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Authors

Jimenez-Izal, Elisa

Liu, Ji-Yuan

Alexandrova, Anastassia N

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Germanium as key dopant to boost the catalytic performance of small platinum clusters for alkane dehydrogenation

Elisa Jimenez-Izal,^{a,b,*} Ji-Yuan Liu,^c Anastassia N. Alexandrova,^{d,e}

^a *Kimika Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU), and Donostia International Physics Center (DIPC), P. K. 1072, 20080 Donostia, Euskadi, Spain*

^b *IKERBASQUE, Basque Foundation for Science, Bilbao, Euskadi, Spain*

^c *Key Laboratory for Advanced Materials, Center for Computational Chemistry and Research Institute of Industrial Catalysis, School of Chemistry and Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P. R. China*

^d *Department of Chemistry and Biochemistry, University of California, Los Angeles, 607 Charles E. Young Drive, Los Angeles, California 90095-1569, United States*

^e *California NanoSystems Institute, Los Angeles, California, 90095, United States*

Corresponding Authors E-mail: elisa.jimenez@ehu.eus

Abstract

Pt is the most active pure metal for the dehydrogenation of light alkanes, to produce light alkenes, like ethylene and propylene. These compounds are exceedingly important products in the chemical industry. Pt, however, suffers from a low selectivity, tending to fully dehydrogenate hydrocarbons to pure carbon and giving rise to coking that blocks the active sites, deactivating the catalyst. Different dopants or co-alloying agents have been proposed to tune its selectivity and produce catalysts with longer lifetimes, such as Sn, B and Si. However, often, the improved selectivity is achieved at the expense of catalytic activity. In this work we study MgO-supported Pt clusters and show that nanoalloying Pt with Ge can lead to an improved

selectivity by halting deeper dehydrogenation that leads to coke, without harming the activity towards alkane dehydrogenation as compared to pure Pt clusters. Moreover, Ge reduces the propensity of Pt nanoclusters to deactivate via Ostwald ripening, and reduces the binding energy to carbon. Therefore, Ge-doped Pt nanocatalyst are more selective and resistant to deactivation. The effect of alloying Pt with Ge has an electronic origin: Ge quenches the unpaired electrons in the metal clusters, which are needed to activate alkenes for dehydrogenation.

1. INTRODUCTION

Light olefins are among the most important organic molecules, with the highest production volumes in the world. It is estimated that 400 million tons of olefins are produced per year¹, ethylene being the most predominant olefin in the global market.² Ethylene is a major intermediate in the chemical industry, used to synthesize a wide variety of compounds, such as polyethylene. Ethylene is, in addition, a good model molecule to investigate the dehydrogenation of light alkanes, because it is a desired product of partial dehydrogenation, yet small enough to make modeling manageable. Although traditionally light alkenes are obtained from petroleum derived nafta, this process has important drawbacks, such as the low selectivity and the reliance on the dwindling petroleum reserves. An alternative route is the catalytic dehydrogenation of alkanes.^{3,4} Currently the main challenge of catalytic alkane dehydrogenation is to achieve competitive catalyst selectivities and stabilities. Low selectivity leads to a rapid catalyst deactivation by carbon deposits (coke) that block the active sites.

Platinum is the most active pure metal for light alkane dehydrogenation due to its superior activation of C–H bonds and low activity toward C–C cleavage. However, Pt binds alkenes strongly, thus preventing their desorption from the catalyst surface, and promoting further dehydrogenation eventually leading to coking. Therefore, even though Pt-based catalysts

exhibit high activity in dehydrogenation reactions, the catalyst stability and selectivity are still severe problems in industry. Different strategies have been proposed to improve the catalytic performance of Pt. Doping Pt with Sn is one of the most widely used strategies. Alloying Pt with Sn reduces the acidity of the metal and introduces geometric effects collectively decreasing the affinity towards alkenes, and also provides nucleation sites for Pt redispersion for supported Pt catalysts.⁵⁻⁹ Other promoters such as Zn,¹⁰ In^{11,12} or Ga¹³⁻¹⁶ have been proposed to enhance the catalytic performance of Pt. Deactivation due to coke, however, is still a major problem.^{17,18}

Oxide supported Pt nanoparticles, and also clusters made of just a few atoms, where most of the atoms are at the surface and available to interact with the reactants, are key to optimize the use of the precious metal in catalysis. Furthermore, they often display superior catalytic performance, and they serve as model catalysts for the active sites. Using such models, in our previous joint theoretical and experimental studies, we identified B as a dopant or co-alloying agent for MgO and α -Al₂O₃-supported Pt nanocatalysts, to increase the thermal stability and selectivity of dehydrogenation of alkane to alkene.^{19,20} It was shown that boration reduces the sintering of the nanoclusters and weakens the interaction of the catalyst with ethylene, increasing its selectivity and therefore, its lifetime. Very recently we screened a number of other possible dopants: N, Al, Si, P, S, Cl, with the aim of finding alternatives to known B and Sn, for boosting the catalytic performance of Pt.²¹ Si was revealed as the best dopant in the series, as it favors stopping dehydrogenation of alkanes at alkenes, thus increasing significantly the selectivity and resistivity of Pt.²¹ Moreover, both Si and B, would slow down the sintering of Pt nanoparticles via Ostwald ripening. In the present work, by comparing surface supported Pt₃ and Pt₇ clusters with Pt₂Ge and Pt₇Ge respectively, we show that Ge outperforms both B, and Si, as it is able to improve the selectivity of Pt without harming its activity towards ethane dehydrogenation.

