Published in final edited form as:

Top Catal. 2018 August 1; 61(12-13): 1290–1299. doi:10.1007/s11244-018-0992-4.

How Au Outperforms Pt in the Catalytic Reduction of Methane towards Ethane and Molecular Hydrogen

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Abstract

Within the context of a “hydrogen economy”, it is paramount to guarantee a stable supply of molecular hydrogen to devices such as fuel cells. At the same time, catalytic conversion of the environmentally harmful methane into ethane, with a significantly lower Global Warming Potential, turns into a highly desirable challenge. Herein we propose a first-step novel proof-of-concept mechanism to accomplish both tasks simultaneously. For that purpose we provide transition-state barriers and reaction Helmholtz free energies obtained from first-principles Density Functional Theory by taking account vibrations for $2\text{CH}_4(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g}) + \text{H}_2(\text{g})$ to show that molecular hydrogen can be produced by subnanometer Pt_{38} and Au_{38} nanoparticles from natural gas. Interestingly, the active sites for the reaction are located on different planes on the two nanoparticles, effectively differentiating the working principle of the two metals. The analysis shows that the *complete* cycle to reduce CH_4 can be performed on Au and Pt with similar efficiencies, but Au requires only half the working temperature of Pt. This substantial decrease of temperature can be traced back to several intermediate steps, but most crucially to the final one where the catalyst must be cleaned from $\text{H}(\star)$ to be able to restart the catalytic cycle. This simple study case provides useful guidelines to capitalize on finite-size effects in small nanoparticles for the design of new and more efficient catalysts. Interestingly, present results obtained for the intermediate steps of the catalytic cycle show an excellent agreement with previous experimental evidence. Finally, we stress the importance of including the final cleaning steps to start a new fresh catalytic cycle.

Keywords

Nanoparticle catalyst; Methane reduction; Ethane evolution; Hydrogen production; Density functional theory; Phonons; Thermodynamics; Transition-state

1 Introduction

The steam reforming process, in which methane and water react over a Ni catalyst, is the most widely used commercial source for the production of molecular hydrogen.[1] The rate-limiting step in this reaction is the dissociative chemisorption of methane: a single C–H bond breaks as the molecule collides with the metal surface, leaving chemisorbed H(*) and CH₃(*) fragments. Several experimental and theoretical groups have studied this reaction, mostly on Ni and Pt surfaces, and molecular beams have been used to measure how the dissociative sticking probability varies with the translational and vibrational energy of methane.[2–7] Typically, the barriers for dissociation on these surfaces are relatively large[8] and the dissociative sticking probabilities are small. Nevertheless, it has been found that reactivity increases dramatically with increasing collision energy and vibrational excitation of the molecule, as well as substrate temperature.

Nanostructured versions of the most common catalysts are appealing candidates to open new routes that enhance the efficiency of this energy-intensive reaction. Some of their advantages are the following: (i) Nanoparticles possess large effective surface areas in the nanoparticle. Hence more active sites will be available to react with the gas-phase molecules participating in the reaction, substantially increasing the multidirectional sticking probability (and thereby the catalytic activity); and (ii) the high morphological versatility of nanoparticles provides a wide multiplicity of available sites. If the reaction is structure-sensitive, those multiple sites contribute differently to the overall catalytic activity, and geometry optimization is paramount to enhance the catalyst's performance.[9]. In addition, modern theoretical chemistry computational approaches can already provide realistic descriptions of catalytic nanoparticles. Instead of describing complex nanostructures using approximations such as Wulff constructions, it is preferable to simulate entire nanoparticles where terraces, edges, and corners coexist and finite-size effects are observed.[10–12] Understanding the interplay between those size and geometry factors can ultimately provide realistic models of catalytic processes.[13]

Methane is the primary component of natural gas and shale gas. It is extremely flammable and may form explosive mixtures with air. It is also violently reactive with oxidizers, halogens, and some halogen-containing compounds, and an efficient asphyxiator, able to displace oxygen in a closed space. These properties, together with the fact that it is one of the primary greenhouse gasses with a Global Warming Potential (GWP) of 25, compared to 5.5 for ethane and 1 for CO₂ (taken as reference) over a 100-year period,[14,15] make the development of efficient catalysts for the selective transformation of methane a task of paramount importance. The activation of methane often requires high temperatures, which results in undesirable products such as CO and CO₂. Additionally, there is a continuous natural supply of methane via the bacteria (methanotrophs)), unlike ethane that is mainly produced from other secondary non-natural processes, is oxidized rapidly in the atmosphere by the hydroxyl radical, and it is quite short-lived (about 2 months).[16]

Multiple natural and industrial ways of producing methane exist: from the biological methanogenesis[17] and fermentation of organic matter to serpentinization[18] and the well-known centenary Sabatier and Fischer-Tropsch processes, among others; all of them efficient

sources of methane. In striking contrast, apart from the combustion which results in the harmful CO and CO₂ products,[19,20] not so many ways to reduce methane are available. One of the few clean processes to reduce methane is found naturally in the Earth's atmosphere, where it is photo-chemically transformed into ethane and molecular hydrogen. Indeed, atmospheric ethane results from the photochemical action of sunlight on methane gas: ultraviolet photons with wavelengths shorter than 160 nm can photo-dissociate the methane molecule into a methyl radical and a hydrogen atom, $\text{CH}_4(\text{g}) \rightarrow \text{CH}_3(\text{g}) + \text{H}(\text{g})$. When two methyl radicals recombine the result is ethane ($2\text{CH}_3(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$), which can be accompanied by the generation of molecular hydrogen. Although ethane is still a greenhouse gas, it is much less abundant than methane (ethane: < 0.01% vs. methane: ~ 0.44% on earth). This photo-dissociation reaction has been analyzed under collision-free conditions for the room-temperature gas-phase dissociation of methane for primary H atom formation, resulting in a photolysis frequency of 121.6 nm, which translates into a photon energy of ≈ 10 eV.[21]

Therefore, the search for catalysts able to carry out the on-surface methane reduction into ethane and molecular hydrogen may prove attractive to transform methane in a clean way with the additional benefit of storing energy in the H–H bond. Apparently, the viability of such an on-surface reaction will be directly linked to a reaction pathway involving kinetic energy barriers that can be overcome with moderate molecular collision energies, vibrational excitation of the molecule, and substrate temperature. Such conditions are needed to make the steam reforming catalyst industrially appealing.

