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Insights from methane decomposition on nanostructured palladium

Sergey M. Kozlov [a,*], Konstantin M. Neyman [a,b,*]

[a] Departament de Química Física and Institut de Quimica Teòrica i Computacional (IQTCUB), Universitat de Barcelona, C/Martí i Franquès 1, 08028 Barcelona, Spain
[b] Institució Catalana de Recerca i Estudis Avançats (ICREA), 08010 Barcelona, Spain

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ABSTRACT

Despite progress in the understanding of how nanostructuring affects activity of heterogeneous catalysts, there are still fundamental questions to be answered. Do nanoparticle edges have the same catalytic properties as steps on single-crystal surfaces? How much does the increased structural flexibility of nanoparticles contribute to their activity? How do reaction barriers depend on the nanoparticle size? Herein we address these questions regarding an exemplary reaction sequence of complete methane dehydrogenation. Using density functional theory methods we calculate energy profiles of this reaction on edges of 1.2 nm large Pd_{79} and 1.6 nm large Pd_{140} particles as well as on Pd(111) and steps on Pd (211) single-crystal surfaces. The barriers of the two slowest reaction steps, $CH_4 \rightarrow CH_3 + H$ and $CH \rightarrow C + H$, notably decrease in the following series of substrates: $Pd(1\,1\,1) \gtrsim Pd(2\,1\,1) > Pd_{140} > Pd_{79}$. Importantly, these barriers differ by $\geqslant$20 kJ/mol on Pd_{140} and Pd(211), whereas the differences between the barriers on Pd(111) and Pd(211) are only $\leqslant$11 kJ/mol. Also, the structural flexibility contributes to higher reactivity several times stronger for Pd_{79} than for Pd(111). All calculated elementary steps follow Brønsted–Evans–Polanyi relationships. This study advances the understanding of heterogeneous catalysis by shedding light on several fundamental questions concerning structure–property relationships in nanostructured catalysts.

1. Introduction

Chemical industry widely relies on nanostructuring of heterogeneous catalysts to increase their surface area and per gram efficiency [1–3]. The catalytic activity of many materials is known to strongly depend on their (nanoscale) structure, in particular, on the size of catalyst particles [4–6]. As a consequence, understanding of structure–property relationships is one of the essential requisites for the effective development of improved catalysts [7]. For example, low-coordinated atoms on catalyst surface often form active sites with notably altered properties, which in some cases may govern the overall performance of the catalyst [8–10]. Most catalysts contain low-coordinated atoms on edges of catalyst particles and on steps on catalyst surface as well as on some other irregular structural features that may appear as a result of certain preparation procedures. Whereas numerous experimental and theoretical investigations revealed higher activity of steps compared to the respective terraces e.g. Refs. [11–13], the activity of edges of catalyst particles is much less studied [8,14,15]. In fact, it is often assumed to be identical to the activity of surface steps [10,12,16]. The only justification for this assumption seems to be common similarity between coordination numbers of atoms on surface steps and atoms on nanoparticle (NP) edges. However, recent transmission electron microscopy (TEM) studies with atomic resolution suggest that structural relaxation of the catalyst is altered near nanoparticle edges [17]. The higher structural flexibility of NPs compared to extended surfaces is also discussed in the literature [18,19]. Nevertheless, it is still unclear how much does the flexibility of NPs contribute to the kinetics of catalyzed reactions. Another important aspect is that the strong dependency of properties of nanoparticulate catalysts on the particle size may have two different explanations. On the one hand, properties of each active site may alter with the nanoparticle size leading to the change in the overall activity of the catalyst. On the other hand, the mere variation of the relative abundance of various types of active sites with NP size may alter catalytic activity, while the activity of each particular type of active sites remains unchanged [5,10,20].

Thus, currently there is still a lack of detailed scientific evidence elucidating how nanostructuring affects heterogeneous catalysts, which calls for a dedicated study. Such study is easier to perform using so-called computational experiments, i.e. simulations, rather

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[*] Corresponding authors at: Departament de Química Física and Institut de Quimica Teòrica i Computacional (IQTCUB), Universitat de Barcelona, C/Martí i Franquès 1, 08028 Barcelona, Spain (K.M. Neyman).

E-mail addresses: sergey.m.kozlov@ub.edu (S.M. Kozlov), konstantin.neyman@icrea.cat (K.M. Neyman).

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than laboratory experiments. Among the advantages of the computational approach for such a fundamental investigation are the following: (1) absolute control over the catalyst structure and the nature of the active site under scrutiny, (2) the ability to analyze each elementary reaction individually, and (3) straightforward procedures to obtain real (not apparent) reaction and activation energies. Moreover, it seems hardly possible to design an experiment, where the effect of NP flexibility on its catalytic activity can be measured directly.

Herein we study an exemplary chain of reactions, complete methane dehydrogenation on Pd, taking place on catalysts nanostructured in different manners. In particular, we use density functional theory (DFT) methods to calculate energy profiles of the reaction on terraces of Pd(111) single-crystal surface and steps on Pd(211) surface as well as on edges of Pd_{79} and Pd_{140} nanoparticles. This variety of systems allows us investigating (1) differences in reactivities of steps on extended surfaces and NP edges and (2) the effect of the NP size on catalytic properties of particular active sites. Moreover, via in-depth analysis of the obtained results we also shed light on (3) the influence of the flexibility of the catalyst structure on its reactivity, and (4) the reliability of Brønsted–Evans–Polanyi (BEP) relationships for prediction of the effects of nanostructuring on surface reactivity of materials. To the best of our knowledge the present study is the first to address in detail point (1), whereas point (3) was so far addressed only in insufficient detail [18,19] and points (2) and (4) were studied just for one-step reactions of O_2 and H_2O dissociation on Pt nanoparticles [21,22].

