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Title: Escaping scaling relationships for water dissociation at interfacial sites of zirconia-supported Rh and Pt clusters

Year: 2019

Version: Published version

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Please cite the original version:

Kauppinen, M. M., Korpelin, V., Verma, M. A., Melander, M. M., & Honkala, K. (2019). Escaping scaling relationships for water dissociation at interfacial sites of zirconia-supported Rh and Pt clusters. *Journal of Chemical Physics*, 151(16), Article 164302.
<https://doi.org/10.1063/1.5126261>

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Cite as: J. Chem. Phys. **151**, 164302 (2019); <https://doi.org/10.1063/1.5126261>

Submitted: 02 September 2019 . Accepted: 02 October 2019 . Published Online: 22 October 2019

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ABSTRACT

Water dissociation is an important reaction involved in many industrial processes. In this computational study, the dissociation of water is used as a model reaction for probing the activity of interfacial sites of globally optimized ZrO₂ supported Pt and Rh clusters under the framework of density functional theory. Our findings demonstrate that the perimeter sites of these small clusters can activate water, but the dissociation behavior varies considerably between sites. It is shown that the studied clusters break scaling relationships for water dissociation, suggesting that these catalysts may achieve activities beyond the maximum imposed by such relations. Furthermore, we observed large differences in the thermodynamics of the water dissociation reaction between global minimum and near-global minimum isomers of the clusters. Overall, our results highlight the uniqueness of interfacial sites in catalytic reactions and the need for developing new concepts and tools to deal with the associated complexity.

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I. INTRODUCTION

The dissociation of water into hydroxyl and hydrogen species plays a key role in many industrially relevant processes, such as the water-gas shift (WGS) reaction and steam reforming. The water dissociation reaction has been studied computationally over a number of different systems such as clean metal surfaces [e.g., Cu(111),¹ Au(111),¹ Pt(111),^{1,2} Rh(111)^{1,2}] and unsupported metal clusters (e.g., Cu,³ Au,³ Pt,² and Rh²). Varying activation energies are reported for ideal metal surfaces, ranging from as low as 0.67⁴ to 0.96¹ eV on Ni(111), ~0.8 eV over Pt(111)^{1,5} and Rh(111),^{2,6} and even as high as ~2 eV over Au(111).^{1,7} Numerous studies strongly advocate the vital role of support, and the metal-support interface, for the overall catalytic activity.^{6,8–12} Therefore, both the metal and the support should be considered when investigating such systems computationally. The choice of the supported metal catalyst model is nontrivial; typical models employ either supported finite clusters

or nanorods, and different metal-support combinations have been investigated (e.g., Au/MgO,⁷ Cu/ZrO₂,¹³ Rh/ZrO₂,⁶ Ni/Al₂O₃,⁹ and Pt/CeO₂¹⁰). In contrast to clean metal surfaces, on the metal-support interfaces such as Ni/Al₂O₃,⁹ Rh/ZrO₂,⁶ Cu/ZrO₂,¹³ and Au/TiO₂,¹⁴ the barriers are reported to be much lower than those on the corresponding pure metals.

In our current study, we use globally optimized supported clusters to model zirconia-supported rhodium and platinum catalysts. Both materials have been found to be active toward the WGS reaction,^{15,16} and Rh/ZrO₂ is also active for H₂ oxidation¹⁷ and the partial oxidation of methane.¹⁸ Recent studies have highlighted the importance of considering the catalyst as an ensemble of clusters with similar energies rather than as the static minimum energy structure.^{19–22} While the clusters may spend most of their time as the global minimum (GM) structure, at reaction conditions there is available energy for them to isomerize to one of the structures lying only slightly higher in energy. These near-global minimum (NGM)

structures can be more reactive than the most stable isomer and may even dominate catalytic activity while being minority species.²⁰ With this in mind, we have investigated the GM as well as NGM structures of zirconia-supported rhodium and platinum clusters of different sizes.

Multiple ways to escape traditional scaling relations have been proposed for heterogeneous catalysts,²³ among which the fluxionality under reaction conditions²⁴ and the presence of multiple different adsorption sites²⁵ are highly relevant for small, supported clusters. The absence of scaling relations makes it difficult to predict activation energies; however, it also provides a way to improve catalyst performance beyond a previously proposed maximum.²⁶ The Brønsted–Evans–Polanyi (BEP) relation²⁷ between the reaction energy and barrier for water dissociation over extended transition metal surfaces has been established before, and oxygen atom adsorption energy was found to be a good descriptor for the reaction.²⁸ Over unsupported Rh and Pt nanoparticles, the transition state (TS) energies were found to correlate well with water adsorption energies across different sites.² The descriptors in this case were the projected d-band center and coordination number of the surface atoms forming the site, which also correlated linearly with the transition state energies.² However, the extended surfaces were observed to not fit in the same scaling relation as the nanoparticles.

In this study, we focus on the water dissociation reaction at the perimeter sites of GM and NGM isomers of supported Rh and Pt clusters. The activation energies are compared to the reaction energies in order to establish a BEP relation to predict the activity of interfacial sites toward water dissociation. Transition-state scaling between the initial (or final) state and the transition state energy is also evaluated. Next, we compare the thermodynamics of the water dissociation reaction on the GM and NGM structures. Finally, we screen hydrogen adsorption sites on the clusters, and the adsorption energies are compared to the strain-adjusted generalized coordination numbers (SGCN)²⁹ of the sites, as well as the smooth overlap of atomic position (SOAP)³⁰ descriptor. Our results further highlight the importance of thorough consideration of the interface sites of small fluxional clusters and the heterogeneity and catalytic behavior found at the perimeter of such clusters.