In this communication we describe, from a first-principles modeling standpoint, a viable mechanism for the complete catalytic cycle of the reaction $2\text{CH}_4(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g}) + \text{H}_2(\text{g})$ on the truncated octahedra subnanometer Pt₃₈ and Au₃₈ nanoparticles. This particular shape displays a high *surface-to-volume* ratio for a 38-atoms cluster, is very stable, and contains short (111) and (100) terraces where active undercoordinated atoms are abundant.

The reaction starts with two gas-phase methane molecules being reduced on one terrace of the nanoparticles. The elementary steps are: (i) sequential adsorption / dissociative chemisorption of two methane molecules, $2 \times (\text{CH}_4(\text{g}) \rightarrow \text{CH}_3(*) + \text{H}(*))$, where * denotes a free adsorption site; (ii) associative desorption of ethane, $2\text{CH}_3(*) \rightarrow \text{C}_2\text{H}_6(\text{g})$; and, finally, (iii) associative desorption of molecular hydrogen, $2\text{H}(*) \rightarrow \text{H}_2(\text{g})$. The facets where the cycle is completed are different for Pt and Au: four-atom (100) terraces, and seven-atom (111) terraces, respectively. Although the catalytic cycle is energetically viable on both Pt₃₈ and Au₃₈ nanoparticles, our calculations predict that the limiting step of the reaction, which is the cleaning of the nanoparticle from poisoning H(*), can be achieved on Au₃₈ at about half the temperature required for Pt₃₈. All stationary configurations (initial, transition, and final states) have been obtained from first-principles Density Functional Theory (DFT) calculations. The energies for these states have been used to determine the canonical probabilities for a thermal fluctuation to overcome kinetic barriers along the reaction path, yielding the time scale for the reaction. Our mechanism offers a viable and clean route for: (i) the catalytic reduction of methane towards ethane and molecular hydrogen; and (ii) within the context of a “hydrogen economy”, the stable supply of molecular hydrogen to technologically and industrially attractive devices such as fuel cells.

2 Computational Methods and Models

2.1 Ab-initio Electronic Energies

The total energies and forces were minimized using DFT as implemented in the plane-wave package QUANTUM ESPRESSO.[22] Within the DFT+D formalism, a semi-empirical van der Waals (vdW) R^{-6} correction has been used to add long-range dispersive forces.[23–25] This vdW contribution to the total energy is almost negligible around the transition-states. It only becomes significant (>15%) when the distances between the adsorbates and the nanoparticles increase to values $> 4\text{Å}$, which only matters for a good description of energies at asymptotic distances. The Perdew-Burke-Ernzerhof (PBE) parametrization has been used for the exchange and correlation potential.[26] The ionic cores were described by Projector Augmented Wave (PAW) method.[27] All atoms in the nanoparticles were free to move in all directions. The atomic relaxations were carried out with conjugate gradient minimization scheme until the maximum force on any atom was below 0.01 eVÅ^{-1} . Geometrical optimization was performed with a plane-wave cutoff of 500 eV. The nanoparticles were simulated in a cubic box of $30 \times 30 \times 30\text{ Å}^3$; the smaller distance between images was larger than 20 Å . The Brillouin zone was sampled at the Gamma point only. The Fermi level was smeared with the Methfessel-Paxton approach with a Gaussian width of 0.01 eV, and all energies were extrapolated to $T=0\text{K}$. [28] All these parameters yield total electronic energies with accuracies of $E \approx \pm 0.01\text{ eV}$ (converged to a precision better than 10^{-6} eV). DFT adsorption energies for H_2 , CH_4 and C_2H_6 were calculated with respect to the clean optimized nanoparticles and the gas-phase species in the following way: $E_{\text{ADS}} = E_{A,*} - E_{A,*} - E_A$, where $*$ represents the clean nanoparticle, and A and $(A,*)$ are the gas-phase and adsorbed states for a given species. The gas-phase references were calculated in the same cubic box of $30 \times 30 \times 30\text{ Å}^3$ using the Gamma point only. These values have been corrected with Helmholtz's free energies derived from vibrational modes of the different configurations. Apart from the enthalpies of adsorption, dissociation and desorption (H), the important feature to ascertain the feasibility of a particular state is the height of the barrier (E) at the transition-state (TS). The TSs have been investigated within the climbing-image nudged elastic band (CI-NEB) method,[29–31] where the initial, final, and all the intermediate states (12 image states for all the barriers have been analyzed) were completely free to relax.

2.2 Thermochemistry

The influence of temperature on the energetics of the different steps has been analyzed by introducing the effect of vibrations on the system. For each stationary quasi-equilibrium state reported in Figures 2-4 we have computed the frequencies of the vibrational modes. A model of harmonic independent oscillators has been used to compute the partition function in the canonical ensemble, where the system is in contact with a thermostat at temperature T :[32]

$$Z(N, V, T) = \prod_i \frac{e^{-\frac{\hbar w_i}{2k_B T}}}{1 - e^{-\frac{\hbar w_i}{k_B T}}} \quad (1)$$

The number of particles N is fixed, and the volume V corresponds to a zero stress condition. The origin for energies is taken at the bottom of the harmonic well. To ensure convergence of the series we include modes $w > 1 \text{ cm}^{-1}$ only; a reasonable approximation at the temperatures of interest.