2. METHODS

We performed PW-DFT calculations using PAW pseudopotentials²² and the PBE²³ functional, with the Vienna Ab initio Simulation (VASP) package.²⁴⁻²⁸ The DFT-D3 scheme was used to account for the dispersion interactions.²⁹ We used MgO as a model support, as was justified previously.²¹ In the initial test, triatomic Pt₃ and Pt₂Ge clusters are supported on a MgO(100) 3 x 3 x 3 unit cell. Larger clusters, Pt₇ and Pt₇Ge, on a bigger 4 x 4 x 3 slab were then considered. The MgO slab is composed of six layers. The bottom two layers of the support were fixed at the positions of the bulk, while the top four layers, as well as the clusters on top of the slab, are allowed to relax. A vacuum separation of about 15 Å between repeating cells in z direction was added. The applied convergence criteria for geometry (SCF) relaxation was set to 10⁻⁵ (10⁻⁶), and the plane wave cutoff energy was 450 eV. A 1 x 1 x 1 Γ -centered *k*-point grid was used for surface calculations. The calculations were spin-unrestricted. In the case of Pt₂Ge supported on MgO(100), the global minimum was found manually, with linear and triangular clusters as starting geometries, deposited on all possible binding sites and in all the possible orientations. To search for the global and local minima of Pt₇Ge on MgO(100), and the most stable binding configurations of adsorbates on the clusters, we used several different techniques implemented in our in-house PGOPT package, as explained in ref. 21. Transition states were found using the Climbing Image Nudged Elastic Band (CINEB). In these calculations, clusters were supported on a two-layers MgO(100) surface slab, where the bottom layer was fixed and the top layer with the cluster was relaxed. The convergence criterion for residual force in the TS calculations was set to 0.02 eV•Å⁻¹. TSs were confirmed by phonon calculations at the Γ point.

Several energetic characteristics were calculated to account for the cluster stability against sintering and coking. First, the sintering energy, i. e., the energy penalty for one Pt atom to dissociate from the cluster on the support was calculated as:

$$(1) E_s = E(\text{PtX})_{\text{supported}} + E(\text{Pt})_{\text{supported}} - E(\text{Pt}_2\text{X})_{\text{supported}} - E(\text{surf})$$

where $E(\text{PtX})_{\text{supported}}$ is the energy of the supported PtX dimer (i. e. after losing one Pt atom) on MgO, $E(\text{Pt})_{\text{supported}}$ is the energy of a Pt atom supported on MgO, $E(\text{Pt}_2\text{X})_{\text{supported}}$ stands for the energy of the supported Pt₂X trimer on MgO, and $E(\text{surf})$ for the energy of the pristine MgO(100) surface. A larger **positive** sintering energy means that the cluster needs more energy to lose one Pt atom, therefore, it is more stable and less likely to break apart.

The adsorption energy of the cluster to the surface was calculated as:

$$(2) E_{\text{ads}} = E(\text{Pt}_n\text{X})_{\text{supported}} - E(\text{surf}) - E(\text{Pt}_n\text{X})_{\text{gas}},$$

where $E(\text{Pt}_n\text{X})_{\text{supported}}$ is the energy of the Pt_nX cluster on MgO, $E(\text{surf})$ is the energy of the pristine MgO(100) surface, and $E(\text{Pt}_n\text{X})_{\text{gas}}$ the energy of the Pt_nX cluster in gas phase.

Finally, the binding energy of the supported catalyst to carbon was calculated as:

$$(3) \text{BE}[\text{C}] = E(\text{C-Pt}_n\text{X})_{\text{supported}} - E(\text{Pt}_n\text{X})_{\text{supported}} - E(\text{C})_{\text{gas}}$$

where $E(\text{C-Pt}_n\text{X})_{\text{supported}}$ is the energy of the Pt_nX cluster on MgO with one C atom attached, $E(\text{Pt}_n\text{X})_{\text{supported}}$ is the energy of the Pt_nX cluster on MgO, and $E(\text{C})_{\text{gas}}$ the energy of the carbon atom in gas phase.

3. RESULTS AND DISCUSSION

3.1 Small-size clusters supported on MgO(100)

The study of three atoms clusters supported on MgO, for the screening purposes, allows the reduction of the computational cost due to the smaller configurational space and the required unit cell. For this reason, and following the scheme used in our previous work, we started by exploring Pt₂Ge and comparing its electronic and energetic characteristics to pure Pt

