Atomistic Modeling of Plasma-Assisted Catalysis: Opportunities and Challenges

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DOE Center Plasma Interactions with Complex Interfaces
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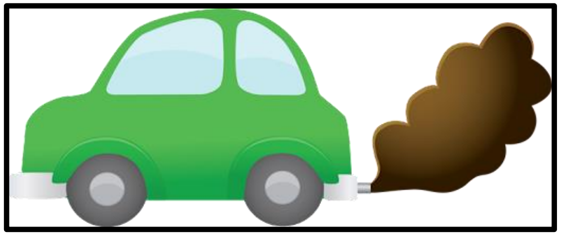
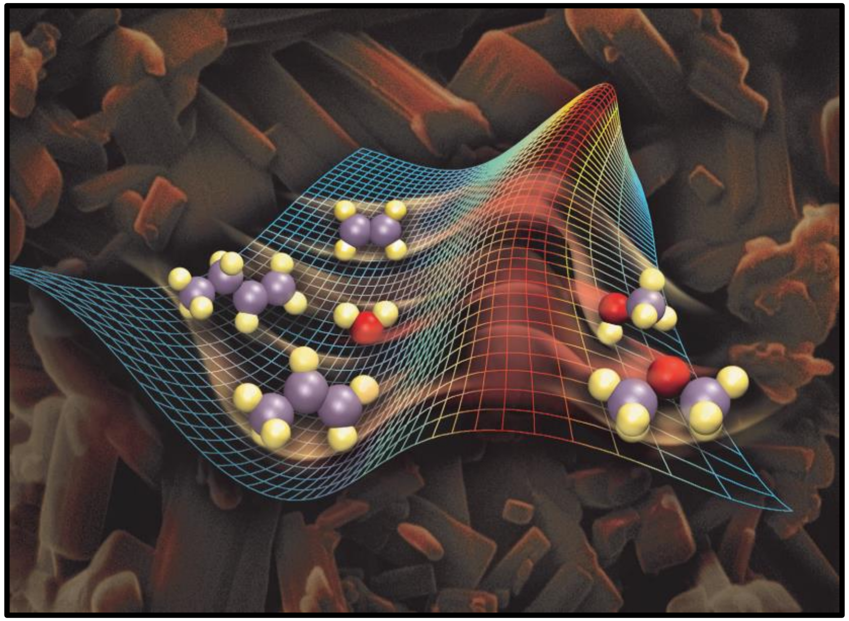
CATALYSIS IS AN ENABLING TECHNOLOGY

- **Catalysis is used in most chemical and energy conversion processes**



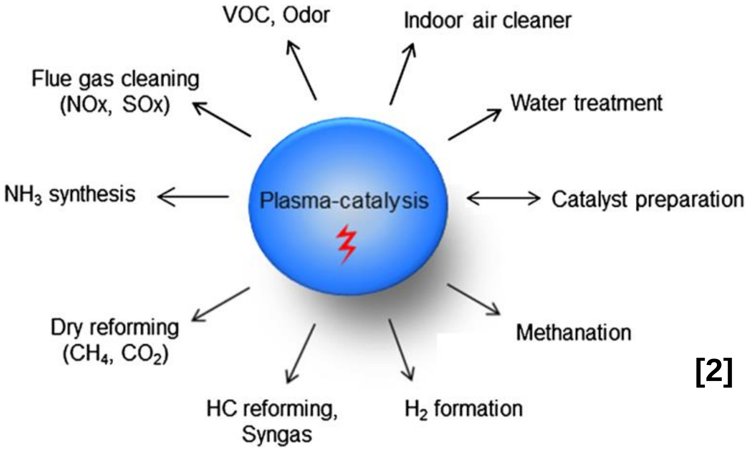


- **Reacting molecules (at left) acquire energy to climb the energy barrier and convert into product molecules (at right).[1]**

[1] Basic Research Needs for Catalysis Science, Department of Energy (2017).

WHY PLASMA CATALYSIS?

- **Possibility of low-temperature operation and improved activity and selectivity makes nonthermal plasmas an exciting complement to thermocatalytic processes.**



[2]

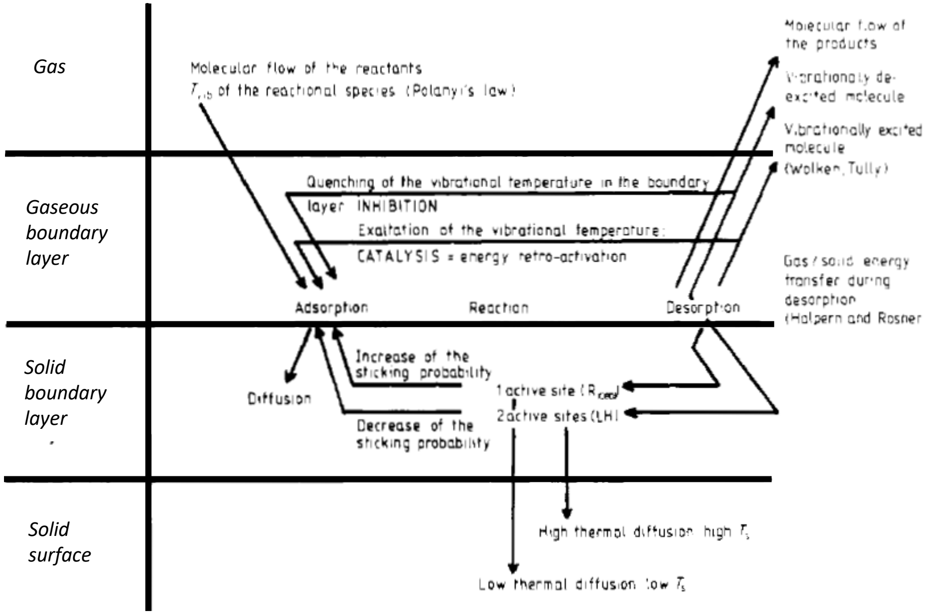
- ***1986*: An early report of the synergistic effects of the interaction of plasma and catalyst.[1] Low-temperature plasma with a WO_3 surface for $N_2 + O_2 \rightleftharpoons 2NO$ and $2NH_3 \rightleftharpoons N_2 + 3H_2$.**
- ***Plasma Roadmaps and recent reviews*:[3-5] (1) Need to identify the interactions taking place between plasmas and catalysts & (2) Complex mechanism of plasma catalysis is far from understood.**

→ Computational catalysis can help!