All the thermodynamic magnitudes can be obtained from the partition function, in particular the contribution of vibrational modes to the Helmholtz's free energy:[33]

$$F = -k_B T \ln(Z) \quad (2)$$

This free energy is used to include the effect of temperature in the energies of the different steps and on the largest barrier (limiting step). To further interpret these results it is also possible to break up Helmholtz's function in the associated vibrational entropies and internal energies as follows:

$$\begin{cases} S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \\ U = F + TS \end{cases} \quad (3)$$

2.3 Au₃₈ and Pt₃₈ Geometrical Models

The shape of the Pt₃₈ and Au₃₈ nanoparticles corresponds to a truncated octahedron with minimum and maximum *atom-to-atom* nanoparticle diameters of 7.3 and 8.5 Å for Pt₃₈, and 7.6 and 8.9 Å for Au₃₈ (see Figure 1). There are eight (111) and six (100) terraces that are denoted 111T and 100T, respectively. At the intersection of neighboring facets there are 12 edges between neighboring (111) facets, and 24 edges between neighboring (100) facets. These are denoted 111E and 100E, respectively. Finally, there are twenty-four corners at the intersection between two neighboring (111) and (100) terraces; these are called kinks. These atoms, together with the eight central atoms of (111) terraces (called centers), are the only two non-equivalent atoms in the outer shell of the nanoparticle. The outer shell has 32 atoms while the inner core of the nanoparticle consists of a regular 6-atom octahedron.

Pt and Au nanoparticles have been chosen because they show high catalytic efficiencies in numerous technological and industrial processes. Particularly, in the field of heterogeneous catalysis, platinum and its alloys have been successfully used in many catalytic applications, including the water-gas shift,[34–36] fuel cells and light harvesting.[13,37–39] Moreover, gold nanoparticles have also been used as efficient catalysts in a number of chemical

reactions.[40] Interestingly enough, gold surfaces can be used for selective oxidation reactions,[41,42] but can also be reductive, as in the case of nitrate reduction.[43] Additionally, Pt@Au composite nanoparticles have recently been shown to enhance the kinetics of the oxygen reduction reaction (ORR), and oxygen evolution reaction (OER) in rechargeable Li–O₂ cells.[44]

3 Results and Discussion

3.1 Reaction Path Description: Energetics and Transition-State Barriers

In gas phase, the reaction $2\text{CH}_4(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g}) + \text{H}_2(\text{g})$ is endothermic, requiring approximately 0.7 eV to proceed (17 kcal/mol). Moreover, it has a large kinetic barrier of about 6.2 eV at the initial step of CH₄ dehydrogenation.

In the presence of Au₃₈ and Pt₃₈ the reaction proceeds following some elemental steps shown schematically in Figures 2-4. While the overall reaction enthalpy is obviously not modified by the presence of the catalyst, the barrier of the rate-limiting step is reduced to $\approx$ 1 eV for Au and 2 eV for Pt (see below). In black, we show the DFT internal electronic energies for each of the equilibrium configurations. In blue ($T = 0$ K) and red ($T = 400$ K) we give the corrections to these values obtained from the vibrational Helmholtz's free energy. The origin is always set out in the first step to facilitate comparisons. Although the zero-point energy correction for each phase in the reaction can be substantial due to the fair number of modes involved, differences between them amount to fractional corrections of 15% or less for $T=0$ K. At nonzero temperatures, however, these differences increase due to the disparate nature of vibrations on the two metals and the different relevant adsorption sites. In particular, the whole pathway for Au transforms from endothermic to quasi-exothermic, except for the last steps where the enthalpy of reaction is recovered. It is interesting to notice that at 400 K the population of the intermediate steps in Au is significantly increased because of thermodynamical equilibrium. As a whole, Au is "softer" than Pt and the contribution to Helmholtz's free energy is larger. On the other hand, Pt is more active chemically and makes the reaction exothermic even for very low temperatures, but the final steps become more costly.

To facilitate its analysis the whole process has been divided in the following eight steps:

- **1. Methane adsorption.** The reaction starts with the adsorption of a CH₄ molecule on a favorable site on the nanoparticle. For Pt₃₈ this is the top of a kink atom (black dots in the inset of Figure 2A). The molecule is physisorbed by one of the H atoms on the nanoparticle with an equilibrium distance of 2.12 Å from the Pt atom. The adsorption energy is -0.12 eV. For Au₃₈, in contrast, the same process takes place on a kink atom on a (111) facet (black dots in the inset of Figure 2B). The equilibrium distance is 3.13 Å, and the adsorption energy is -0.06 eV. We observe that the interaction with Au is weaker compared with Pt because the different chemical activity of both species.
- **2. Methane dehydrogenation.** We consider the elementary dissociative reaction $\text{CH}_4(\star) \rightarrow \text{CH}_3(\star) + \text{H}(\star)$. On Pt₃₈, one hydrogen atom from the adsorbed methane molecule moves to the closest 100E bridge edge (blue dots in the inset

of Figure 2A). The total energy is reduced by -0.24 eV (exothermic) and the kinetic barrier is 0.70 eV. On Au₃₈, this is an endothermic process that requires about 0.69 eV of extra energy and has a barrier of 0.86 eV at T=0 K, which reduces substantially the required energy by 0.46 eV at T=400 K. H is adsorbed on-bridge at the closest 111E edge (blue dots in the inset of Figure 2B). The larger barrier is related to the weaker interaction between Au and methane compared to that for Pt and methane. This apparent disadvantage will turn out to be beneficial at the end of the process when the nanoparticle needs to be restored to its original state. Indeed, it is known that a single Pt atom can dehydrogenate methane without a barrier, while on a surface a barrier appears due to the increased coordination of Pt to other Pt atoms.[6]