The present study deals with analysis of reaction and activation energies of C–H bond scissions, $CH_x \rightarrow CH_{x-1} + H$ ($x = 1$–4), occurring on a series of model catalysts composed of crystalline fcc Pd. Hence, possible inaccuracy due to the approximate form of the exchange–correlation functional used in calculations would lead to a systematic error that does not vary too much between considered systems and reactions. That is, qualitative conclusions of the present study as well as relative values are unlikely to be critically affected by the choice of the particular computational method, whereas absolute values may be less precise.

The focus of the present work on methane decomposition is due to both the simplicity of this reaction and its relevance to many industrial processes. Indeed, methane is a naturally abundant fuel also used as reactant in such applications as acetic acid production [23], NO reduction [24], as well as CO_2 [25,26] and steam [27] reforming reactions, which require dedicated catalysts to be performed efficiently. Despite certain controversy [28–30], some studies of methane oxidation on Pd-based catalysts concluded that metallic Pd is active in methane activation [30–32]. Since close-packed surfaces of Pd are rather inert toward methane [30,33,34], it is particularly interesting to investigate methane dissociation on nanostructured Pd. Note that previously methane decomposition has been calculated only on single-crystal surfaces of Pd [30,35].

In most applications nanostructured Pd catalysts contain Pd particles of several nanometers in size located on a support with high surface area. At least in the case of particularly inactive supports [36,37], such catalysts can be simulated by unsupported *scalable with size* (SwS) nanoparticle models [38–40]. These models are designed so that their properties are not exactly the same as properties of much larger species, but should smoothly approach them with growing NP size. One could also expect properties of NP terraces to converge to properties of respective single-crystal surfaces with the increasing nanoparticle size. At the same time, properties of NP edges do not have to converge to properties of steps on single-crystal surfaces, due to intrinsic structural differences between these two entities. Scalable with size nanoparticle models should feature a bulk-like lattice structure (like bigger particles) and a shape in line with the Wulff construction.

Note that smooth dependency of calculated adsorption energies on the NP size occurs only for nanoparticles above a certain critical size. Below this size particles belong to the so-called "every atom counts" regime, where their properties may significantly change upon addition or removal of even a single metal atom [41–43]. In turn, the value of the critical size strongly depends on the particular transition metal as well as the nature of the considered adsorbate [44–46], which forces one to perform a scalability with size check for each particular case. For Pd already truncated octahedral Pd_{79} NPs fulfill SwS criteria, which explains their numerous applications in computational studies [47–49].

One could expect from Brønsted–Evans–Polanyi relationships that the smooth dependency of adsorption energies on the size of SwS NPs would result in a similarly smooth trend for activation energies. Yet, it is still unclear how accurate are BEP relationships for nanostructured catalysts [22]. At the same time, there are only few studies explicitly considering the dependency of reaction [21] and diffusion [50,51] barriers on the size of scalable with size nanoparticles. (Similar studies on nanoparticle models that are not SwS are more common [52–54].) Also in some studies the surface reactivity of SwS NPs has been calculated without addressing their size dependency [8,55,56]. Moreover, to the best of our knowledge reactivity of NP edges is yet to be compared to that of steps on single-crystal surfaces.

It is important to mention at this point that many [21,37,57] but not all [19,47,55] species adsorb more strongly on nanoparticle edges than on NP terraces. Furthermore, only if the products of a given reaction are stabilized more on NP edges than the reactants, the exothermicity of the reaction increases. Thus, there is no reason to assume that activation energy of any elementary step should be lower on nanoparticle edge than on NP terrace.

2. Computational details and employed models

The computational parameters in this study were chosen to be as similar as possible to those of Ref. [8], which addressed methane dehydrogenation on Pt(111) single crystals and Pt_{79} NPs and yielded results in line with molecular beam experiments. VASP software [58] was used to perform periodic calculations with rPBE exchange–correlation functional [59], which was shown to yield reasonable results for H interaction with Pd among other systems [37]. To evaluate the role of dispersive interactions for methane activation empirical DFT-D3 corrections [60] were applied to rPBE functional in some calculations. Eigenstates of valence electrons were calculated using plane-wave basis sets with the cutoff of 415 eV. First order Methfessel–Paxton smearing of 0.1 eV was applied to the occupation numbers [61]. The presence of core electrons was accounted via projector augmented wave technique [62]. All calculations except those for gas-phase CH_x species and H atoms were performed in spin-unpolarized fashion, which does not introduce any significant inaccuracy [63]. $5 \times 5 \times 1$ and $7 \times 5 \times 1$ Monkhorst–Pack meshes of k-points were used to sample the reciprocal space in calculations of Pd(111) and Pd(211) slabs, respectively. Calculations of NP models were performed at Γ-point in the reciprocal space. Geometry optimization was performed until forces on C, H and certain Pd atoms (see details below) became less than 0.2 eV/nm. Transition states were pre-optimized with nudged elastic band method [64] and refined using dimer method [65]. Vibrational frequencies were calculated using finite differences method with 3 pm displacements applied to C and H atoms. All transition states featured exactly one imaginary vibrational frequency.