II. COMPUTATIONAL DETAILS

All density functional theory (DFT) calculations were carried out in the projector-augmented wave (PAW)³¹ formalism of DFT as implemented in the GPAW 1.4.0 package.^{32–34} The Perdew–Burke–Ernzerhof (PBE) functional^{35,36} was used to describe the exchange and correlation effects under the generalized gradient approximation (GGA). The core electrons of all elements were described by PAW setups in the frozen-core approximation. Setups with 15 and 16 valence electrons were used for Rh and Pt, respectively. The maximum spacing for the real-space grid basis was 0.2 Å, a value our group has previously used successfully for related systems.^{2,6,37–39} The reciprocal space was sampled at the Γ point.

The interface model was built using 13 and 19 metal atom clusters (Pt and Rh) dispersed over monoclinic zirconia, $m\text{-ZrO}_2(\bar{1}11)$, as support. The Rh₁₃, Rh₁₉, Pt₁₃, and Pt₁₉ clusters supported on $m\text{-ZrO}_2(\bar{1}11)$ were modeled using the globally optimized geometries discovered in previous work by our group.³⁹ In that study, the

global optimizations using a genetic algorithm (GA) were carried out for three sizes (13, 19, and 43 atoms) of Rh and Pt clusters over the $m\text{-ZrO}_2(\bar{1}11)$ support. For each M/ZrO₂ system, three optimization runs were performed starting from randomly generated populations. The offspring was created using cut-and-splice crossover (70% probability) and mutation (30% probability) operations. First, metal atoms were allowed to relax ($f_{\text{max}} = 0.08 \text{ eV/\AA}$) over a fixed 3×3 single layer ZrO₂ surface. The resulting structures from all GA runs were merged, and for the 60 lowest energy structures, the metal fragments were cut and adsorbed over a 2 layers thick (bottom layer fixed) 3×3 ZrO₂ support. Finally, the optimization runs were carried out until the maximum residual forces reached below $0.05 \text{ eV/\AA}$. Overall, ~9900 M/ZrO₂ structures were screened. For further details, please see Ref. 39.

The $m\text{-ZrO}_2(\bar{1}11)$ support was selected because of its representation of the most stable polymorph at the considered WGS reaction conditions and $(\bar{1}11)$ being the most stable facet. The oxide support was described by a slab model consisting of 3×3 unit cells with a thickness of two stoichiometric layers. All global minimum (GM) Rh₁₃/ZrO₂, Rh₁₉/ZrO₂, Pt₁₃/ZrO₂, and Pt₁₉/ZrO₂ catalyst structures are depicted in Fig. 1. We also employed near-global minimum (NGM) isomers lying higher in energy studied by our research group³⁹ to compare the energetics with their respective global minimum catalytic systems (see Fig. 1). The NGM clusters were chosen based on geometrical as well as energetic considerations; we picked NGM geometries that were noticeably different from the GM clusters and whose energies were within roughly 1 eV of the global minima. The relative instabilities of the chosen NGM isomers of Rh₁₃, Rh₁₉, Pt₁₃, and Pt₁₉ clusters compared to their respective GM clusters were calculated as 0.80, 1.33, 0.56, and 0.35 eV, respectively. The gas-phase reference for molecular water was computed in a nonperiodic cell of size $17.5 \times 16.0 \times 16.6 \text{ \AA}$.

In the geometry optimizations, the bottom layer of the zirconia slab was kept frozen to its initial geometry, while the top zirconia layer, the metal cluster, and the adsorbed atoms were allowed to relax until the maximum residual force reached below $0.05 \text{ eV \AA}^{-1}$. We consider this an acceptable criterion, considering the large sizes of our systems with about 2000 valence electrons; the choice is also consistent with our work on the global optimization of these clusters.³⁹ The transition state structures of water dissociation reactions at various interfacial sites were located using the climbing-image nudged elastic band (CI-NEB) method.^{40–43} The obtained transition state structures were confirmed by harmonic vibrational analysis with the presence of an imaginary frequency mode corresponding to the reaction coordinate.

The adsorption energies of molecular and dissociated water were computed as

$$E_{\text{ads}} = E_{\text{total}} - E_{\text{M}_X/\text{ZrO}_2} - E_{\text{H}_2\text{O}(\text{g})}, \quad (1)$$

where E_{total} is the energy of the optimized supported cluster and the water molecule (or dissociated water). $E_{\text{M}_X/\text{ZrO}_2}$ is the energy of the supported metal cluster, where M corresponds to either Pt or Rh and X is either 13 or 19. $E_{\text{H}_2\text{O}(\text{g})}$ is the computed energy of the gas-phase water molecule under nonperiodic boundary conditions. The reaction energy of water dissociation is defined as

$$\Delta E = E_{\text{ads}}(\text{OH} + \text{H}) - E_{\text{ads}}(\text{H}_2\text{O}). \quad (2)$$

FIG. 1. Structure geometries of (a) global minimum and (b) near-global minimum zirconia-supported Rh_{13} , Rh_{19} , Pt_{13} , and Pt_{19} clusters. Rh, Pt, and O atoms are colored blue, purple, and light gray, respectively. High-coordinated Zr atoms are colored dark gray, while lower-coordinated Zr are colored white.

