Promoter-poison partnership protects platinum performance in coked cluster catalysts

Patricia Poths,∗† Harry W. T. Morgan,† Guangjing Li,‡ Autumn Fuchs,‡ Scott L. Anderson,∗‡ and Anastassia N. Alexandrova∗†¶

†Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, CA 90095, USA
‡Department of Chemistry, University of Utah, Salt Lake City, UT, 84112, USA
¶California NanoSystems Institute, Los Angeles, CA, 90095, USA

E-mail: patriciapoths@chem.ucla.edu; anderson@utah.edu; ana@chem.ucla.edu

Abstract

Deactivation via coking due to a lack of selectivity is a persistent problem for the longevity of Pt-based dehydrogenation catalysts. Ge as a promoter improves the experimental selectivity and stability of subnano Pt clusters. The origin of this improvement is self-limiting coking, to form a Pt$_4$GeC$_2$ cluster which is more stable and selective than the bare Pt$_4$Ge cluster. In this paper we compare the dehydrogenation abilities of Pt$_4$ and Pt$_4$C$_2$ with and Pt$_4$Ge and Pt$_4$GeC$_2$ with DFT calculations in order to explore the origin of self-limiting coking in the presence of Ge. The unique stability of Pt$_4$GeC$_2$ is attributed to electron donation from Ge to the C$_2$ atoms. This prevents the coke from drawing electrons from the Pt, which is the origin of deactivation via coking. Thus, we identify an electronic mechanism for coke deactivation and then use an electronically driven doping strategy to improve catalyst longevity. This differs from the common perception of coke deactivated via steric blocking of active sites.
Furthermore, Pt$_4$C$_2$ and Pt$_4$GeC$_2$ show differences in kinetic accessibility of different isomers, which brings us into a new paradigm of sub-ensembles of isomers, where the dominant active sites are determined by kinetic stability under reaction conditions, rather than Boltzmann populations.

**Introduction**

The formation of coke, or carbonaceous deposits, is a persistent problem for dehydrogenation catalysts, as it results in their rapid deactivation. Deactivation is typically attributed to physical blocking of active sites on the catalyst. Coke formation on Pt-based alkane dehydrogenation catalysts originates from the lack of selectivity of the catalyst; side reactions for deeper dehydrogenation past alkenes and C-C cracking contribute to coke formation. Approaches to preventing coke formation include co-feeding H$_2$, changing Pt nanoparticle size, and dopants or promoters such as Sn, Ge, Si, Ga, Zn, and B. These approaches all favor desorption of the desired alkenes over deeper dehydrogenation (or cracking) reactions.

Coke formation typically occurs in two stages; an initial fast coking regime, and a later regime where the buildup of further coke is much slower, which indicates that early coking stages change catalysts selectivity to limit further coking. This change in selectivity has been attributed to carbon blocking the most reactive and least selective sites, which can catalyze side-reactions leading to coke formation. An additional explanation is that the presence of carbon can modify olefin adsorption strength on a surface, and increase the energy barrier for C-H activation. Coke may therefore deactivate Pt catalysts via an electronic interaction, in addition to steric blocking.

The interaction between metal and coke influencing selectivity is reminiscent of dopants or promoters; the selectivity improvement from adding Sn or Ge to the Pt catalyst comes at the cost of activity, though not to the same extent as coking. Sn is the most widely-used dopant for Pt, though Ge has been found to produce similar improvements in stability against cok-
XPS of subnano PtSn clusters shows a shift to lower binding energies, implying that Sn tends to donate electrons to Pt. However, there have been reports that PtSn catalysts build up more coke than their pure Pt analogues, suggesting that they are not simply resistant to the build-up of coke, but that their activity persists despite partial coking. The contrast between the electronic and steric mechanisms of coking, and the role of doping are represented in Figure 1.