- **3–4. Adsorption and dehydrogenation of a second methane molecule.** At this point CH₃(*) is adsorbed atop a kink (2.07 Å) on the platinum 100T terrace, and H(*) atom is adsorbed on-bridge near a 100E edge (1.77 Å). The previous steps 1 and 2 are repeated at a neighboring site with a second methane molecule adsorbed atop a vicinal empty kink (black dots in the insets of Figure 2). The second adsorbed CH₄ molecule loses again one H atom that is adsorbed on-bridge in the remaining symmetrical empty 100E edge of the same (100) facet for Pt₃₈ (blue dots in the inset of Figure 2A), and in the remaining symmetrical empty 100E edge of the same (111) facet for Au₃₈ (blue dots in the inset of Figure 2B). Steps 3 and 4 are similar to 1 and 2 in enthalpy, barriers and respective optimum sites for both Pt and Au, cf. Table 1.
- **5–6. Associative desorption of ethane: 2CH₃(*) → C₂H₆(g).** After the two consecutive processes of dissociative chemisorption of methane, the two CH₃(*) fragments adsorbed on neighboring sites combine to produce ethane. Up to now, the barriers on both Pt and Au are quite similar, being the main difference the exothermic versus endothermic reaction steps. The process of associative desorption of ethane raises the first important difference in terms of kinetic barriers: 1.24 eV for Pt compared to 0.87 eV for Au. The reaction on both substrates is exothermic, but is more stable on gold, namely -0.32 eV compared to -0.07 eV for platinum, accompanied by a similar reduction in the barrier. These barriers are plotted together in Figure 5 (red for Pt, and blue for Au). The significance in time, or in working temperature, is shown in Figure 6C; the difference in barriers implies approximately a 100 K higher temperature on Pt to get the process completed in the same time.
- **7–8. Associative desorption of H₂.** The most substantial difference between the two catalysts is found in the associative desorption of H₂. In the presence of chemisorbed H(*), a known poison for the reaction,[45,46] the first dehydrogenation step of the next cycle would become significantly more difficult, and the barriers would grow accordingly. Therefore, it is imperative to remove atomic hydrogen from the nanoparticle. A convenient way of desorbing it is by forming molecular hydrogen.

On Pt₃₈ two H(•) remain adsorbed on-bridge at 100E opposite edges of the same (100) facet (step 7 of Figure 2A). The H-cleaning process will be completed in this nanoparticle by the migration of one of the H(•) atoms (denoted H_A•) to be adsorbed on-bridge in the closest 100E edge (denoted H_B•), shown in step 7' of Figure 2A. This migration allows for the formation, and subsequent desorption, of an H₂ molecule from the two adsorbed H(•) atoms, leaving Pt₃₈ clean and ready to start over a new catalytic cycle (step 8 of Figure 2A).

On the other hand, on Au₃₈ the two H(•) remain adsorbed on-bridge at the 111E mirror edges of the same (111) facet (step 7 of Figure 2B). Atomic H diffusion on Au nanostructures is fast and efficient,[47] which facilitates the recombination and subsequent desorption of an H₂ molecule, leaving Au₃₈ clean in its initial configuration (step 8 of Figure 2B).

At T=0 K the barrier for this final step in Pt is 2.06 eV for Pt and 0.62 eV for Au. Temperature effects suggest that these values could typically end up around 2 and 1 eV (see Figure 6B). The difference in estimated times to complete this step amounts to several orders of magnitude (see Figure 6C). Regarding thermodynamics, the reaction enthalpies for Pt and Au are 1.33 eV and 0.18 eV, respectively, cf. Figures 3 and 4. These values are robust estimations since they are related to global energy conservation on the whole cycle. Therefore, this last step reinforces the fact that catalysis on Au should be more attractive than on Pt for this particular reaction, implying a higher working temperature on Pt of at least 100 K.

At this point it is important to remark that all different non-equivalent adsorption sites for the intermediates participating in the catalytic cycle have been checked for both Pt₃₈ and Au₃₈ nanoparticles. Here we only report the most stable ones (which agree well with those reported in previous literature for these nanoparticles, e.g. Refs. [9,12]) to construct the most viable and realistic reaction path as given above. Table 1 summarizes the energies used to draw Figures 3 and 4. Besides, we have also analyzed several possible secondary reaction pathways deviating from the catalytic cycle proposed here. As an example, we have computed the barriers for subsequent dehydrogenations of CH₃(•) (in steps 3–4) towards CH₂(•)+H(•), CH(•)+2H(•) and C(•)+3H(•). The computed transition-state barrier for CH₃(•) → CH₂(•)+H(•) are 3.6 and 4.1 eV on Pt₃₈ and Au₃₈, respectively, which renders this step, and the ones derived from it, energetically unlikely. Moreover, we have checked minimum-energy pathways (MEPs) and transition-state (TS) barriers on other adsorption sites for all the participating adsorbates, where the intensity of the adsorption was weaker, also resulting in larger kinetic barriers that hinder the advance of the whole catalytic cycle. Additional plausible competing channels for the proposed reactions, such as H₂ molecular associative desorption from adsorbed CH₄(•) and CH₃(•), or dehydrogenation of the adsorbed final C₂H₆(•) have also been carefully checked, yielding very large barriers that prevent the evolution of those secondary reaction channels. All these attempts reinforce our confidence on the reaction path proposed in this study.