A. Generalized coordination numbers

Following Ref. 44, the generalized coordination number (GCN) of cluster atom i is defined as

$$\text{GCN}(i) = \sum_j^{n_i} \frac{\text{CN}(j)}{\text{CN}_{\max}(j)}, \quad (3)$$

where j runs over the nearest neighbors of atom i , n_i is the number of nearest neighbors for atom i , $\text{CN}(j)$ is the conventional coordination number of atom j , and $\text{CN}_{\max}(j)$ is the maximum coordination number of atom j (12 for an fcc metal; 7 for Zr; and 3 or 4 for O). To account for bridge and hollow sites s , the definition is extended as follows:

$$\text{GCN}(s) = \frac{\text{CN}_{\max}(\text{fcc})}{\text{CN}_{\max}(s)} \sum_j \frac{\text{CN}(j)}{\text{CN}_{\max}(j)}. \quad (4)$$

Here, $\text{CN}_{\max}(s) = 12, 18, 22$, or 26 , for top, bridge, 3-fold, or 4-fold hollow sites, respectively, and $\text{CN}_{\max}(\text{fcc}) = 12$. The index j runs over the nearest neighbors of the atoms that define the adsorption site, without double-counting any atoms. This is a slightly generalized version of the definition in Ref. 44 to allow for the inclusion of atoms other than fcc metals.

The GCNs were refined by considering strain effects for the metal cluster atoms.²⁹ This is done by including a factor describing the ratio of the optimal bulk bond length d_{bulk} to the particular metal-metal bond length $d(i, j)$,

$$\text{SGCN}(i) = \sum_j \frac{d_{\text{bulk}}}{d(i, j)} \frac{\text{CN}(j)}{\text{CN}_{\max}(j)}, \quad (5)$$

where SGCN denotes strain-adjusted GCN. A similar strain adjustment can be written for Eq. (4). In the site calculations, if a neighbor of the site was coordinated to multiple site-defining atoms, the average distance was used to determine the strain adjustment.

III. RESULTS

A. Water adsorption and dissociation at global minimum cluster-support interfaces

The molecular adsorption of water at interfacial sites of the zirconia-supported global minimum Rh_{13} , Rh_{19} , Pt_{13} , and Pt_{19} clusters was thoroughly screened. The starting geometries were chosen based on results from previous studies concerning water adsorption on Rh and Pt,² ZrO_2 ,³⁷ and the Rh-ZrO₂ interface,⁶ which show that water should preferably adsorb on the oxide sites rather than on the metal. Therefore, we initially deposited molecular water on each of the Zr top sites in the immediate vicinity of the clusters, sitting almost horizontally with one hydrogen pointing toward the cluster. The optimized adsorption geometries are depicted in Fig. 2 along with their adsorption energies as bar charts. The data can also be found in the [supplementary material](#) in a tabular form (Table S1). Please note that the geometry optimizations were performed for one deposited water molecule at a time, and in Fig. 2, for brevity's sake, the molecules are shown in a single image with the cluster being in its optimized geometry.

Upon optimization, some water molecules moved far away from the cluster, while some moved to be adsorbed on a Rh/Pt top site instead of the Zr top site (labeled 5 and 7 for Rh_{13} and 7, 9, and 11

FIG. 2. (a) H_2O adsorption geometries and (b) molecular and dissociative adsorption energies on global minimum Rh_{13} , Rh_{19} , Pt_{13} , and Pt_{19} clusters. Oxygen atoms that are not part of the support are colored red, while hydrogen atoms are colored light blue. For the rest of the atom colors, please refer to Fig. 1. H_2O molecules are labeled clockwise starting from H_2O indicated in each case with a red circle (labeled “1”). The H_2O adsorption energies are indicated with gray bars, while $\text{OH} + \text{H}$ adsorption energies are indicated with blue bars.

for Pt_{13} in Fig. 2). All such water molecules were initially deposited on high-coordinated Zr atoms (colored dark gray in Fig. 2). While most surface Zr atoms are bound to 6 lattice oxygens, the high-coordinated ones are bound to 7, rendering them unable to adsorb water at all. The molecules that moved far away from the cluster were omitted from Fig. 2 as well as further calculations since they were deemed to be too far from the interface to be activated by it.

The adsorption energies display significant variation along the perimeters of all clusters. For instance, over $\text{Rh}_{13}/\text{ZrO}_2$ and $\text{Rh}_{19}/\text{ZrO}_2$, the adsorption energies range from -0.99 to -0.32 eV and from -0.96 to -0.45 eV, respectively. This roughly spans the whole range of adsorption energies previously calculated for $\text{Rh}(111)$ and $m\text{-ZrO}_2(\bar{1}11)$ surfaces, with the weakest adsorption energy being comparable to that of $\text{Rh}(111)$ (-0.34 eV)² and the strongest to that of $m\text{-ZrO}_2(\bar{1}11)$ (-1.01 eV).³⁷

Over $\text{Pt}_{13}/\text{ZrO}_2$ and $\text{Pt}_{19}/\text{ZrO}_2$, the adsorption energies range from -1.04 to -0.29 eV and from -0.95 to -0.42 eV, respectively. Like in the case of Rh clusters, the strongest adsorption energies are comparable to the adsorption energy found on bare zirconia, and the weakest are similar to the adsorption energy found on $\text{Pt}(111)$.²