and other doped Pt clusters, namely Pt₂Sn, Pt₂B, and Pt₂Si. The most stable structure of MgO deposited Pt₂Ge is shown in Figure 1. Ge preferentially binds between the two Pt atoms, not in a direct contact with the surface, unlike B and Si that both bind to the surface oxygen. To explore how Ge affects the propensity of Pt to sinter, we calculated the adsorption energy of the cluster to the surface (related to the cluster coalescence mechanism of sintering), and the sintering energy (related to the Ostwald ripening sintering mechanism).^{19,21} Pure Pt has the largest (best) adsorption energy, although it is known that Sn and B mitigate sintering. This suggests (in agreement with the literature³⁰⁻³²) that particle coalescence is not the prevalent sintering mechanism, and instead at this size regime the Ostwald ripening dominates. The sintering energies that are the indicators of the sintering tendencies by Ostwald ripening are given in Table 1. The previously reported agents (Sn, B, and Si) improve the sintering energy. Importantly, Ge also has a very positive impact, i.e. significantly increases the sintering resistance with respect to pure Pt, and to all cluster alloys except for Pt₂B. To estimate the likelihood of deactivation of platinum via coke deposition, we calculated the binding energy of one C atom, BE[C], as a first approximation. C binding can be related to coke initiation on the catalyst. This approximation was shown to be reliable in the past.^{19-21,33} As it can be seen in Table 1, alloying Pt with Ge has an enormous effect on the BE[C], reducing it by 2.5 eV, the largest effect among all the Pt₂X considered. Therefore, it is expected that Ge will both slow down the sintering, and make the catalyst more resilient to carbon deposits. Calculated Bader atomic charges to some extent illuminate this result. Like B and Si added to Pt clusters, Ge is positively charged. Pt atoms in all doped clusters have a larger negative charge as compared to that in pure Pt clusters, but the effect of Ge is milder than the effect of B or Si. Hence, it is likely that Ge brings the most adequate charge to Pt, mitigating its affinity to carbon while also increasing the penalty for cluster dissociation during sintering.

Table 1. Energetic and electronic properties of Pt₂X (X = Ge, B, Si, Sn) deposited on MgO(100). Sintering energy, E_s, adsorption energy, E_{ads}, and binding energy to C, BE[C], are given in eV. ΔQ_{cluster}, ΔQ_{Pt}, and ΔQ_X are the total Bader charge on the cluster, Pt, and X, respectively.

| Cluster | E _s | E _{ads} | BE[C] | ΔQ _{cluster} | ΔQ _{Pt} | ΔQ _X |
|-------------------------|----------------|------------------|--------------|-----------------------|------------------|-----------------|
| Pt₂Ge | 2.61 | -3.27 | -5.88 | -0.55 | -1.20 | 0.65 |
| *Pt ₃ | 2.07 | -4.18 | -8.36 | -0.58 | -0.58 | - |
| *Pt ₂ B | 2.79 | -3.88 | -6.19 | -0.21 | -1.69 | 1.45 |
| *Pt ₂ Si | 2.30 | -3.11 | -6.09 | -0.11 | -2.22 | 2.12 |
| *Pt ₂ Sn | 2.13 | -2.83 | -6.22 | -0.39 | -1.09 | 0.69 |

*Data taken from reference 19.

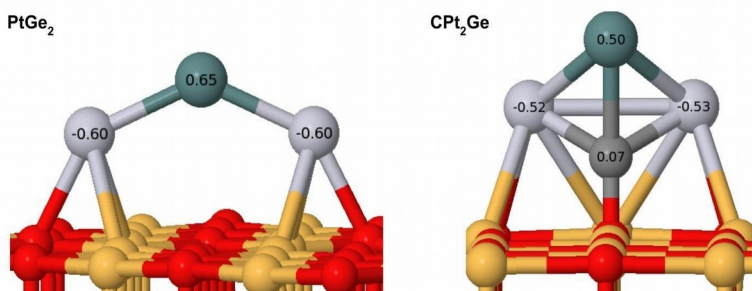


Figure 1. Putative global minima of Pt₂Ge on MgO(100) (left), and C-Pt₂Ge (right). Bader charges are depicted on the atoms. O, Mg, Pt, Ge and C are depicted in red, orange, grey, dark green and dark grey, respectively.

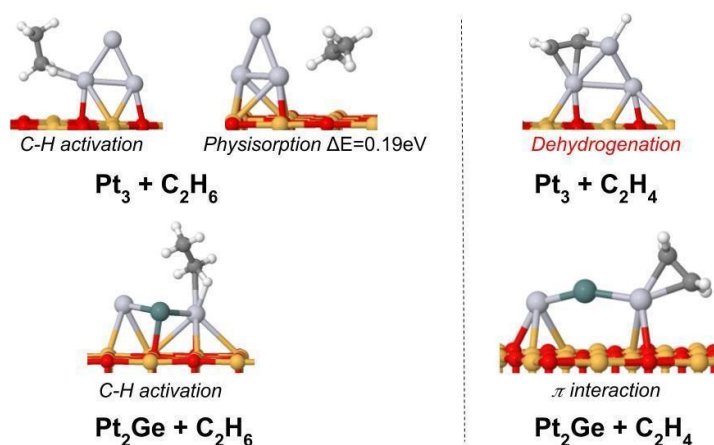


Figure 2. The most stable configurations of ethane and ethylene adsorbed on Pt₃ (top, from reference 19), and on Pt₂Ge (bottom). Energy differences are in eV. O, Mg, Pt, Ge, C, and H are depicted in red, orange, grey, dark green, dark grey and white, respectively.

