2}, the effect of varying \( \nu \) between \( 10^{13} \text{ s}^{-1} \) to \( 10^{15} \text{ s}^{-1} \) was tested, and found to shift the \( \theta(E_{\text{des}}) \) distribution by only \( \sim 7\% \).

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure_s3.png}
\caption{Mass 36 desorption (HCl) during the first C$_2$D$_4$ TPD for Pt$_n$Sn$_x$/SiO$_2$. No HCl is detected in subsequent runs.}
\end{figure}
**XPS Characterization of Carbon Deposition.** Because the C 1s photoemission cross section is quite small,\(^8\) and carbon is deposited only on the clusters, it was difficult to quantify carbon deposition for samples of the sort discussed above. To increase the carbon coverage, we prepared Pt\(_4\)/SiO\(_2\) and Pt\(_4\)Sn\(_{3.3}\)/SiO\(_2\) samples with twice the usual cluster coverage, and subjected them to eight sequential C\(_2\)D\(_4\) TPD/R runs. The results are compared in Fig. S4. A broad C 1s peak is observed for the blank SiO\(_2\) substrate, attributed to adventitious carbon remaining after the substrate was cleaned by annealing in O\(_2\). The binding energy is in the range expected for partially oxidized carbon, as might be expected after annealing in O\(_2\).

For Pt\(_4\)/SiO\(_2\) after C\(_2\)D\(_4\) TPD/R, this adventitious carbon feature is still present, as expected, but a sharper C 1s feature appears at lower binding energy, which we attribute to carbon deposited on the Pt clusters by C\(_2\)D\(_4\) dehydrogenation. Subtracting the contribution from adventitious carbon, the intensity of this low binding energy feature corresponds to eight TPD/R runs having deposited ~1.5 C atom/Pt atom.

**Figure S4.** Comparison of C 1s XP spectra for an SiO\(_2\) substrate, a Pt\(_4\)/SiO\(_2\) sample, and a Pt\(_4\)Sn\(_{3.3}\)/SiO\(_2\) sample, subjected to eight sequential C\(_2\)D\(_4\) TPD/R runs.
The lower frame of the figure shows analogous data for Pt₄Sn₃.₃/SiO₂ after eight C₂D₄ TPD runs. No increase in carbon intensity was observed, compared to the SiO₂ substrate, consistent with the TPD/R results showing no significant D₂ desorption from the Sn-alloyed clusters.

**Fig. S5** shows the fit for TPD spectra. Here, we use the first C₂D₄ TPD run from Pt₄/SiO₂ as a representative example; this method was carried out for all energy desorption profile plots in this paper. Fits were performed using a two component model, representing low temperature and high temperature feature. Using these fits, the desorption profile was computed and plotted as a function of binding energy. This model makes the critical assumption of first order desorption kinetics. While we expect some 2nd order behavior for surface-bound C₂D₄, i.e., dissociative adsorption \( \rightarrow \) recombinative desorption, the first order fit was carried out simply to approximate the binding energies for comparison to DFT studies.

**Figure S5.** 1st C₂D₄ TPD from Pt₄/SiO₂. The spectrum was fit with low(blue) and high(red) temperature components. The fits can be used to calculate energy desorption profiles.
Desorption energy distributions for Pt$_7$/SiO$_2$ and Pt$_7$Sn$_{6.3}$/SiO$_2$ were calculated as described above. Briefly, the first C$_2$D$_4$ TPD from Pt$_7$/SiO$_2$ was fit with a low and high temperature component and then modeled using a first order kinetics relation. The same was done for the second C$_2$D$_4$ for the Pt$_7$Sn$_{6.3}$/SiO$_2$ sample.

![Arrhenius fits for the C$_2$D$_4$ TPD from Pt$_7$/SiO$_2$ and Pt$_7$Sn$_{6.3}$/SiO$_2$ spectra in Fig. 1.](image)

**Figure S6.** Arrhenius fits for the C$_2$D$_4$ TPD from Pt$_7$/SiO$_2$ and Pt$_7$Sn$_{6.3}$/SiO$_2$ spectra in Fig. 1.
Figure S7. Thermally-accessible geometries of $(\text{C}_2\text{H}_4)_2/\text{Pt}_4/\text{SiO}_2$ obtained from global optimization calculations along with their Boltzmann populations at 700 K.
Figure S8. Thermally-accessible geometries of \((\text{C}_2\text{H}_4)_2/\text{Pt}_4\text{Sn}_3/\text{SiO}_2\) obtained from global optimization calculations along with their Boltzmann populations at 700 K. Note that the ensemble is dominated by \(\text{C}_2\text{H}_4\) \(\pi\)-binding mode.
Table S1. All reaction barriers of C$_2$H$_4$/Pt$_4$/SiO$_2$ and C$_2$H$_4$/Pt$_4$Sn$_3$/SiO$_2$ obtained from CI-NEB calculations along with their contribution to the final $k_{\text{cat}}$ at 700 K.