The bare $\text{ZrO}_2(\bar{1}11)$ presents four Zr atoms per unit cell, and water adsorption energies vary from one Zr top site to the next.³⁷ The weakest adsorption energy on the pristine zirconia corresponds to the high-coordinated Zr cation, and as discussed above, water cannot adsorb atop these Zr at the interface. Another factor is the formation of hydrogen bonds to the surface oxygen atoms, which is different from one site to the next.³⁷ However, the rest of the variance in adsorption strength cannot be explained only by comparing the Zr sites to those on pure zirconia. One possible explanation could be that the presence of the metal cluster changes the

coordination of the Zr cations as well as the surface oxygen atoms; however, the irregular shape and size of the clusters means that the effect is unpredictable.

Dissociative adsorption geometries of water at the global minimum clusters were optimized for the same interface sites as the molecular adsorption. Starting geometries were constructed by moving one of the hydrogen atoms to the nearest promising adsorption site (e.g., nearest hollow) on the metal, with OH staying at the original water adsorption site. Geometries were allowed to fully relax, and in some cases, hydrogen diffused quite far away from the initial placement. In the case of the Pt_{13} cluster, three dissociated water structures (H_2O labeled 2, 3, and 12) preferably have the hydrogen sitting on an interfacial surface oxygen atom instead of the metal site. The OH species generally stayed near their initial positions, with some of them moving closer to the cluster to bind through the O atom to both Zr and Rh. This bridge-bonded geometry was previously also found for the nanorod model of the Rh-ZrO_2 interface.⁶ On the Rh_{13} cluster, two structures (H_2O labeled 5 and 7) were found with OH preferably binding to a Rh top site, which was the original H_2O adsorption site for them. The same applies for Pt_{13} structures with H_2O labels 7, 9, and 11.

As in the case of molecular water, dissociative adsorption energies vary significantly from site to site (see Fig. 2 and Table S1 in the supplementary material for details). On average, the water dissociation reaction is mildly exothermic at the Rh cluster interfaces but slightly endothermic at the Pt cluster interfaces. On the extended $\text{Rh}(111)$ surface, the reaction has been found to be weakly exothermic by ~ 0.1 eV,^{2,6} while on the extended $\text{Pt}(111)$ surface, the reaction is moderately endothermic by ca. 0.3 eV.^{2,45} The difference in reaction energies between Rh and Pt has previously been shown to be less

pronounced for gas-phase nanoclusters than for extended surfaces.² Here, although the average reaction energies between the clusters are comparable to each other, comparing reaction energies between roughly equivalent sites reveals how different the water dissociation energetics are between the clusters. For instance, H₂O label 1 occupies the same Zr top site on all systems, and while the molecular adsorption energies are very similar, the OH + H adsorption energies and therefore the reaction energies are different. One explanation may be that the hydrogen adsorption strength varies since it adsorbs on completely different sites on the clusters. Furthermore, the Zr sites are not exactly equivalent due to the presence of the clusters. In general, all of the clusters include some sites at their perimeter where water dissociation is thermodynamically more favorable than on the extended metal (111) and *m*-ZrO₂(111) surfaces and some sites where water dissociation is unfeasible.

In order to supplement the results obtained from the adsorption energy calculations, we analyzed the scaling between molecular and dissociated water adsorption energies. The obtained scaling plots of OH + H vs H₂O adsorption energies show very poor R² values for all clusters (see Figs. S1–S4 of the [supplementary material](#) for details), except for Rh₁₃/ZrO₂ which has a slightly better value (R² = 0.80, slope = 0.71). Thus, the energies of the initial and final states of the dissociation reaction do not scale with each other at the Rh₁₉, Pt₁₃, and Pt₁₉ cluster perimeters. For these clusters, a particular site may bind both molecular water and dissociated water equally well, or it might bind one weaker or stronger than the other. Note that only sites for which activation energies were determined are included in the scaling relationships and that sites where dissociation does not occur “across” the interface (H₂O adsorbs on metal/OH and H both adsorb on oxide or metal) were excluded from the analysis. The exclusion of outliers does not lead to any significant improvement of the R² values, except for Rh₁₃/ZrO₂ for which there is no scaling (R² = 0.18) between the initial and final state energies if all sites are included.

B. Activation energies

A thorough screening of transition state (TS) structures at the interfacial sites was carried out over the Pt₁₃/ZrO₂ and Rh₁₃/ZrO₂ clusters. To reduce the computational cost, five transition state calculations across the interface were performed over the Pt₁₉/ZrO₂ and Rh₁₉/ZrO₂ clusters. Over the M₁₉ (M = Rh or Pt) clusters, we selected water molecules for TS calculations solely based on geometry so that each water is adsorbed on a Zr top site with one hydrogen pointing toward the cluster (see Tables S2 and S3 in the [supplementary material](#)). The transition state structures corresponding to the lowest barriers are depicted in Fig. 3. All activation energies pertaining to each cluster are supplied in Tables S2 and S3 of the [supplementary material](#) along with the corresponding imaginary frequencies, as well as O–H and M–H bond lengths.

