CO Oxidation By Pt Single Atoms and Pt_nO_x Clusters on Ceria

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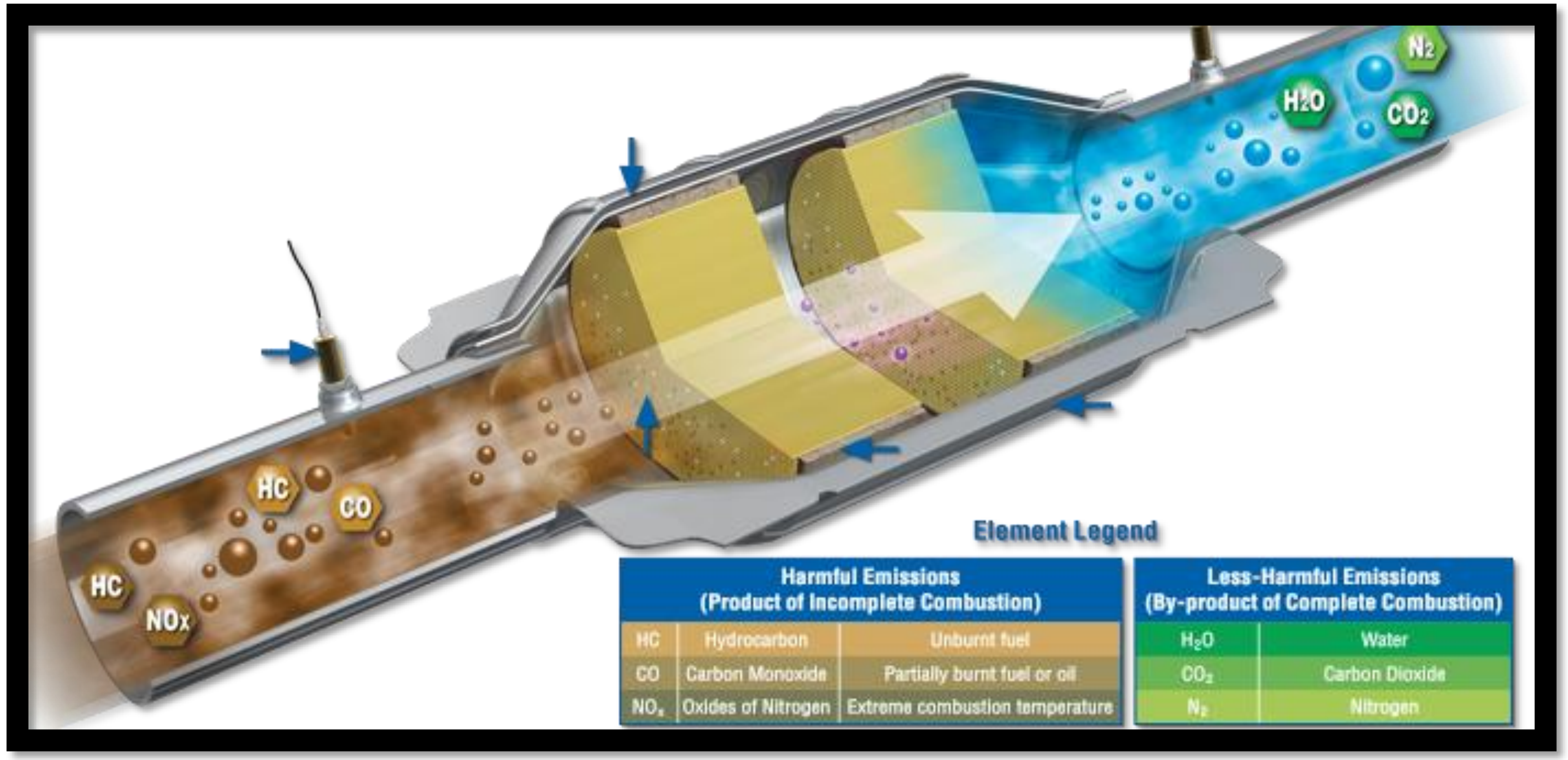
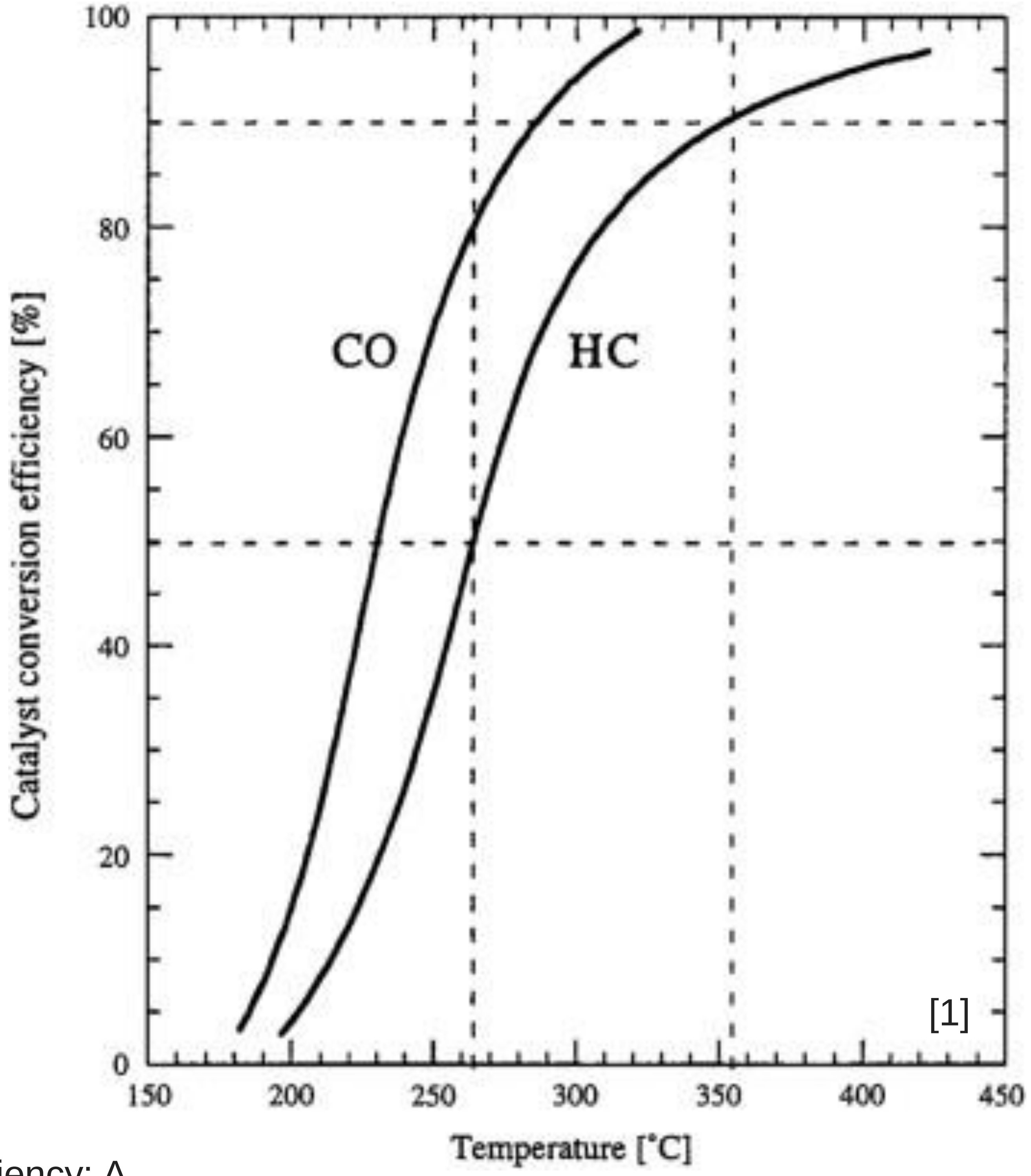
Low-temperature CO oxidation on PGM/CeO_x

Platinum group metals (PGM) dispersed on ceria supports need to be more active in eliminating CO emissions below 150 °C during engine cold start.

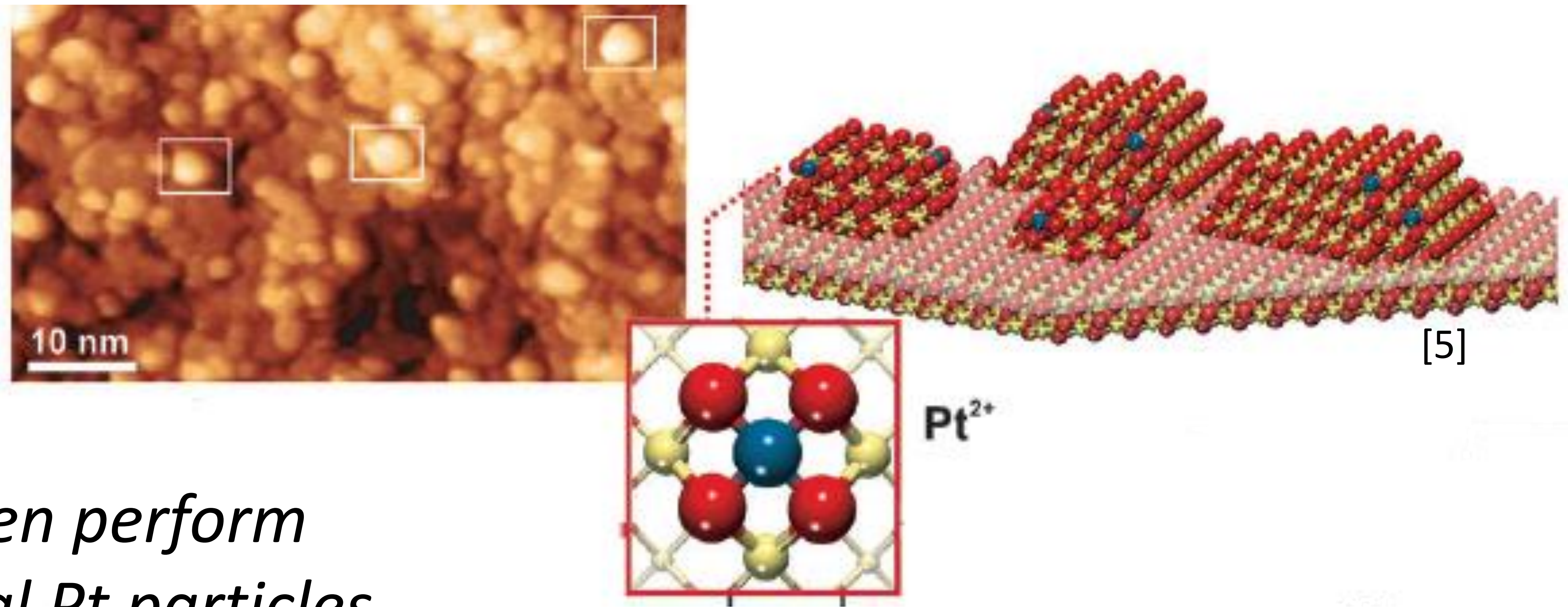




[1]. Roberts, Andrew, Richard Brooks, and Philip Shipway. "Internal combustion engine cold-start efficiency: A review of the problem, causes and potential solutions." *Energy Conversion and Management* 82 (2014): 327-350.

Pt_1 single-atoms supported on oxides is of interest for low-temperature CO oxidation

Pt_1 catalysts using CeO_2,[1-2] Al_2O_3,[3] and KLTL zeolite[4] supports were probed for CO oxidation.



Unfortunately, such Pt_1 catalysts often perform similar to or worse than conventional Pt particles.

<u>At 150 °C</u>

Pt_1/CeO_2: TOF ($\times 10^2\ s^{-1}$) of 0.05–9.2

Pt particle/CeO_2: TOF ($\times 10^2\ s^{-1}$) of 0.4–35

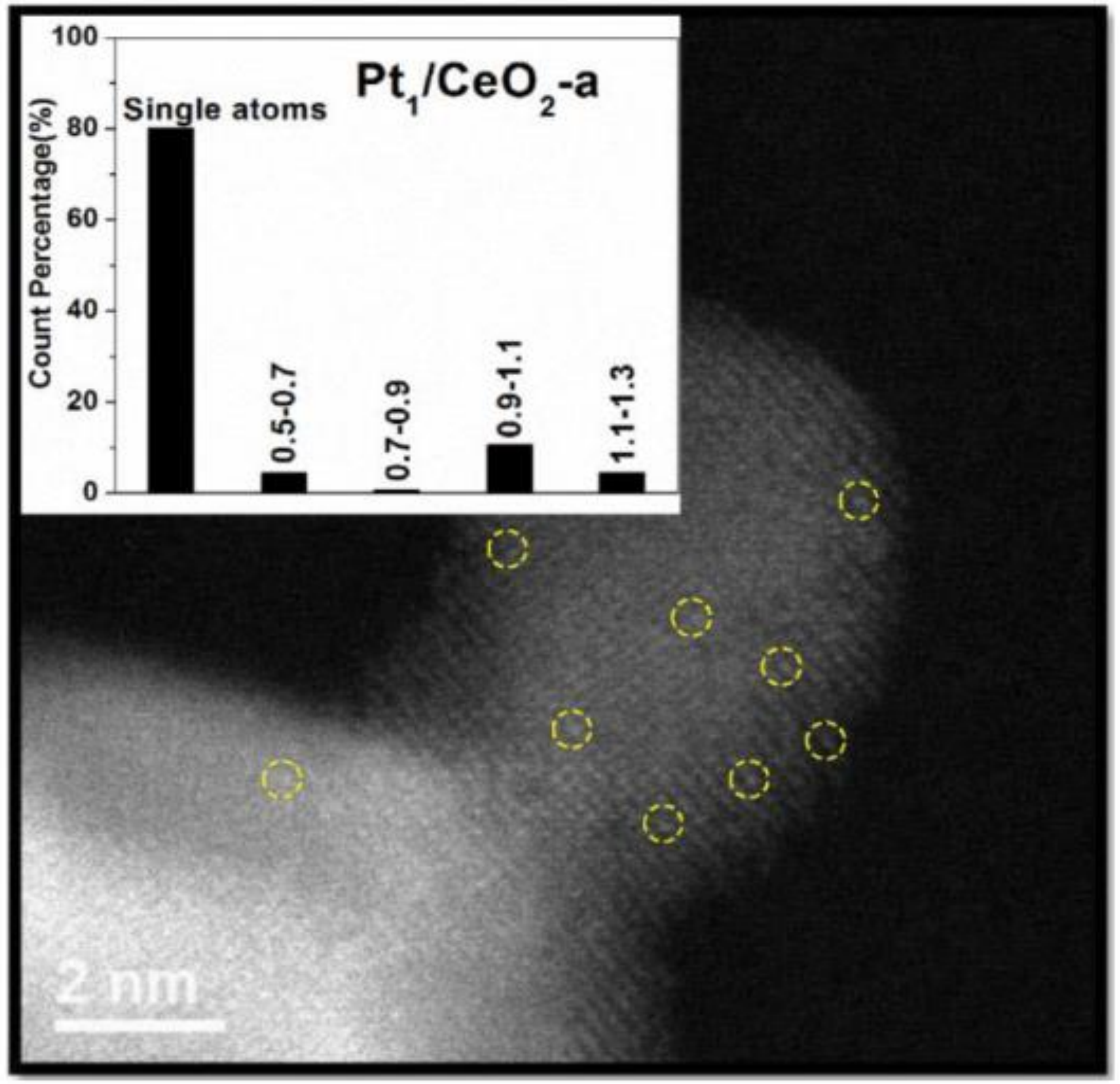
The question arises whether a multi-atom catalytic site (ensemble of M-O_x species) will increase the catalytic performance under oxygen rich conditions

[1]. J. Jones, H. Xiong *et al. Science* 353 (2016); [2]. L. Nie, D. Mei, *et al. Science* 358, (2017); [3]. Z. Zhang *et al. Nat. Commun.* 8 (2017);
[4]. J. D. Kistler *et al. Angew. Chem. Int. Ed.* 53 (2014); [5]. A. Bruix, Y. Lykhach *et al. Angew. Chem.* 53 (2014)

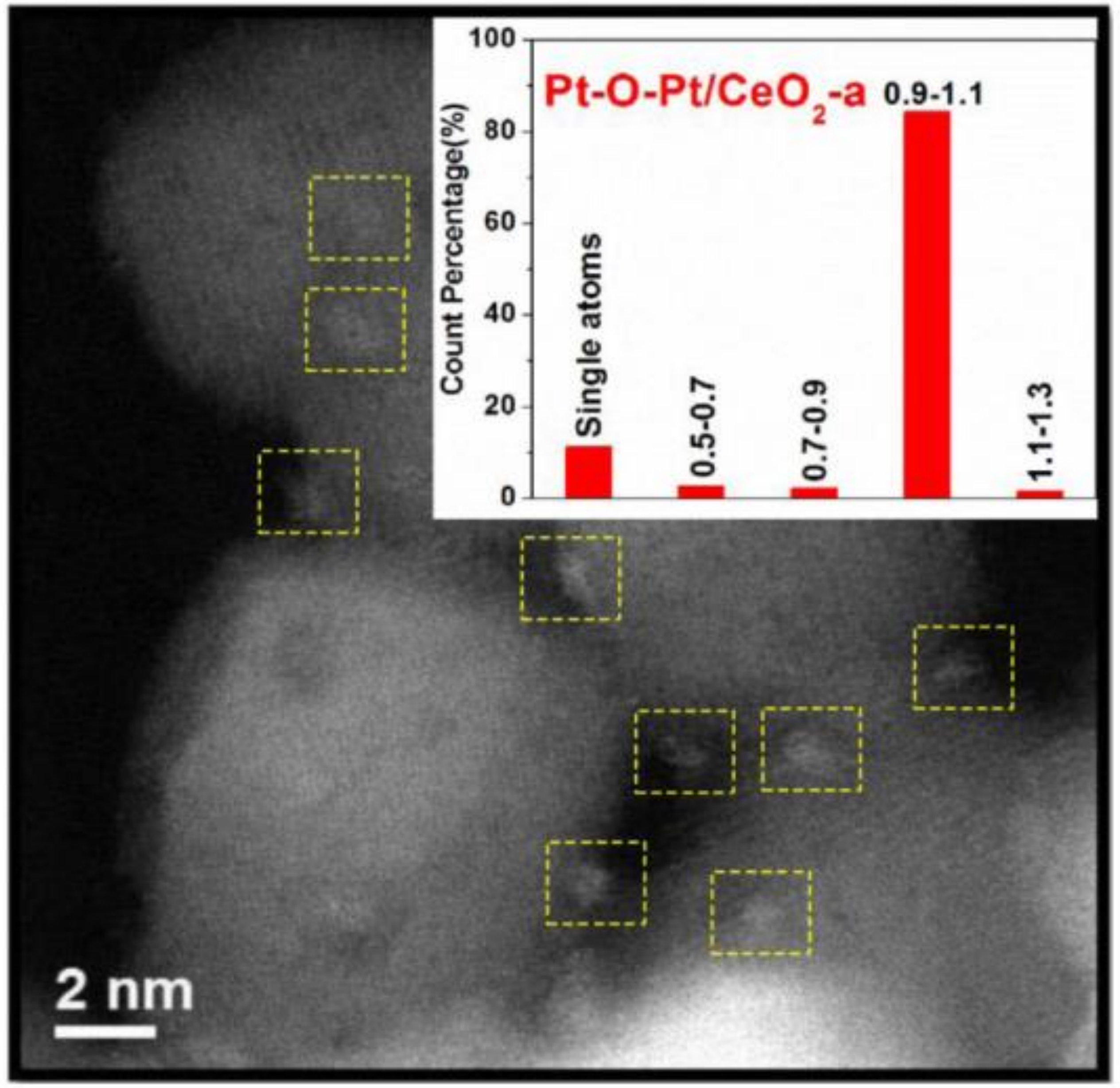
Experimental synthesis of Pt_1/CeO_2 and Pt-O-Pt/CeO_2

ceria support (10-30 nm particles)