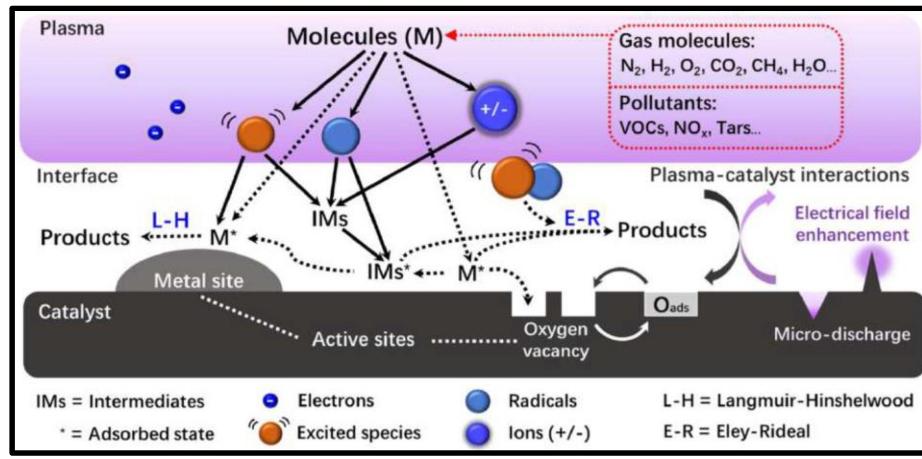
[1] C. Gicquel C *et al., J. Phys. D: Appl. Phys.* 19 (1986).
[2] H. Kim *et al., Plasma Chem. Plasma Process* 36 (2016).
[3] S. Samukawa *et al., J. Phys. D Appl. Phys.* 45 (2012). [2012 Plasma Roadmap]
[4] S. Zhang and G. Oehrlein, *J. Phys. D: Appl. Phys.* 54 (2021).
[5] A. Bogaerts *et al., J. Phys. D Appl. Phys.* 53 (2020). [2020 Plasma Catalysis Roadmap]

ATOMISTIC MODELING CAN AID UNDERSTANDING OF PLASMA-ASSISTED CATALYSIS

- **Atomic scale modeling provides microscopic insights at a level of detail that may be inaccessible to experiments.**



- **Possible reactional mechanisms during plasma catalysis.[1]**

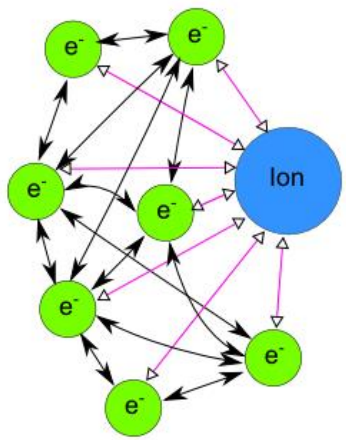


- **Schematic representation of several factors active in plasma catalysis.[2]**

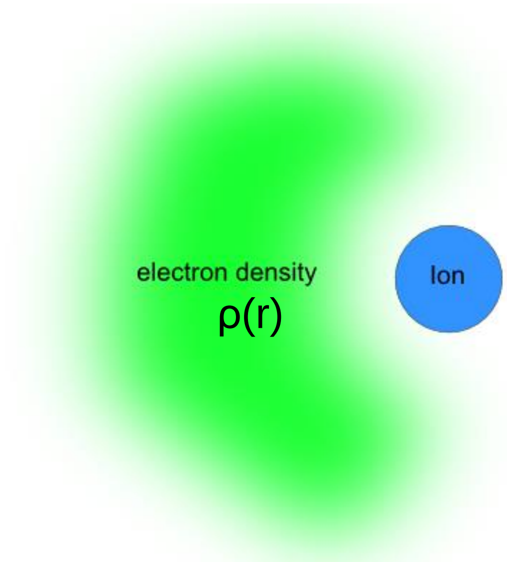
[1] C. Gicquel C *et al., J. Phys. D: Appl. Phys.* 19 (1986).
[2] A. Bogaerts *et al., J. Phys. D Appl. Phys.* 53 (2020).