The first results suggest that Ge could be a very promising alloying agent for Pt. To assess the selectivity of Ge-doped Pt in alkane dehydrogenation, we explored the interaction of Pt₂Ge with ethane (reactant) and ethylene (desirable product). Ideally the reactant would be activated, and the product would desorb or at least interact weakly with the catalysts. Deeper dehydrogenation leads to coke, and this is indeed what happens in the case of pure Pt.²¹ ethylene spontaneously dehydrogenates when put in contact with Pt₃ (Figure 2, top right). When ethylene interacts with Pt₂Ge, however, no dehydrogenation is observed. It is well-established that ethylene can bind Pt either in the di-σ mode, a precursor of dehydrogenation, or in the π mode, which is more likely to desorb.³⁴⁻³⁷ Pt₂Ge binds ethylene only in the π mode,

as pictured in Figure 2 bottom right. No competing thermally-accessible configurations were found for this system. Thus, Ge should radically improve the selectivity of Pt₂Ge compared to pure Pt₃, favoring alkene desorption. Moreover, Ge promises a better selectivity with respect to the previously studied Pt₂B and Pt₂Si.²¹ First, the more reactive di- σ mode interaction is not energetically competitive, unlike in B and Si doped clusters. Second, ethylene should be easily desorb from Pt₂Ge because its binding energy to the cluster is smaller (-1.21 eV in Pt₂Ge; -1.43 eV in Pt₂B; -1.92 eV in Pt₂Si; -2.43 eV in Pt₃).

A problem of B and Si might be that their reactivity with alkene is reduced at expense of the reactivity with the reactant (alkane). In other words, B and Si-doped Pt does not activate C-H in ethane as effectively as pure Pt does. On the other hand, the results for Ge suggest that it might actually preserve the activity of Pt toward alkane dehydrogenation. Indeed, when the catalysts bind ethane, Pt₃ activates one of the C-H bonds elongating it from 1.11 to 1.18 Å (Fig. 2), but Pt₂B and Pt₂Si activate the C-H bond less (to 1.13 Å), whereas Pt₂Ge activates C-H even more than pure Pt, elongating it up to 1.21 Å. Furthermore, while for Pt₃, Pt₂B, and Pt₂Si the physisorption of ethane is energetically competitive with the activated geometry, for Pt₂Ge is not.

We further computed the barriers for ethane dehydrogenation on Pt₃ and Pt₂Ge. The calculated reaction profiles are shown in Figure 3. The barriers for ethane dehydrogenation in both pure Pt and Ge-doped Pt clusters are very small, 0.17 and 0.05 eV respectively. In agreement with the elongation of the C-H bonds in the adsorbed geometries, the dehydrogenation proceeds more readily, i. e., with a smaller energetic barrier, on the Ge-doped cluster. Thus, in the Pt₂Ge clusters, Ge causes Pt to interact less strongly with ethylene improving its selectivity, while preserving and even enhancing its catalytic activity toward ethane dehydrogenation.

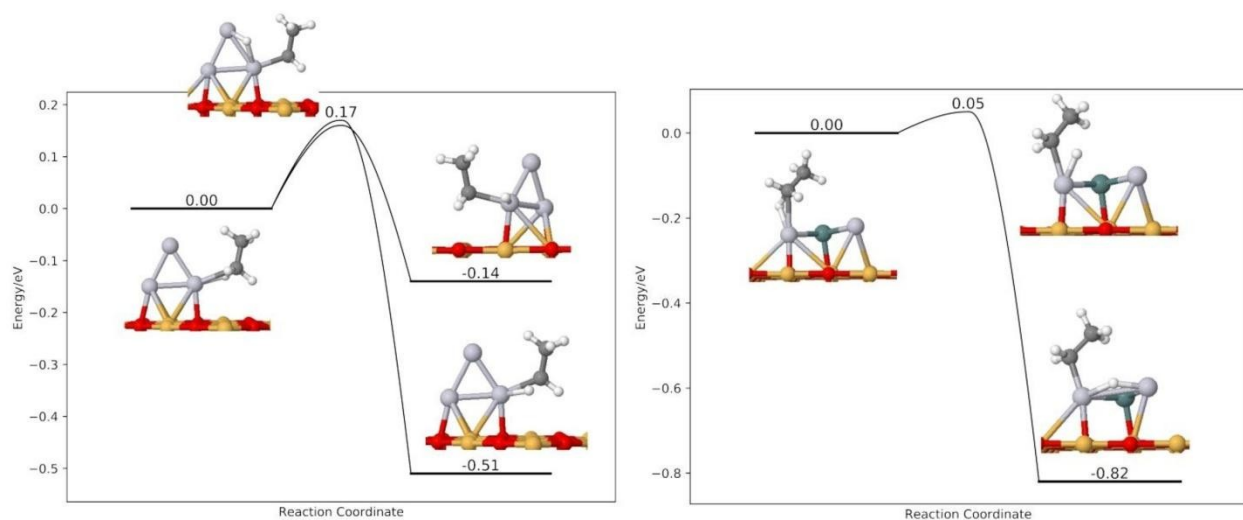


Figure 3. Reaction pathway for direct ethane dehydrogenation on Pt₃ (left) and Pt₂Ge (right). Activation energies are given in eV. O, Mg, Pt, Ge, C and H are depicted in red, orange, grey, dark green, dark grey and white respectively.

3.2 Larger size cluster supported on MgO(100)

Next, we explored the larger Pt₇Ge cluster supported on MgO(100). We chose this system because it is experimentally known that Pt₇ exhibits the highest activity toward the undesirable ethylene dehydrogenation as compared to Pt₄ and Pt₈ on alumina,³³ and B was experimentally shown to extend its lifetime.²⁰ Because the computational cost is enormous, we focus the structural search for reagent-bound systems on the most stable identified Pt₇Ge isomers. We considered the interactions of these isomers with carbon and ethylene, i.e. the most important adsorbates reporting on the likely selectivity and durability of the catalyst.