| C$_2$H$_4$/Pt$_4$/SiO$_2$ | Path-1 (eV) | Path-2 (eV) | Path-3 (eV) | Path-4 (eV) | P$_{700K}$  |
|--------------------------|-------------|-------------|-------------|-------------|------------|
| I                        | 0.95        | 1.13        | 3.18        | 3.40        | 76.71%     |
| II                       | 1.77        | 1.95        | 3.11        | 4.23        | 23.02%     |
| III                      | 1.29        | 1.30        | 2.20        | 2.23        | 0.01%      |

| C$_2$H$_4$/Pt$_4$Sn$_3$/SiO$_2$ | Path-1 (eV) | Path-2 (eV) | Path-3 (eV) | Path-4 (eV) | P$_{700K}$  |
|--------------------------------|-------------|-------------|-------------|-------------|------------|
| I                              | 1.29        | 1.39        | 1.77        | 2.15        | 69.03%     |
| II                             | 1.00        | 1.55        | 2.22        | 3.12        | 27.45%     |
| III                            | 1.62        | 2.97        | 4.14        | 6.99        | 6.70%      |

Figure S9. Reaction profiles of breaking C-H bond obtained from CI-NEB calculations for (a) C$_2$H$_4$/Pt$_4$/SiO$_2$ and (b) C$_2$H$_4$/Pt$_4$Sn$_3$/SiO$_2$. The reaction barrier corresponding to the highest populated C$_2$H$_4$/Pt$_4$Sn$_3$/SiO$_2$ isomer is 0.3 eV higher than that of C$_2$H$_4$/Pt$_4$/SiO$_2$. The reaction coordinate is defined as the root mean square distance from the reactant, which can be found in the computational methods section.
Table S2. Charge on the cluster, ethylene binding mode, and Boltzmann population at 700 K obtained for C₂H₄/Pt₄/SiO₂, (C₂H₄)₂/Pt₄/SiO₂, C₂H₄/Pt₄Sn₃/SiO₂, and (C₂H₄)₂/Pt₄Sn₃/SiO₂.

| Isomer   | Q_{cluster}(e) | C₂H₄ Binding mode   | P_{700K}     |
|----------|----------------|----------------------|--------------|
|          |                | Pt₄                   | Pt₄Sn₃       |              |              |
| C₂H₄/Pt₄Sn₃/SiO₂ | –0.15          | 0.39                               | di-σ         | π                    | 76.71%       | 69.03%       |
| I        | –0.11          | 0.46                               | π            | π                    | 23.01%       | 27.45%       |
| II       | –0.10          | 0.43                               | π            | π                    | 0.25%        | 2.32%        |
| III      | –0.12          | 0.50                               | π            | π                    | 0.01%        | 0.7%         |
| IV       | –0.12          | 0.50                               | di-σ         | π                    | 0.01%        | 0.3%         |
| V        | –0.14          | 0.32                               | di-σ         | π                    | <0.01%       | 0.2%         |
| (C₂H₄)₂/Pt₄Sn₃/SiO₂ | –0.04          | 0.31                               | π, di-σ      | π, π                 | 99.88%       | 57.33%       |
| I        | –0.16          | 0.56                               | π, π         | π, di-σ              | 0.06%        | 37.42%       |
| II       | –0.11          | 0.58                               | π, π         | π, π                 | 0.05%        | 4.69%        |
| III      | –0.19          | 0.45                               | π, di-σ      | π, π                 | <0.01%       | 0.56%        |

Table S3. Ensemble averaged first and second C₂H₄ binding energies on Pt₄/SiO₂ and Pt₄Sn₃/SiO₂ calculated at 700 K.

| Structure    | E_{b1}(eV) | E_{b2}(eV) |
|--------------|------------|------------|
| Pt₄/SiO₂     | –1.91      | –1.76      |
| Pt₄Sn₃/SiO₂  | –1.11      | –1.04      |
Figure S10. (a) 3 most populated C$_2$H$_4$/Pt$_4$/SiO$_2$ isomers used in CI-NEB calculations and (b) all 12 products (4 for each structure) obtained by cleaving every C-H bond in C$_2$H$_4$ on Pt$_4$/SiO$_2$. 
Figure S11. (a) Three most populated C$_2$H$_4$/Pt$_4$Sn$_3$/SiO$_2$ isomers used in CI-NEB calculations and (b) all 12 products (four for each structure) obtained by cleaving every C-H bond in C$_2$H$_4$ on Pt$_4$Sn$_3$/SiO$_2$. 
Figure S12. Transition state structures corresponding to all 12 different pathways of C-H bond dissociation on Pt$_4$/SiO$_2$ obtained from CI-NEB calculations.
Figure S13. Transition state structures corresponding to all 12 different pathways of C-H bond dissociation on Pt₄Sn₃/SiO₂ obtained from CI-NEB calculations.
**Figure S14.** C-C and C-Pt Bond distance, and $\angle$HCC and $\angle$PtCC bond angle during the MD simulations of C$_2$H$_4$/Pt$_4$/SiO$_2$. The time step is 1 fs and the total run time is 10 ps.
Figure S15. C-C and C-Pt Bond distance, and $\angle$HCC and $\angle$PtCC bond angle during the MD simulations of C$_2$H$_4$/Pt$_4$Sn$_3$/SiO$_2$. The time step is 1 fs and the total run time is 10 ps.
Figure S16. All structures corresponding to an extreme in bond distance or bond angle during the MD simulations of C2H4/Pt4/SiO2 with their corresponding value.
Figure S17. All structures corresponding to an extreme in bond distance or bond angle during the MD simulations of C\textsubscript{2}H\textsubscript{4}/Pt\textsubscript{4}Sn\textsubscript{3}/SiO\textsubscript{2} with their corresponding value. Note that at 5.059 ps C\textsubscript{2}H\textsubscript{4} is almost detached from the cluster.
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