Sub-nano clusters are promising catalysts due to their high atom utility, and ability to outperform bulk-like catalysts by breaking scaling relations. Pure Pt clusters have been studied as alkane dehydrogenation catalysts, as have various dopants to improve catalyst selectivity, including B, Si, Ge, Sn, and S. Surface-supported clusters are fluxional, isomerizing rapidly under the high temperatures of real reactions such that metastable structures are thermally populated. Higher-energy isomers often show greater catalytic activity than the global minimum isomer. If the kinetic barriers for isomerisation are low, then the isomer populations will be determined by a Boltzmann distribution. If a cluster were to have high isomerisation barriers then the ensemble would not thermally equilibrate, and macroscopic properties would be determined by the reduced set of accessible isomers, which could be useful if the prevalent isomers have superior activity.

Our most recent work focused on Al₂O₃-supported PtGe subnanoclusters, which were pre-
pared experimentally after Ge was theoretically predicted to be a suitable dopant.\textsuperscript{7} We found that not only were the prepared Pt\textsubscript{4}Ge clusters reasonably stable and selective, but that they slowly converted to a partially-coked form, Pt\textsubscript{4}GeC\textsubscript{2}, which was stable against further coking.\textsuperscript{29} This parallels the behavior of PtSn nanoparticles which remain active and stable despite building up more coke than their pure Pt analogues.\textsuperscript{24} Transforming a poisoning process into in-situ catalyst synthesis by doping, illustrated in the right-most part of Figure 1 is a powerful new strategy in catalyst design. To apply this strategy to other reactions, we must first understand the fundamental chemistry behind the efficacy of Pt\textsubscript{4}GeC\textsubscript{2}. In this paper we investigate the electronic synergy between Ge and coke in Pt\textsubscript{4} clusters in the context of ethane dehydrogenation with a combination of DFT calculations and experiment. For the DFT calculations, we focus on the “pristine” clusters Pt\textsubscript{4} and Pt\textsubscript{4}Ge, and their partially coked counterparts Pt\textsubscript{4}C\textsubscript{2}, and Pt\textsubscript{4}GeC\textsubscript{2}. After obtaining the ensemble of isomers, we perform transition state calculations to obtain barriers and determine the reactivities of these isomers towards ethane and ethylene dehydrogenation. Detailed bonding analyses of the interaction between Ge and C\textsubscript{2} provides deeper chemical insights into activity and stability trends. With supporting experimental evidence from ISS and TPD data, we observe that Ge mitigates the deactivating effect of C towards ethane dehydrogenation, and improves the selectivity towards ethylene desorption.

**Results and discussion**

**Pt\textsubscript{4} and Pt\textsubscript{4}C\textsubscript{2}**

Pt, in the bulk or in the nanoparticle/cluster form, is a facile catalyst for ethane dehydrogenation, and Pt\textsubscript{4} is no exception to this, proving to bind ethane and activate C-H bonds with low activation barriers based on DFT calculations (vide supra). However, Pt suffers from lack of selectivity, and it has been shown both experimentally and computationally to dehydrogenate ethylene and acetylene, leading to rapid deactivation by coking. “Complete
dehydrogenation” of ethane adsorbed on Pt$_4$ forms a Pt$_4$C$_2$ cluster, which may be seen as the first step of coking. To assess theoretically the effects of this initial coking on catalytic activity and selectivity in subsequent reactions we must first explore the isomeric ensembles of Pt$_4$ and Pt$_4$C$_2$. Here we explore the initial coking product Pt$_4$C$_2$ and directly compare it to Pt$_4$GeC$_2$, which is found to be selective and stable against further coking.$^{29}$ Furthermore, this gives us useful information about early stages of coking. Relevant isomers for Pt$_4$C$_2$/Al$_2$O$_3$ obtained via global optimization can be seen in Figure 2(a); see Figure S1 for the Pt$_4$/Al$_2$O$_3$ and Pt$_4$C$_2$/Al$_2$O$_3$ full ensembles. The C atoms are mostly 3-coordinate while the Pt atoms are on the edges of the clusters, so incorporation of C into the Pt$_4$ cluster does not block Pt sites. Incorporation of C into the Pt cluster results in dramatic structural differences between the Pt$_4$ and Pt$_4$C$_2$ ensembles. Clearly, the earliest stages of coke formation induce structural reorganization.

To compare the reactivity and selectivity of Pt$_4$/Al$_2$O$_3$ and Pt$_4$C$_2$/Al$_2$O$_3$, we computed the binding modes of ethane, ethylene, and acetylene to the thermally accessible isomers of both clusters. The accessible binding modes can be seen in Figure S2. We then computed the first C-H activation barriers for low-energy binding modes as a descriptor for the activity or selectivity of Pt$_4$/Al$_2$O$_3$ and Pt$_4$C$_2$/Al$_2$O$_3$.

Reactivity studies of fluxional systems are challenging because we must understand the contribution of each isomer to the overall reactivity. Using the Curtin-Hammet principle, where the distribution of products is determined by the free energy difference between the two transition states, $\Delta\Delta G^\ddag$, we consider the isomer with the lowest transition state energy relative to the global minimum the driver of reactivity for that step.$^{33,34}$ To show this for our multi-component systems, we plot barriers on bar charts where all energies are given relative to the global minimum for that composition in Figure 2(b,c). Therefore, according to the Curtin-Hammet principle, the most reactive isomers are the ones with the lowest bar tops in Figure 2(b,c).

C-H activation barriers for Pt$_4$ and Pt$_4$C$_2$ are shown for ethane in Figure 2(b) and for ethy-
lene in Figure 2(c). Results for acetylene can be found in Figure S3 along with details of all computed barriers (Figure S4). Figure 2(b) shows that Pt$_4$ is an active dehydrogenation catalyst for ethane, with computed transition state energies as low as 0.29 eV above the ground state. When C$_2$ is added to the Pt$_4$ cluster, the barriers for ethane C-H activation increase to 0.64 eV, showing that a small amount of coke has a large deactivating effect. We also see an increase in the lowest ethylene C-H activation barrier for Pt$_4$C$_2$ relative to Pt$_4$, indicating an increase in selectivity (Fig. 2(c)). This agrees with literature; even the inclusion of a small amount of carbon on Pt, either in bulk, or larger more bulk-like NPs will dramatically reduce the activity towards ethane dehydrogenation, while improving selectivity towards ethylene. The charge distributions in Figure 3(a,b), calculated using QTAIM, reveal details of the mechanism of electronic deactivation. The carbon atoms are negatively charged, having drawn electron density away from the platinum atoms, as expected from
Pauling electronegativity values\textsuperscript{36} A similar charge-transfer effect has been observed experimentally in S-doped Pt catalysts by XPS and CO stretching frequencies\textsuperscript{27} With this in mind, we next investigate the effect of Ge doping on catalyst stability and selectivity.

\textbf{Pt\textsubscript{4}Ge and Pt\textsubscript{4}GeC\textsubscript{2}}

Pt\textsubscript{4}Ge is a stable and selective candidate catalyst for ethane dehydrogenation\textsuperscript{29} and both experiment and theory suggest that the partially coked species Pt\textsubscript{4}GeC\textsubscript{2} is actually the stable form of the catalyst. The low-lying isomers of Pt\textsubscript{4}GeC\textsubscript{2} fall into two groups - those with separated C atoms, and those with a C–C dimer, both of which are shown in Figure 4(a) (see figure S5 for the full Pt\textsubscript{4}Ge and Pt\textsubscript{4}GeC\textsubscript{2} ensembles). Note the similarities in the Pt-C binding between Pt\textsubscript{4}C\textsubscript{2} (Figure 2a) and Pt\textsubscript{4}GeC\textsubscript{2} (Figure 4a); the inclusion of C\textsubscript{2} induces similar restructuring with and without Ge. This means that Ge in Pt\textsubscript{4}GeC\textsubscript{2} is not altering the reactivity due to a stabilization of Pt core structures different from those of Pt\textsubscript{4}C\textsubscript{2}. As a result, the stabilization of Pt\textsubscript{4}GeC\textsubscript{2} against further coking and deactivation must have an electronic cause.

Consider the lowest-energy isomer of Pt\textsubscript{4}GeC\textsubscript{2} with a bonded C–C dimer (Figure 4(a), right side), which lies just 0.06 eV above the global minimum isomer (which has separated C atoms, Figure 4(a), left side), and compare it to the corresponding isomer of Pt\textsubscript{4}C\textsubscript{2}. There are several reasons for focusing on these C-C bonded isomers. The isomer populations would be thermally equilibrated, and thus dominated by the global minimum structures if the barriers to isomerisation were low (e.g. in undoped Pt\textsubscript{7})\textsuperscript{28} but in this case, the computed barrier is \(~1.33\) eV, indicating that interconversion should be slow. Furthermore, based on the active structures for ethylene dehydrogenation, we expect that the C-C bonded isomer should dominate Pt\textsubscript{4}GeC\textsubscript{2} formation, and remain dominant because of the high isomerization barrier. This is important because the global minimum isomer of Pt\textsubscript{4}GeC\textsubscript{2}, with separated C atoms, is predicted to be unreactive towards ethane, based on its lack of chemisorption of ethane in DFT calculations (Figure S6), whereas the C-C bonded isomer should be reactive,
based on our activation energy calculations.

Figure 3(a,b) shows these active isomers of Pt\textsubscript{4}C\textsubscript{2} and Pt\textsubscript{4}GeC\textsubscript{2} annotated with atomic QTAIM charges. The large positive charge on Ge indicates electron-donating behaviour, while the negative charges on C show electron acceptance, in agreement with electronegativities. The Pt atomic charges vary, but the sums (-0.10 for Pt\textsubscript{4}C\textsubscript{2}, -0.50 for Pt\textsubscript{4}GeC\textsubscript{2}) indicate that electron donation from Ge to Pt compensates for the electron depletion by transfer to carbon.

![Figure 3: Electronic structure and bonding properties of active isomers of Pt\textsubscript{4}(Ge)C\textsubscript{2}. (a,b) Structures of Pt\textsubscript{4}C\textsubscript{2} and Pt\textsubscript{4}GeC\textsubscript{2} on Al\textsubscript{2}O\textsubscript{3} with Pt shown in grey, C in brown, and Ge in purple, Al in blue, and O in red. Each atom is labelled with its computed QTAIM charge, and $\Sigma q_{Pt}$ denotes the sum of the Pt charges. (c,d) Projected density of states (PDOS) plots for the 2s, p orbitals of carbon annotated with $p_z$ Mulliken populations. The 2s PDOS is in black, $p_x$ in orange, $p_y$ in red, and $p_z$ in purple. (e,f) ICOHP plots for the C 2p\textsubscript{z} - C 2p\textsubscript{z} interaction, annotated with the C-C atomic ICOBI.]

To further study the bonding in Pt\textsubscript{4}GeC\textsubscript{2} and Pt\textsubscript{4}C\textsubscript{2}, we devised simple gas-phase models by taking the cluster structures from periodic optimization and deleting the support entirely. The models are validated by their QTAIM charge distributions, which show the same trends as the supported clusters. The molecular clusters, QTAIM charges, and MO diagrams are
shown in Figure S7. The MO diagrams show that the Ge atom in Pt₄GeC₂ is in the +2 oxidation state; the lowest three unoccupied levels have predominant Ge 4p character, while the Ge 4s-based MO is found far below the HOMO. The LUMO of Pt₄C₂, which corresponds to the HOMO in Pt₄GeC₂ after accepting an electron pair from Ge, is C-C π bonding, so adding Ge to Pt₄C₂ strengthens the C-C bonding.

Returning to the supported cluster model, Figure 3(c,d) shows the projected density of states (PDOS) for the carbon 2p orbitals in Pt₄C₂ and Pt₄GeC₂ respectively. The sharp 2pₓ peak just above E_F in Pt₄C₂ but immediately below E_F in Pt₄GeC₂ suggests a C 2pₓ orbital that is empty in Pt₄C₂ but filled in Pt₄GeC₂. The C 2pₓ orbital is perpendicular to the surface, so this PDOS analysis supports the theory that Ge strengthens C-C π bonding. Mulliken analysis also supports this conclusion, showing an increase in C 2pₓ population from 0.86 to 1.01 on addition of Ge to Pt₄C₂. The most compelling evidence for Ge strengthening C-C bonding is shown in the C 2pₓ COHP plots in Figure 3(e,f), related to the atomic C-C COHP plots previously reported,²⁹ and the integrated crystal orbital bond index (ICOBI) values for the C-C atomic pair. COHP shows the bonding character of electronic states between specific pairs of atoms or orbitals, where bonding states appear to the right of the vertical axis (note that the horizontal axis plots -COHP so that positive values denote bonding orbitals). The PDOS peaks around the Fermi level, as discussed above, are present in the bonding channel on the COHP plots, indicating that these states have strong C-C bonding character. ICOBI is a bond order for pairs of atoms in solids,³⁷ so the increase in C-C ICOBI from 1.20 to 1.55 on addition of Ge is further evidence for a strengthened C-C bond. We can therefore conclude that the Ge dopant donates electrons to C, so Pt remains electron-rich and reactive, while remaining selective.¹⁷,³⁸ The donated electrons occupy a πC−C bonding orbital, so Ge doping strengthens C-C bonding as indicated by the gas phase models.

The isomeric structures for adsorbed hydrocarbons found by global optimization show the consequences of these electronic structure trends. If we compare the first and last isomers of Pt₄C₂ in Figure 2(a) with the isomers of Pt₄GeC₂ in Figure 4(b), we see structural sim-
ilarities, even though these clusters have different reactivities. The binding sites for ethane and ethylene on Pt$_4$C$_2$ and Pt$_4$GeC$_2$ are similar (Figure S1, S5), consistent with the hypothesis that Ge influences reactivity electronically. There is also a significant Ge effect on the energetics of the isomers with separated vs bonded C atoms. In Pt$_4$C$_2$ the C-C bonded isomer lies +0.17 eV above the C-C separated isomer, while in Pt$_4$GeC$_2$ the corresponding gap is reduced to +0.06 eV due to C-C bond strengthening by electron transfer from Ge. Furthermore, the equivalent barrier for breaking the C-C bond in Pt$_4$C$_2$ (1.16 eV) is lower than that for Pt$_4$GeC$_2$ (1.33 eV). See Table S1, and Figure S8 for details.

To quantify the effect of changes in electronic structure on catalytic behavior, 4 shows our previously reported reaction barriers for ethane (Figure 4(b)) and ethylene (Figure 4(c)) plotted in the same style as in Figure 2. There is an increase in the ethane C-H activation barrier upon the deposition of C$_2$, to 0.53 eV but this increase is less than in the absence of Ge, in Figure 2, where the barrier increased to 0.64 eV. Thus, doping with Ge allows the cluster to remain more active for ethane C-H activation after partial coking.

Figure 4(c) shows that the lowest barrier for C-H activation of ethylene increases upon coking, from 1.24 eV in Pt$_4$Ge to 1.41 eV in Pt$_4$GeC$_2$, so the first C$_2$ deposition should hinder further coking. Doping with Ge increases the ethylene dehydrogenation barriers substantially, from 0.66 eV for Pt$_4$ to 1.24 eV for Pt$_4$Ge, so Ge also preserves catalyst activity by reducing the rate of initial coking. Our bonding analysis helps to explain the resistance of Pt$_4$GeC$_2$ to further coking. Dehydrogenation of additional ethylene molecules would result in C-C bond formation between the cluster C$_2$ unit and the subsequently deposited C atoms. Ge strengthens π bonding in the C$_2$ unit which would have to be broken to bind additional coke, so the combined electronic effects of Ge and C$_2$ hinder further coking. This manifests in different binding energies of ethylene to Pt$_4$C$_2$ (-1.85 eV) and Pt$_4$GeC$_2$ (-2.10 eV), for structures where ethylene binds directly to the C$_2$ unit in the cluster (Figures S4 and S9).

C-C cracking is another side reaction which frequently deactivates pure Pt catalysts. In order to assess the role of C-C cracking in coking for Pt$_4$, Pt$_4$C$_2$, Pt$_4$Ge, and Pt$_4$GeC$_2$,
Figure 4: (a) Low-energy isomers of Pt$_4$GeC$_2$. Pt atoms are shown in grey, Ge in purple, and C in brown. Blue polyhedra represent the Al$_2$O$_3$ support. (b,c) Ethane and ethylene (respectively) C-H activation barriers for Pt$_4$Ge and Pt$_4$GeC$_2$ with individual isomer resolution. The bottom of each bar corresponds to the energy of the reactant isomer, relative to the lowest energy isomer for that composition, and the top of each bar corresponds to the transition state energy.

we compared the barrier heights of C-C cracking to C-H activation starting from the same isomer. These are summarized in Table S1, with relevant barriers shown in Figure S10. For Pt$_4$ and Pt$_4$C$_2$, C-C cracking is only faster than dehydrogenation for for bound acetylene, in agreement with literature.\textsuperscript{16,18} For Pt$_4$Ge and Pt$_4$GeC$_2$, on the other hand, we see that the C-C cracking barrier is always higher than the corresponding C-H activation barrier. The addition of Ge therefore eliminates C-C cracking as a possible side-reaction. Doping with Ge and Sn suppresses these side-reactions for bulk and larger NP systems.\textsuperscript{39–41} Ge therefore reduces the tendency to coke not only by raising barriers for deeper dehydrogenation, but also by preventing coke-forming side-reactions. This leads to a difference in the kinetic accessibility of the Pt$_4$C$_2$ and Pt$_4$GeC$_2$ ensembles. Since there are more feasible C-C cracking pathways for Pt$_4$, the isomer with the split C$_2$ unit is kinetically accessible, and plays a role in the catalytic behavior of Pt$_4$C$_2$. The Pt$_4$GeC$_2$ isomer with the split C$_2$ unit is however not
accessible due to higher C-C cracking barriers, despite the fact that it is the putative global minimum. Thus, relative populations of isomer in the ensemble may be determined by relative rates of dehydrogenation and C-C cracking, rather than by their relative energies. Given the large activity differences between isomers, detailed knowledge of all possible reactions would be necessary for quantitative predictions of non-equilibrium ensemble behaviors. This is in agreement with work by Peters, which emphasizes the importance of isomer interconversion flux and reaction production leading to deviations of populations from their equilibrium concentrations. Thus reactivity may not be identifiable from equilibrium populations alone.

Experimental Support

Figure 5: Pt relative intensities from He$^+$ ion scattering spectroscopy of Pt$_4$/alumina (black) and Pt$_4$Ge/alumina (hatched grey). The secondary axis highlights the number of C$_2$D$_4$ molecules adsorbed to Pt sites on Pt$_4$/alumina (red) and Pt$_4$Ge/alumina (hatched light red) per cluster.

For experimental validation of the electronic origin of the Ge effects on coking and stability, we compare our DFT results to ISS and TPD data for Pt$_4$ and Pt$_4$Ge, before and after varying numbers of ethylene TPD cycles. Each cycle involved first saturating the catalysts with C$_2$D$_4$ at 180 K, then heating to drive desorption of either intact C$_2$D$_4$ or of D$_2$, the latter indicating carbon deposition. The TPD data is from previous work, and explored in more detail there. In brief- the as-prepared Pt$_4$ catalyst has a high T desorption peak for
ethylene around 310 K for the first 2 TPD cycles, but which rapidly decreased, indicating rapid loss of strong ethylene binding sites. D$_2$ desorption also rapidly decreases in successive TPD runs. For Pt$_4$Ge, in contrast, the high-T ethylene and D$_2$ desorption features are stable over repeated runs, with much less D$_2$ desorption compared to Pt$_4$. This reflects higher stability and selectivity against coking of the Pt$_4$Ge clusters.