All the Pt₇Ge cluster structures that are predicted to be populated at catalytically relevant temperatures of 700 K²⁰ are shown in Figure 4. Probabilities of the minima to be thermally populated are computed using the Boltzmann statistics, under the assumption that isomers easily interconvert, as we justified previously.³⁸ For this larger cluster, we considered a statistical ensemble of several thermally-accessible geometries

instead of just the global minimum, because, as we showed in numerous works, physical and chemical properties of cluster catalysts are defined by ensembles of metastable states at realistic temperatures.^{20,21,33,38,39} Electronic and structural similarities are found between Pt₂Ge and Pt₇Ge. First, Ge is positively charged (Fig. S1) and, as a result, Pt exhibit larger negative charges than in pure Pt. Second, again, the Ge atom avoids the direct interaction with the surface. On the contrary, B and Si bind between the cluster and the support, whereas Sn, alloys with Pt without obstructing the Pt sites on the surface. At the lowest concentration of Ge explored here, it is not possible to conclude how Ge would distribute in the cluster at higher Ge:Pt proportions, but if Ge tends to bind to the cluster surface it might become necessary a tight control of the dopant concentration in the experiment. The putative global minimum of Pt₇Ge, Isomer I (Fig. 4), has a cage-like structure, whereas most of the other isomers are more planar and tend to be perpendicular to the surface, as found for Pt₅⁴⁰ and some Pt₇²¹ isomers on MgO(100). The structural diversity upon alloying Pt with Ge is similar to pure Pt₇ and not as large as that in Pt₇Si (8 isomers are found significantly populated at 700 K for both Pt₇ and Pt₇Ge, versus 12 isomers for Pt₇Si). We are still discovering the implications of having an ensemble of isomers present in catalysis, rather than just one isomer.^{38,41} It is likely that having fewer isomers present in conditions of catalysis can allow more control of the binding sites. Very diverse population would have binding sites with the right reactivity for every kind of adsorbate and this might lead to undesired side reactions, lack of selectivity, and intensified poisoning of the catalyst. In this respect, it appears that Ge does not increase the population of the Pt₇ structures, unlike Si and B.^{20,21}

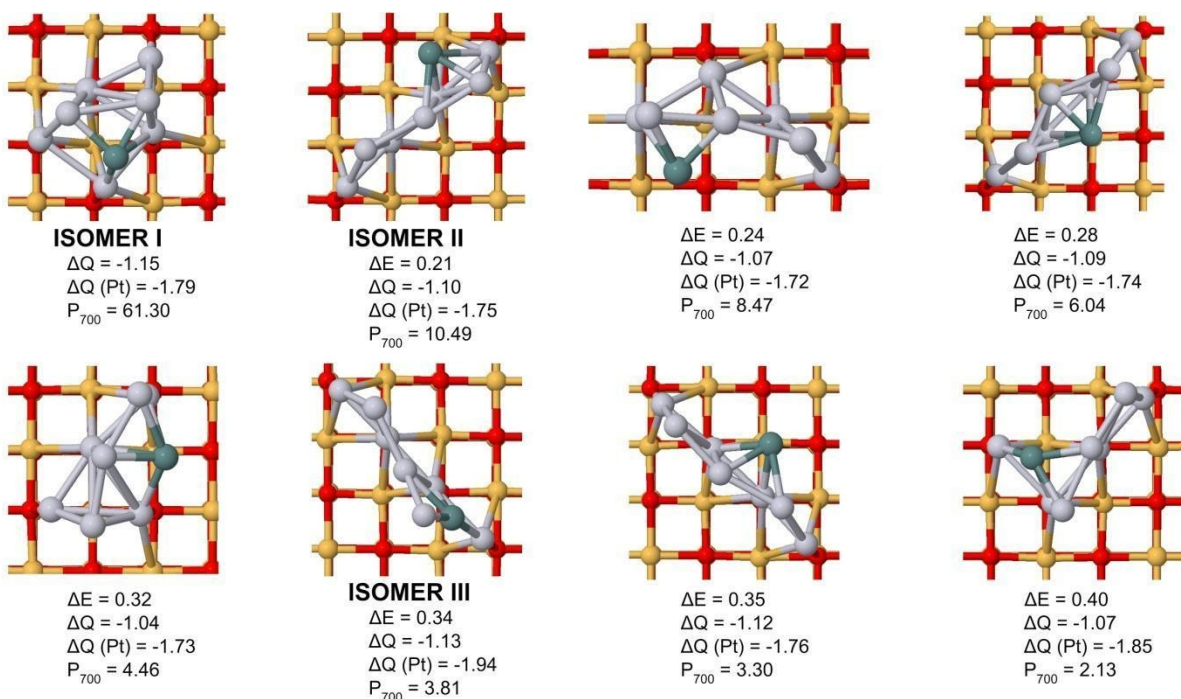


Figure 4. Lowest-energy minima of Pt_7Ge on $\text{MgO}(100)$, with the energy difference of each isomer with respect to the global minima, ΔE , in eV. Charge transfer from the support to the whole Pt_7Ge cluster, ΔQ , and the sum of the Bader charges of every Pt atom forming the cluster, $\Delta Q(\text{Pt})$, and their Boltzmann populations at 700 K are shown. O, Mg, Pt and Ge are depicted in red, orange, grey, and dark green respectively.