Locating transition state structures at the asymmetric metal-oxide interfacial sites has its fair share of complications. We came across a few examples where the dissociation occurred at the nearby metal sites or over the zirconia surface instead of across the interface. Therefore, careful observation is mandatory while dealing with interfacial reactions over asymmetric cluster models. We note that the abovementioned TS cases were removed from our scaling

FIG. 3. Transition states corresponding to the lowest water dissociation barrier.

relationships, but full data and further discussion are provided in Table S3 and Sec. I of the [supplementary material](#).

The forward activation energies over the Pt₁₃ and Rh₁₃ clusters range from 0.60 to 1.13 eV and from 0.48 to 0.81 eV, respectively. Over the Pt₁₉ and Rh₁₉ clusters, the forward activation energies range from 0.35 to 0.76 eV and from 0.40 to 0.88 eV, respectively. The varying nature of the activation energies, even between Zr sites that are equivalent on the bare surface, can partially be attributed to the different Zr coordinations due to cluster asymmetries. Therefore, similar to the adsorption strengths of H₂O and OH + H, there is no predictability between the type of Zr site and barrier height. The M₁₉ and Rh₁₃ clusters exhibit a similar range of barriers, whereas Pt₁₃ has slightly higher barriers. Interestingly, over Rh clusters, lower barriers often correspond to lower water binding strengths, but Pt clusters show mixed behavior and there is no relation between adsorption energies and barriers.

The smallest calculated activation energies are lower compared to clean Rh(111) and Pt(111) surfaces and unsupported Rh₁₄₇ and Pt₁₄₇ metal nanoparticles (~0.72 eV).^{1,2,6} The present metal-oxide interfaces also perform better in terms of activation energy compared to the Cu/ZrO₂¹³ and Au/MgO interfaces⁷ for the activation of water. Evidently, the results for Rh-based clusters are in good agreement with the Rh/ZrO₂ rod model interface (E_{act} = 0.35 eV) previously studied by our research group.⁶ The lowest activation energies over the Rh₁₉ and Rh₁₃ clusters differ only by 0.05 eV and 0.13 eV from that on the rod model interface. The larger difference observed for Rh₁₃ may be explained by its smaller size.

Although the barriers obtained for the activation of water over the present cluster interfaces are lower or similar compared to various metal-oxide catalysts, they are still higher compared to the pure zirconia surface. Our research group has previously found the activation of water over pure zirconia to be spontaneous and mildly

exothermic.⁶ Therefore, the water activation might occur over zirconia first, followed by hydrogen diffusion to the metal frame. The diffusion of a hydrogen atom on $m\text{-ZrO}_2(\bar{1}11)$ is likely a complex process, as there exist multiple possible pathways for diffusion. Under reaction conditions, the behavior is further complicated by the adsorbate (e.g., hydroxyl) coverage of the surface.⁴⁶ As an example, we have simulated the diffusion of H from a 2-coordinated lattice oxygen atom to the nearest lattice oxygen on the ideal $m\text{-ZrO}_2(\bar{1}11)$ surface and found the activation energy to be fairly high at about 1.3 eV. We emphasize that this value corresponds to one possible route out of many, and a thorough analysis of diffusion pathways is required to definitively describe the diffusion behavior.

The presence of hydrogen at the metal site is desired for further reaction with CO in the WGS process because, as previously observed, CO strongly prefers metal sites.^{6,7,13} Interestingly, we found a few cases in our study where the water molecule preferably dissociated onto a ZrO_2 lattice oxygen next to the cluster. In these cases, H_2O is initially hydrogen bonded to a 2-coordinated surface oxygen atom, facilitating the dissociation onto it. The barriers for such dissociations range between 0.04 and 0.75 eV, meaning that the cluster can impede the ordinarily spontaneous dissociation on zirconia to varying degrees. With regard to the diffusion of H from oxide to metal, we found two paths on Pt_{13} with diffusion barriers of 0.60 and 1.10 eV. On a Rh/ZrO_2 rod model using similar computational methods as in the present work (please see Ref. 6 for details), the oxide-to-metal H diffusion barrier was found to be 0.62 eV. These barriers are of comparable magnitude to those of water dissociation across the cluster-oxide interface, suggesting that both pathways could supply H to the cluster.

The Brønsted–Evans–Polanyi (BEP) relationships based on forward activation energies and reaction energies were studied in order to further analyze the results obtained from the calculations. They demonstrated weak trends over Rh_{13} , Rh_{19} , and Pt_{13} clusters, as indicated by low R^2 values. Interestingly, the Pt_{19} cluster delivers an improved trend ($R^2 = 0.83$) compared to the other systems. We note that the M_{19} relationships contained only five data points, and therefore, a slight difference in correlation cannot be ruled out with a larger number of data. A BEP relation with an R^2 value of 0.54 has been reported earlier for dissociation over numerous clean metal surfaces.²⁸

We also analyzed the transition state scaling (TSS) relationships based on the adsorption energies of TS and molecular water (initial state) or dissociated water (final state). The Pt_{19} cluster delivered a good linear trend based on the TS and final states of water with an R^2 value of 0.89. This correlation arises from the fact that the TS structures resemble the final states on the Pt_{19} cluster. Other systems expressed no dependencies between two considered parameters. In comparison with the present models, the unsupported Rh and Pt nanoparticles previously investigated by our research group exhibited R^2 values of 0.92 and 0.85, respectively.² Furthermore, we studied the bonding patterns in the TS structures in relation to their adsorption energies. There was no observed correlation between O–H bond lengths and E_{ads} of TS structures over any cluster. The trend between Rh–H bond lengths and E_{ads} (TS) over Rh_{19} showed a little improvement but not to a significant level. Moreover, no dependencies were found in between M–H bond lengths and E_{ads} of TS structures over other clusters.