DENSITY FUNCTIONAL THEORY (DFT) HAS GREATLY ENABLED COMPUTATIONAL CATALYSIS

Many body Perspective

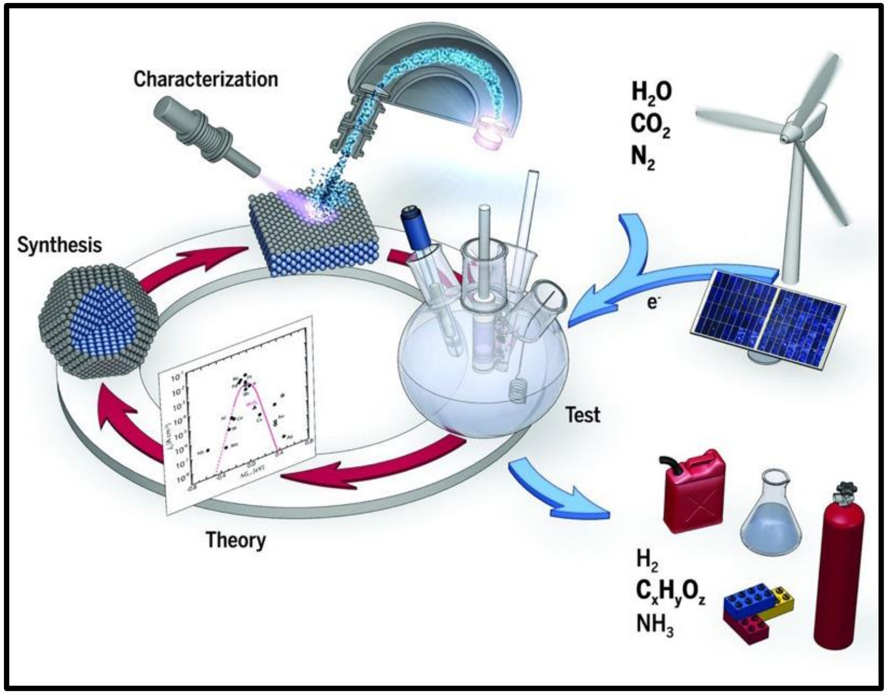


DFT Perspective

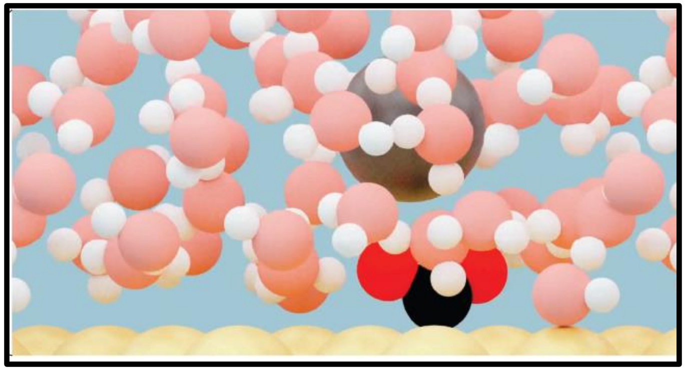


[1] W. Kohn, *Rev. Mod. Phys.* 71 (1999).

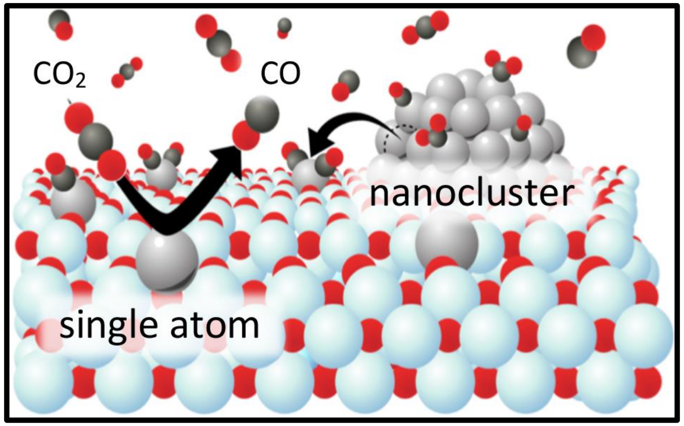
DFT MODELING IS WIDELY USED TO UNDERSTAND AND PREDICT CATALYSTS



- **Combining theory and experiment in electrocatalysis for catalyst discovery.[1]**



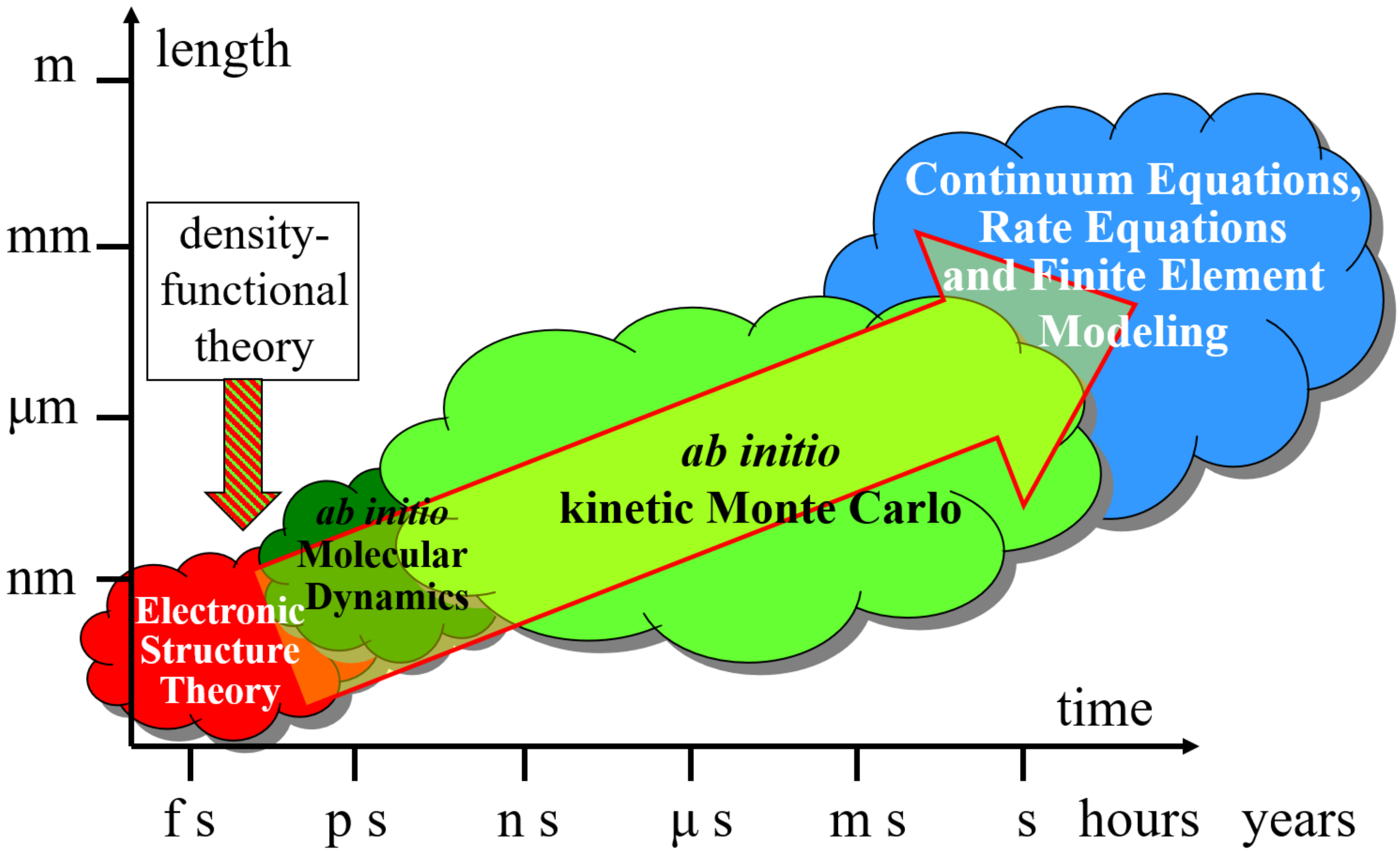
- **Cations play an essential role in CO_2 reduction.[2]**



- **Single metal atoms and nanoclusters often show different selectivity for CO_2 conversion.[3]**

[1] Z. W. Seh *et al., Science* 355 (2017).
[2] L. D. Chen, *Nature Catal.* 4 (2021).
[3] F. Doherty *et al.*, *Catal. Sci. Tech.* 10 5772 (2020).