The proposed catalytic cycle can be understood fairly well by focusing on the highest barriers along the path; this is a good approximation since the exponential Boltzmann factors select the few most relevant steps. We identify two such crucial steps on the transition-states

for the associative desorption of ethane ($\text{TS}_{\text{C}_2\text{H}_6}$, between steps 4 and 5), and the associative desorption of molecular hydrogen (TS_{H_2} , last step).

Regarding the comparison with related available experimental information, we have to point out that several works in the literature have inspired the present study. In particular, those on several faces of Pt, Pd and Ni[6,48–50] and clusters of Pt[51]. These experiments agree in general terms with the adsorption energies and barriers that we obtain, but none of them focuses on the final effort to clean the catalyst and start a new cycle again. The combined experimental and theoretical study of Vajda *et al.* on very small clusters of Pt indeed shows the dehydrogenated propane molecule in a bound state by around 1 eV, which is fully consistent with our predictions (see Figure 3). Finally, the nanoparticles we study have an important feature when compared with surface science experiments: the presence of several orientations on the same system allows for processes to take place in different coordination environments that are close together. In that direction work by Anghel *et al.* on Pt(110)-(1×2), and by Franke *et al.* on Pt(321), also display different orientations close together, and the results of their calculations are fully compatible with our values.

Finally, to analyze the effect of temperature we computed vibrational Helmholtz's free energies for each local equilibrium step and for the transition-state associated to the last one, which we find effectively limits the rate for the whole cycle.

3.2 Associative Desorption of Ethane

First, we analyze the electronic energy in the region around the transition-state for the associative desorption of ethane: $2\text{CH}_3(\star) \rightarrow \text{C}_2\text{H}_6(\text{g})$. In Figure 5 Pt (red) shows a larger barrier than Au (blue) by around 0.37 eV; if the height of the barrier was independent of

temperature, this would determine the reaction to be a factor $e^{-\frac{0.37}{k_B T}}$ times slower on Pt than on Au, i.e. $\approx 10^{-7}$ at $T = 300$ K. Moreover, the final state (desorbed ethane) is ≈ -0.25 eV more stable for Au than for Pt, determining in equilibrium at 300 K a ratio of populations between the initial and final states of $\approx 1 : 10^5$ for Au compared to $1 : 1$ for Pt. Therefore, all these considerations based on chemical arguments favor Au over Pt on this particular step.

Next, we analyzed the effect of temperature on the quasi-equilibrium initial (4) and final (5) states. In Figure 6A we plot the difference between Helmholtz's free energies vs T . The different role of vibrations for $\text{CH}_3(\star)$ and $\text{C}_2\text{H}_6(\text{g})$ is already apparent from the zero-point energies quoted in Table 1, but its evolution with temperature is even more interesting: the molecule becomes less and less stable at high temperatures both for Au and Pt. The reason can be traced back to the entropy S (bottom-right panel of Figure 6A): while the vibrational internal energies U of both Au and Pt (bottom-left panel of Figure 6A) are stabilized by about 100 meV from 4 to 5, the entropic term $-T \times S$ is destabilized by about 200 meV for Pt, and it nearly doubles for Au. Therefore, the softer material (Au) is affected more significantly by temperature and the reaction “changes the trend” (regarding the two considered materials: Pt and Au) due to the mere contribution of zero-point vibrations.

To compute the effect of temperature on this transition-state $\text{TS}_{\text{C}_2\text{H}_6}$ is difficult in view of the large amount of modes needed to be described with enough accuracy. A rigid model for

the barrier where the effect of temperature on the initial and final points is interpolated to the transition-state predicts that at 400 K both barriers would be comparable. Although this procedure is not warranted down to the finest details, it outlines at least the tendency on the barrier as the temperature increases. The rates for this step have been computed by looking at normal modes possessing amplitudes that make the methyl groups approach the barrier simultaneously from both sides. The rate for the transition is then obtained by multiplying the Boltzmann factor (giving the probability to pick up a thermal fluctuation at temperature T to overcome the barrier after “fluctuation”, E) times the number of attempts to pass the barrier given by the frequency of the relevant normal mode, $\Gamma e^{-\frac{\Delta E}{k_B T}}$.

Figure 7 shows esquematically the most relevant vibrational modes, i.e. the modes related to overcoming the highest barriers. For Au (see the left panel of Figure 7) this is the step where the two adsorbed methane molecules couple to form C_2H_6 . Because these vibrations also involve substrate atoms, the relevant frequencies for this process are in a band between 130 and 360 cm^{-1} . On the contrary, for Pt (see the right panel of Figure 7) the highest barrier, i.e. the limiting step, corresponds to the associative desorption of $2H(*)$ to form H_2 . The relevant modes associated to this process are in the range between 550 and 1650 cm^{-1} (again, these modes also involve vibrations of the substrate atoms).

3.3 Associative Desorption of Molecular Hydrogen

The most significant difference arises at the moment of cleaning the substrate to restart the catalytic cycle. This corresponds to the associative desorption of molecular hydrogen. The barrier to form and desorb H_2 on Pt_{38} is $\approx 2\text{ eV}$, doubling the corresponding one on Au_{38} .

In this particular case it is simpler to include the effect of vibrations on the transition-state due to the significant reduction in the number of normal modes involved w.r.t. the previous steps. On the initial configurations (steps 7' and 7 for Pt_{38} and Au_{38} , respectively, in Figure 2) we have six modes associated with two chemisorbed H atoms. On the final configuration only the internal stretch of the hydrogen molecule is left and we can follow the softening of all the modes except one in a quasi-adiabatic picture. Furthermore, hindered rotations here for TS_{H_2} are not an issue due to the simplicity of the geometry (contrasting with the previous $TS_{C_2H_6}$ case). The result of this approach for the relative variation of the barrier with respect to the initial state is given in Figure 6C. In both cases the barrier is lowered by about $0.1\text{--}0.2\text{ eV}$, being again Au more affected than Pt by temperature. In this step, mainly two modes contribute to the process: one around atop sites and the other around the hollow sites, with frequencies of 550 and 1650 cm^{-1} . Again, beside the details for the vibrations behind the transformation, Boltzmann's factors dominate in this range of temperatures and fully determine the time taken for the process.