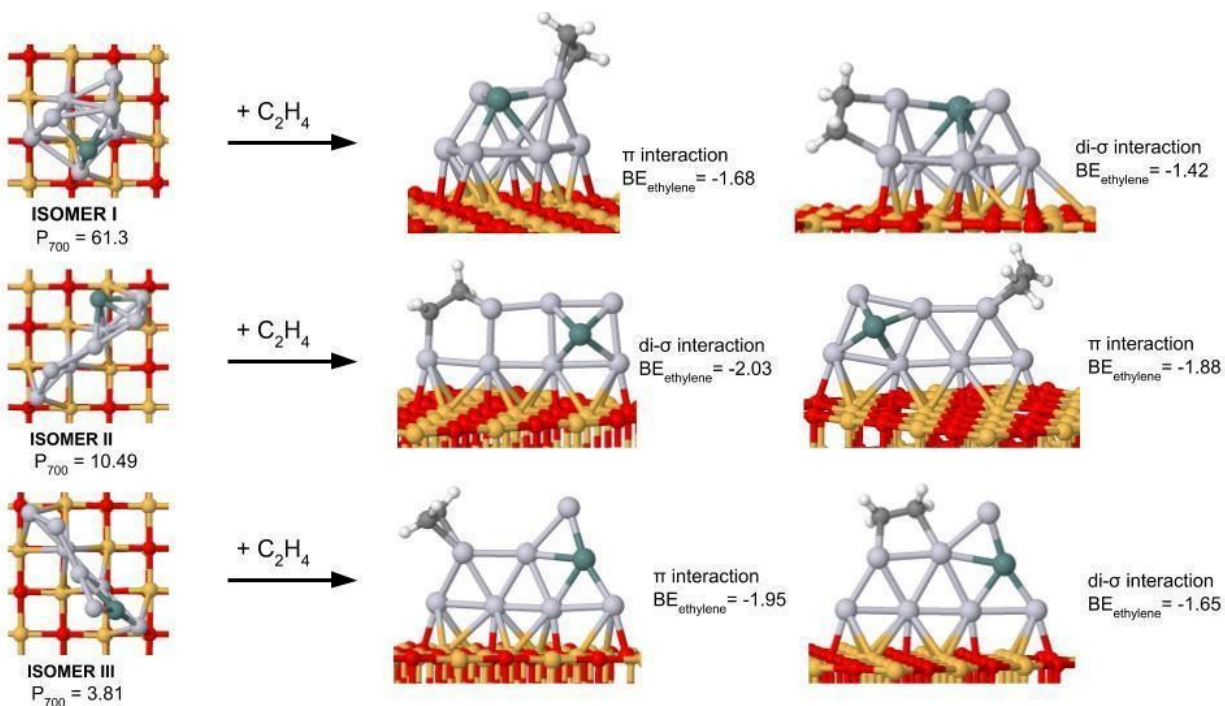


Figure 5. Most stable configurations of ethylene adsorbed on Pt₇Ge Isomer I, II, and III. Binding energies to ethylene (BE_{ethylene}) are given in eV. O, Mg, Pt, Ge, C and H are depicted in red, orange, grey, dark green, dark grey and white respectively.

In our previous work we showed that a low selectivity is correlated with unpaired electrons on the catalysts.²¹ For pure Pt₇, half of the population at 700K contained unpaired electrons, and would therefore be more likely to insert homolytically into the ethylene molecule, bind it in a di- σ mode, and dehydrogenate, often without a barrier. This could be understood by the need to have unpaired spins on adjacent Pt atoms in order to homolytically insert into the ethylene molecule for activation toward dehydrogenation. For Pt₇Si, only 25% of the population had unpaired electrons and these clusters still needed to overcome an energy barrier of 0.6 eV to dehydrogenate ethylene. In the case of Pt₇Ge, all the clusters in the population have a closed-shell electronic structure. Hence, in order for a cluster to activate ethylene, the cluster needs to first unpair some electrons, and undergo the required geometric rearrangement. However, the cost of this isomerization

without ethylene bound is very high; the triplet and higher spin states are not energetically-competitive isomers. We explored the reactivity of the three representative conformers, namely, the two most stable isomers of Pt₇Ge, Isomers I and II, which constitute more than 70% of the population, and Isomer III because it might have an enhanced reactivity since the most exposed Pt atom has a notably large negative charge (-0.46 |e|, Fig. S1).

To analyze the selectivities of these cluster isomers, first we calculated their binding energies to carbon. The resulting most stable structures are shown in Fig. S2. The binding energy to C of Pt₇Ge Isomer I (-7.86 eV) lies between that of the two most stable isomers of Pt₇ (-7.73 and -7.96 eV).²¹ However, Isomers II and III of Pt₇Ge have slightly reduced affinity to C, even smaller than that characteristic of Pt₇Si (-7.57 and -7.51, versus -7.81 eV).²¹ Note that these binding energies, are nevertheless large. Thus, the addition of Ge would not entirely prevent the deactivation of Pt due to coke deposits. However, the marked effect of Ge that we found could indicate that eventually its concentration or conditions could be tuned to improve the catalyst performance. Secondly, we calculated the most stable binding structures of ethylene on the three lowest-energy isomers of Pt₇Ge, as shown in Fig. 5. Importantly, no spontaneous dehydrogenation is found, unlike for Pt₇ and Pt₇Si.²¹ Isomer I, that constitutes 61% of the population at catalytically relevant temperature, binds ethylene preferentially in the weakest π -fashion. The di- σ geometry is 0.26 eV higher in energy. Isomer III has a similar reactivity. For isomer II the order is reversed, where the di- σ structure is more stable than the π structure. Overall, the binding energies to ethylene are smaller than those for Pt₇. Thus, Pt₇Ge clusters favor ethylene desorption rather than further dehydrogenation by weakening the interaction with desired product. Additionally, we calculated the reaction barriers for ethylene dehydrogenation on Pt₇Ge Isomer I and II, by building manually the final products (dehydrogenated ethylene on the doped cluster). In the case of Isomer I, shown in Fig. 6, three different reaction pathways were considered. Note that in these reaction pathways the starting structure for