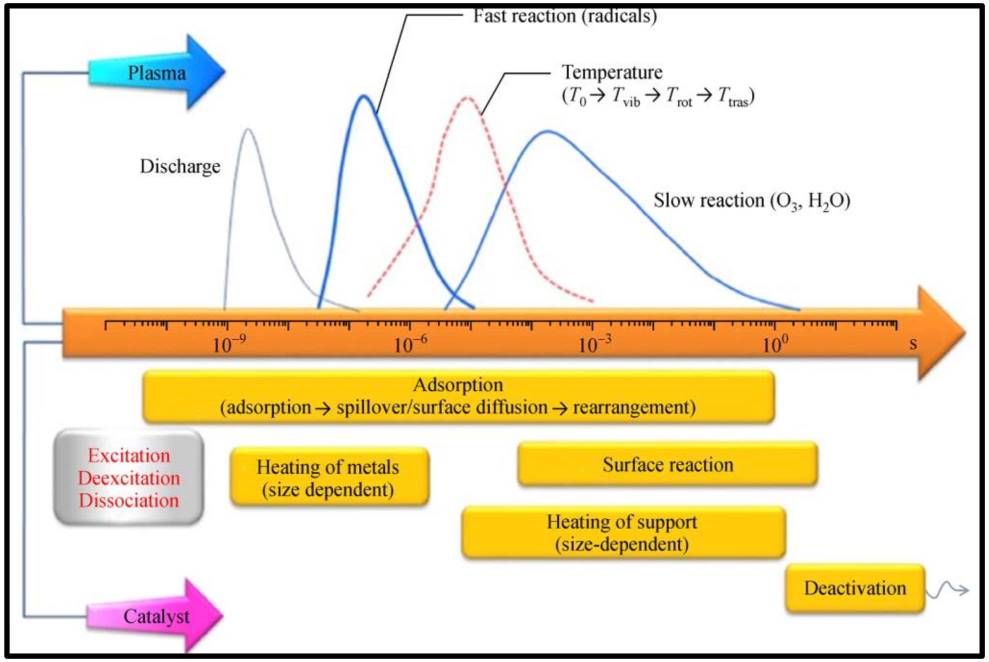
MULTI-SCALE APPROACH FOR MODELING CATALYSTS



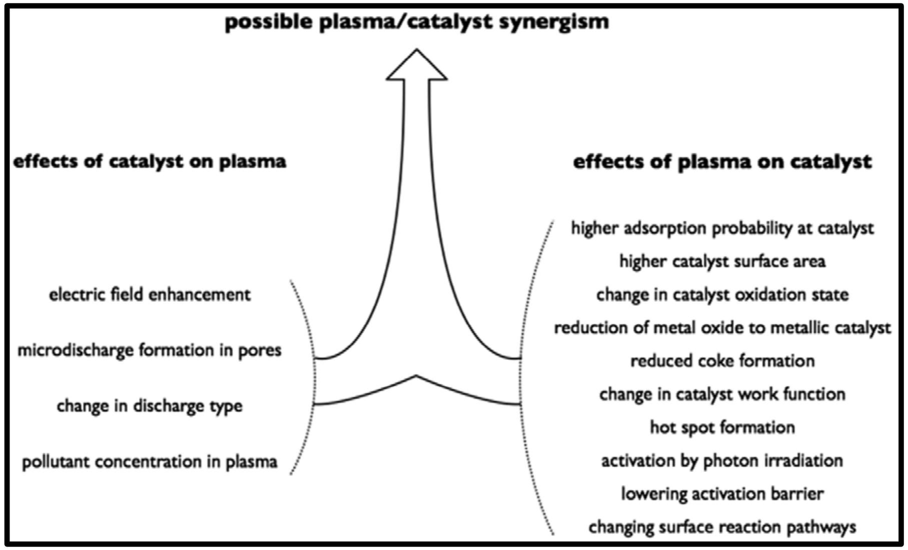
- Image courtesy of K. Reuter, K. Fichthorn, and M. Scheffler

CHALLENGES FOR MODELING PLASMA CATALYSIS

1) Addressing the discrepancy in accessible time and length scales with respect to experiment.[1]



2) Treating all the plasma-specific factors.[2]

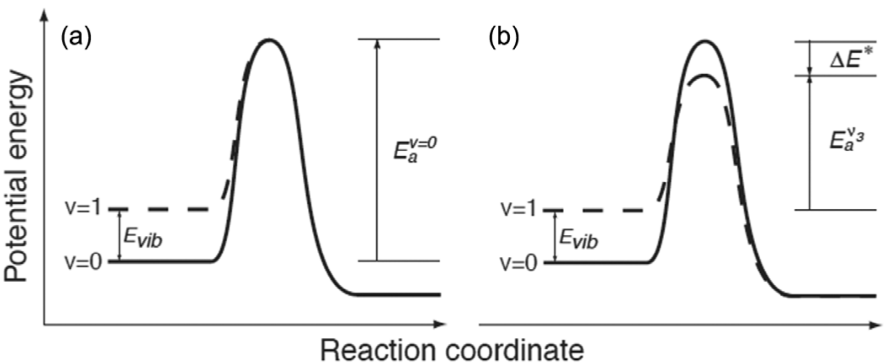


[1] H. Kim *et al., Plasma Chem. Plasma Process.*, 36 (2016).
[2] E. Neyts and A. Bogaerts, *J. Phys. D Appl. Phys.* 47 (2014).