C. Water adsorption over near-global minimum catalytic systems

Next, we address the thermodynamics of dissociative water adsorption over systems with near-global minimum (NGM) cluster isomers and compare the values to those obtained on the global minima. The initial geometries for both molecular and dissociated water were built in the same way as on the GM clusters, and the optimization behavior was similar. Figure 4(a) shows all the considered water molecules at various interfacial sites of NGM isomers of the $\text{Rh}_{13}/\text{ZrO}_2$, $\text{Rh}_{19}/\text{ZrO}_2$, $\text{Pt}_{13}/\text{ZrO}_2$, and $\text{Pt}_{19}/\text{ZrO}_2$ catalytic systems. The adsorption energies of water on the Rh_{13} and Rh_{19} clusters range from -0.99 to -0.64 eV and -0.87 to -0.41 eV, respectively. On the Pt_{13} and Pt_{19} clusters, the corresponding ranges are -0.98 to -0.36 eV and -1.07 to -0.20 eV. These ranges are comparable to those obtained on the GM clusters, which is to be expected, since molecular water usually adsorbs to the oxide Zr top sites in both cases. The adsorption energies are summarized in Fig. 4(b) and reported in detail in the supplementary material (Table S4).

In contrast to the molecular water adsorption energies, the dissociative adsorption energies on the NGM clusters differ from those on the global minima. The dissociative adsorption energies over the NGM isomers are considerably more exothermic; while only one water molecule with dissociative adsorption energy below -1.20 eV was found on the GM clusters, a total of 12 such cases were discovered on the NGM clusters, ranging from -1.83 eV to -1.25 eV. For instance, the most exothermic adsorption energy for dissociated water on GM Pt_{13} is -1.04 eV, while the corresponding figure on the NGM cluster is -1.54 eV (water label 7). To investigate this difference, the OH group of dissociated water label 7 on the NGM Pt_{13} cluster was moved to a Zr top site on a faraway corner of the cluster. As a consequence, the OH + H adsorption energy changed from -1.54 eV to -0.74 eV. This suggests that the stronger dissociative adsorption on NGM sites cannot be attributed (at least solely) to differences in H adsorption sites between the clusters, as similar OH + H adsorption energies were obtained for the global minima when the OH group was placed at the same corner (see Sec. III D).

The stronger OH + H binding on the NGM clusters seems to be related to the deformation of the clusters upon adsorption. Both molecular and dissociated water deform the NGM clusters more than the GM clusters, with the mean metal atom displacement for NGM clusters being roughly 50% higher averaged over all cases. This is evidence of the NGM clusters' higher fluxionality, which stands to reason considering their lower stability compared to the GM clusters. Since the less stable clusters are capable of relaxing to more favorable geometries upon adsorption, the OH + H binding is more exothermic on the NGM clusters than the GM clusters. This effect is not observed for H_2O binding because molecular adsorption causes considerably less cluster deformation than dissociative adsorption. We note that the clusters usually maintain their shapes fairly well even upon dissociative adsorption, however, and significant deformations only occur in a few cases.

Because of the stronger adsorption of dissociated water, the reaction energies for water dissociation on the NGM clusters are more exothermic than those on the global minima. In agreement with the results observed for the GM clusters, the reaction energies are more exothermic for Rh than Pt interfaces. A similar trend

FIG. 4. (a) H₂O adsorption geometries and (b) molecular and dissociative adsorption energies on near-global minimum Rh₁₃, Rh₁₉, Pt₁₃, and Pt₁₉ clusters. Oxygen atoms which are not part of the support are colored red, while hydrogen atoms are colored light blue. For the rest of the atom colors, please refer to Fig. 1. H₂O molecules are labeled clockwise starting from the H₂O indicated in each case with a red circle (labeled “1”). The H₂O adsorption energies are indicated with gray bars, while OH + H adsorption energies are indicated with blue bars.

has been observed earlier for Rh and Pt surfaces and nanoparticles, though in that investigation the difference became insignificant for small (M_{55}) nanoparticles.² Here, the average ΔE is roughly -0.5 eV for both NGM Rh clusters and 0.0 eV for both NGM Pt clusters. The variation in reaction energy is dominated by the variation in dissociative water adsorption energy, as the molecular adsorption energies are rather similar to one another by comparison. The linear scaling behavior between molecular and dissociated water adsorption energy remains similar to the GM case, with no notable correlation.

D. Hydrogen adsorption at various cluster sites

In order to estimate the significance of the H adsorption site to the water dissociation energy, we conducted a thorough screening of the available sites. This was carried out by computing the adsorption energy of dissociated water for various H adsorption sites with the OH group on a Zr top site at a faraway corner of the computational cell. The OH site was chosen to minimize the effect of cluster-OH and H-OH interaction and to eliminate the adsorption energy variation caused by changes in the OH adsorption site. These OH + H adsorption energies are used as a measure of the H binding strength. The optimized locations of the H atoms, color-coded according to the corresponding adsorption energies, are presented in Fig. 5(a). Each OH + H adsorption energy was calculated separately, but all H locations have been collected into the same figure for brevity. This is reasonable because the deformation of the cluster in response to H adsorption was fairly modest: the highest individual metal atom displacement observed was 0.62 Å, while the average displacement was on the order of 0.1 Å.

The OH + H adsorption energies exhibit considerable variation with differing H adsorption sites. For instance, on the Rh₁₃ cluster, the adsorption energy ranges from -0.99 to -0.17 eV depending on the site. Notably, we find no obvious connection between the geometry of the H adsorption site and the adsorption energy on any of the clusters; both top and bridge sites can bind H strongly or weakly, depending on the specific position of the site. This is at least partially explained by the irregularity of the cluster geometries, which results in each adsorption site on the clusters having a unique chemical environment. Only few H atoms relaxed to hollow sites, though, and the binding is fairly weak in these cases. A preference for top and bridge sites has also been reported for both gas-phase and γ -Al₂O₃-supported Pt₁₃ clusters with varying H coverages.^{20,47}

Since the coordination number or location of the hydrogen atom on the cluster does not seem to explain the variation in adsorption energy, we turned our attention to more sophisticated descriptors. In earlier studies, the generalized coordination number (GCN) has been successfully used to explain differences in adsorbate binding between different adsorption sites on nanoparticles.^{2,44} Due to the irregularity of the cluster geometries, we also incorporated the strain adjustment proposed in Ref. 29, resulting in the SGCN descriptor. The OH + H adsorption energies have been plotted against the SGCN values of the H adsorption sites in Fig. 5(b), from which it is evident that these quantities show no correlation with each other. Thus, the SGCN is unable to explain the adsorption behavior of hydrogen on these supported clusters.

Alternatively, the chemical environment can be characterized by the smooth overlap of atomic position (SOAP) descriptor, which we utilized as implemented in the DDescribe 0.2.8 package.^{30,48} SOAP

FIG. 5. (a) Adsorption geometries of all hydrogen atoms on supported global minimum Rh₁₃ (upper-left), Rh₁₉ (upper-right), Pt₁₃ (lower-left), and Pt₁₉ (lower-right) clusters, and (b) plots of OH + H adsorption energies vs SGCN. The colors of the metal atoms correspond to their SGCN values (gradients shown in the figure), while the color gradient of the H atoms corresponds to the adsorption energy of OH + H with OH far away and H at the pictured site (white: −0.01 eV and black: −0.97 eV).

vectors were computed for each H adsorption site on the M₁₃ clusters, with the parameters $n_{\max} = 12$, $l_{\max} = 9$, and $r_{\text{cut}} = 12$ Å. For each cluster, the most strongly hydrogen-adsorbing site was used as the reference to which other sites were compared by SOAP similarity analysis. The dot product and the Euclidean 2-norm were used as similarity metrics. These metrics find no correlation between the OH + H adsorption energy and SOAP similarity to the strongest-adsorbing site. Other SOAP parameter combinations were also explored, but they resulted in the same conclusion. However, we cannot rule out the possibility that, e.g., machine learning could allow SOAP to explain the adsorption behavior.

Further analyses were carried out using the Pt₁₃ cluster as a test case. Explanations for the H adsorption behavior were sought from the Bader charges⁴⁹ and projected d-band centers^{50,51} of the cluster metal atoms, the electrostatic potential surrounding the cluster,⁵² and the Fukui functions of the cluster.⁵³ These methods describe the electronic structure and response of the cluster, thus complementing the geometric descriptors discussed above; the d-band model is a simple approach to rationalize covalent bonding in terms of a Newns–Anderson Hamiltonian, the electrostatic potential map is a measure of Lewis acidity, while Fukui functions characterize the electron donor/acceptor properties. The analyses provided no clear relationship between the H adsorption site and binding strength, indicating that the electronic as well as geometric structures of the supported clusters are quite complicated. Finally, we note a connection between the geometric and electronic descriptors: the SGCN and projected d-band center exhibit a moderate correlation ($R^2 = 0.65$ for Pt₁₃ and 0.45 for Rh₁₃).

IV. DISCUSSION

The elucidation of catalytic activities under the computational framework, while mimicking the experimental conditions, requires

a careful analysis of the nature of catalytic active sites. The formation and understanding of these active sites at the interfaces of supported metal catalysts is complex to pursue due to the irregular shapes of the clusters. Deposition of asymmetric clusters over a catalyst support results in different coordinations of metal atoms throughout the cluster perimeter. Herein, the adsorption analyses at the perimeter of zirconia-supported Pt and Rh clusters report similar challenges. Every interfacial adsorption site over each cluster is found to be unique, and the differences in adsorption energies are notable. The molecular water preferably adsorbs on Zr top sites near the cluster, avoiding adsorption over high-coordinated zirconia atoms. Deformation of the clusters upon molecular adsorption is small, whereas with dissociated water, the clusters show comparatively larger changes in geometry. Overall, the binding of H₂O and OH + H is highly dependent on the adsorption sites over our clusters, making it difficult to predict the pattern.