Therefore, we conclude that temperature-dependent corrections on the initial and final states around the barrier (and on the barrier itself) of this most crucial step do not significantly alter our main conclusions.

Conclusions

We have proposed an energetically-viable mechanism that explains the complete catalytic cycle of $2\text{CH}_4(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g}) + \text{H}_2(\text{g})$ on platinum and gold nanoparticles made of 38 atoms with truncated-octahedron shapes. DFT has been used to obtain transition-state barriers, kinetic rates, and reaction enthalpies. We have also computed the relevant vibrational modes to obtain Helmholtz's free energies.

Using these values we have evaluated the performance of both catalysts. The proposed catalytic reaction is a temperature-activated mechanism that requires to surmount barriers of ≈ 2 eV on Pt_{38} and ≈ 1 eV on Au_{38} . Remarkably, Au nanoparticles outperform those of Pt in several intermediate steps, but most crucially in the final one where $\text{H}(\ast)$ must be removed from the nanoparticles to be able to restart the catalytic reaction. The reason for the improved activity of Au can be rationalized in terms of the equilibrated compromise between the adsorption strength of the adsorbed intermediates. Pt nanoparticles bind adsorbates in a way such that it is more difficult to clean the surface at the end of the cycle. Furthermore, Au is more affected by the operating temperature since its vibrational modes are typically softer than on Pt.

Therefore, the complete catalytic cycle to decompose CH_4 can be performed on Au with similar efficiency than Pt, but using only half the temperature. Such a substantial reduction in the working temperature of the catalyst is appealing from an industrial standpoint and evinces the benefits of using nanostructured catalytic materials in which a compromise exists between the relative strength of the reaction intermediates in complex pathways.

Finally, in conclusion, the results of this work provide: (i) on one side, an excellent starting point to elucidate the optimal particle size for the reduction of methane towards ethylene and hydrogen evolution, capitalizing on geometric and finite-size effects; and (ii) on the other hand, within the context of a "hydrogen economy", a viable route towards the stable supply of molecular hydrogen to technologically and industrially attractive devices such as fuel cells.

Acknowledgments

This work has been financially supported by the Spanish MINECO through Grants MAT2014-54231-C4-1-P (G*SURF) and MAT2017-85089-C2-1-R (FUN-LDS), and the EU via the ERC-Synergy Program through Grant NANOCOSMOS ERC-2013-SYG-610256. JIM acknowledges funding from NANOCOSMOS and "Ramón y Cajal" MINECO Program through Grant RYC-2015-17730, and thanks CTI-CSIC for use of computing resources. FCV received funding from the NWO, Veni project number 722.014.009.

References

1. Achenbach E, Riensche E. Journal of Power Sources. 1994; 52(2):283.doi: 10.1016/0378-7753(94)02146-5
2. Larsen JH, Chorkendorff I. Surface Science Reports. 1999; 35(58):163.doi: 10.1016/S0167-5729(99)00009-6
3. Juurlink L, Killelea D, Utz A. Progress in Surface Science. 2009; 84(34):69.doi: 10.1016/j.progsurf.2009.01.001
4. Utz AL. Current Opinion in Solid State and Materials Science. 2009; 13(12):4.doi: 10.1016/j.cossms.2009.01.004