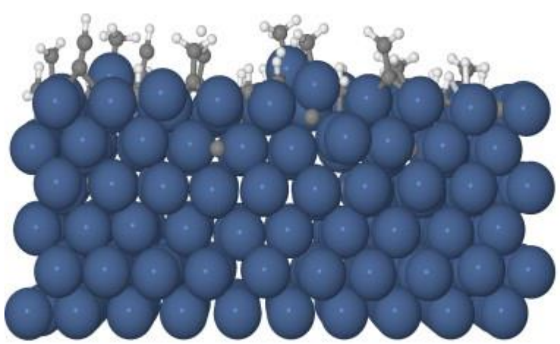
APPLICATIONS OF ATOMISTIC MODELING IN PLASMA CATALYSIS

- **Number of models specifically designed for plasma catalysis and focusing on the combination of both plasma effects and surface effects is limited.**

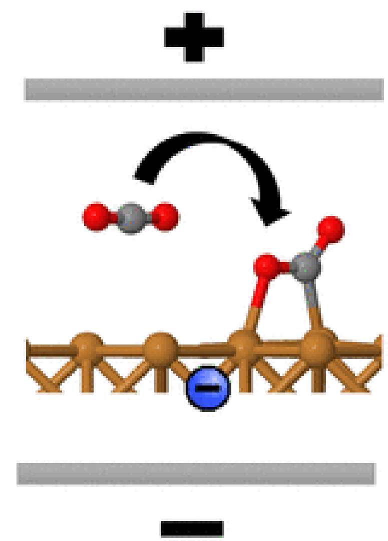
- **Impact of Vibrational Excitations[1-2]**



- **Interaction of Plasma-generated Radicals with Metal Surface[3]**



- **Surface Charging[4]**



[1] R. Smith *et al., Science* 304 (2004).
[2] H. Ma *et al., J. Phys. D Appl. Phys.* 54 (2021).
[3] W. Somers, *Appl. Catal. B: Environ.* 154 (2014).
[4] A. Jafarzadeh *et al., J. Phys. Chem. C* 124 (2020).

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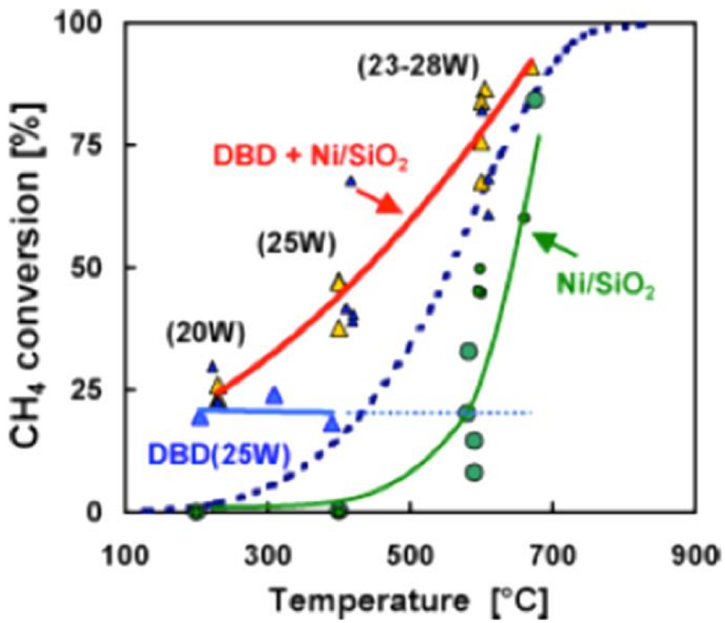
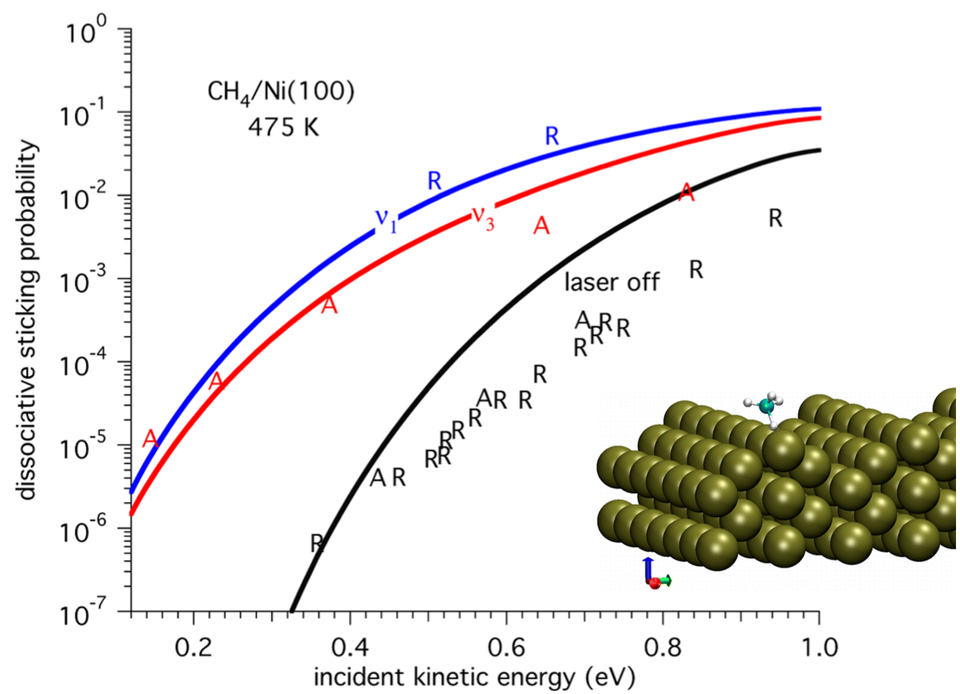
VIBRATIONAL EXCITATIONS IN PLASMA-ASSISTED STEAM METHANE REFORMING



- Synergistic effect for plasma-catalytic CH_4 steam reforming on Ni/SiO_2.[1]

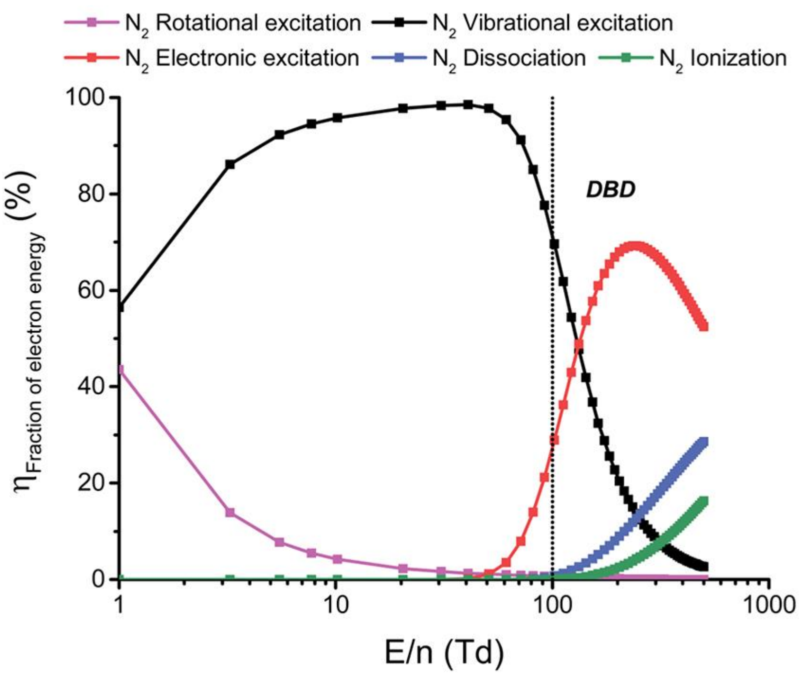
[1] T. Nozaki *et al., Catal. Today* 89, 57 (2004).
[2] T. Nozaki *et al., Catal. Today* 89, 67 (2004).
[3] T. Nozaki, K. Okazaki, *Catal. Today* 211 (2013).
[4] S. Nave *et al., J. Phys. Chem. A* 118 (2014).

- Attributed to vibrationally excited CH_4 molecules reacting on Ni surface (symmetric stretch v_1).[1-4]



- Dissociative sticking probability vs translational energy for CH_4 on Ni(100). CH_4 is initially in the ground (black), $1v_3$ (red), or $1v_1$ (blue) vibrational state. Symbols are experimental data from the groups of Utz (A) and Beck (R).[4]

VIBRATIONAL EXCITATIONS IN PLASMA-ASSISTED AMMONIA SYNTHESIS

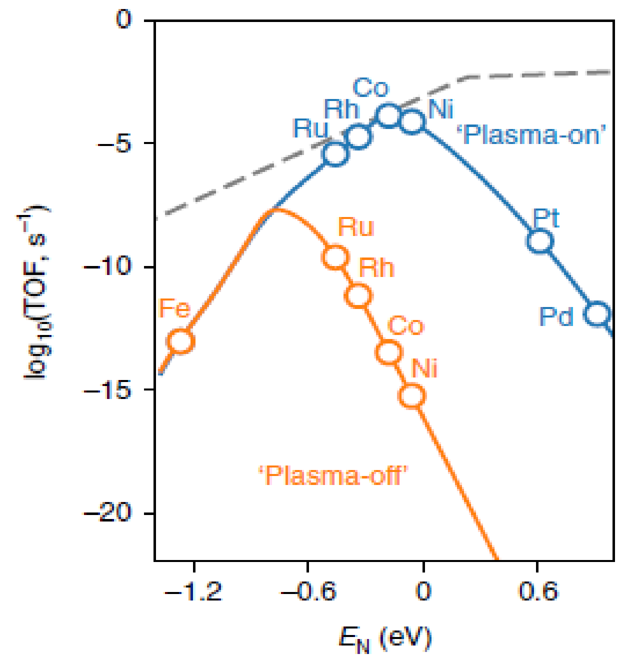


- Electron energy loss channels in N_2 plasma.[1]

- Postulated that plasma helps to dissociate N_2 via vibrational excitations and produces H* radicals.

- No general agreement on the relative importance of any particular activation channel.

- **Used DFT modeling + microkinetic model. Modified the N_2 dissociation rate to be an explicit function of N_2 vibrational state.[2]**

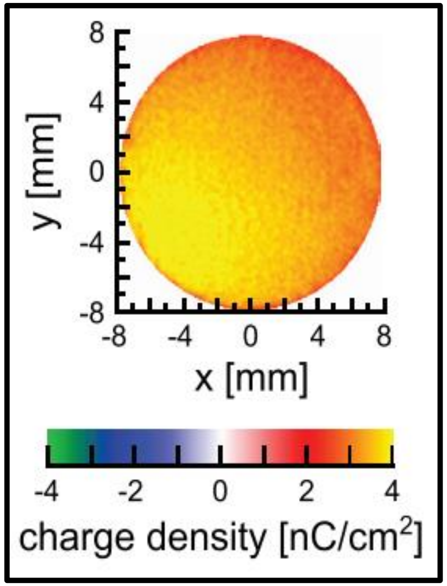


- ***Not optimal to simply use the best thermal catalyst in plasma catalysis.***

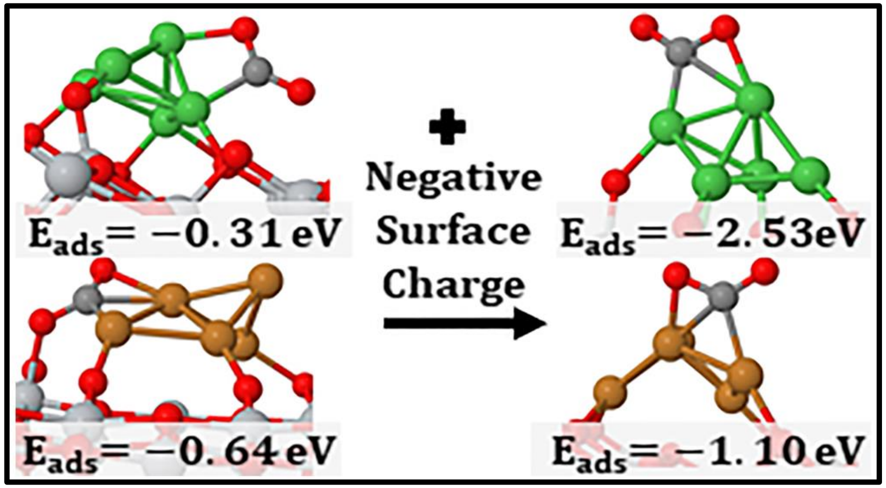
[1] P. Mehta *et al., ACS Energy Lett.* 4 (2019).
[2] P. Mehta *et al., Nat. Catal.* 1 (2018).

ROLE OF PLASMA-INDUCED SURFACE CHARGING ON CO_2 CONVERSION

- **Plasma-assisted catalysis powered by renewable energy has promise for CO_2 conversion.**
- **Surfaces exposed to a gas discharge accumulate a negative charge.**
- **How plasma modifies the catalyst through *surface charging* is not well-understood.**



- **Plasma-induced surface charge accumulating on borosilicate glass.[1]**



- **CO_2 Activation on Cu_5 and Ni_5 Nanoclusters on TiO_2: Effect of Plasma-Induced Surface Charging.[2-3]**

[1] R. Tschiersch *et al., J. Phys. D: Appl. Phys.* 50 (2017).
[2] K. Bal *et al.*, *Plasma Sources Sci. Technol.* 27 (2018).
[3] A. Jafarzadeh *et al.*, *J. Phys. Chem. C* 123 (2019).

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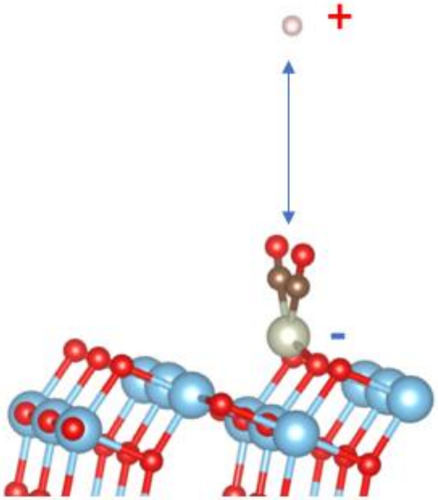
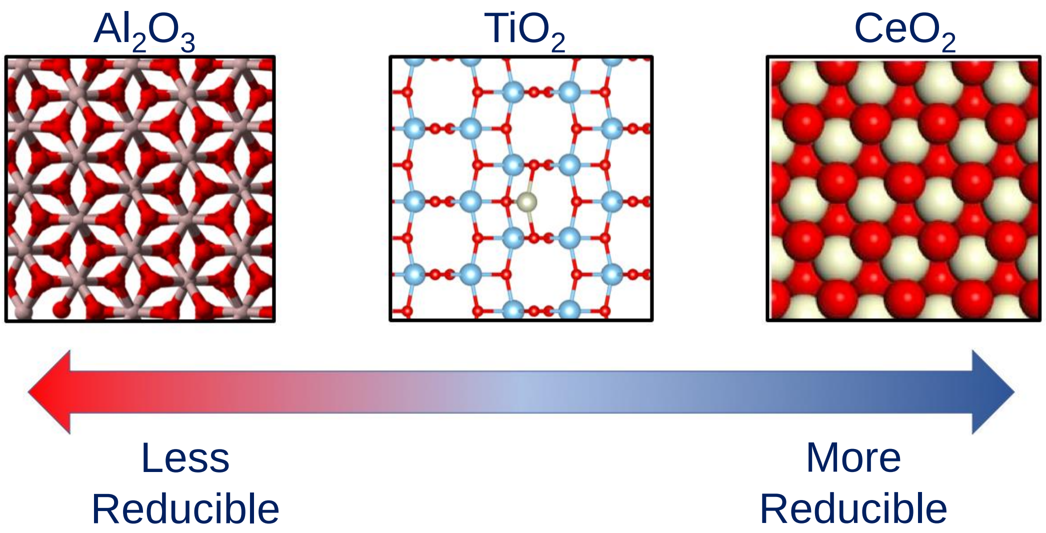
UNDERSTAND SURFACE CHARGING FOR CO_2 REDUCTION ON SINGLE ATOM CATALYSTS

1. How does charging impact the catalytic properties of different transition metal single atoms?
2. How does the support material alter the localization of the extra imparted charge?
3. Does surface charge alter the reaction mechanism of CO_2 reduction on a single-atom catalyst?

Frank Doherty
(PhD student)





- ***Surface Charging Methodology:***

K. Bal *et al. Plasma Sources Sci. Technol.* 27 (2018)

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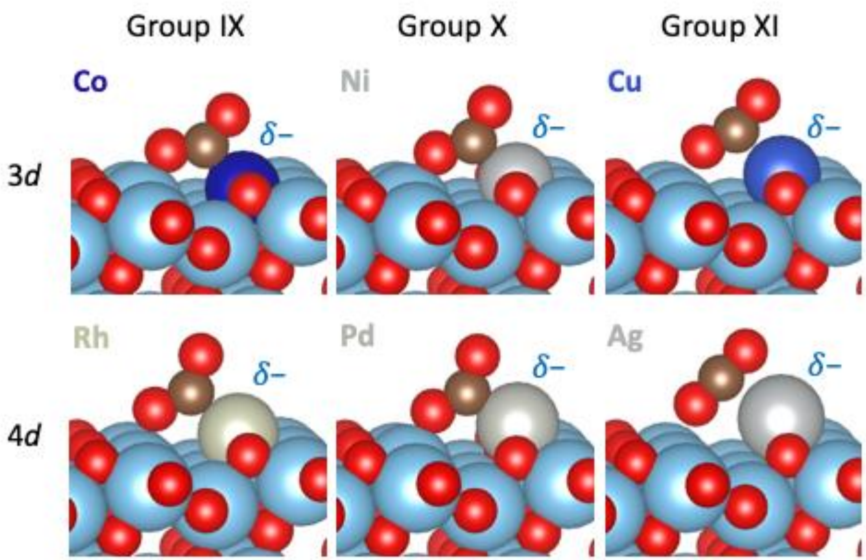
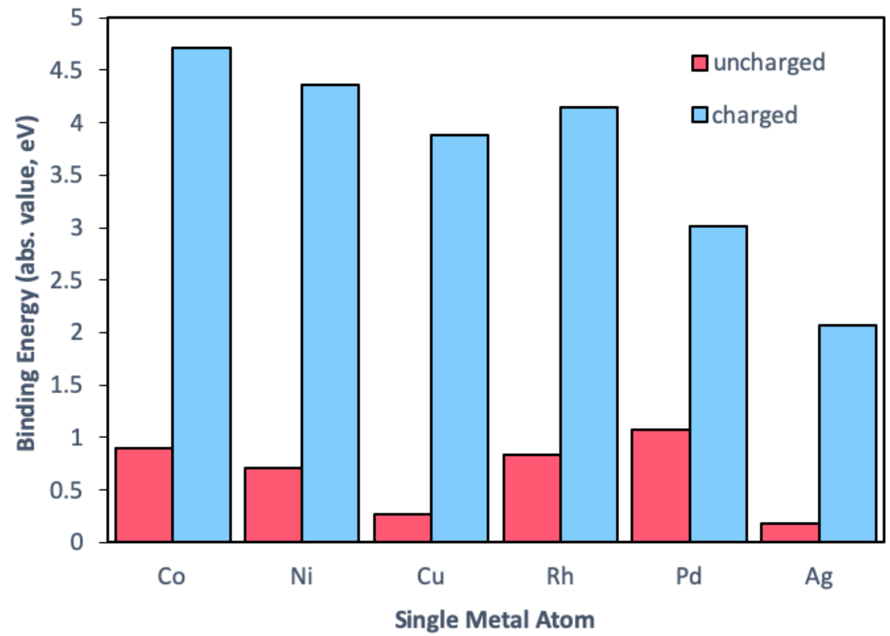
SURFACE CHARGING ON CO_2 ADSORPTION