ethylene dehydrogenation is the di- σ geometry, albeit the π -adsorbed ethylene is the most stable structure. The reason is that, as mentioned above, the di- σ binding mode of ethylene on Pt is considered precursor of further dehydrogenation, whereas the π bonded species is more likely to desorb.³⁴⁻³⁷ Therefore, the dehydrogenation of ethylene on Pt is expected to occur from the di- σ geometry. In the most favorable case, the reaction needs to overcome a barrier of 0.53 eV. This barrier is similar to that found for Pt₇Si, but unlike for Pt₇Si, in this case the reaction is endothermic. For Isomer II, ethylene dehydrogenation is even less favorable. As shown in Fig. 7, two different reaction pathways were computed. The first one leads to a dehydrogenated structure that is thermodynamically more stable than the starting di- σ conformation. But the reaction barrier is very large (1.30 eV). In the second mechanism, the barrier is similar to that for Isomer I, 0.49 eV, and the reaction is again endothermic. Thus, in-line with energetic, geometric, and electronic characteristics, the kinetics of ethylene dehydrogenation is suggestive of great catalyst selectivity induced by alloying Pt₇ with Ge.

Finally, we analyzed the effect of adsorbate coverage on the prediction of this study, by binding two ethylene molecules on Pt₇Ge. The resulting most stable configurations are shown in Fig. S3. The co-adsorption favors the weaker π binding mode, and slightly reduces the binding energies to the catalyst, implying that the predicted selectivity would be preserved or even enhanced at higher coverage. Because the selectivity improvement shown in the present work is driven by thermodynamics, it will be markedly notable at high reaction conversions or when the catalytic reaction is closer to the equilibrium.

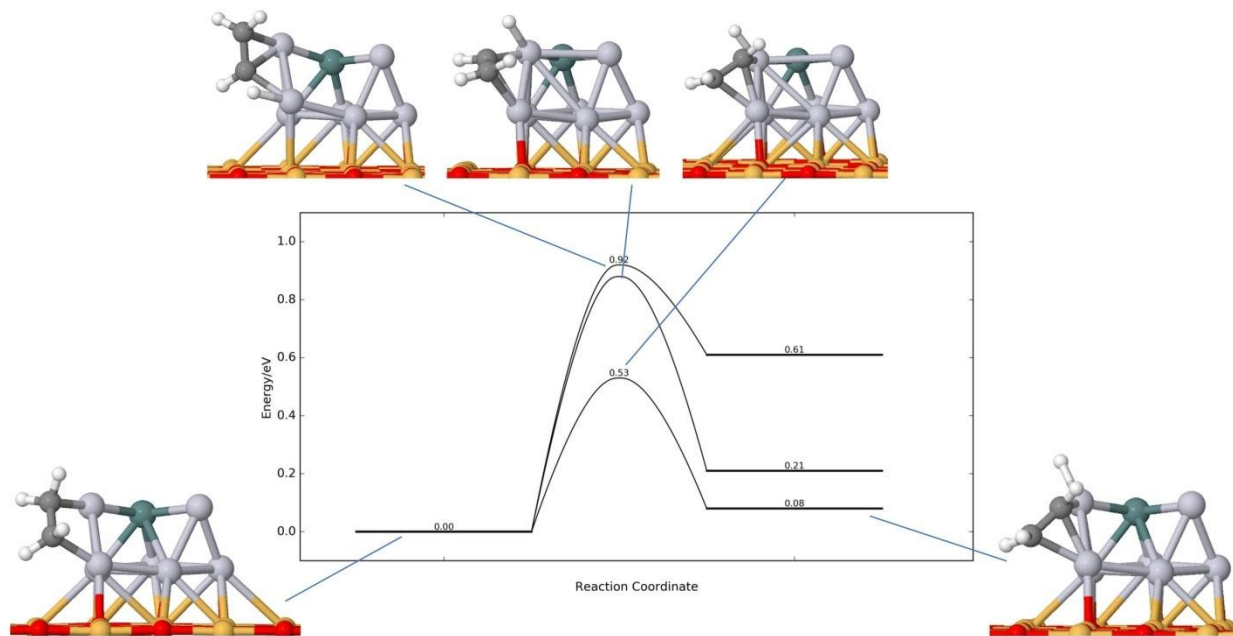


Figure 6. Reaction pathways for direct ethylene dehydrogenation on Pt₇Ge, Isomer I, with TSs and the final product structures shown. Activation energies are given in eV. O, Mg, Pt, Ge, C and H are depicted in red, orange, grey, dark green, dark grey, and white respectively.