ISS allows us to track changes induced by TPD cycles in the surface layer of the catalysts, which can be compared to the estimated total number of strong ethylene binding sites per clusters, estimated prior to each TPD cycle (details in SI). For Pt$_4$/Al$_2$O$_3$, the “as-prepared” Pt ISS intensity reflects a catalyst where essentially all the Pt atoms are in the He$^+$-accessible surface layer. The Pt intensities were attenuated, relative to those for the as-prepared catalyst, by factors of 15%, 45%, and 70%, respectively, after 1, 6, and 21 TPD runs, reflecting shadowing/blocking of He$^+$ scattering by bound C atoms. Note, however, that after 6 TPD runs, 6 to 8 C atoms per Pt$_4$ cluster were estimated to be present, but more than half of the Pt atoms remained He$^+$-accessible, whereas saturating the Pt clusters with CO molecules resulted in much larger (~80%) attenuation of Pt ISS signals. This supports our results showing restructuring of Pt$_4$ upon the addition of C$_2$, which has also been seen experimentally on the surfaces of larger NPs. The number of ethylene molecules adsorbed in strong binding sites decreases more rapidly after each TPD run, by factors of 48%, 68% and 80%, respectively, after 1, 6 and 21 runs. The decline in strong ethylene binding sites is partly offset by an increase in weak binding sites. Thus, the combination of ISS and TPD suggests that while there is some steric site blocking by carbon deposition, the larger effect on ethylene binding is electronic, decreasing the binding energies such that few strong binding sites remain. Because these strong binding sites are responsible for the dehydrogenation activity, the catalyst deactivates.

For Pt$_4$Ge the as-prepared ISS intensity was 21% lower than for as-prepared Pt$_4$, attributed to Ge atoms partially shadowing or blocking He$^+$ scattering from Pt. The attenuations of the Pt ISS signal, relative to as-prepared Pt$_4$Ge, were 22%, 44%, and 70% after 1, 6, and
21 TPD runs respectively, similar to Pt$_4$. In contrast, the loss of strong of ethylene binding sites per Pt$_4$Ge was much smaller than for Pt$_4$, at 5%, 24%, and 44%, respectively. Pt$_4$Ge clusters were estimated to have a total of ~2 C atoms present per cluster after 6 TPDs - just one third of the number deposited per Pt$_4$. Thus, experiment shows that there is less, but still significant coking on Pt$_4$Ge, that similar fractions of the initial Pt atoms remain in the surface layer, and that the loss of strong ethylene binding sites is inhibited by Ge. This, too, supports our conclusions that Pt$_4$Ge restructures upon the addition of C$_2$, and that the improved stability of Pt$_4$GeC$_2$ arises from electronic effects due to the interaction between the Ge, Pt, and C.

**Conclusions**

We have studied the electronic behavior of four dehydrogenation catalysts, Pt$_4$, Pt$_4$C$_2$, Pt$_4$Ge, and Pt$_4$GeC$_2$, all supported on Al$_2$O$_3$, to explore the role that Ge plays in mitigating deactivation via coke formation. Pt$_4$ is predicted to be a potent ethane dehydrogenation catalyst, but suffers from poor selectivity, driving deep dehydrogenation that leads to carbon deposition and catalyst deactivation. Coke formation induces restructuring of the cluster core, and increases the energy barriers for ethane and ethylene C-H activation, while also decreasing adsorption energies. The partially coked Pt$_4$C$_2$ is therefore more selective, but much less active than the uncoked catalyst. This deactivation is attributed to electronic effects, as coke formation does not primarily block sites, but changes the electronic properties of the cluster, with the C$_2$ unit withdrawing electron density from Pt.

Pt$_4$Ge is already more selective than Pt$_4$, due to higher ethylene C-H activation barriers, while retaining the same activity towards ethane. However, it is the interaction between Ge and C$_2$ that results in “coke-resistance”. Pt$_4$GeC$_2$ has a similar ethane C-H activation barrier to Pt$_4$Ge, and even higher ethylene C-H activation barriers. Ge donates electrons to the C$_2$ unit, preventing the depletion of electron density on Pt, allowing it to retain ac-
tivity despite some coke formation. Additionally, as Ge strengthens the C-C π-bond, the binding of further coke to the C₂ unit is discouraged, as it would require the disruption of the bonding C-C interaction. Thus, Pt₄GeC₂ is an active dehydrogenation catalyst despite carbon deposition, with desirable selectivity arising from the interaction between Ge and C₂. The ab initio results are substantiated by experimental results, which demonstrate that the physical loss of ethylene binding sites during coking is insufficient to explain loss of activity, reflecting that the effect observed for both Pt₄ and Pt₄Ge is electronic rather than steric. The cooperative interaction between Ge and C₂ invites us to see the two species as co-dopants for Pt₄, where Ge as a promoter prevents the poisoning effect of C₂ alone. This conclusion sheds new light on the report in literature that “coke-resistant” Pt-Sn¹,²⁴ or Pt-Ge catalysts⁶ remain active despite coke buildup. We believe that the observations reported here may help explain the behavior of a broader class of coke-resistant catalysts, and should be applicable to other compositions and reactions.

Methods

Computational Methods

Calculations on surface-supported clusters were performed using plane-wave DFT in VASP,⁴⁴ using the PBE exchange-correlation functional,⁴⁵ PAW pseudopotentials,⁴⁶ and a plane-wave cut-off of 500 eV. Unit cells were constructed from a 5-layer 3x3 supercell of Al₂O₃ with a 15 Å vacuum gap. Transition states were calculated using the climbing-image nudged elastic band (CI-NEB) method implemented in VTST.⁴⁷,⁴⁸ QTAIM analysis was performed using the Bader code developed by the Henkelman group.³⁵,⁴⁹ Global optimizations were performed with a BLDA approach⁵⁰ to generating chemically-reasonable initial structures, both for cluster structure sampling, and adsorbate binding sampling. The in-house codes PGOPT and GOCIA were used to run the optimizations. Local-basis projections for bonding analysis were performed with LOBSTER,⁵¹ using the
PBEVaspFit basis set and a projection basis of 5p5d6s for Pt, 4s4p for Ge, 3s3p for Al, and 2s2p for C and O. All projections reported less than 1.2% charge spilling.

DFT calculations on gas-phase models were performed with the Amsterdam Density Functional (ADF) package, version 2019.304, using the PBE functional. Slater-type basis sets of triple-ζ + polarization quality were used on all atoms, with orbitals up to 4d (Pt), 3d (Ge) and 1s (C) included in the frozen core.

**Experimental Methods**

The relative intensities in He$^+$ ion scattering spectroscopy (ISS) was summarized from the series of ISS previous results for Pt$_4$/alumina and Pt$_4$Ge/alumina. The relative intensities are calculated by taking the average Pt ISS signals of the first 3 data points of the corresponding series of ISS, of which the ISS signals are calculated by integrating the background subtracted Pt integrated intensities normalized to the total integrated ISS signals for the full ion scattering spectrum that remain relatively invariant to compensate for the fluctuation of He$^+$ ions scattered. The Pt ISS signals for the as deposited samples are extrapolated, to reveal what the initial Pt ISS signals would be at, from the gradual leveled curve rising from the ISS intensities after some exposure of the samples under He$^+$ ions; the extrapolated numbers are close to their corresponding Pt ISS signals post 750 K heat treatment, thus indicating the presence of adventitious adsorbates or H and Cl atoms present on the sample surfaces as well as that the clusters do not sinter much after a single heat treatment on the sample surface.

The C$_2$D$_4$ adsorbed molecules per cluster are calculated from the sum of the high temperature C$_2$D$_4$ desorption peaks (attributed to C$_2$D$_4$ binding to Pt) and half of the D$_2$ desorbed molecules (as each C$_2$D$_4$ produces 2 D$_2$ molecules) in the temperature programmed desorption from our previous work.
References

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Supporting Information Available

Computed ensembles for Pt$_4$, Pt$_4$C$_2$, Pt$_4$Ge, and Pt$_4$GeC$_2$ both bare and with adsorbed C$_2$H$_6$, C$_2$H$_4$, and C$_2$H$_2$. MO analysis of Pt$_4$C$_2$ vs. Pt$_4$GeC$_2$. Structures corresponding with C-H activation and C-C cracking NEBs. Comparison between C-H and C-C breaking barriers.

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