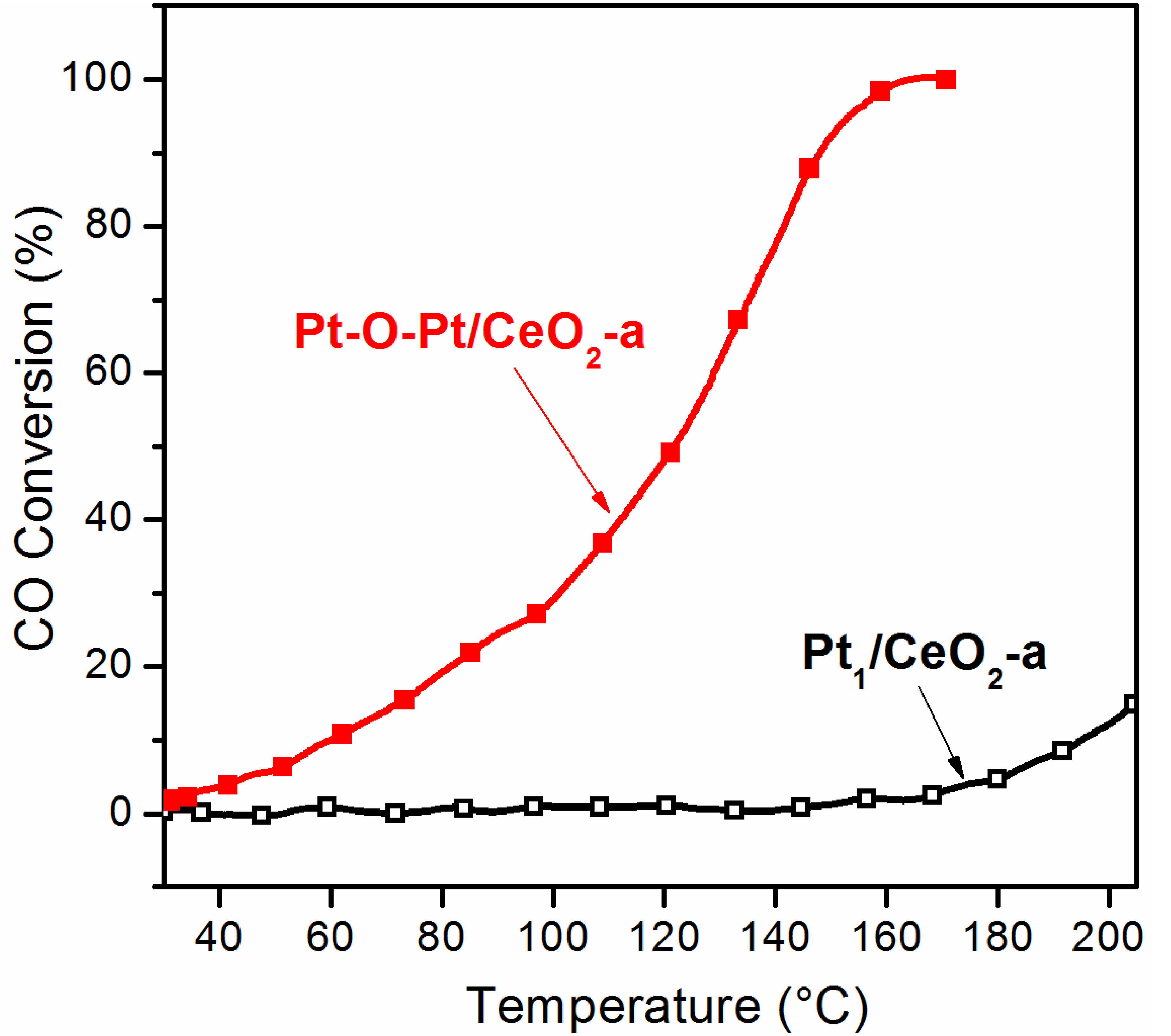
Pt_1 single-atom catalyst

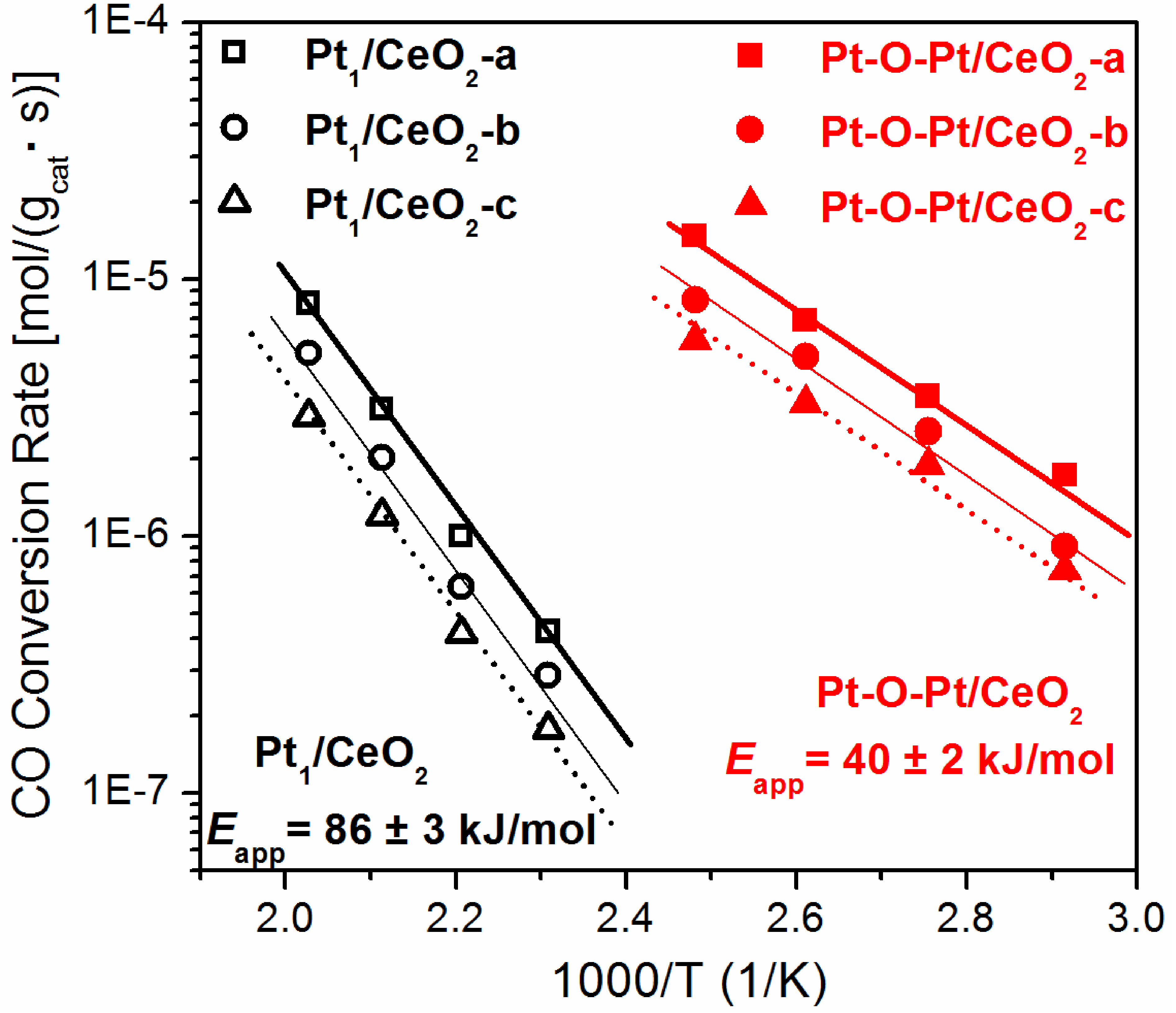


0.9 - 1.1 nm Pt-O-Pt catalyst



Our experiments show the 1 nm Pt-O-Pt/CeO_2 clusters are much more active than Pt_1/CeO_2 at low temperatures





CO oxidation light-off performance ([CO] = 0.1%, [O_2] = 5 %, balanced with N_2)

Study low-temperature CO oxidation by Pt_1 and ~1 nm Pt oxide clusters (Pt-O-Pt) on ceria

Goal

Understand the intrinsic activity difference and mechanism of Pt_1/CeO_2 and Pt-O-Pt/CeO_2

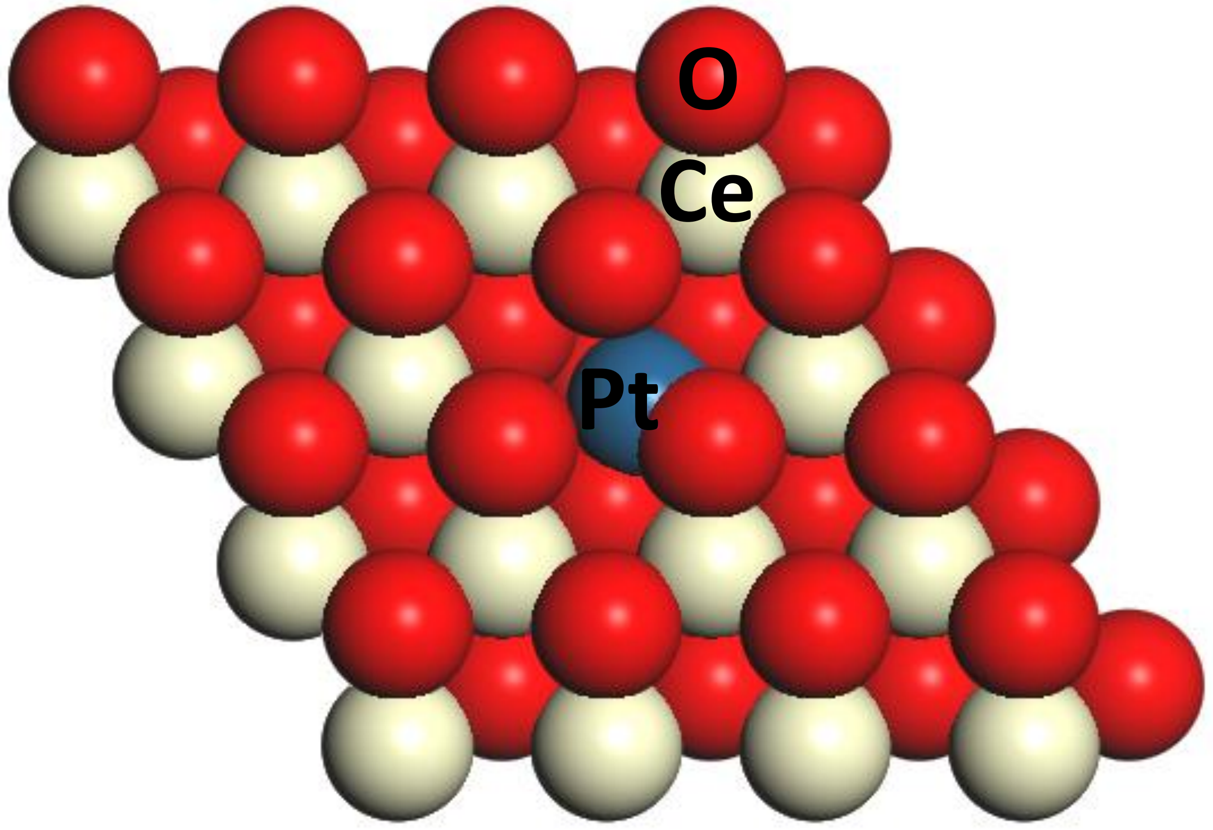
Reaction conditions

- *Low temperature: $T < 150$ °C*
- *Oxygen rich feed: $[CO]:[O_2] = 1:50$*
- *'Water free' conditions*

Hui Wang et al. *Nature Communications* 10.1 (2019): 1-12.

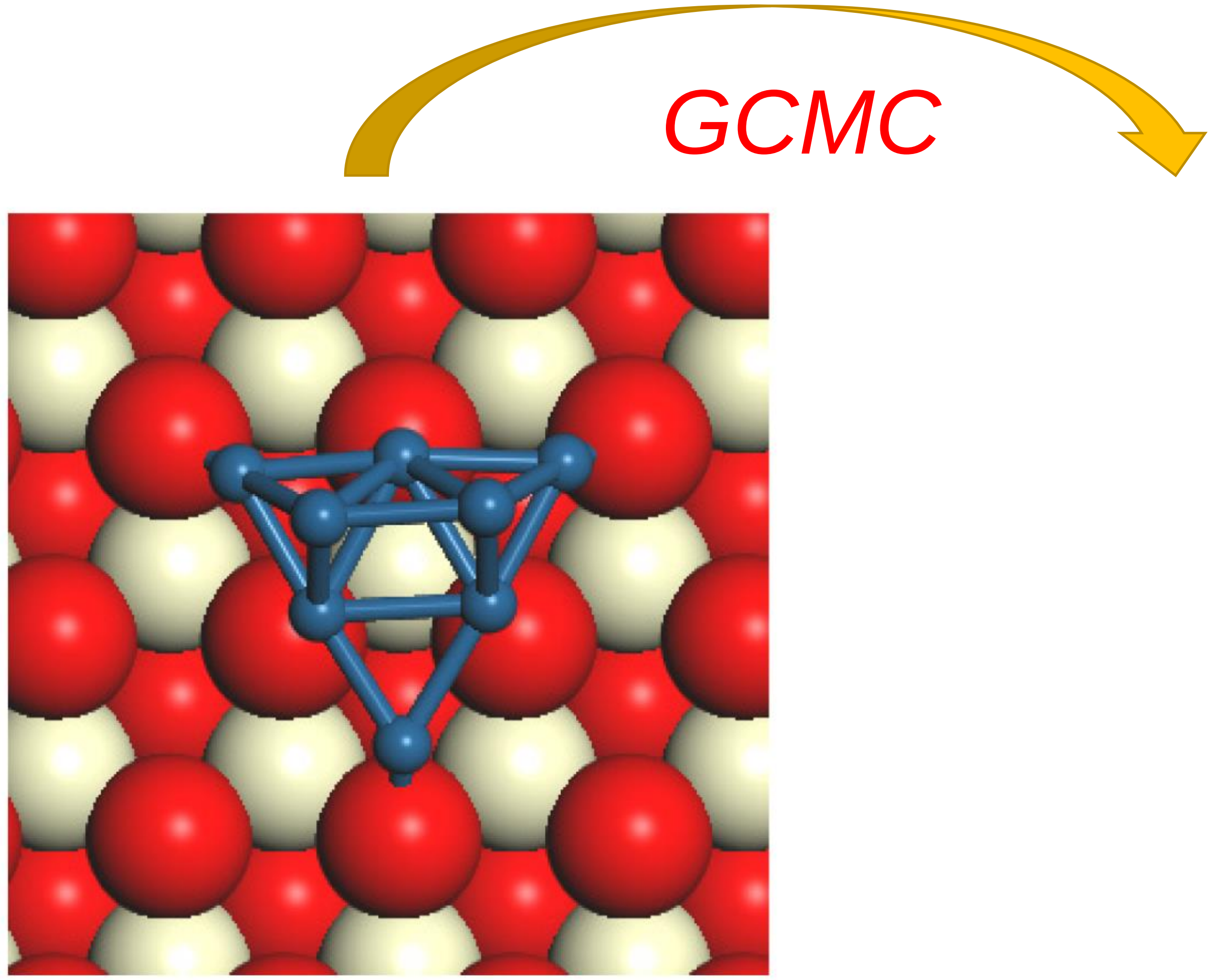
Perform DFT modeling to understand the structure and activity of Pt_1/CeO_2 and Pt_xO_y/CeO_2

- Density functional theory (DFT) calculations were done using VASP software.
- Cluster structure search using genetic algorithm + grand canonical Monte-Carlo (GA+GCMC).[1]
- CeO_2(111) used as the model support (experiment used 10-30 nm ceria particles).
- Surface oxygen vacancies are filled (oxygen-rich conditions).



Stable Pt_1/CeO_2(111) configuration

μ (T = 350 K, P_{O2} = 0.05 bar)



Pt_8/CeO_2

[1] J-X. Liu,… E. J. Hensen *JACS* 140.13 (2018): 4580-4587.

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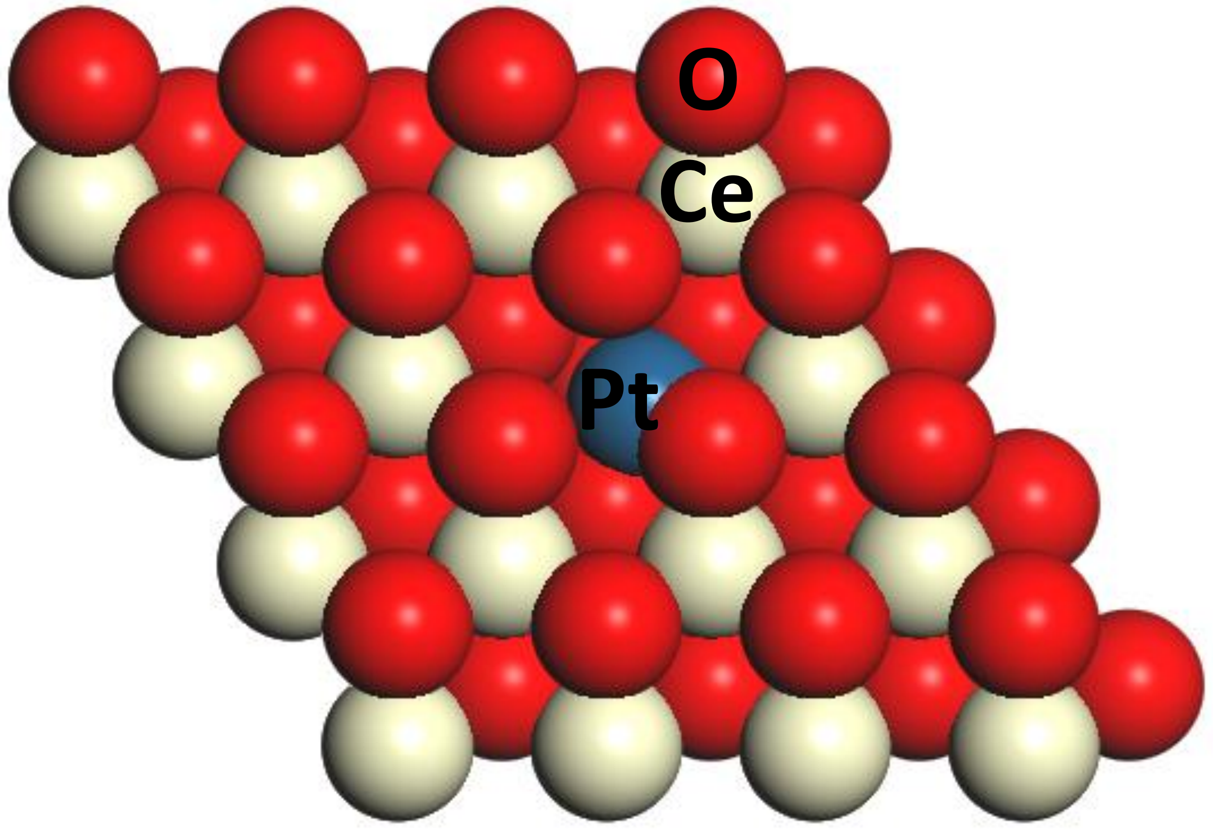

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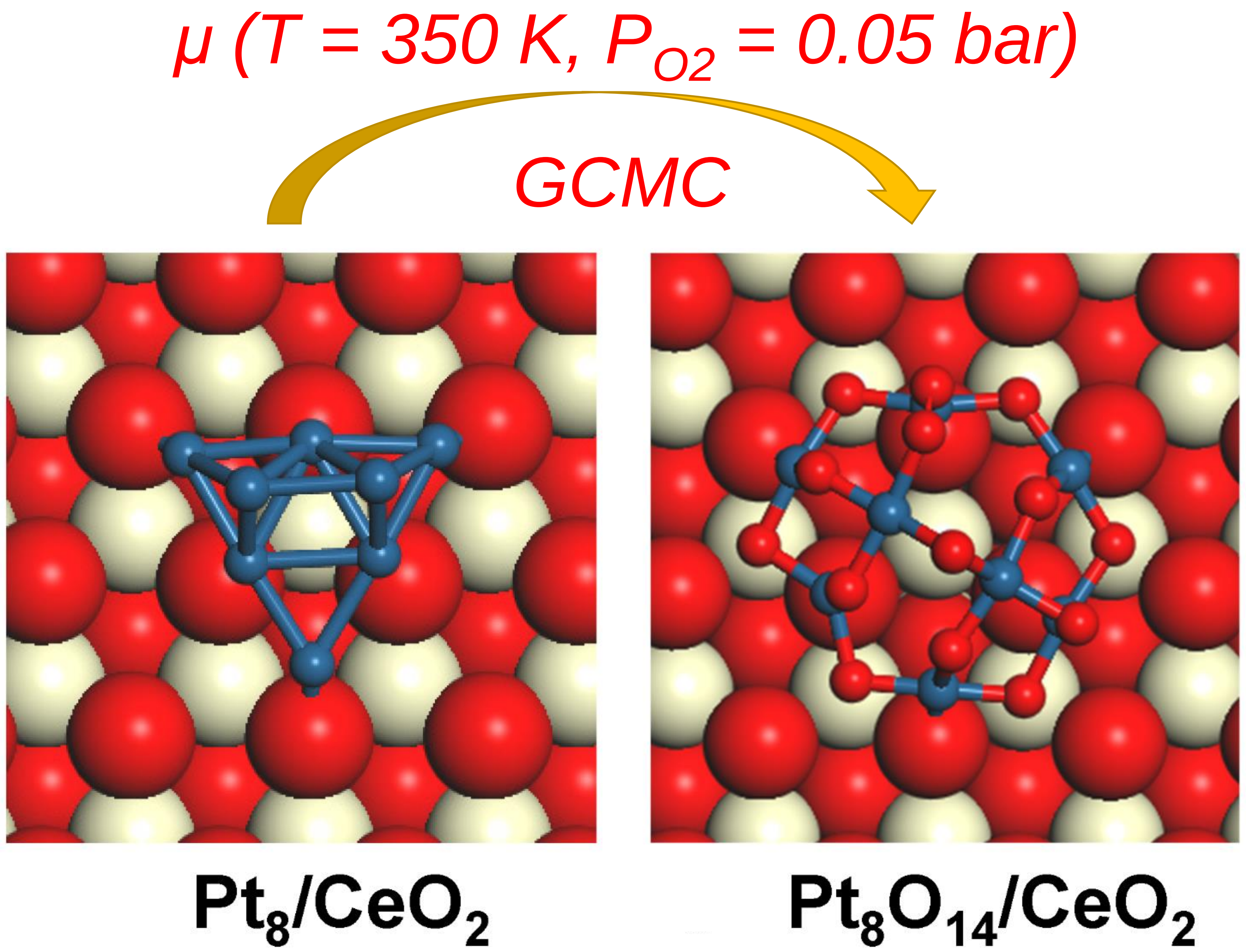
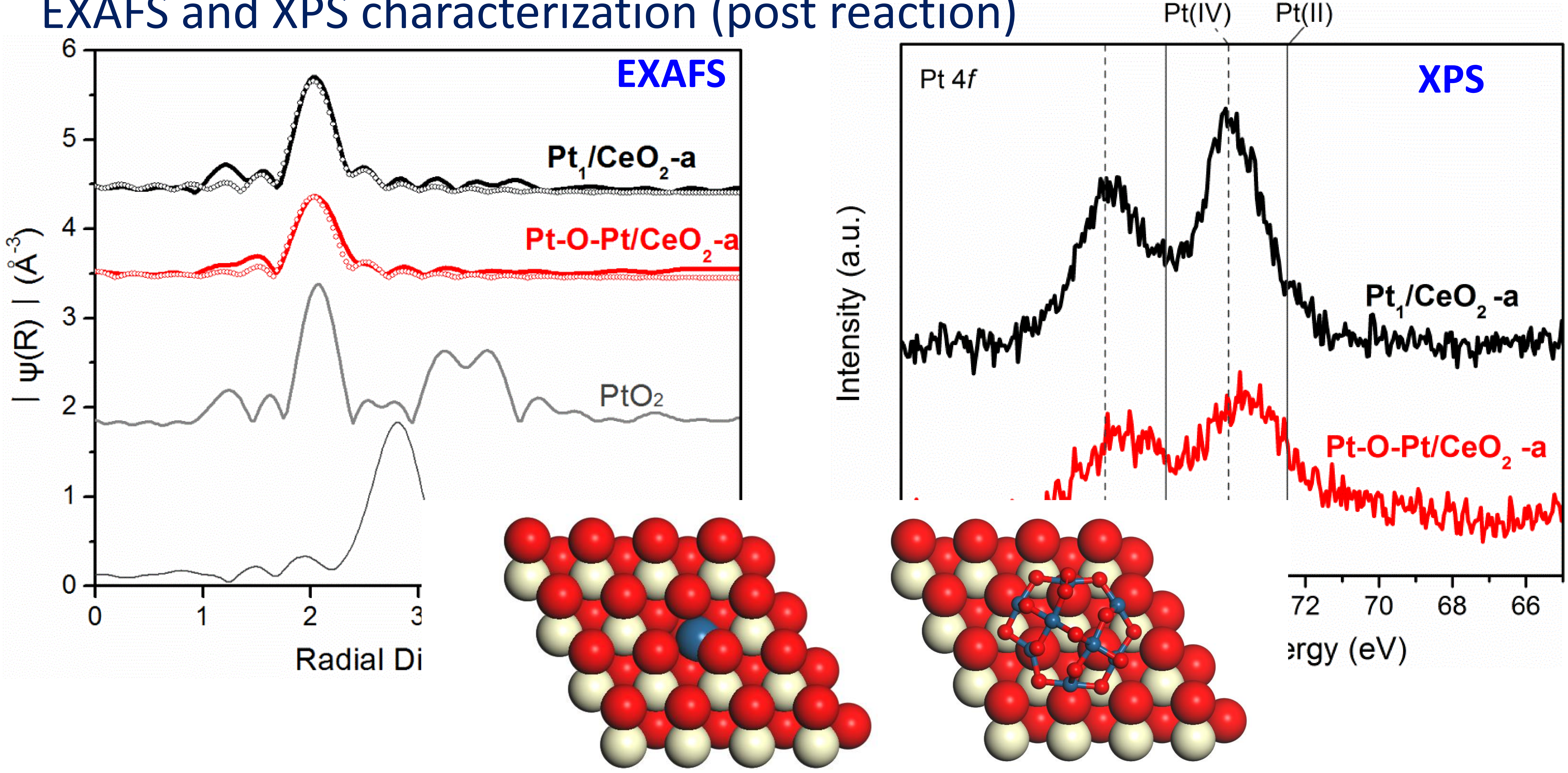


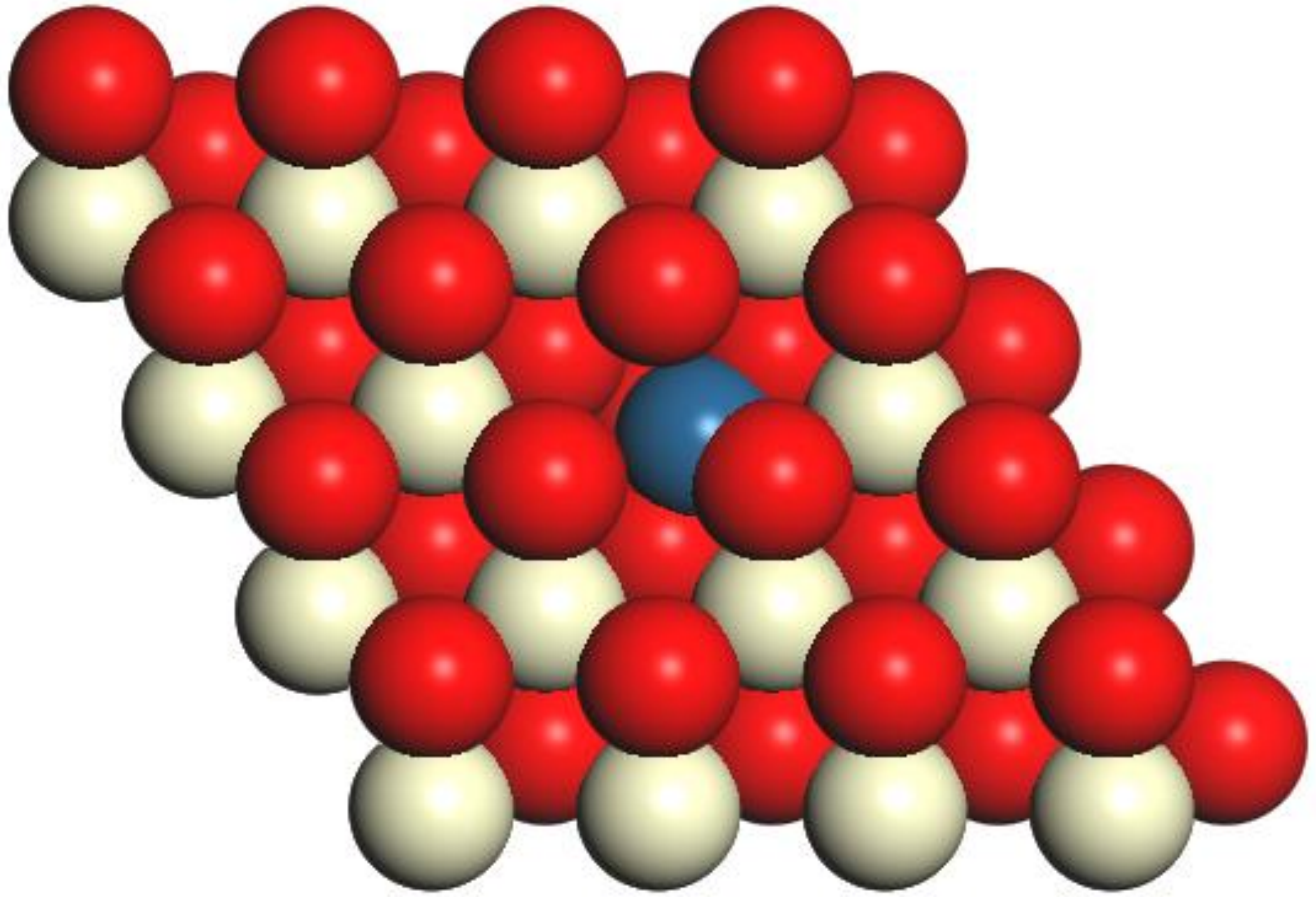
[1] J-X. Liu,… E. J. Hensen *JACS* 140.13 (2018): 4580-4587.

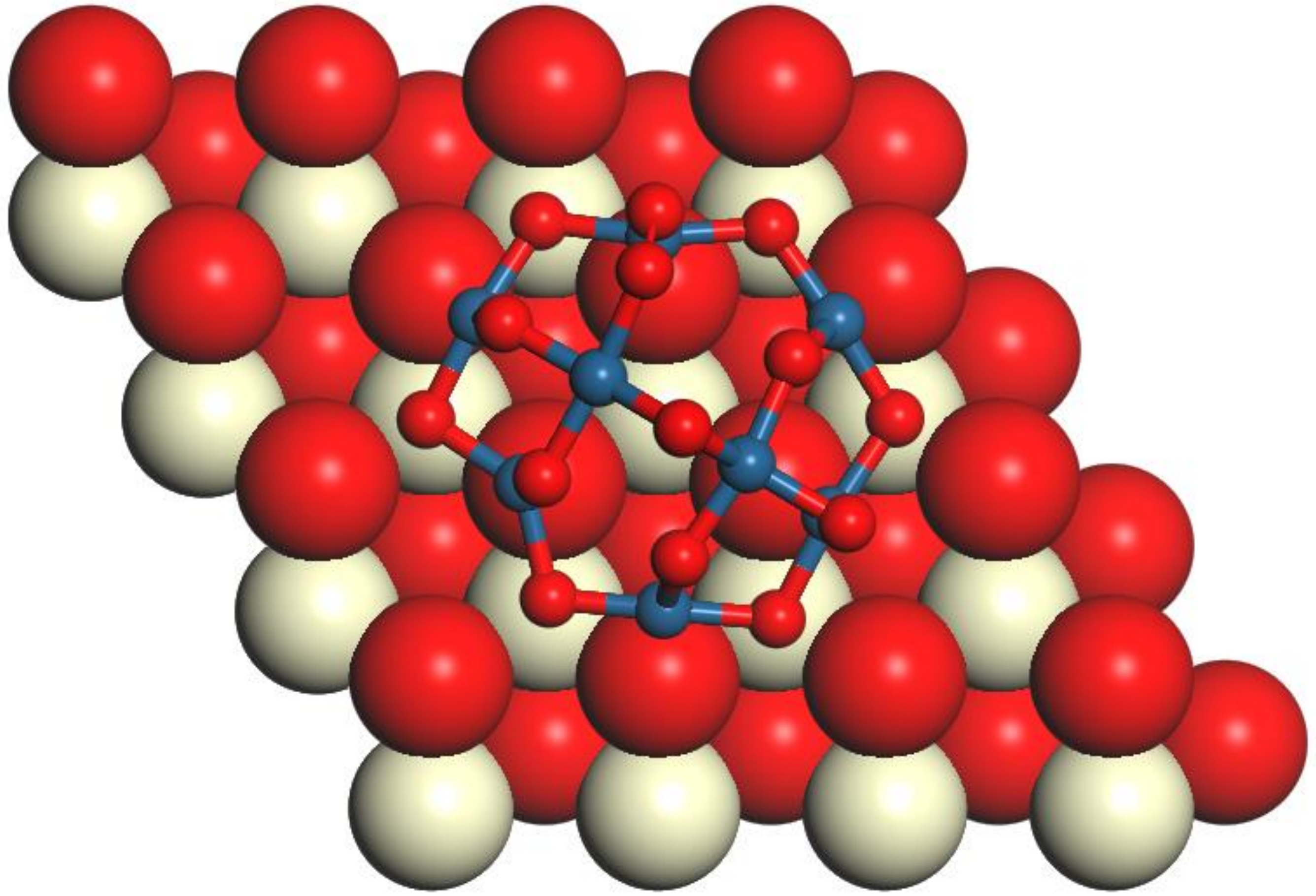
Pt_1/CeO_2 and Pt_8O_{14}/CeO_2 models are consistent with EXAFS and XPS characterization (post reaction)



Bader charge Pt_1/CeO_2 (+1.51) < Pt_8O_{14}/CeO_2 (+1.23 ± 0.21)

Study the mechanism of CO oxidation on $Pt_1/CeO_2(111)$ and $Pt_8O_{14}/CeO_2(111)$ under oxygen-rich conditions





→Surface oxygen vacancies will be rapidly filled under our oxygen-rich conditions and low-temperature.[1-2]

Three CO oxidation pathways:

1. At the metal-support interface

2. At the Pt_8O_{14} cluster edge

3. On Pt_8O_{14} cluster

[1] M. Fronzi *et al. J. Chem. Phys.* 131 (2009)

[2] V. Botu, R. Ramprasad, A. Mhadeshwar. *Surf. Science* 619 (2014)

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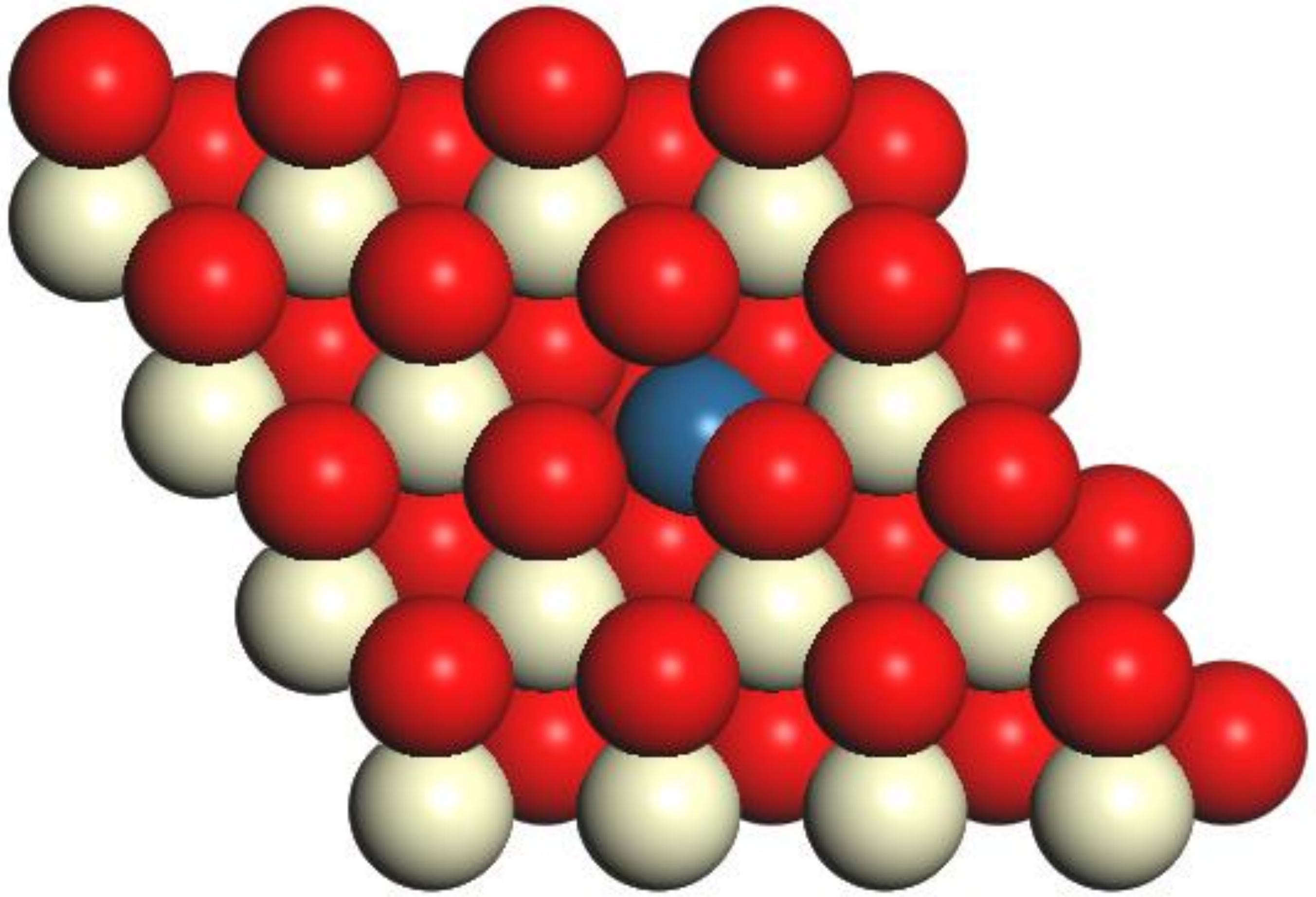

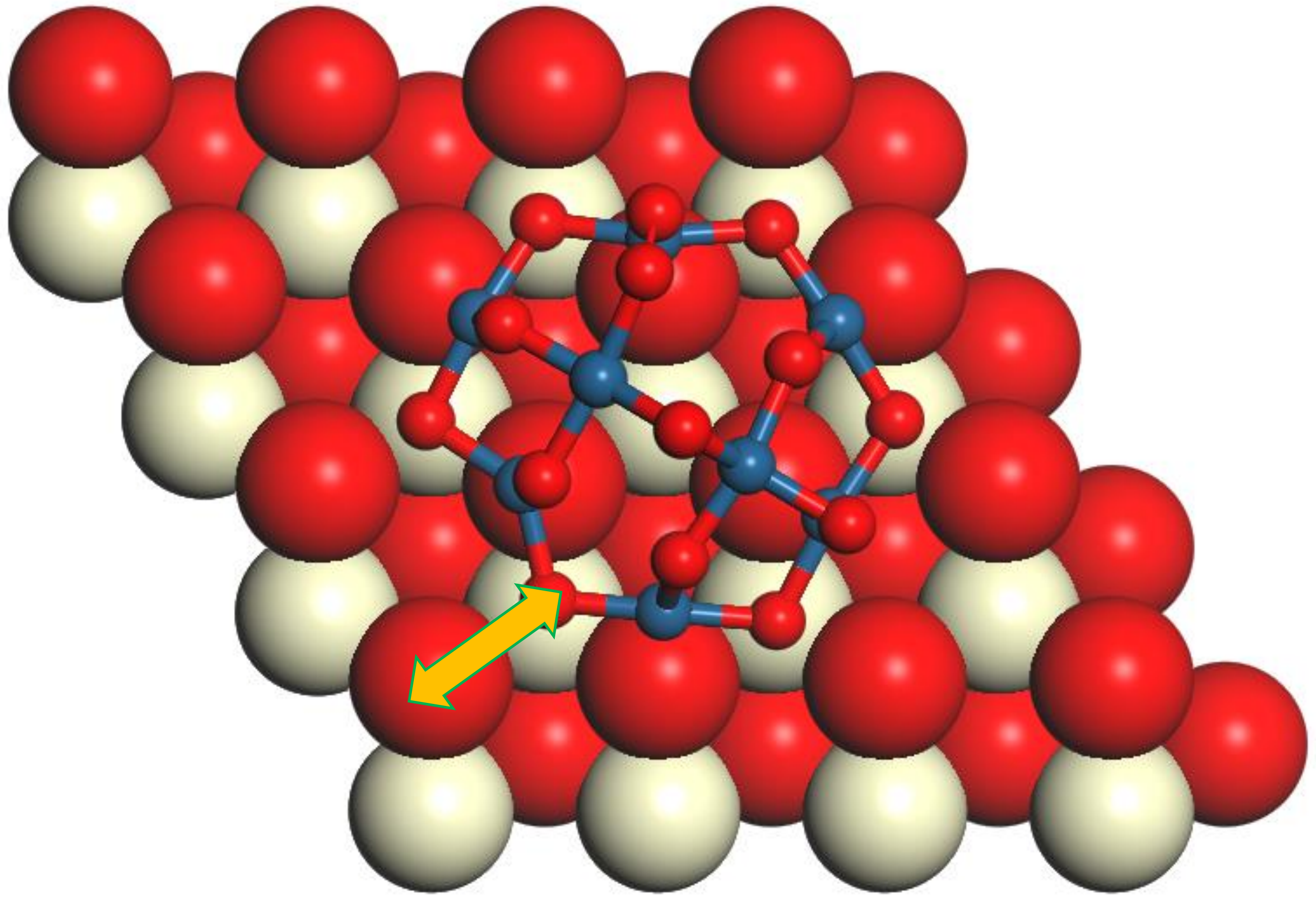

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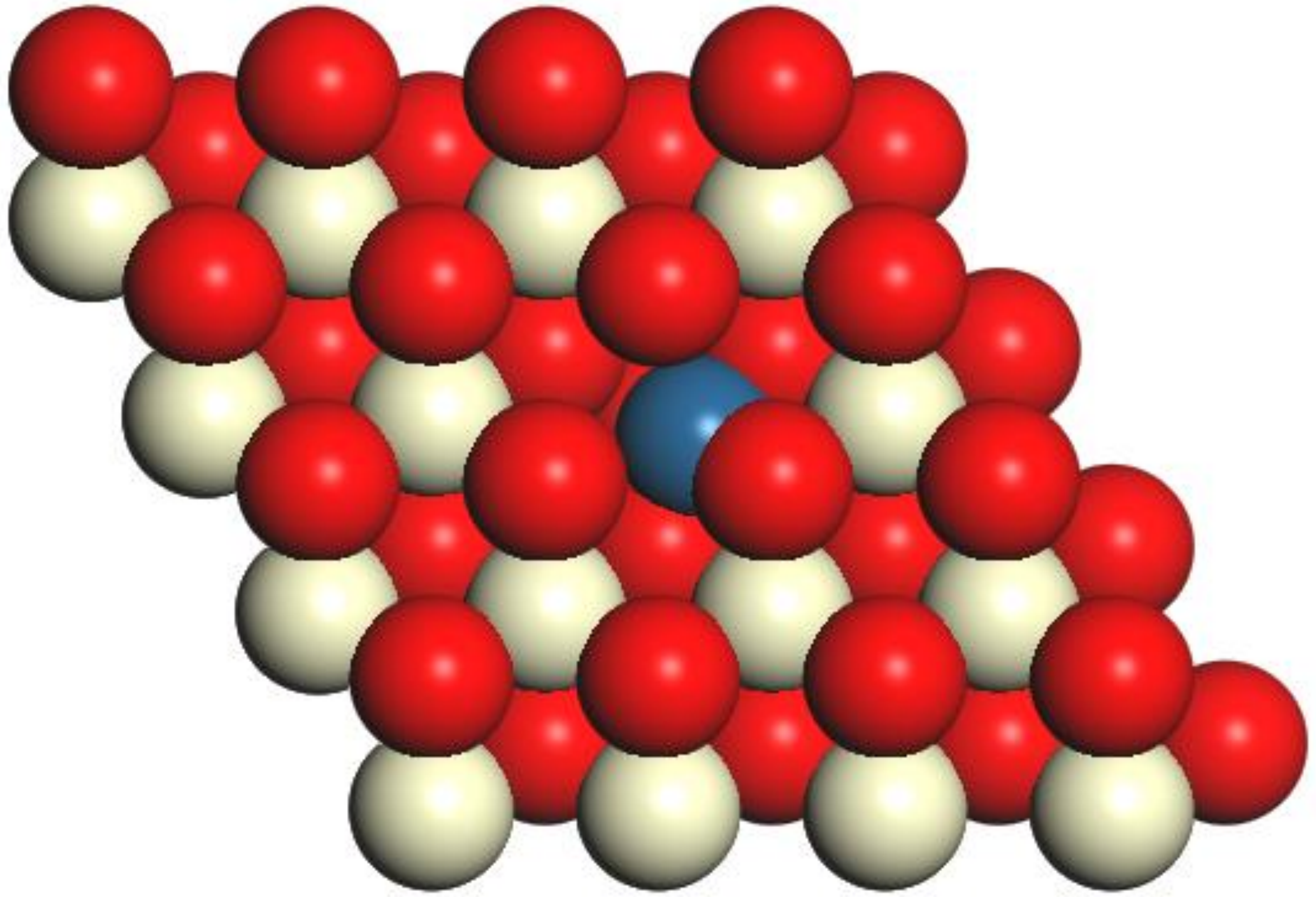

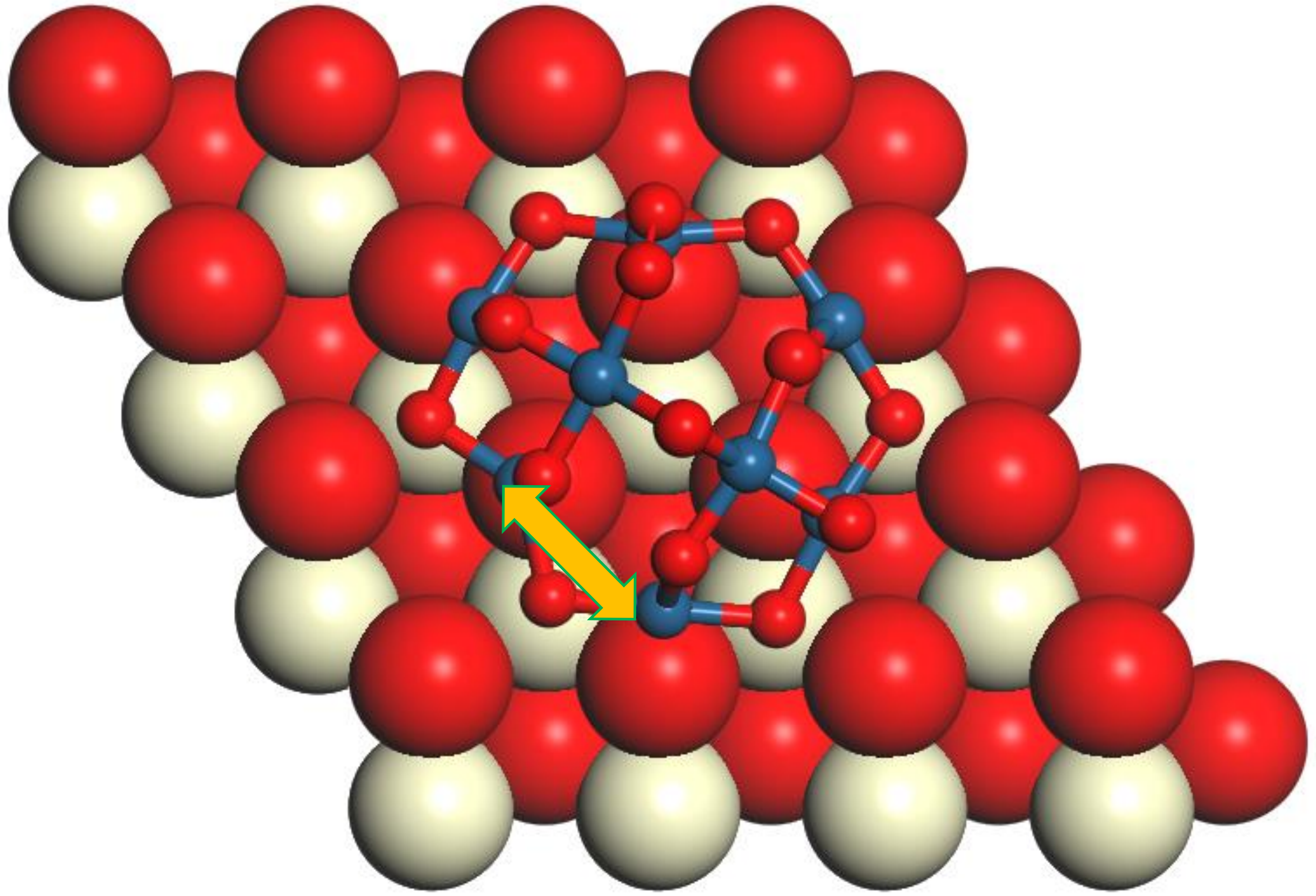

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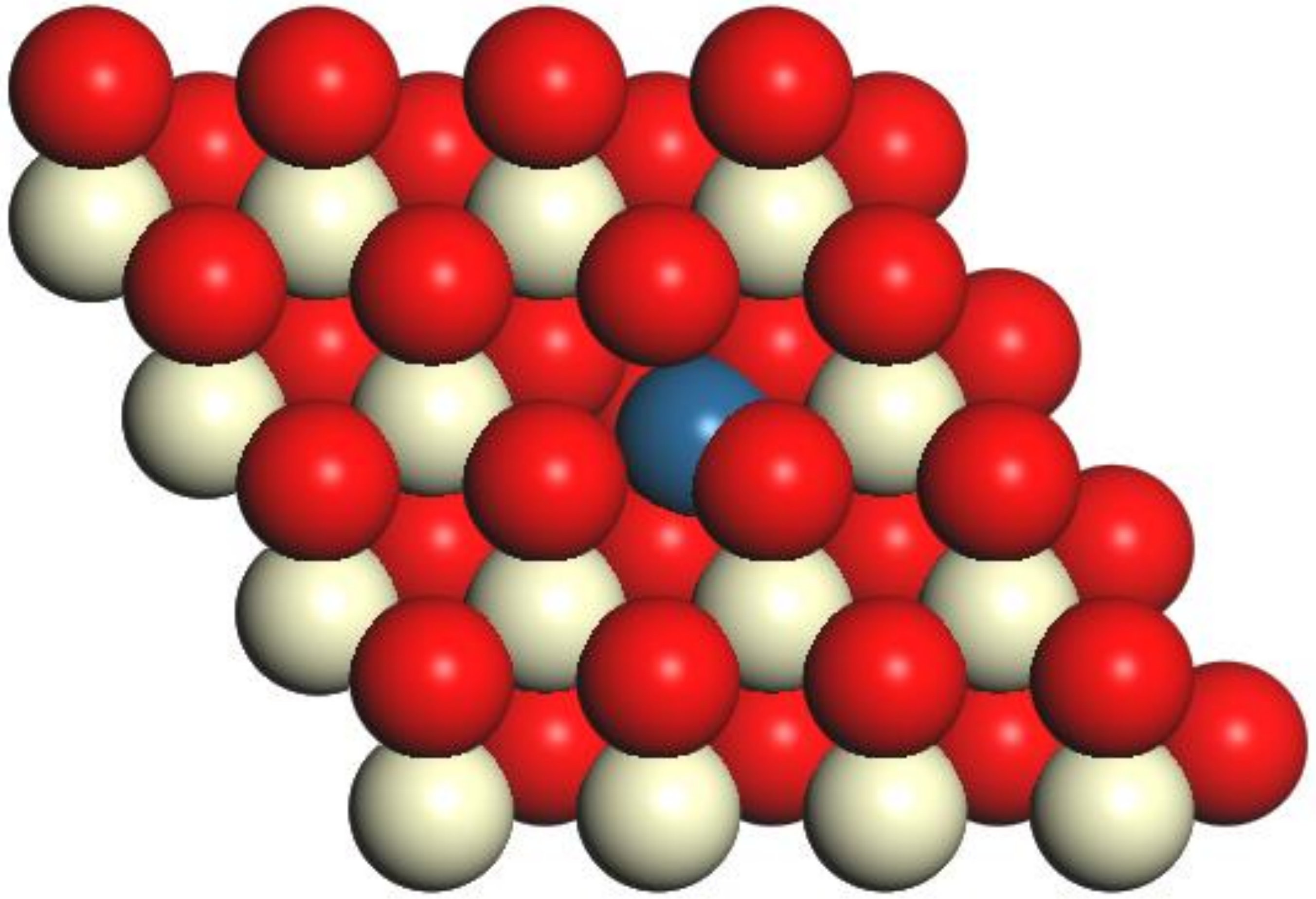

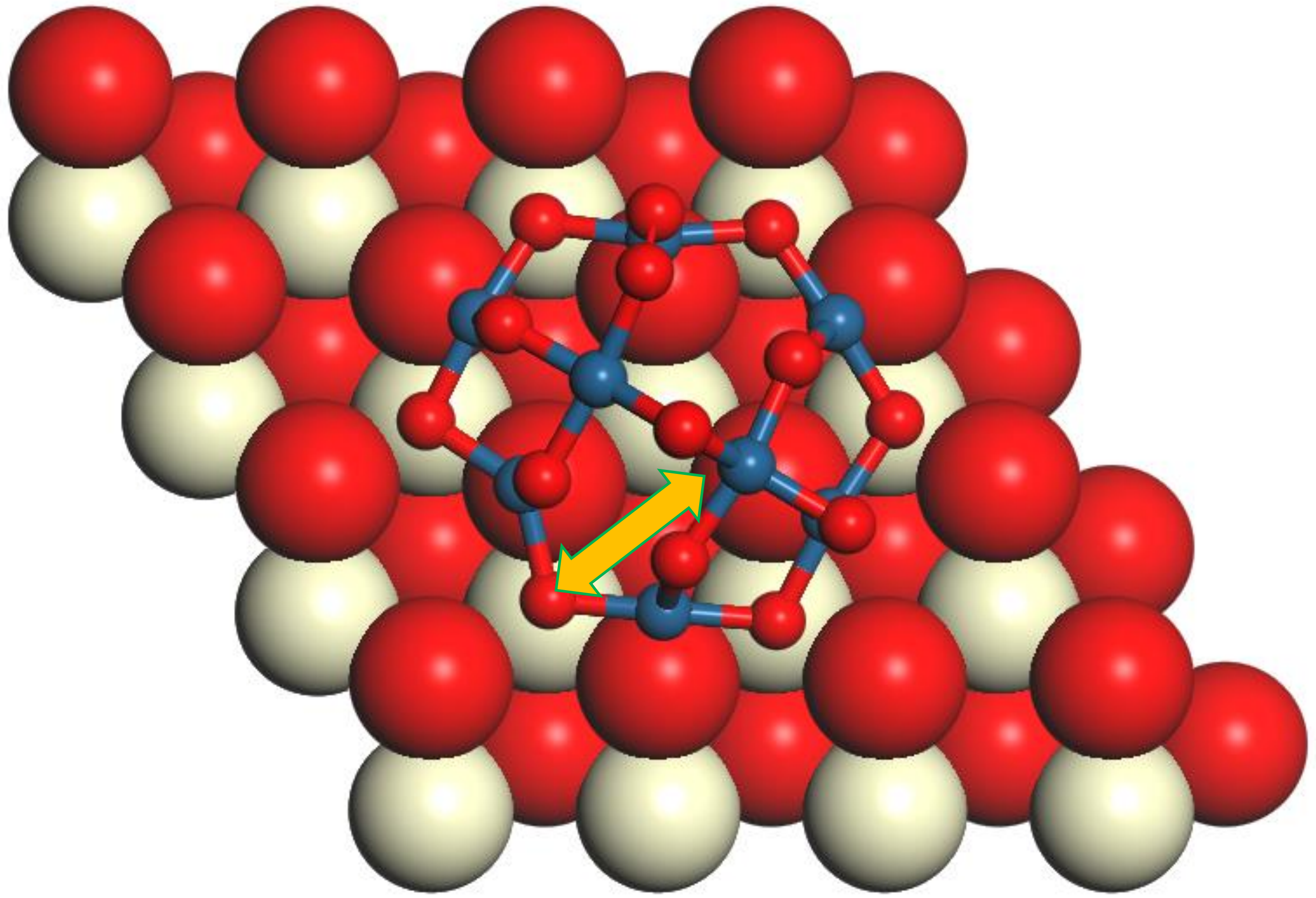

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Microkinetic modeling for mechanistic hypothesis testing of CO oxidation by Pt_1 /CeO_2(111) and Pt_8O_{14}/CeO_2(111)

$$r_i = \sum_{j=1}^{N} \left(k_j v_i^j \prod_{k=1}^{M} c_k^{\ v_k^j} \right)$$

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^{\ddagger}}{RT}}$$

$$X_{RC,i} = \frac{k_i}{r} \left(\frac{\partial r}{\partial k_i} \right)_{k_{j \neq i}, K_i} = \left(\frac{\partial \ln r}{\partial \ln k_i} \right)_{k_{j \neq i}, K_i}$$

Use MKMCXX[1] mean-field microkinetic modeling software.

Inputs to software

✓ Adsorption energies of reactant, intermediates, and product

✓ Forward and backward reaction barriers

✓ Temperature, pressure

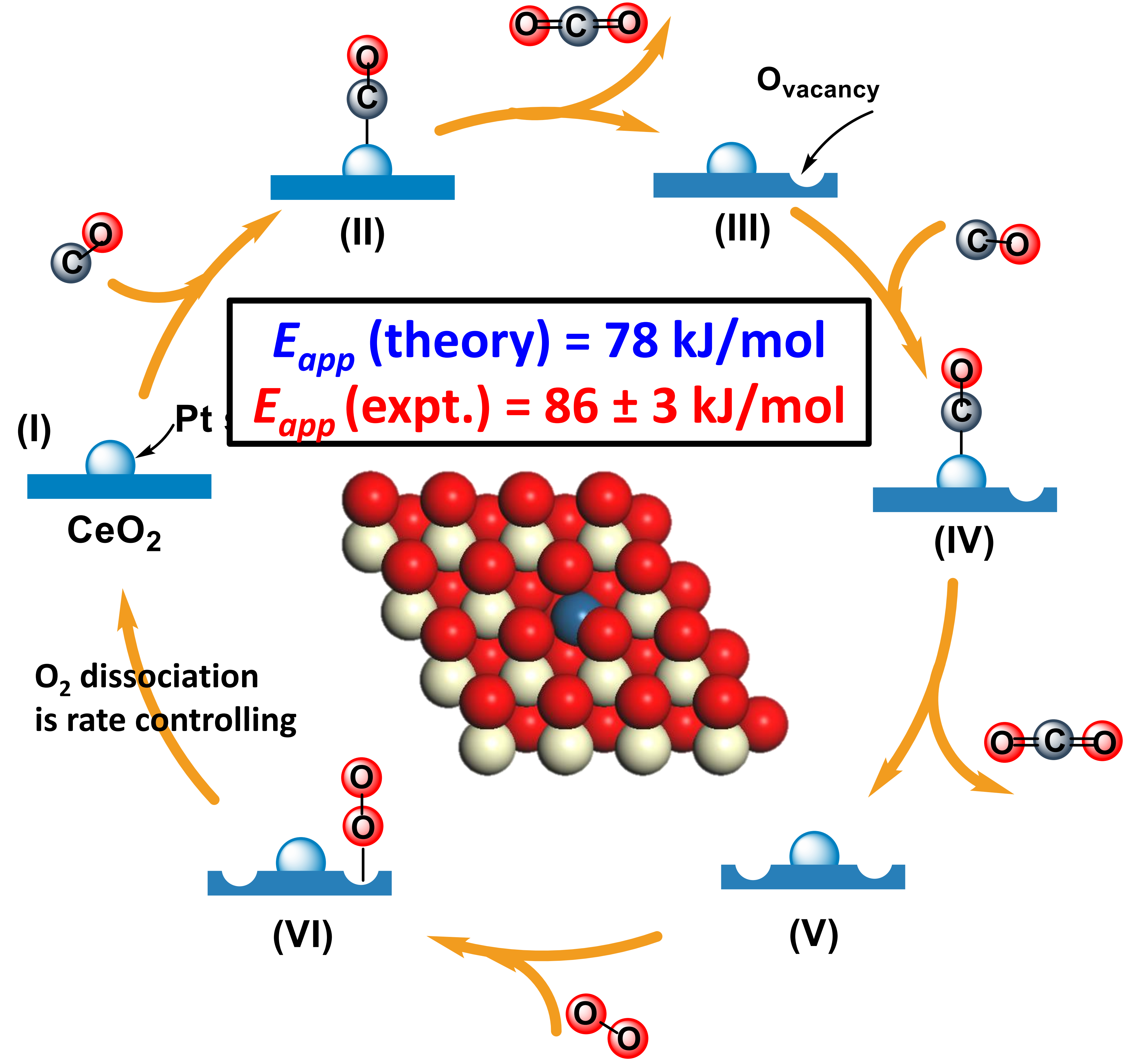
Output:

✓ Reaction rate, coverages, apparent activation barrier

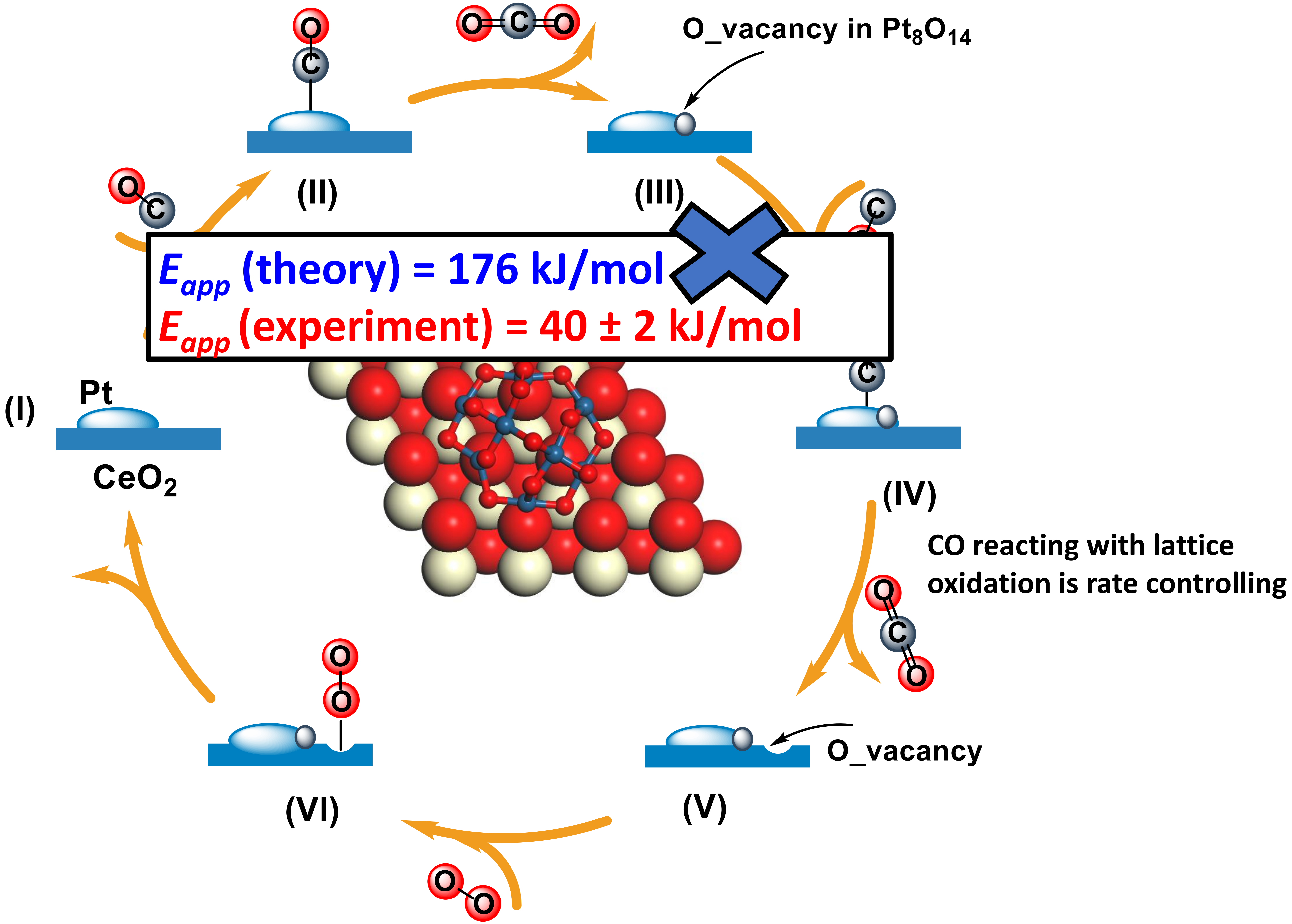
[1] https://www.mkmcxx.nl/

[1a] Filot, Ivo AW, Rutger A. van Santen, and Emiel JM Hensen. "The optimally performing Fischer–Tropsch catalyst." *Angewandte Chemie International Edition* 53.47 (2014): 12746-12750.

CO oxidation on $Pt_1/CeO_2(111)$ follows MVK mechanism



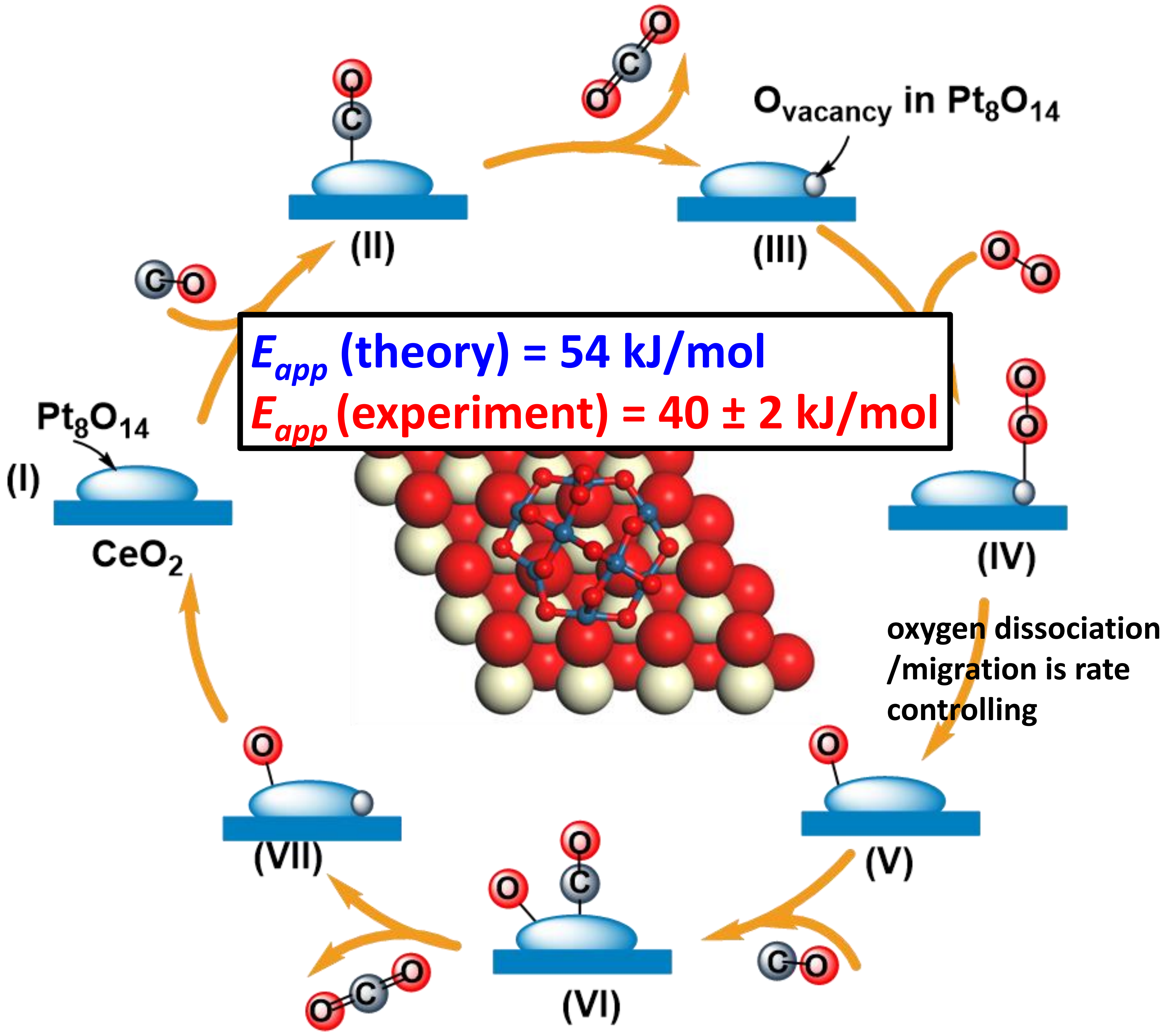
CO oxidation at Pt_8O_{14}/CeO_2 interface



E_{app} (theory) = 176 kJ/mol

E_{app} (experiment) = 40 ± 2 kJ/mol

CO oxidation at Pt-O-Pt in Pt_8O_{14} is favored



CO oxidation at Pt-O-Pt in Pt_8O_{14} is favored based on microkinetic modeling

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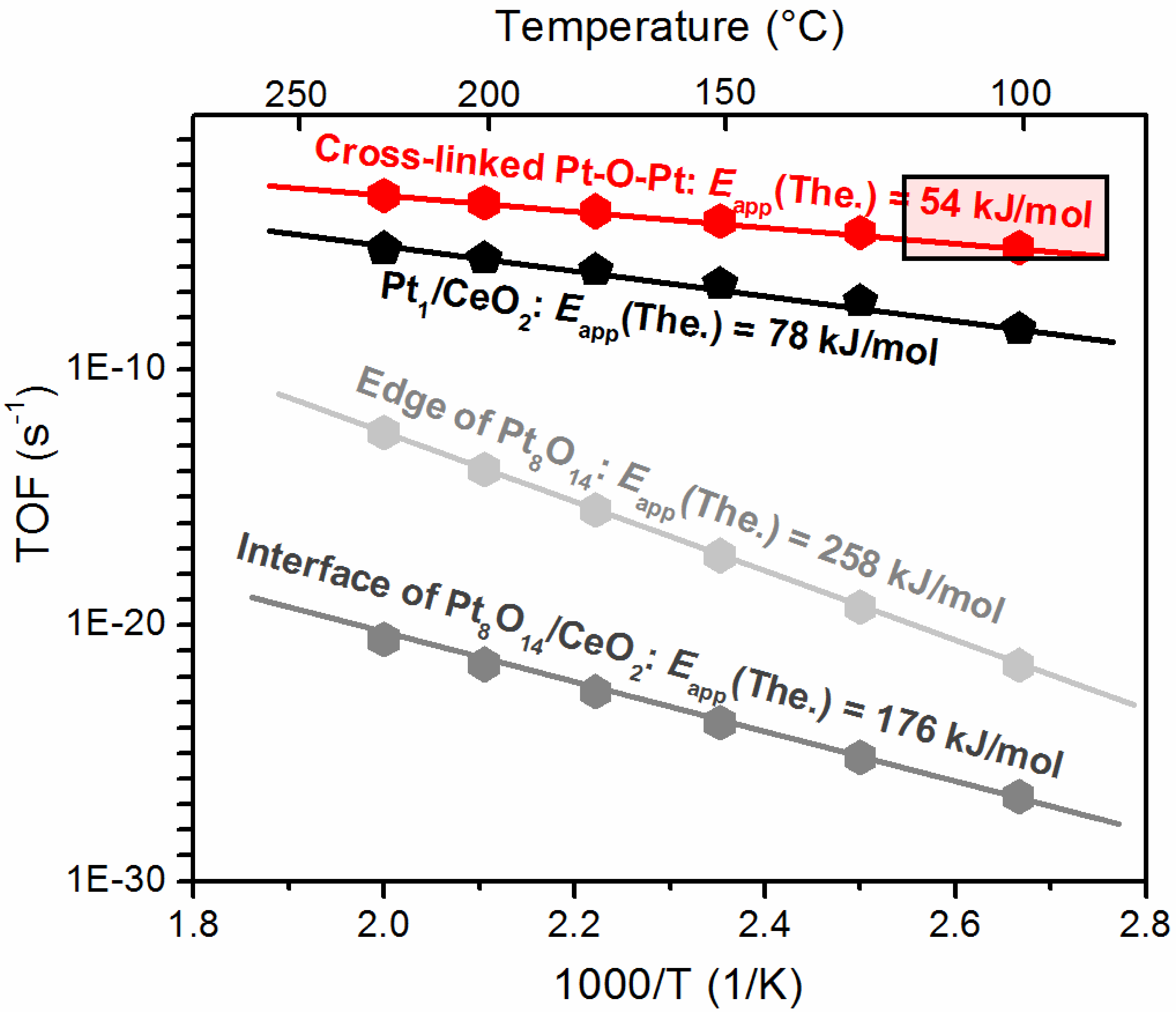
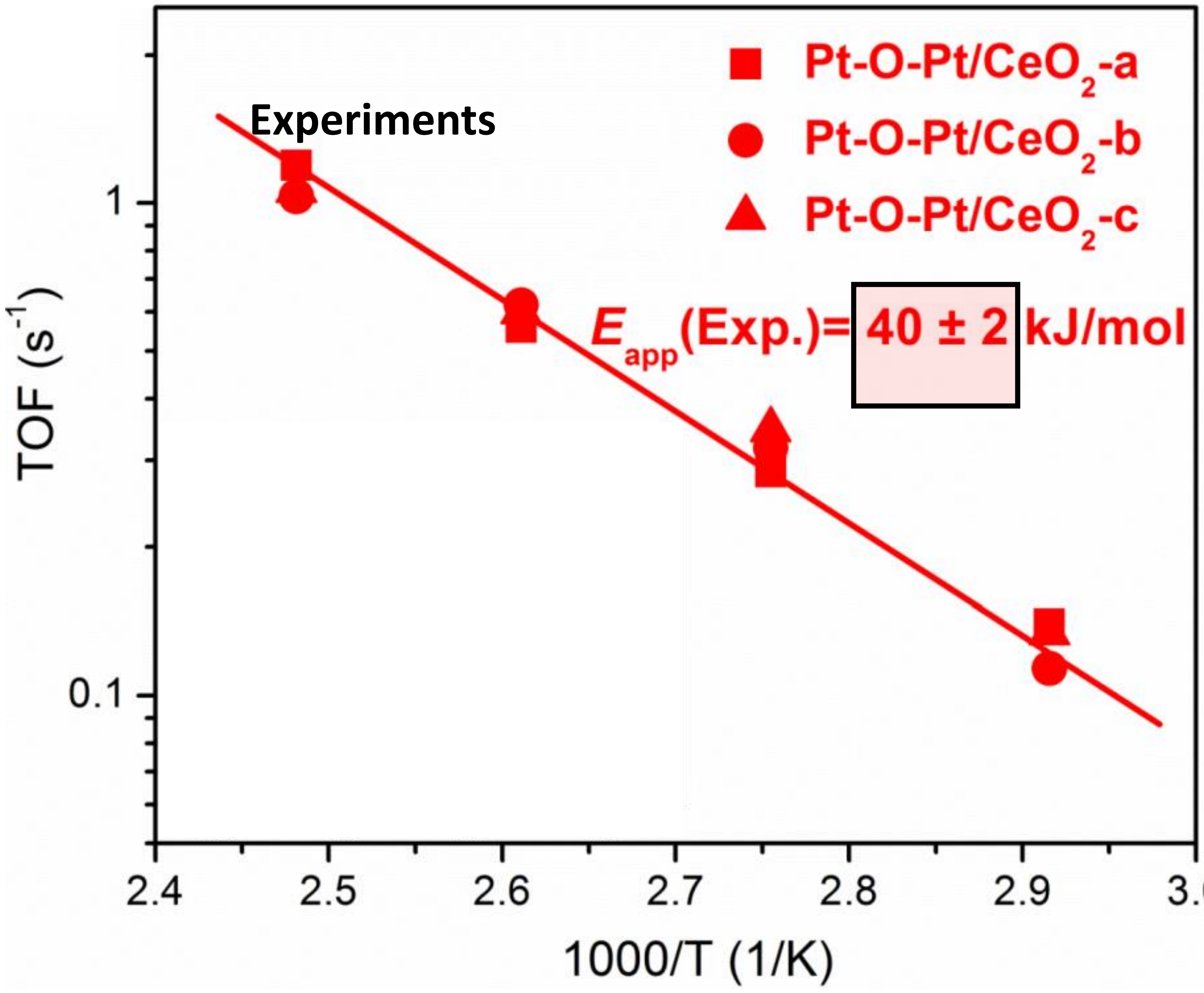
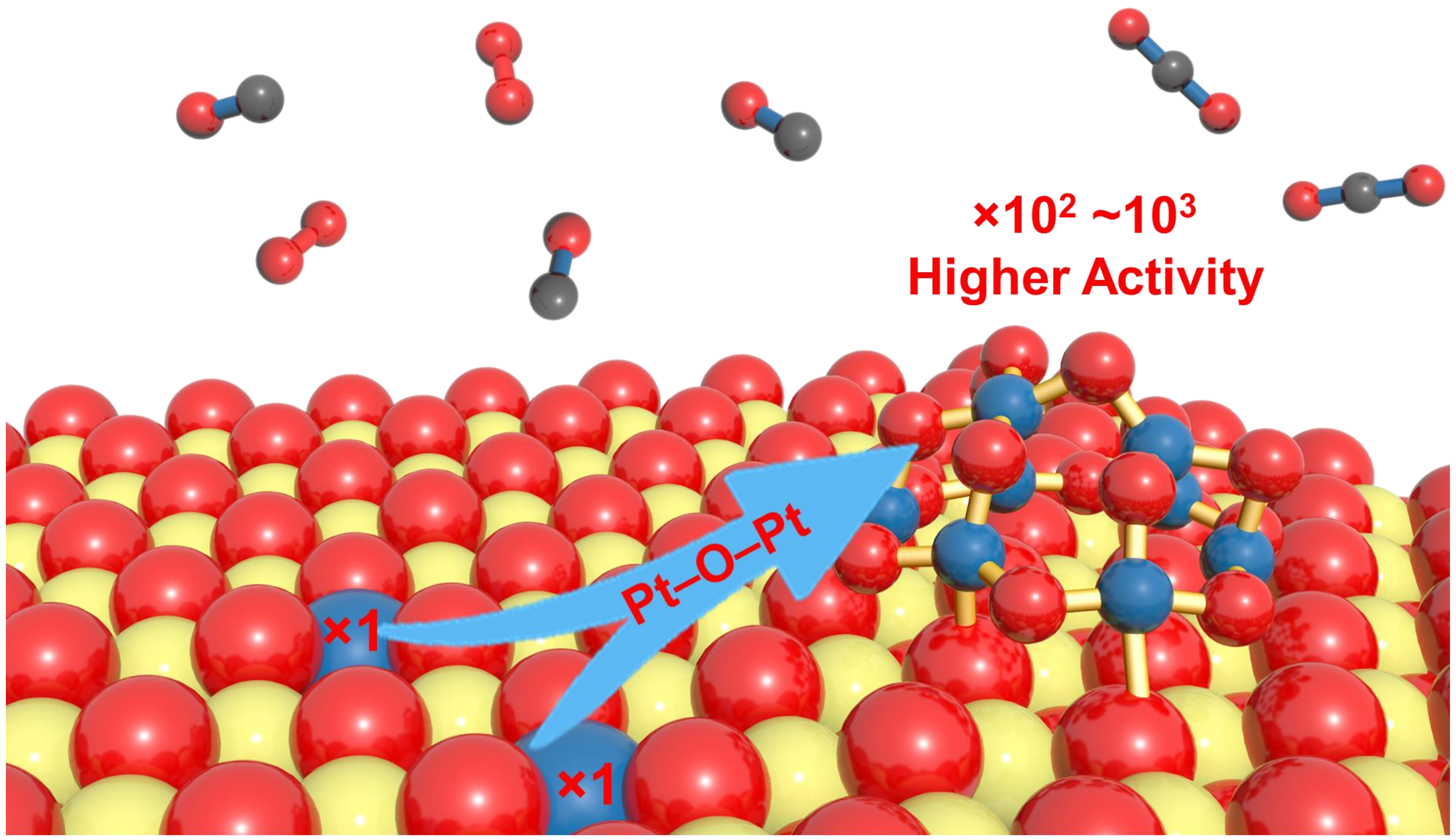


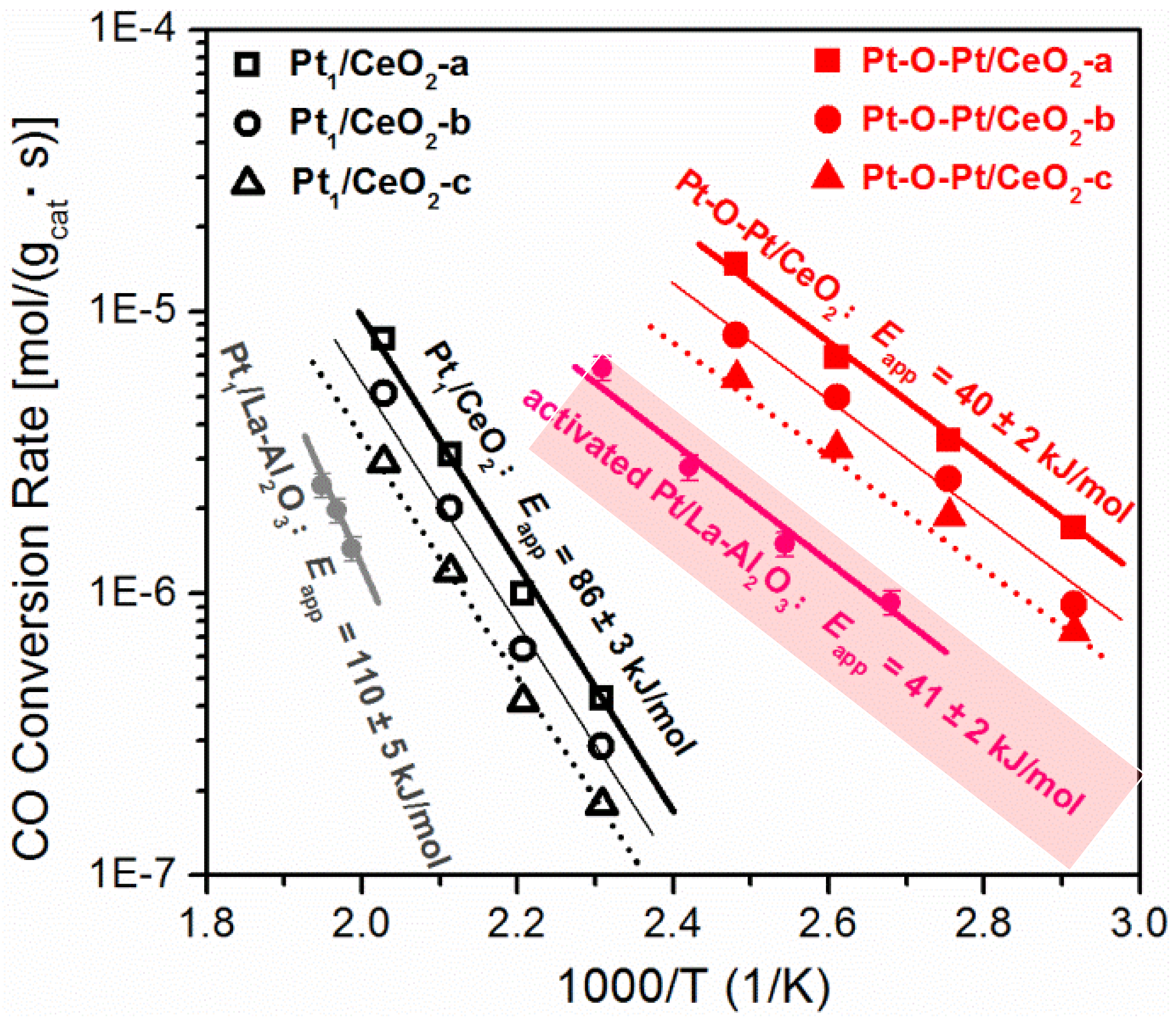


Pt-O-Pt/CeO_2 has 100-1000*x* higher TOF than Pt_1/CeO_2 for low-temperature CO oxidation

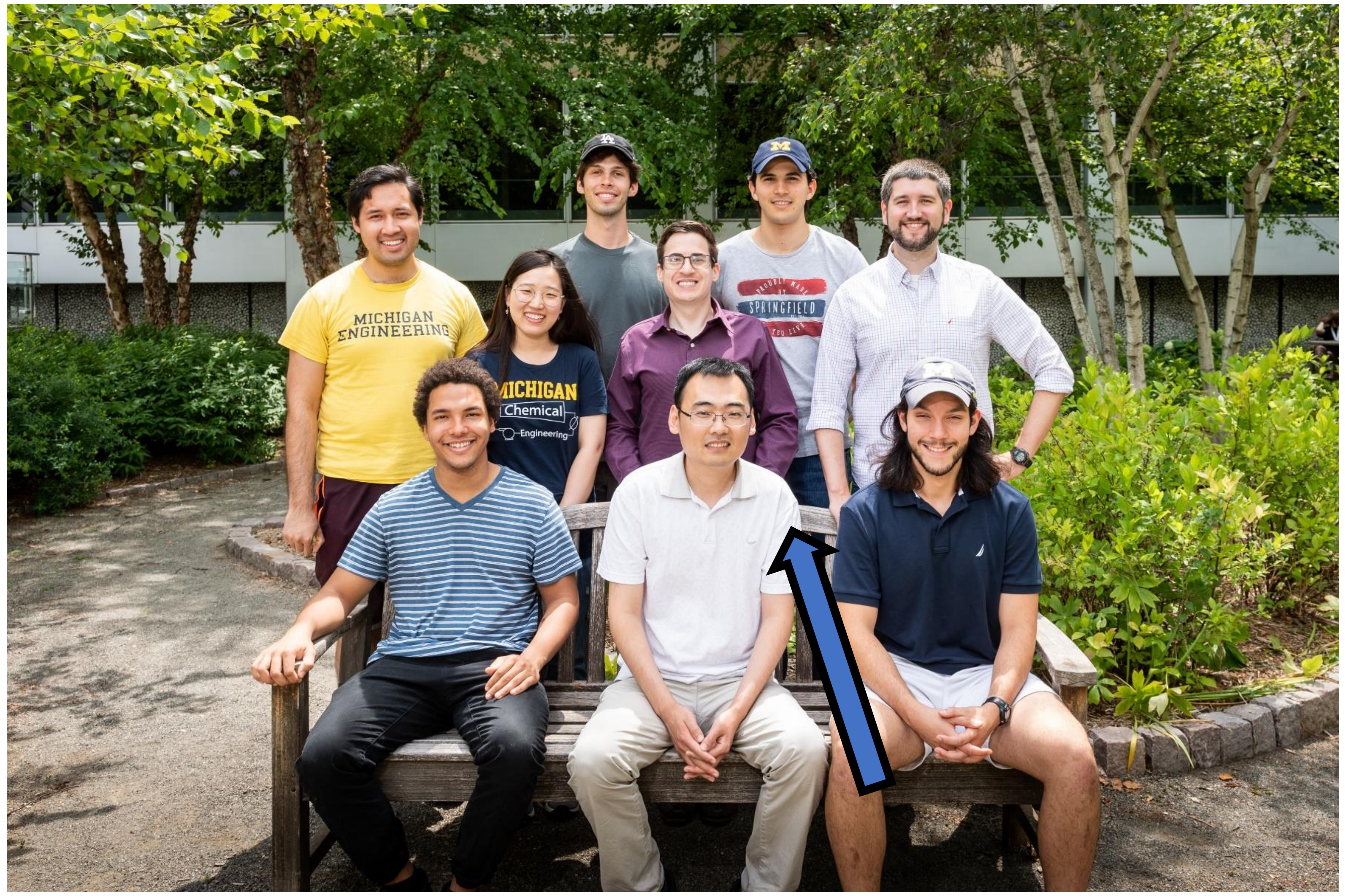
1) Semi-quantitative structural and kinetic agreement found between experiment and models for both the Pt-O-Pt/CeO_2 and Pt_1/CeO_2 systems.

2) High catalytic activity may arise from the Pt-O-Pt unit in Pt-O-Pt/CeO_2 under these O_2-rich conditions.





Acknowledgements



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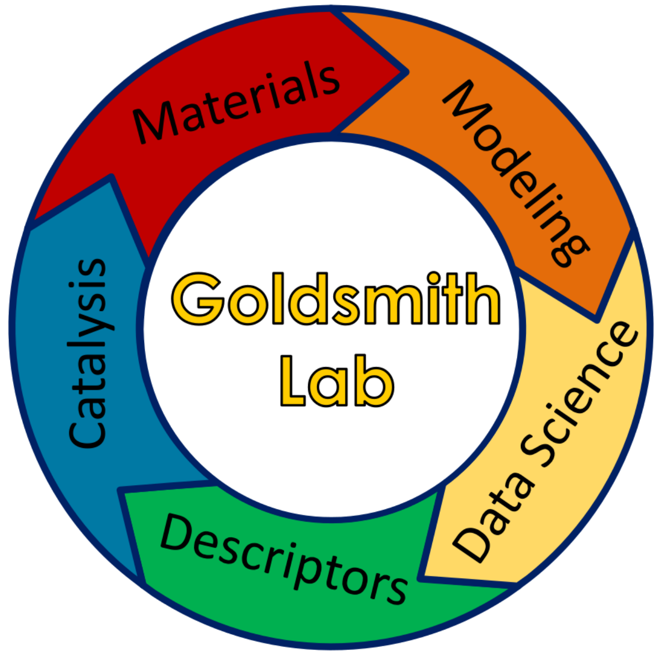

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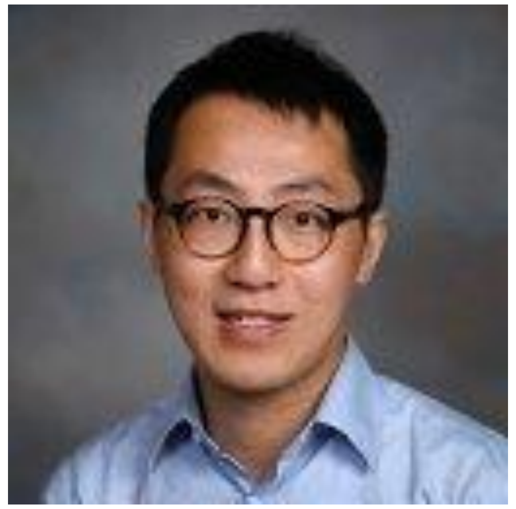
Ming Yang (General Motors)



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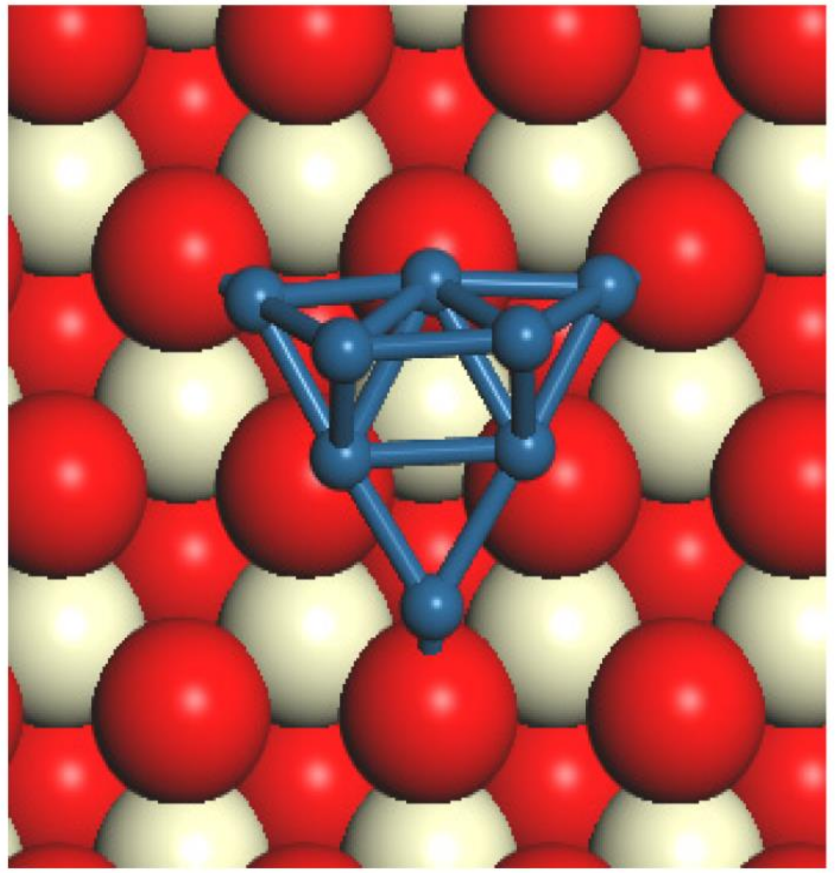
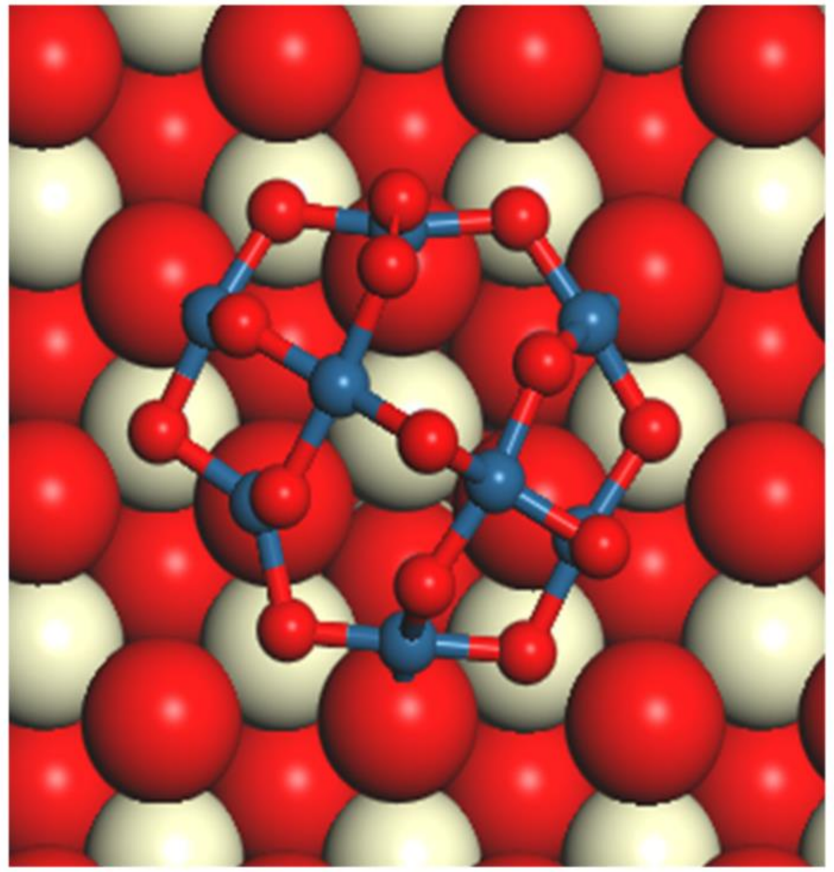
Supporting Information

(1) Structure identified by Genetic Algorithm



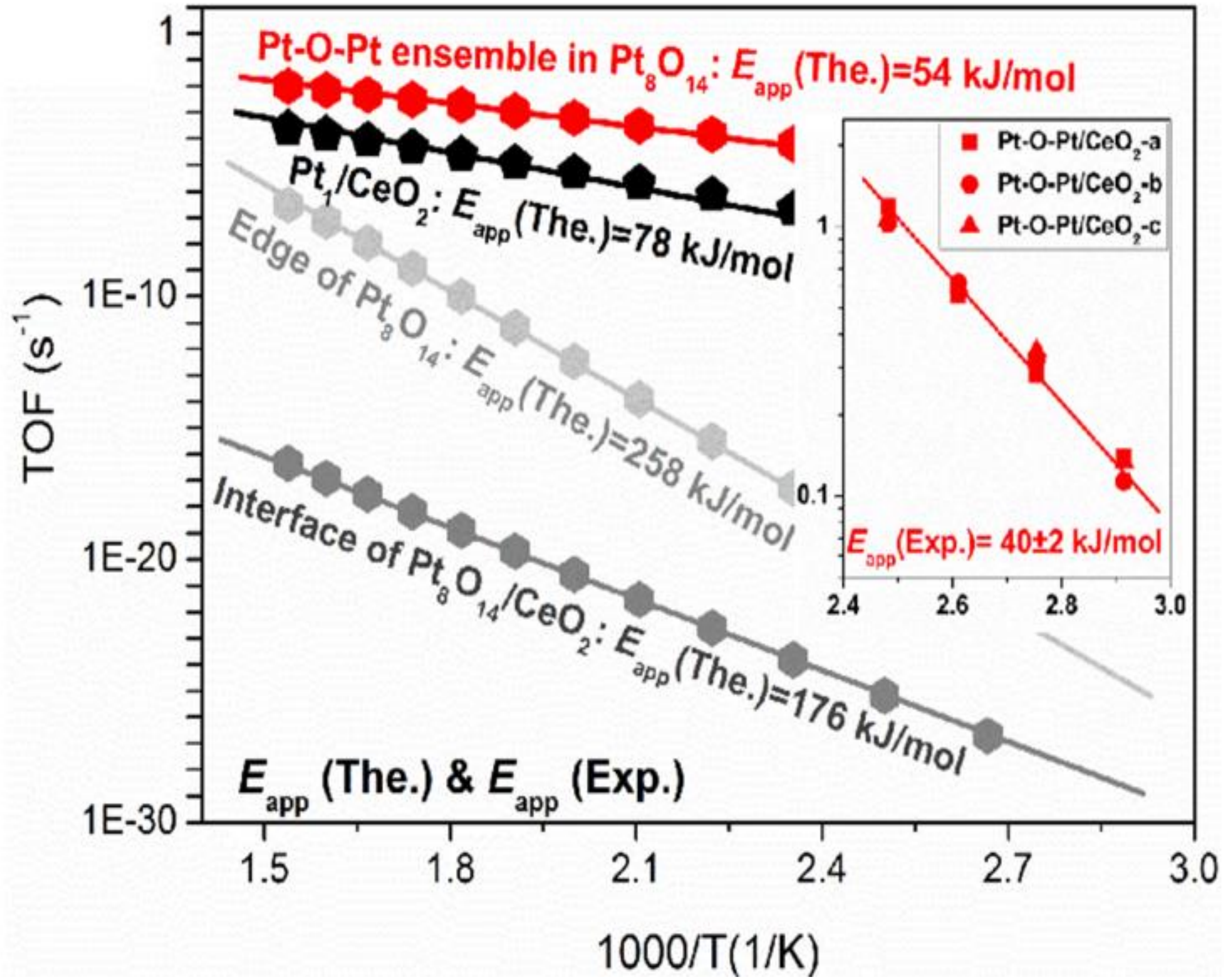
Pt_8/CeO_2

(2) Structure identified under reaction conditions by Genetic algorithm + Grand Canonical Monte Carlo

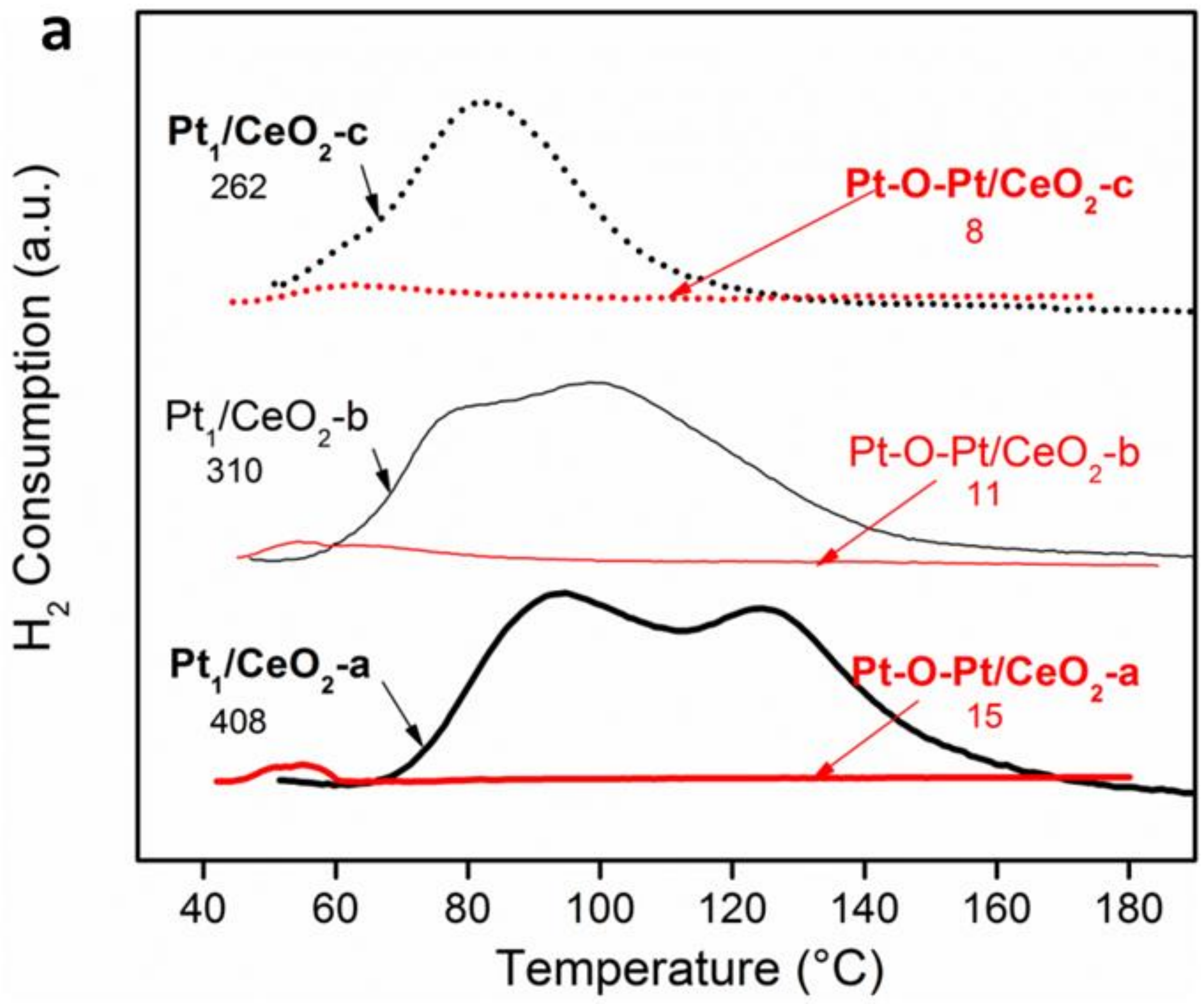


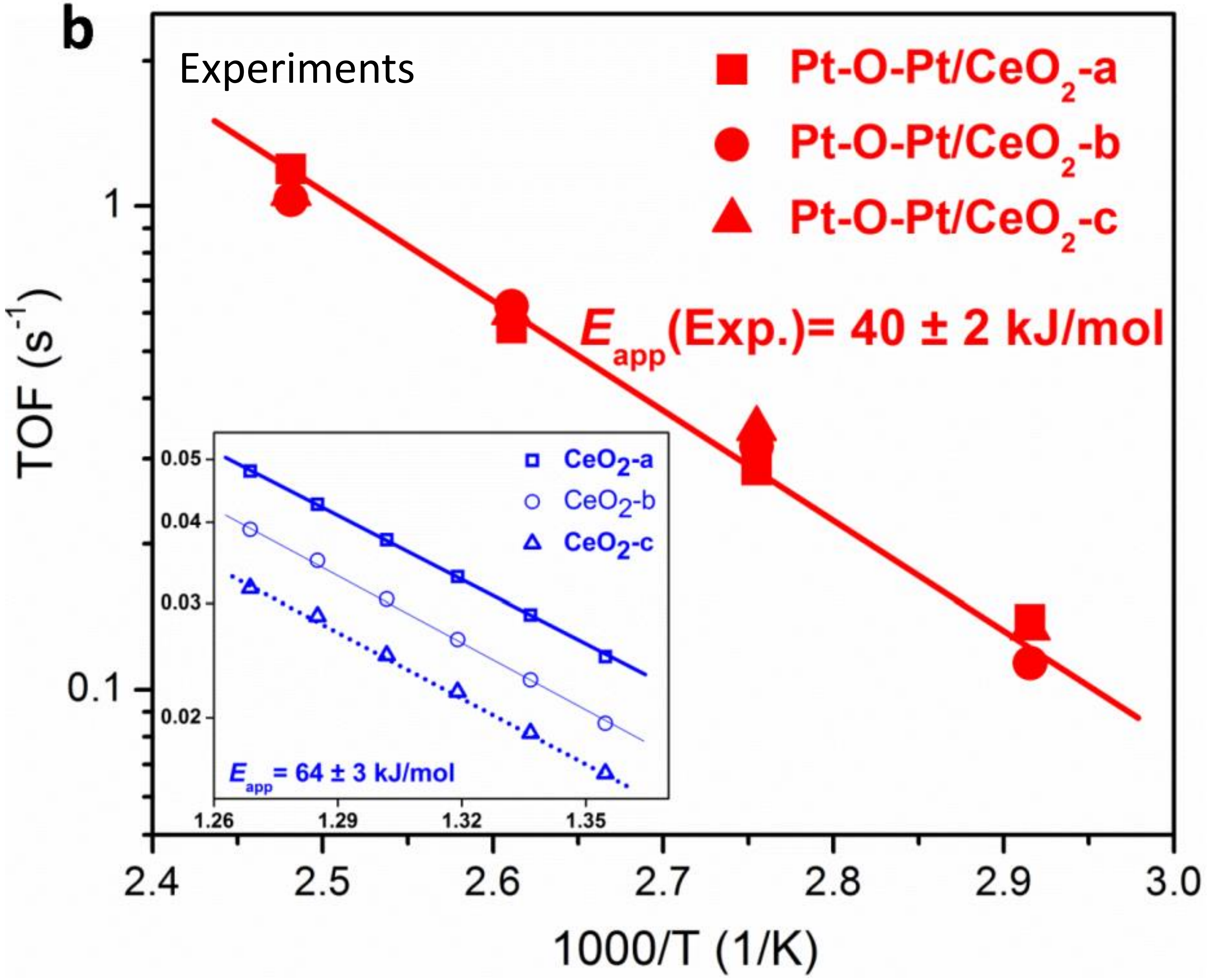
Pt_8O_{14}/CeO_2

(3) Microkinetic modeling of hypothesized mechanisms and comparison with experimental measurements



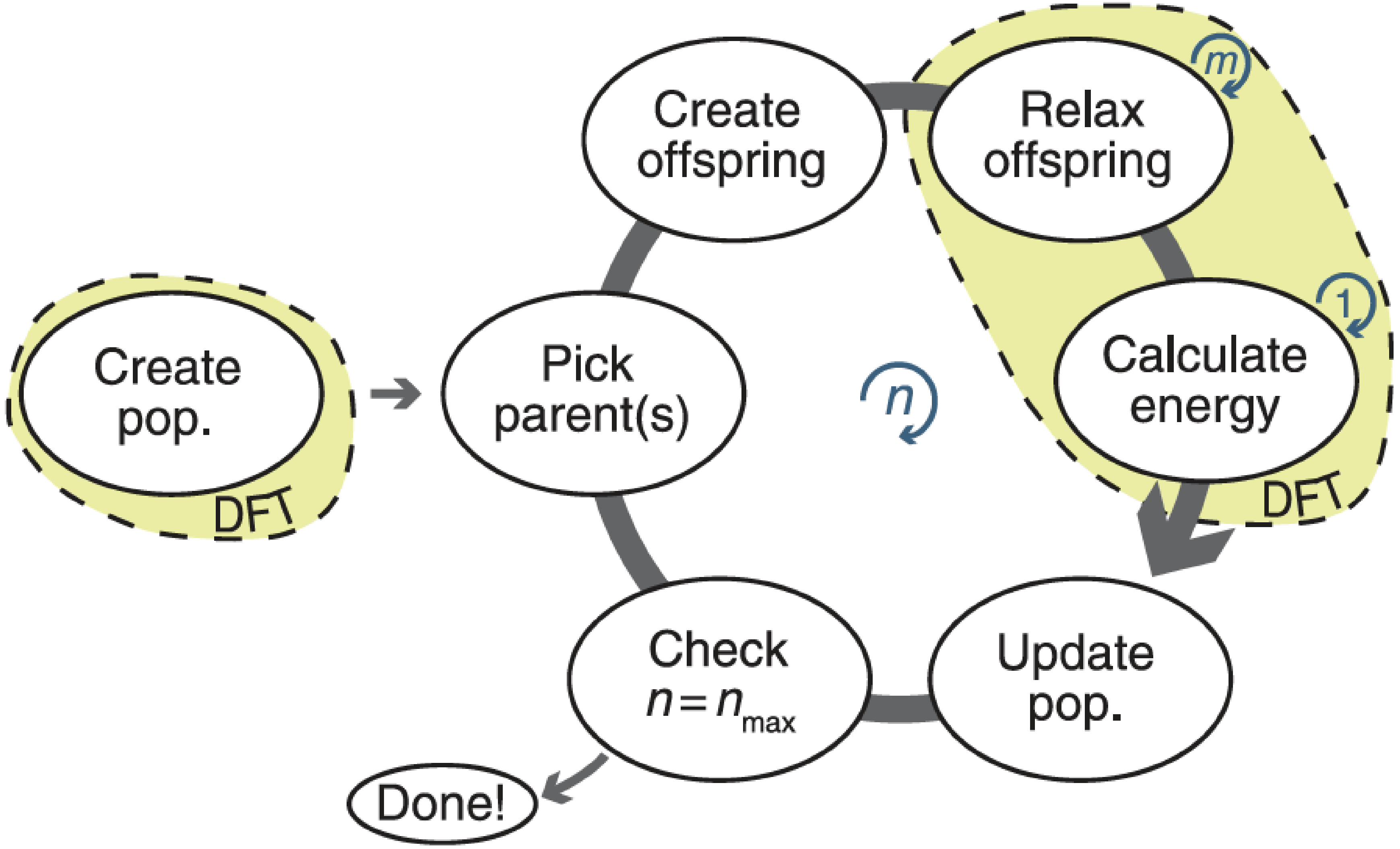
Impact of the ceria support is minimal in this temperature range, compared to the cluster structure



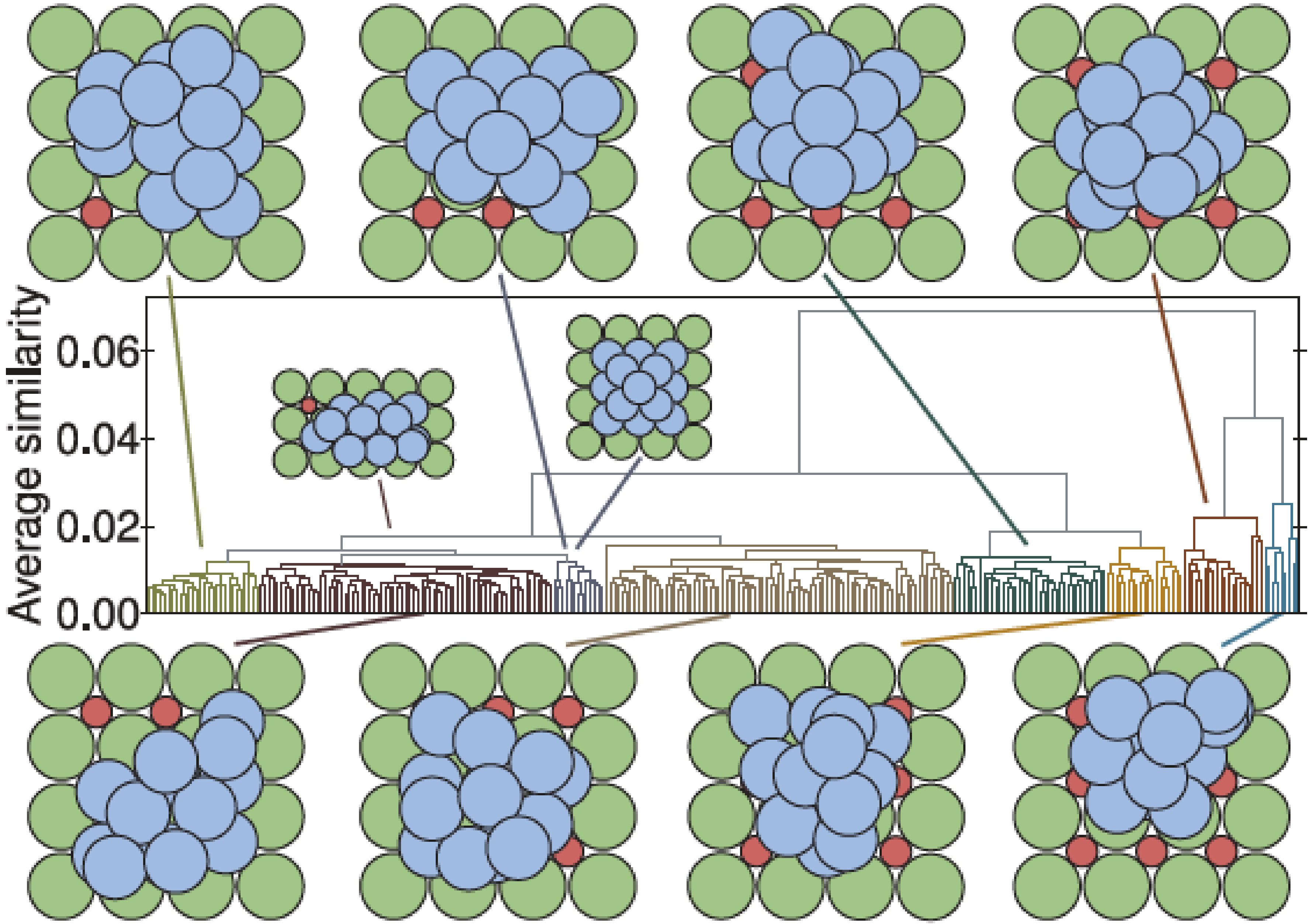


Cluster structure optimization using a genetic algorithm (GA)

Standard GA workflow[1-2]

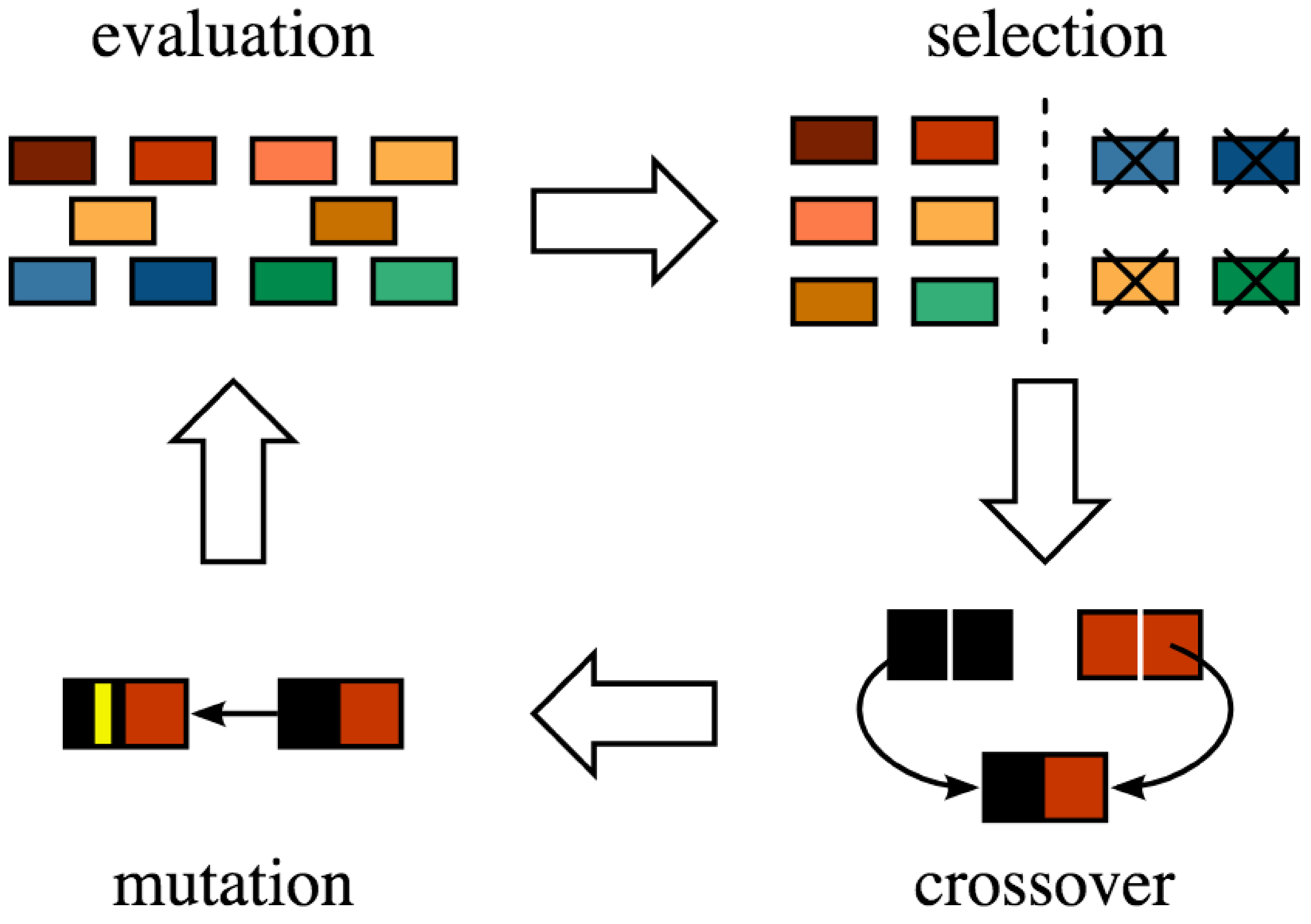


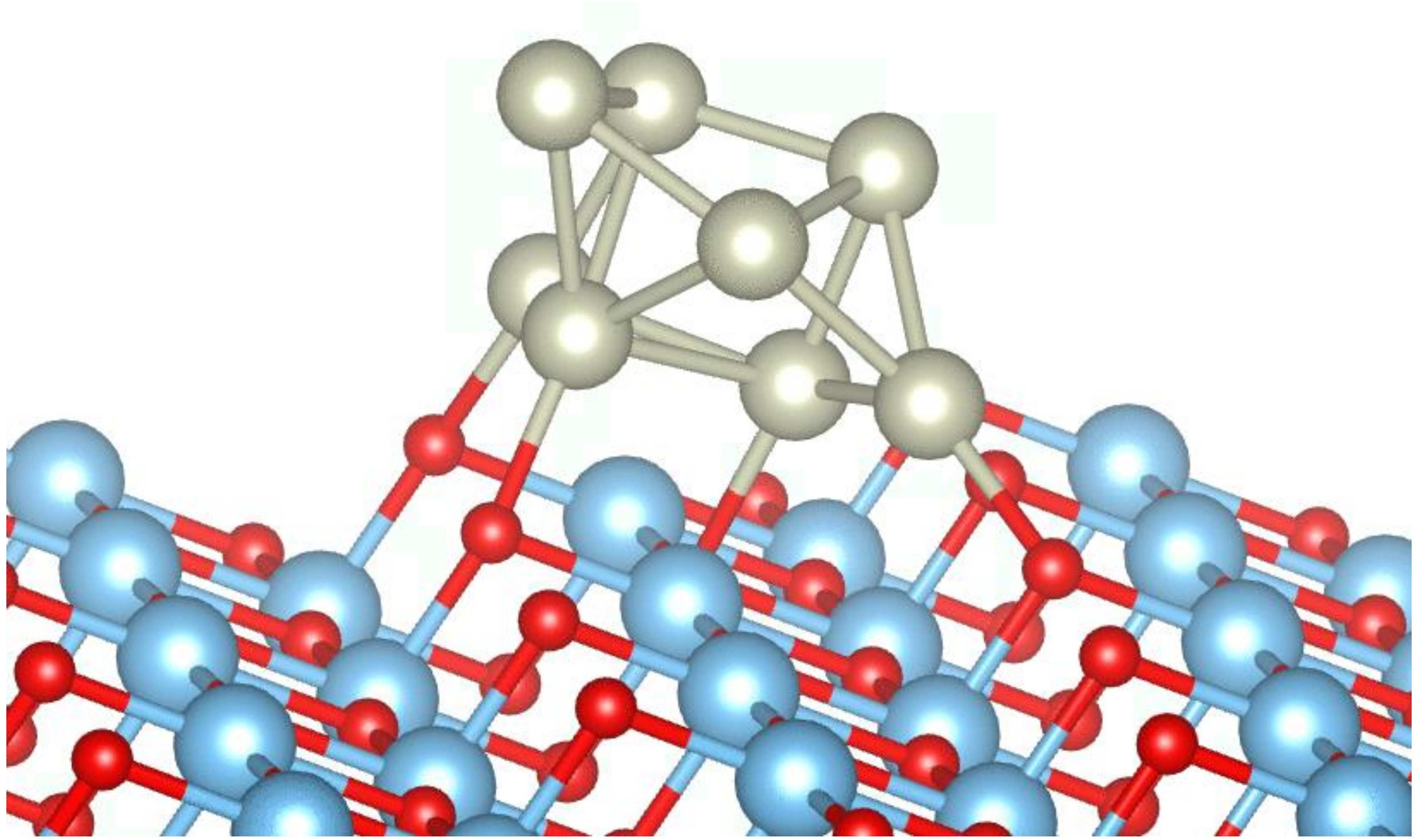
Example[1]: Pt_{13}/MgO



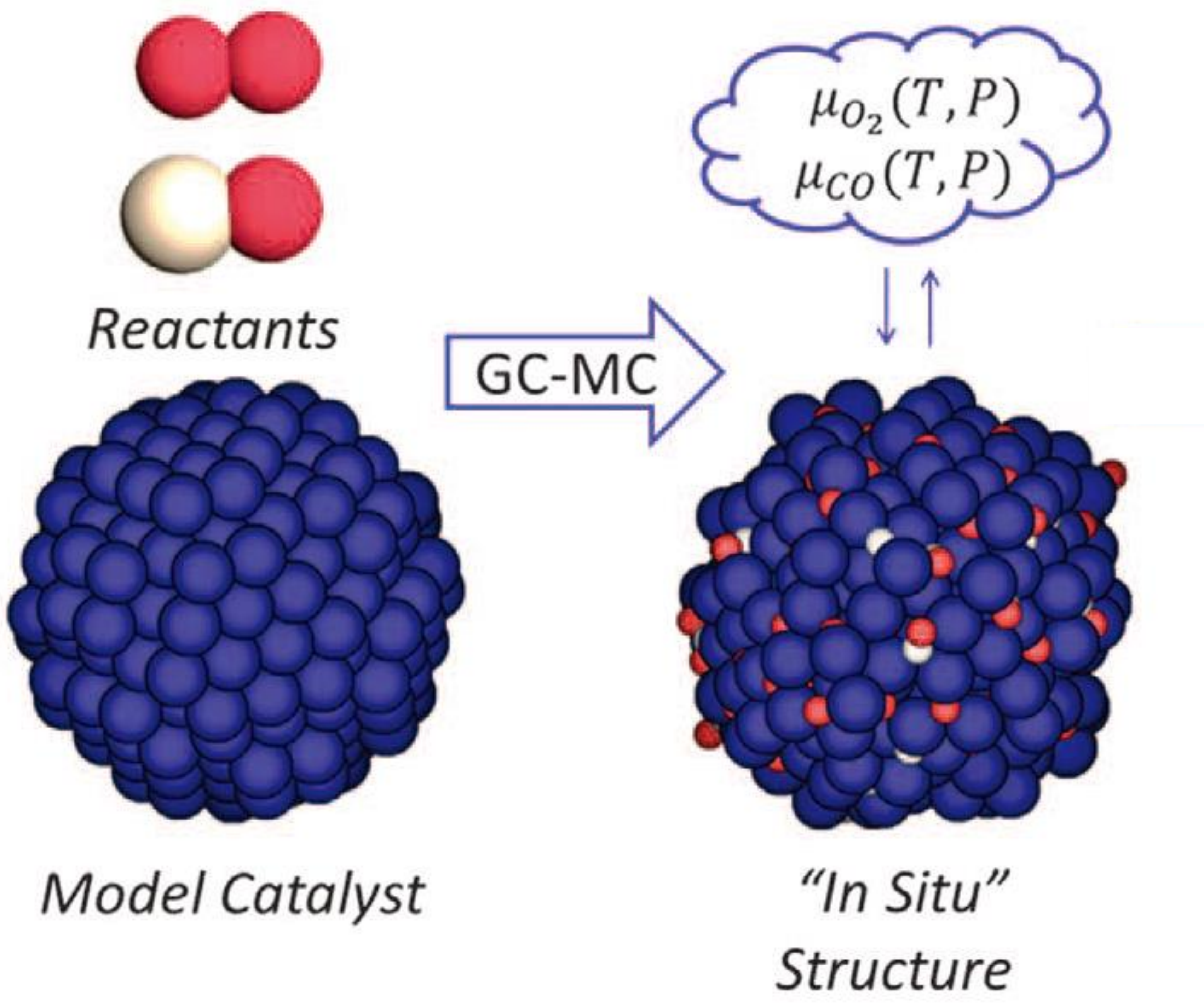
[1] E. L. Kolsbjerg, A. A. Peterson, B. Hammer. *Phys. Rev. B* 97 (2018)
[2] D. M. Deaven and K.-M. Ho. *Phys. Rev. Lett.* 75 (1995)

Example of the genetic algorithm applied to Rh_8/TiO_2





Grand Canonical Monte Carlo (GCMC) to model structure of nanoclusters under reaction conditions



For grand canonical ensemble:

$\mu_{gas}(P,T)$ = *Constant*

Monte Carlo moves

- Addition of reactants
- Deletion of reactants
- Movement of reactants
- Metal atom migration

[1] A. C. T. van Duin *et al. NPJ. Comput. Mater.* 2 (2016)
[2] T. P. Senftle, R. J. Meyer, M. J. Janik, A. C. T. Van Duin, *J. Chem. Phys.* 139 (2013)
[3] Frenkel D, Smit B. Understanding molecular simulation: from algorithms to applications. Academic Press; (2002)