5. Han D, Nave S, Jackson B. The Journal of Physical Chemistry A. 2013; 117(36):8651.doi: 10.1021/jp402987w [PubMed: 23634878]
6. Anghel AT, Wales DJ, Jenkins SJ, King DA. Phys Rev B. 2005; 71 113410. doi: 10.1103/PhysRevB.71.113410
7. Bengaard H, Nørskov J, Sehested J, Clausen B, Nielsen L, Molenbroek A, Rostrup-Nielsen J. Journal of Catalysis. 2002; 209(2):365.doi: 10.1006/jcat.2002.3579
8. Juurlink LBF, McCabe PR, Smith RR, DiCologero CL, Utz AL. Phys Rev Lett. 1999; 83:868.doi: 10.1103/PhysRevLett.83.868
9. Calle-Vallejo F, Martínez JI, García-Lastra JM, Sautet P, Loffreda D. Angewandte Chemie International Edition. 2014; 53(32):8316.doi: 10.1002/anie.201402958 [PubMed: 24919964]
10. Kleis J, Greeley J, Romero NA, Morozov VA, Falsig H, Larsen AH, Lu J, Mortensen JJ, Dulak M, Thygesen KS, Nørskov JK, et al. Catalysis Letters. 2011; 141(8):1067.doi: 10.1007/s10562-011-0632-0
11. Viñes F, Gomes JRB, Illas F. Chem Soc Rev. 2014; 43:4922.doi: 10.1039/C3CS60421G [PubMed: 24473497]
12. Calle-Vallejo F, Sautet P, Loffreda D. The Journal of Physical Chemistry Letters. 2014; 5(18): 3120.doi: 10.1021/jz501263e [PubMed: 26276322]
13. Calle-Vallejo F, Tymoczko J, Colic V, Vu QH, Pohl MD, Morgenstern K, Loffreda D, Sautet P, Schuhmann W, Bandarenka AS. Science. 2015; 350(6257):185.doi: 10.1126/science.aab3501 [PubMed: 26450207]
14. Shindell DT, Faluvegi G, Koch DM, Schmidt GA, Unger N, Bauer SE. Science. 2009; 326(5953): 716.doi: 10.1126/science.1174760 [PubMed: 19900930]
15. Pachauri RK, Reisinger A. IPCC Fourth Assessment Report: Climate Change 2007 (AR4). Intergovernmental Panel on Climate Change; 2007. URL <http://www.ipcc.ch>
16. Aydin M, Verhulst KR, Saltzman ES, Battle MO, Montzka SA, Blake DR, Tang Q, Prather MJ. Nature. 2011; 476(7359):198.doi: 10.1038/nature10352 [PubMed: 21833087]
17. Daniels L. Trends in Biotechnology. 1984; 2(4):91.doi: 10.1016/S0167-7799(84)80004-9
18. McCollom T. Proceedings of the National Academy of Sciences. 2012; 109(49):E3334.doi: 10.1073/pnas.1214629109
19. Tsang W, Hampson RF. Journal of Physical and Chemical Reference Data. 1986; 15(3):1087.doi: 10.1063/1.555759
20. Lee JH, Trimm DL. Fuel Processing Technology. 1995; 42(2):339.doi: 10.1016/0378-3820(94)00091-7
21. Lauter A, Lee K, Jung K, Vatsa R, Mittal J, Volpp HR. Chemical Physics Letters. 2002; 358(34): 314.doi: 10.1016/S0009-2614(02)00625-5
22. Giannozzi P, Baroni S, Bonini N, Calandra M, Car R, Cavazzoni C, Ceresoli D, Chiarotti GL, Cococcioni M, Dabo I, Corso AD, et al. Journal of Physics: Condensed Matter. 2009; 21(39) 395502. URL <http://stacks.iop.org/0953-8984/21/i=39/a=395502>.
23. Grimme S. Journal of Computational Chemistry. 2006; 27(15):1787.doi: 10.1002/jcc.20495 [PubMed: 16955487]
24. Elstner M, Hobza P, Frauenheim T, Suhai S, Kaxiras E. The Journal of Chemical Physics. 2001; 114(12):5149.doi: 10.1063/1.1329889
25. Dunitz JD, Gavezzotti A. Accounts of Chemical Research. 1999; 32(8):677.doi: 10.1021/ar980007+
26. Perdew JP, Burke K, Ernzerhof M. Phys Rev Lett. 1996; 77:3865.doi: 10.1103/PhysRevLett.77.3865 [PubMed: 10062328]
27. Kresse G, Joubert D. Phys Rev B. 1999; 59:1758.doi: 10.1103/PhysRevB.59.1758
28. Methfessel M, Paxton AT. Phys Rev B. 1989; 40:3616.doi: 10.1103/PhysRevB.40.3616
29. Berne BJ, Cicotti G, Coker DF, editors Classical and Quantum Dynamics in Condensed Phase Simulations. World Scientific Publishing Company; 1998. URL <http://www.librarything.com/isbn/9810234988>
30. Henkelman G, Jonsson H. The Journal of Chemical Physics. 2000; 113:9978.doi: 10.1063/1.1323224

31. Henkelman G, Uberuaga BP, Jónsson H. *The Journal of Chemical Physics*. 2000; 113:9901.doi: 10.1063/1.1329672
32. Kardar M. *Statistical Physics of Fields*. Cambridge University Press; 2007.
33. Hill TL. *Statistical Thermodynamics*. Dover; 1987.
34. Knudsen J, Nilekar AU, Vang RT, Schnadt J, Kunkes EL, Dumesic JA, Mavrikakis M, Besenbacher F. *Journal of the American Chemical Society*. 2007; 129(20):6485.doi: 10.1021/ja0700855 [PubMed: 17469820]
35. Ding K, Gulec A, Johnson AM, Schweitzer NM, Stucky GD, Marks LD, Stair PC. *Science*. 2015; 350(6257):189.doi: 10.1126/science.aac6368 [PubMed: 26338796]
36. Andersson KJ, Calle-Vallejo F, Rossmeisl J, Chorkendorff I. *Journal of the American Chemical Society*. 2009; 131(6):2404.doi: 10.1021/ja8089087 [PubMed: 19166291]
37. Mu Y, Liang H, Hu J, Jiang L, Wan L. *The Journal of Physical Chemistry B*. 2005; 109(47): 22212.doi: 10.1021/jp0555448 [PubMed: 16853891]
38. Perez-Alonso FJ, McCarthy DN, Nierhoff A, Hernandez-Fernandez P, Strebel C, Stephens IEL, Nielsen JH, Chorkendorff I. *Angewandte Chemie International Edition*. 2012; 51(19):4641.doi: 10.1002/anie.201200586 [PubMed: 22461415]
39. Wang X, Yu JC, Yip HY, Wu L, Wong PK, Lai SY. *Chemistry A European Journal*. 2005; 11(10): 2997.doi: 10.1002/chem.200401248
40. Thompson DT. *Nano Today*. 2007; 2(4):40.doi: 10.1016/S1748-0132(07)70116-0
41. Masatake H, Tetsuhiko K, Hiroshi S, Nobumasa Y. *Chemistry Letters*. 1987; 16(2):405.doi: 10.1246/cl.1987.405
42. Falsig H, Hvolbæk B, Kristensen I, Jiang T, Bligaard T, Christensen C, Nørskov J. *Angewandte Chemie International Edition*. 2008; 47(26):4835.doi: 10.1002/anie.200801479 [PubMed: 18496809]
43. Calle-Vallejo F, Huang M, Henry JB, Koper MTM, Bandarenka AS. *Phys Chem Chem Phys*. 2013; 15:3196.doi: 10.1039/C2CP44620K [PubMed: 23344855]
44. Lu YC, Xu Z, Gasteiger HA, Chen S, Hamad-Schifferli K, Shao-Horn Y. *Journal of the American Chemical Society*. 2010; 132(35):12170.doi: 10.1021/ja1036572 [PubMed: 20527774]
45. Fromm E. *Poisoning of Hydrogen Reactions*. Springer; Berlin Heidelberg: 1998. 123–155.
46. Thomas JP, Chopin CE. *Modeling of Hydrogen Transport in Cracking Metal Systems*. John Wiley & Sons, Inc; 2013. 223–242.
47. Martínez JI, Abad E, González C, Flores F, Ortega J. *Phys Rev Lett*. 2012; 108 246102. doi: 10.1103/PhysRevLett.108.246102
48. Jiang B, Yang M, Xie D, Guo H. *Chem Soc Rev*. 2016; 45:3621.doi: 10.1039/C5CS00360A [PubMed: 26100606]
49. Nave S, Tiwari AK, Jackson B. *The Journal of Physical Chemistry A*. 2014; 118(41):9615.doi: 10.1021/jp5063644 [PubMed: 25153478]
50. Franke JH, Kosov DS. *The Journal of Chemical Physics*. 2015; 142(4) 044703. doi: 10.1063/1.4906151
51. Vajda S, Pellin MJ, Greeley JP, Marshall CL, Curtiss LA, Ballentine GA, Elam JW, Catillon-Mucherie S, Redfern PC, Mehmood F, Zapol P. *Nat Mater*. 2009; 8(3):213.doi: 10.1038/nmat2384 [PubMed: 19202544]