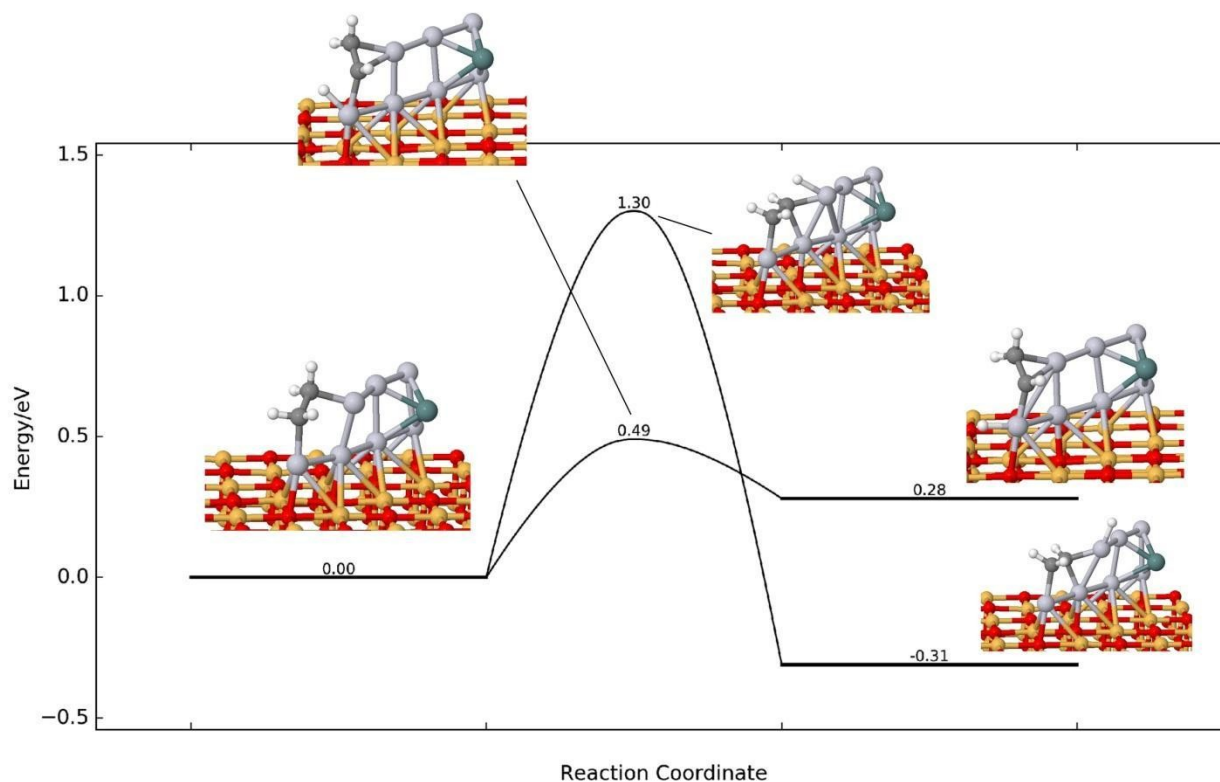


Figure 7. Reaction pathway for direct ethylene dehydrogenation on Pt₇Ge Isomer II. Activation energies are given in eV. O, Mg, Pt, Ge, C and H are depicted in red, orange, grey, dark green, dark grey and white respectively.

4. CONCLUSIONS

The catalytic selectivity of Pt in the dehydrogenation reactions of light alkanes is a crucial factor that influences the durability of the catalysts, due to the formation of coke deposits that deactivate it. In previous works B, Si, and Sn were proposed as alloying main-group agents for Pt. B and Si promote ethylene desorption, thus halting deeper dehydrogenation leading to coke. However, the activity toward the initial step of alkane dehydrogenation to alkene is also reduced on PtB and PtSi. In this work we compared MgO-supported Pt₃ and Pt₇ with Pt₂Ge and Pt₇Ge respectively and we showed that, at least for these cluster sizes, Ge is an optimal dopant to tune the selectivity of Pt. In our model studies, alloying Pt with Ge decreases the affinity of pure metallic clusters toward alkenes and thus also favors alkene desorption. Importantly, it does so without harming the activity towards alkane dehydrogenation as compared to pure Pt. In addition, for the smallest clusters sintering by Ostwald ripening is less likely for PtGe clusters compared to Pt alone, as predicted by energetic metrics of sintering. Moreover, Ge reduces very significantly the affinity to carbon, promising to enhance the resistance of the catalyst to deactivation by coking. For the larger Pt₇ and Pt₇Ge clusters, an ensemble of many cluster states accessible at catalytic temperatures is considered, and it is seen that the effect of Ge on the selectivity is preserved at this larger size, expanding ensemble of states, and also at increasing ethylene coverage. The effect of the Ge dopant on the selectivity is traced down to the electronic effect. Ge quenches spins on Pt atoms in these larger clusters, which are needed for the insertion into the double bond of alkenes in the activated di-σ configuration. The exact mechanisms by which the presence or lack of unpaired electrons affects the

reactivity of Pt clusters towards ethylene and ethane will be the subject of further studies.

Finally, despite the significant effort to make this study realistic, it remains a model. In a real catalytic system many cluster sizes and compositions would be present simultaneously, and the support would not be uniform. Following the presented initial indications of the Ge doping effect on the selectivity, further work is needed to assess its generality and practical advantage.

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TOC Graphics:

