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<https://escholarship.org/uc/item/9r3096k4>

Journal

The journal of physical chemistry letters, 11(8)

ISSN

1948-7185

Authors

Guo, Han
Sautet, Philippe
Alexandrova, Anastassia N

Publication Date

2020-04-01

DOI

10.1021/acs.jpclett.0c00548

Peer reviewed

Reagent Triggers Isomerization of Fluxional Cluster Catalyst via Dynamic Coupling

Han Guo^[a], Philippe Sautet^{[a,b,c]}, and Anastassia N. Alexandrova^{*[a,c]}*

[a] Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, CA 90095-1569 (USA)

[b] Department of Chemical and Biomolecular Engineering, University of California, Los Angeles, Los Angeles, CA 90095-1569 (USA)

[c] California NanoSystems Institute, Los Angeles, CA 90095 (USA)

AUTHOR INFORMATION

Corresponding Authors

Anastassia N. Alexandrova – Email address: ana@chem.ucla.edu

Philippe Sautet – Email address: sautet@ucla.edu

ABSTRACT Metallic cluster catalysts have many thermodynamically-accessible isomers with diverse active sites and low reaction barriers, and lately a strong hypothesis emerged that the many catalysts states collectively drive the catalysis. However, it remained a hypothesis that catalyst isomerization is actually kinetically feasible in reaction conditions. Using high-temperature dynamics simulations and sampling a range of orientations and vibrational energy distributions, we probe how thermal effects and molecular events affect cluster catalyst dynamics. We show that even such a delicate affair as a dissociation or scattering of a methane molecule on the heavy and thus slow Pt_{13} cluster triggers substantial isomerization of the catalyst, far beyond thermal at 700 K. A kinetic coupling between the methane activity and cluster catalyst dynamics is observed. In return, the thermal dynamics of the cluster affects the methane reaction and scattering probabilities. Hence, molecular events at the surfaces of fluxional cluster catalysts should facilitate population of an ensemble of the catalyst states in reaction conditions, with implications for available active sites, reaction mechanisms, and apparent rates.

TOC GRAPHICS

Sub-nano transition metal clusters exhibit remarkable and tunable catalytic activities. However, recently, their incredible complexity began to transpire, specifically because they have many structural isomers that appear to be thermodynamically-accessible under realistic conditions of catalysis: high temperatures (500-700 K) and pressures of gasses.¹⁻⁷ While it is unclear whether or not all or most of those isomers can actually be kinetically reached in the time-scales that would make them important for the reaction mechanism, this assumption was bravely made. On the basis of this assumption, a theory was constructed that a cluster catalyst may be better viewed not as a single structure (the global minimum), but as a statistical ensemble of many (all thermodynamically-accessible) states, giving rise to multiple accessible reaction pathways operating concurrently.^{8,9} In some cases, metastable catalyst structures and/or stoichiometries were predicted to be more catalytically active than the global minimum, and even dominate the catalytic functionality.^{2,3,7,9,10} In several cases, this theory was in fact essential to explain the experiment,^{2,4,9,10} and that strengthened the underlying thermodynamics-based hypothesis. For example, theory and experiment suggested that ethylene dehydrogenation on alumina-supported size-selected Pt₇ clusters is catalyzed by the group of metastable, flatter Pt₇ isomers, which becomes more prevalent upon increasing ethylene coverage.⁴ However, most of the mechanistic studies of catalytic processes on cluster do not involve catalyst isomerization as part of the reaction coordinate, and the dynamics of catalyst isomerization is also not probed. It is therefore still not proven whether it is the full ensemble of the thermodynamically-accessible catalyst states, a small subset in this ensemble, or just a few or even one catalyst structure should be involved in the mechanism, and whether the answer to this question is general or system-specific.

The key open question in this complex picture of cluster catalysis is the relative timescales of the reaction and of the catalyst isomerization. It is unknown whether or not full or partial

thermodynamic equilibration of the cluster catalyst can occur on the timescale of the reaction. It is also unclear if the reaction can dynamically couple to the catalyst isomerization, or even happen concurrently with it. On high-index transition metal surfaces, the motion of metal atoms is too slow on reaction timescales to couple to the reaction dynamically.¹¹ However, metal clusters are more flexible. Some cluster isomerizations were found to have low barriers, which can get even lower in the presence of adsorbed small molecules.^{3,5,12–16} Hence, more intense dynamics is to be expected for these catalysts.

We report a direct dynamic study to probe the isomerization of clusters induced by small molecule adsorption/reaction, occurring concurrently with the native, thermal cluster fluxionality, and facilitating it. We focus on alkane dehydrogenation and our model system consists of CH₄ reacting on a gas phase Pt₁₃ cluster. Methane C-H dissociation is also the rate-limiting step in the steam reforming reaction.¹⁷ We probe the extent and timescale of the dynamic coupling between cluster catalyst isomerization and the reaction or scattering of the reactant. We distinguish between the adsorption/reaction-induced and the intrinsic thermal cluster fluxionality. The dynamic coupling could be different from what is seen from the reaction potential energy surface (PES). The coupling would be weak, if the adsorption/reaction-induced fluxionality is small, though the cluster could isomerize in the course of the reaction at high temperature. Hence, this study employs *ab initio* molecular dynamics (AIMD), in the NVE ensemble, combined with the quasi-classical trajectory (QCT) method, in which the vibrational zero-point energy (ZPE), or ZPE+ $h\nu$ is initially imparted to the molecule.^{18–21} All electronic structure calculations are performed using the DFT-based Vienna *ab initio* simulation package (VASP).^{22–26} Additional details can be found in the supporting information (SI). The initial velocities and geometries of the cluster and methane are generated by a homemade code written in Python language. Note that the purpose of this study is

not to reproduce any catalytical experimental result, but to have some insights in the coupling between cluster fluxionality and molecular reaction/adsorption. Thus, to reduce computational cost, we performed simulations in the gas phase, without the sampling of possible coverage with other adsorbates, and considered only one methane molecule hitting the cluster on only one impact site.

We first located the minimum energy path (MEP) for methane dissociation on the site characterized by the lowest TS-energy on the global minimum of Pt_{13} (Figure 1).^{3,7} Unlike reactions on Pt surfaces, where the minimum in the entrance channel corresponds a physisorbed state²⁷, on Pt_{13} methane is activated at this minimum with one C-H bond elongated by 0.06 Å. CH_4 is weakly bound to Pt_{13} (adsorption energy 0.21 eV) with a C-Pt distance of 2.5 Å, only 0.4 Å longer than that for adsorbed CH_3 . The onset of attraction between CH_4 and Pt_{13} occurs rather late, with 0.1 eV stabilization only at a Pt- CH_4 distance of 3.7 Å. Given this shallow adsorption well, the associated structural changes in Pt_{13} are minor in the entrance channel. Only the impact Pt atom recoils to the cluster by a small distance when CH_4 approaches.

The C-H dissociation barrier is 0.136 eV (0.062 eV after zero-point energy (ZPE) correction), relative to the methane activated state, which is much lower than that on Pt surfaces, which is 0.833 eV on Pt(111)²⁷ and 0.522 to 0.688 eV on Pt(211)²⁸, relative to the physisorption well (results obtained with the PBE functional, without ZPE correction). After dissociation, the H atom moves to the neighboring bridge site on the cluster. The cluster structural changes during and after methane dissociation are also small on the MEP (Figure 1).

Figure 1. Potential energy and structures along the MEP for CH_4 dissociation on Pt_{13} . The distance along the reaction coordinate, s , is defined as the geometry difference between two structures defined by $(ds)^2 = \sum_{n=1}^{18} \sum_{i=1}^3 (dx_{ni})^2$, where x_{ni} is the i^{th} Cartesian coordinate of atom n , and the reaction coordinate is set to zero at the TS.

However, the MEP may not represent the large number of reaction paths starting from an ensemble of states of the Pt_{13} cluster, and the distribution of vibrational states, orientations, and velocities of CH_4 . The changes in Pt atom velocities upon molecular impact may also induce cluster rearrangement. AIMD was used to simulate CH_4 impinging on Pt_{13} , on the impact site shown in Figure 1, at cluster temperatures of 400 and 700 K. To model the effect of cluster temperature, different velocities and displacements from the global minimum have been assigned to Pt atoms through an appropriate sampling. More details can be found in the supporting information (SI). CH_4 is initially placed at 4.5 Å from the impact Pt atom, where the interaction between them is weak, with an incident energy of 0.19 eV, well above the dissociation barrier in order to minimize quantum effects such as tunneling²⁹. Note that the lowest excited triplet electronic state of Pt_{13} is at 0.36 eV, and thus, the collisions with methane should not cause non-adiabatic transitions to this triplet state. However, there are other spin states that may be accessible

through spin-orbit coupling (the vertical excitation energies, and adiabatic energy differences are shown Table S1 in the SI). While the spin can change in BOMD, judging by the spin states of the products, most of the time the trajectories remain on the triplet electronic state. Thus, not including spin-orbit coupling should not change the overall qualitative picture. The initial vibrational states of CH₄ sample a Boltzmann distribution,^{19,20} and the molecular orientation is randomly sampled. 128 production trajectories are propagated with a time step of 0.5 fs for 1 ps at each temperature. At the end of the simulations, we observed three outcomes: reaction, trapping and scattering.

CH₄ is considered to have arrived at the impact site when the distance between the C and Pt atoms first reaches 3.0 Å. With the CH₄ initial velocity of 0.015 Å/fs, this process takes ca. 100 fs (Figure 2). Although the mass of Pt is relatively large, the calculated Root-Mean-Square Displacement (RMSD) between the cluster structure at time t and its initial structure ($t=0$) shows that cluster fluxionality is appreciable during the first 100 fs. As CH₄ approaches Pt₁₃, the cluster deviates gradually from the initial structure, and the RMSD in Pt₁₃ reaches 0.15 - 0.2 Å when CH₄ arrives at the impact site (Figure S2).

In order to find out whether these structural changes are driven by the collision of CH₄ or exclusively by thermal effects, we performed 128 reference simulations at each temperature with CH₄ removed, the initial state of Pt₁₃ being identical. In Figure 2, we plot the structural divergence of one reaction trajectory with respect to its methane-free counterpart, defined as the RMSD between the two trajectories.

When methane approaches the impact site, the divergence averaged over all Pt atoms is less than 0.003 Å, two orders of magnitude smaller than the total structural change of the cluster during the same time. Similar behavior has been found for all three types of trajectories (Figure S3). Thus, when CH₄ approaches Pt₁₃, the motion of the cluster is driven by thermal effects.

Figure 2. Structural divergence between one reaction trajectory and its reference trajectory without CH_4 for the impact Pt atom (red line) and Pt_{13} (black line) at 400 K. The dissociating C-H bond length (green dashed line) and the Pt-C distance (blue dashed line) are also shown. The first vertical dashed line shows methane's arrival time (97.5 fs) and the second vertical dashed line is the reaction starting time (161 fs).

After the CH_4 arrival, the production trajectories start to diverge from their reference trajectories. We define the CH_4 dissociation threshold as the time when the C-H bond reaches 1.3 Å before dissociation. In most of the reaction trajectories, CH_4 dissociation starts within 150 fs after it arrives at the impact site, and takes only 50 fs on average to complete. During this short time, the cluster cannot adapt its configuration and relax to the MEP, even though the interaction between CH_4 and the cluster is relatively strong. In 6 out of 52 trajectories (Figure S5), CH_4 remains trapped in the energy well before dissociating, and Pt_{13} has the time to adjust its configuration, with the divergence increased to 0.10 Å before the dissociation starts, while one of the C-H bonds is activated with an increase in bond vibration amplitude.

For the scattering trajectories, CH_4 is considered to have left the cluster when the distance between the C and Pt atoms reaches 3.0 Å for the last time. Two thirds of the scattered molecules

leave the cluster immediately ($t_{\text{left}} - t_{\text{arrived}} < 200$ fs) after impinging (Figure 3b). The primary effect of CH₄ in these trajectories is the collision, adding a regular vibration along the molecular incident direction to the impact Pt atom, (Figure S4c). In the remaining trapped-then-desorb trajectories, CH₄ impinging creates a vibration along the incident direction and the CH₄-cluster interaction changes the motion of the impact Pt atom in an irregular way, which will further affect other Pt atoms.

Figure 3. Structural divergences between reaction trajectories and their corresponding reference trajectories without CH₄. Results are shown for (a) CH₄ arrival time (red points) and reaction starting time (blue points) for reaction trajectories at 400 K and (b) CH₄ arrival time (red points) and leaving time (blue points) for scattering trajectories at 400 K. (c, d) RMSD averaged over each type of trajectories relative to the equilibrium structure (global minimum) at 400 K and 700 K. The results include only immediately dissociated and scattered cases.

Although CH₄-induced cluster fluxionality is minor during CH₄ dissociating or scattering, there is a significant delayed response, whereby the impact of CH₄ can promote the isomerization of Pt₁₃. Figure 3c,d shows the type-averaged RMSD from different trajectories relative to the initial

state of Pt_{13} . Assisted by CH_4 , the average RMSDs of all types of production trajectories increase much faster after the collision, compared to the reference trajectories (except the scattering cases at 700 K, in which both thermally and CH_4 -induced isomerizations were pronounced), suggesting facilitated cluster structural change. One reason for that is the energy transfer from methane to clusters as shown in the top-right corner figure in Figure 4. The reactive trajectories have the largest increases in RMSD, due to the energy released from methane dissociation transferring into the cluster and the adsorption of the dissociating H and CH_3 . Hence, cluster isomers with different structures, energies, and barriers to interconversion can be reached more easily in these trajectories.

In order to probe Pt_{13} isomerization, we extracted the structures at 500 fs after CH_4 dissociation or scattering, or at 1000 fs for trapping trajectories, removed CH_4 , and optimized the Pt_{13} geometries to the nearest minima using the conjugate gradient method. For comparison, we also optimized the structures taken from the same time points in the reference trajectories. All these structures in the exit channel are compared to the initial structures. At 400 K, none of the reference structures are relaxed to any other isomers, i.e. they always return to the global minimum and no spontaneous thermal isomerization is seen, within the limited time of AIMD. This does not mean that thermal isomerization is completely inaccessible, but it is significantly hindered, especially compared to the production trajectories. In 4 production trajectories, including 2 reaction trajectories and 2 scattering trajectories, the cluster transforms into two different isomers (Figure 4). The first one, obtained from a reaction trajectory, has the same geometry as the global minimum, but it is structurally inverted by crossing an isomerization barrier. The second isomer is 0.26 eV higher in energy, with minor structural changes compared to the global minimum.

This methane-induced isomerization is more pronounced at higher cluster temperature of 700 K (Figure 4). To aid the analysis, Figure 5 shows the RMSD(bonds) between the optimized initial structures and the optimized production (horizontal axis) or reference (vertical axis) structures at 700 K. RMSD(bonds) is computed on the basis of Pt-Pt bond lengths, to eliminate the contributions from the rotations and translations. In Figure 5, the points along the $x = y$ line represent thermal isomerization, while those along the $y = 0$ line are isomerization events induced by CH_4 collision and dissociation. The remaining points, except those at the origin, are rearrangements driven by a combination of both effects. In 24 of 128 production trajectories, the cluster rearranges to isomers different from the initial and reference structures, and can be grouped into 13 different isomers (Figure 4).

The reactive collisions are more efficient than non-reactive ones, with an interconversion rate of $27.3 \pm 6.7 \%$. As mentioned before, one reason for that is the collision energy and the energy released from methane dissociation being transferred to the cluster. The other reason is the adsorption of methyl group and H atom. In order to analyze the effect of the adsorbates, we optimized the structures extracted from the exit channel of the reaction trajectories, without removing CH_3 and H. After dissociation, CH_3 remains adsorbed at the impact site, except for very few cases (1 of 52 at 400 K and 3 of 44 at 700 K), while the H atom moves all around the cluster within the 1000 fs. The adsorption of CH_3 and H changes the cluster structure. For example, after the adsorption of CH_3 and H, the global minimum of Pt_{13} has structural changes of $0.027 - 0.157 \text{ \AA}$ in terms of RMSD(bonds) relative to the original structure. These changes are smaller than the RMSD(bonds) between different Pt_{13} isomers ($0.063 - 0.337 \text{ \AA}$). More importantly, adsorbates can change the relative energies of different cluster isomers. As shown in Figure S8, some higher-energy Pt_{13} isomers, after CH_3 and H adsorption, have lower energies than other lower-energy Pt_{13}

isomers. Note that, our sampling of Pt_{13} with adsorbates is far from complete. Global optimization needs to be done for further investigating the thermodynamic effect of adsorbates, which is beyond the scope of this study.

Figure 4. Optimized Pt_{13} geometries in the exit channel of the production trajectories, which are different from the optimized initial structures and the optimized reference structures. The impact Pt atoms are shown in blue. The numbers in the first row under each isomer represent the energies, where the number in bold is the electronic energy and the number in italic font is the free energy, both relative to the global minimum. The number in the second row shows the spin multiplicity of each isomer. The numbers in parentheses are the number of isomerized structures in each type, (#reaction, #trapping, #scattering). The figure on the top-right corner shows the distribution of energy transfer from CH_4 to Pt_{13} for scattering trajectories at 700 K.

AIMD reached some but not all of the known isomers of Pt_{13} ^{3,7} within the energy range of 0.23 eV from the global minimum. This could be because of the insufficient sampling, and/or the kinetic inaccessibility of some of the isomers. We conclude that cluster fluxionality driven by CH_4 is minor in the process of CH_4 approaching, immediately dissociating, or scattering from the cluster.

However, the energy transfer from collision and reaction of CH₄ can promote subsequent cluster rearrangement, leading to many different isomers, and providing new active sites for the catalyzed reaction.

Finally, cluster thermal fluxionality may influence the reaction probability for CH₄. Table 1 lists the percentage of trajectories of each type as a function of cluster temperature. The probability of non-reacted methane trapping increases at lower temperatures. Scattering, on the other hand, is greatly increased at 700 K compared to 400 K. It might seem surprising that the immediate dissociation probability at 400 K is ~10 % higher than that at 700 K.

Figure 5. RMSD(bonds) between the optimized initial structures and the optimized production (horizontal axis) or reference (vertical axis) structures at 700 K. The colors represent structural types.

An analysis of this result shows that the calculated reaction probability might be influenced by two conflicting factors. First, more cluster structures have large displacements from the equilibrium at 700 K (Figure S6). In some of these structures, the considered impact site, which has the lowest barrier to dissociation in the equilibrium structure, may no longer be a low-barrier site. This gives rise to more scattered molecules at 700 K. In trajectories with cluster RMSD larger

than 0.35 Å when CH₄ arrives, only 14.3 ± 7.6 % (3 out of 21) of the molecules dissociate, which is lower than the total reaction probability. This effect is impact site- and system- dependent. If metastable structures are more catalytically active, the reaction probability will be larger at higher temperature.

Table 1. Percentage with statistical error of trajectories in each type at 400 K and 700 K

Cluster temperature	400 K		700 K	
Reaction (immediately reacted)	$35.9 \pm 4.2 \%$	$40.6 \pm 4.3 \%$	$25.0 \pm 3.8 \%$	$34.4 \pm 4.2 \%$
Reaction (trapped first)	$4.7 \pm 1.9 \%$		$9.4 \pm 2.6 \%$	
Trapping	$25.0 \pm 3.8 \%$		$4.7 \pm 1.9 \%$	
Scattering (immediately scattered)	$20.3 \pm 3.6 \%$	$34.4 \pm 4.2 \%$	$50.8 \pm 4.4 \%$	$60.9 \pm 4.3 \%$
Scattering (trapped first)	$14.1 \pm 3.1 \%$		$10.2 \pm 2.7 \%$	

On the other hand, although the trapping probability is larger at a lower cluster temperature, the reaction probability for the trapped molecules is larger at a higher temperature. One reason for that is the increased energy transfer from the hotter cluster to the adsorbed CH₄. Thus, due to the shallow adsorption well and low barrier, the temperature-dependent behavior of the system is less predictable, and an accurate estimation of the reaction probability should average over all accessible catalyst structures.

Finally, we note that the model chosen in this study is very simple. The cluster is in only one global minimum form before methane arrival, not covered with adsorbates of varying nature and number, and not supported. Methane arrives only at just one site, and one molecule at a time. In addition, non-adiabatic transitions that may occur during the trajectories are not treated with precision, and DFT lacks static electron correlation that would be required to describe the PES regions on non-adiabatic coupling. These deficiencies would affect the rates of transitions. Nevertheless, the key qualitative results are informative for the field of catalysis.

We find that a rich ensemble of Pt cluster structures is reached upon methane attack on the global minimum of Pt₁₃. Slower Pt cluster dynamics makes the majority of the cluster response to be not concurrent with the methane collision or dissociation, but following it with a delay. It has been largely unknown whether or not the ensemble of low-energy cluster catalyst states can actually be reached in catalytic conditions. Our results suggest that reactive and non-reactive collisions with molecules facilitate isomerization of the catalyst, and lead to population of many new cluster isomers, which then begin presenting new active sites for the reaction. Given that some of those metastable cluster states have lower reaction barriers for methane dissociation,⁷ the catalyst isomerization has important consequences for the apparent mechanism and rate of the catalyzed reaction. In return, cluster temperature also affects the reaction probability for methane. Hotter clusters promote methane scattering and reduce the probability of trapping, and the reaction probability is balanced by two factors: more energy is transferred from cluster to methane, and more of the less reactive isomers are accessible for hotter clusters.

AUTHOR INFORMATION

Notes

Any additional relevant notes should be placed here.

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work was supported by DOE-BES Award DE-SC0019152, and used resources of the National Energy Research Scientific Computing Center (NERSC), a U.S. Department of Energy (DOE) Office of Science User Facility operated under Contract No. DE-AC02-05CH11231, and the Argonne Leadership Computing Facility (ALCF) Facility, a DOE Office of Science User Facility supported under Contract DE-AC02-06CH11357, provided by the Innovative and Novel Computational Impact on Theory and Experiment (INCITE) program.

Supporting Information Available:

Computational methods and additional computational results (supporting figures)

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