Fig. 1. Perpendicular view to a (100) terrace (left panel) and to a (111) edge (right panel) of the Pt₃₈ and Au₃₈ nanoparticles (truncated octahedron) included in this study, where T stands for terrace and E for edge.

Fig. 2.

Pictorial sketch of the different intermediate stages along the whole catalytic cycle $2\text{CH}_4(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g}) + \text{H}_2(\text{g})$ on Pt_{38} (panel A) and Au_{38} (panel B) nanoparticles. The top views of the four-atom (100) and seven-atom (111) facets, where the catalytic cycle is completed on Pt and Au, respectively, are also given as insets in both panels.

Fig. 3.

Computed reaction pathway (including enthalpies and transition-state barriers) for the whole catalytic $2\text{CH}_4(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g}) + \text{H}_2(\text{g})$ cycle completed on the Pt_{38} nanoparticle. Labels 1-8 correspond to the geometries depicted in panel A of Figure 2. DFT energies (black), Helmholtz free-energies at $T=0\text{K}$ (blue) and Helmholtz free-energies at $T=400\text{K}$ (red).

Fig. 4.

Computed reaction pathway (including enthalpies and transition-state barriers) for the whole catalytic $2\text{CH}_4(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g}) + \text{H}_2(\text{g})$ cycle completed on the Au_{38} nanoparticle. Labels 1-8 correspond to the geometries depicted in panel B of Figure 2. DFT energies (black), Helmholtz free-energies at $T=0\text{K}$ (blue) and Helmholtz free-energies at $T=400\text{K}$ (red).

Fig. 5. Schematics of the initial (IS), transition (TS) and final (FS) states for the elementary step $2\text{CH}_3(^*) \rightarrow \text{C}_2\text{H}_6(^*) + 2\text{H}(^*)$ on the Pt_{38} (top panel) and Au_{38} (bottom panel) nanoparticles. The middle panel shows the CI-NEB energy barriers for Pt_{38} (red) and Au_{38} (blue) nanoparticles.

Fig. 6.

A) (Top) Difference of Helmholtz's free energies (in eV) as a function of temperature (in K) between steps 5 and 4 (associative desorption of ethane) in Au (yellow) and Pt (grey). (Bottom-left) Internal vibrational energy (in meV) and entropic contribution (in meV) to the free energy plotted in the top panel (bottom-right). B) Helmholtz's free energy barrier (in eV) as a function of temperature (in K) at the transition-state for associative desorption of molecular hydrogen; steps 6 and 8 in Au (yellow) and Pt (grey). C) Typical times to overcome the transition-state barrier for the associative desorption of ethane (Au in solid yellow and Pt in solid grey), and the associative desorption of molecular hydrogen (Au dotted yellow and Pt dotted grey).

Fig. 7. (Left panel) Relevant normal modes with amplitudes directed towards the transition-state for the formation (and subsequent desorption) of C₂H₆ on Au₃₈ (ranging between 130 and 360 cm⁻¹). (Right panel) Relevant normal modes with amplitudes directed towards the transition-state for the formation (and subsequent desorption) of H₂ on Pt₃₈ (ranging between 550 and 1650 cm⁻¹).

Table 1

All values in eV. For each elemental step i (labels 0 to 8) we give the increment in the internal electronic energy, U_e , w.r.t the step 0, zero-point vibration Helmholtz's free energy at T=0 K, F_0 , increments with respect to the first step, F_0 , and Helmholtz's free energy increment at T=400 K, F_{400} .

i	U_e	F_0	F_0	F_{400}
Pt ₃₈				
0	0	2.45	0	0
1	-0.13	2.41	-0.04	-0.40
2	-0.37	2.32	-0.13	-0.35
3	-0.50	2.29	-0.16	-0.41
4	-0.68	2.19	-0.26	-0.40
5	-0.75	2.30	-0.15	-0.28
6	-0.63	2.31	-0.14	-0.18
7	-0.56	2.29	-0.16	-0.20
8	+0.77	2.26	-0.19	-0.21
Au ₃₈				
0	0	2.45	0	0
1	-0.06	2.44	-0.01	-0.36
2	+0.63	2.30	-0.15	-0.46
3	+0.54	2.30	-0.15	-0.64
4	+0.87	2.14	-0.31	-0.86
5	+0.55	2.33	-0.12	-0.57
6	+0.59	2.33	-0.12	-0.25
8	+0.77	2.26	-0.19	-0.21