In this work, all screening was done by manually constructing plausible initial guesses for geometry optimizations. This approach is good when the system is simple and only a moderate number of structures are required for screening. Manual screening in complicated systems, such as these clusters, is somewhat arduous and may cause a sampling bias: catalytically significant structures can be missed if the human building the initial structure does not realize their importance. This is highlighted especially when the behavior of the system at hand is difficult to predict. In the case of the H screening discussed in Sec. III D, for instance, a more complete description of hydrogen adsorption on the clusters could be obtained by conducting a thorough, automated scan of the adsorption energy as a function of H position.⁵⁴ Such an approach would avoid human sampling bias and also provide a larger quantity of data without an extensive manual setup. Of course, such a comprehensive scan would also require using more computational resources or lowering the level of theory.

Linear regressions using physics-based descriptors were found unable to rationalize the observed variations in adsorption, reaction, and transition state energies. In addition to linear regression, the data could be analyzed using more refined regression models which are rapidly gaining traction⁵⁵ as means to describe chemical systems. For instance, the physics-based descriptors used herein could be taken as input parameters (features) used for training a supervised regression or neural network algorithm. Such an approach can possibly describe the data as a nonlinear function of several physically meaningful features.⁵⁵ Alternatively, the data could be analyzed using automatized and more abstract featurization approaches such as SOAP used in this work. While abstract features may alleviate manual labor, they may also provide a qualitative understanding of the important features or descriptors. Whether physics-based or more abstract featurization is used, large data sets are needed to obtain a reliable machine learning model—obtaining this data from DFT may well become the bottleneck for the machine learning approaches.

Water adsorption strength over clean metal surfaces is often reported to be weak compared to that on pure zirconia;^{1,2,6,7,37} therefore, the support is needed for overall catalytic activity. According to previous works, zirconia alone cannot catalyze the WGS reaction.^{6,16} As the water activation behavior of Rh(111) and Pt(111) are quite similar,² the Pt(111) surface could be expected to perform similarly toward WGS. Therefore, even though the interfacial sites make up a minority of the whole system, they can play a key role in the catalytic activity. In line with previous results, molecular water binds at the present interface sites with moderate strengths and displays lower dissociation barriers than on the pure metal surfaces.^{1,2,6} Our present study shows that water dissociation can take place across the interface, thereby supplying hydrogen to the metal cluster for further reaction with CO in the WGS process.

The presence of NGM isomers highlights the importance of considering the ensemble of structures instead of focusing only on the GM isomer.¹⁹ Our study shows that molecular water adsorption is rather similar between GM and NGM structures, but a considerable difference is observed for OH + H adsorption, which may be partially attributed to the cluster deformations. Consequently, the results based on NGM isomers raise numerous questions: (i) at elevated temperatures, what is the extent of fluxionality during the reaction? (ii) how does cluster fluxionality affect the reaction mechanism and minimum energy pathways? (iii) how and to what extent do surface species modify the cluster geometry? Note that we exclude kinetics over NGM clusters, and the present comments are based on thermodynamic analysis. Moreover, only low-coverage cases were considered; higher adsorbate coverages may introduce larger structural deformations than those observed here, in particular, if the adsorbates are included in the global optimization.

Finally, the breaking of energy scaling relationships is an inherent way to overtake the maximum catalytic activities proposed based on volcano plots.⁵⁶ In our study, the linear scaling relationships between adsorption energies of H₂O and OH + H over all GM and NGM clusters show, at best, poor correlations. As meaningful BEP and TS scaling relationships were also not observed, we are unable to predict activation energies based on adsorption or reaction energies over these clusters. This is perhaps unsurprising given that scaling relations assume that the initial structures as well as the transition state and final structures are relatively similar across the studied

sites. Our results demonstrate that simple scaling relationships do not hold for these zirconia-supported Rh and Pt clusters and, consequently, interfacial sites may display unexpected catalytic behavior. This calls for systematic computational and experimental studies on atomically well-defined clusters in order to better understand these systems and formulate new concepts for the prediction of catalytic properties.

V. CONCLUSIONS

We have investigated the dissociation of water over globally optimized Rh and Pt clusters on *m*-ZrO₂(111). It was observed that the adsorption and reaction properties of the system are complex and cannot be easily predicted from simple geometric or electronic structure measures of the cluster or from scaling relations. Three main factors likely contribute to this complexity: (i) the irregular morphology of the clusters, (ii) the small size of the clusters, and (iii) the low symmetry of the support. Together these factors result in very intricate properties for the clusters and cause every adsorption site to be unique.

As the properties of a cluster are highly dependent on its exact geometry, and there exist multiple cluster isomers that are close in energy to the GM structures, focusing only on the most stable geometry provides a limited view of a catalytic system. Indeed, we found that NGM clusters can bind dissociated water more strongly than the GM clusters. This effect could stabilize cluster geometries that are less favorable on the bare surface, further increasing the number of thermodynamically feasible structures in the H₂O/M/ZrO₂ system.

The aspects mentioned above indicate that there is potential for rich catalytic chemistry on small, fluxional clusters. Our results reinforce the necessity of using an ensemble model comprising a variety of cluster geometries to gain a complete picture of the catalytic process.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for the complete water adsorption and dissociation data, including adsorption and reaction energies, activation energies, TS bond lengths, imaginary frequencies, and scaling relationship plots.

ACKNOWLEDGMENTS

The work was funded by the Academy of Finland, Project Nos. 307853 and 317739, and the University of Jyväskylä. The electronic structure calculations were made possible by the computational resources provided by the CSC—IT Center for Science, Espoo, Finland (<https://www.csc.fi/en/>). V.K. thanks Mr. Lauri Himanen from Aalto University for fruitful discussions on SOAP.

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