- CO_2 adsorption strength studied across six transition metals.

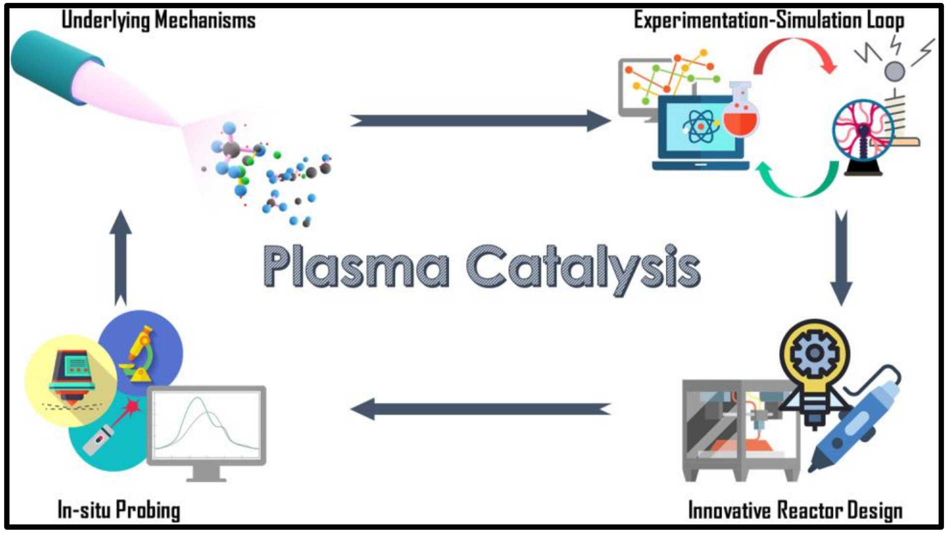


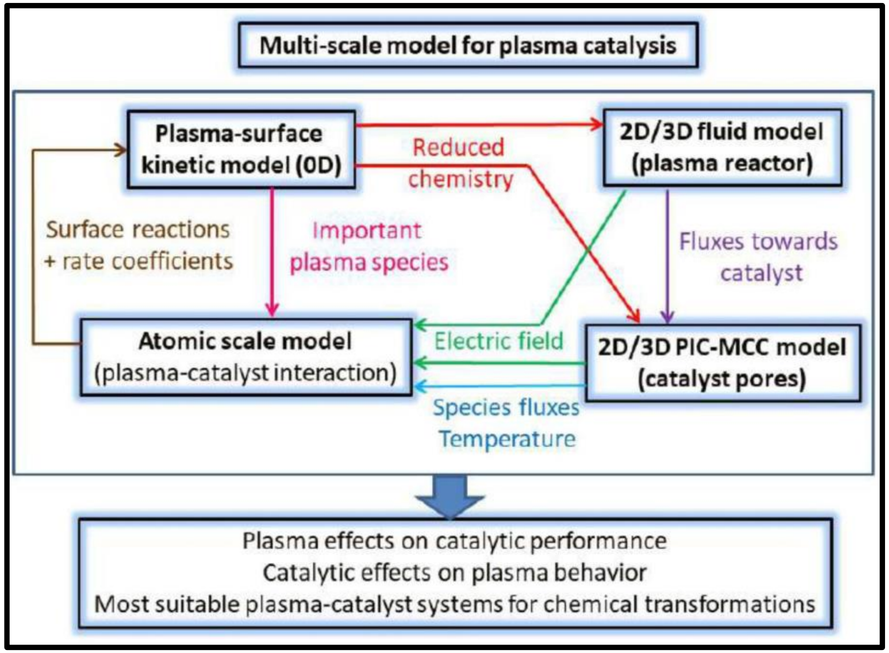


- Stronger CO bond on charged surface may change the preferred mechanism.
- Cu and Ag typically act as noble metals but show comparable binding to other metals once charged.
- Greater adsorption of molecular species in plasma systems compared to thermocatalytic has been observed, which may partially be due to surface charging.

OPPORTUNITIES FOR ATOMISTIC MODELING

- **Bringing specific plasma factors into the atomistic simulations.**
  - **Treating radicals and electronically excited states of molecules.**
  - **Treat vibrationally excited states of species interacting with surface.**
  - **Include electric field effects.**
- **Combine atomistic modeling with mesoscale and macroscale plasma models.[1]**
- **Experiments which enable a 1-to-1 comparison with simulations.**
- **Aid rational design of catalysts tailored to plasma environment.**





[1] A. Bogaerts *et al., J. Phys. D Appl. Phys.* 53 (2020). [2020 Plasma Catalysis Roadmap]

ACKNOWLEDGEMENTS

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Frank Doherty (UofM)

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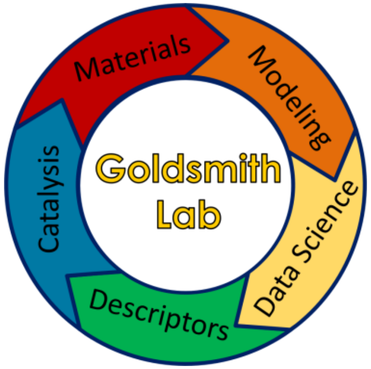

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Yudong Li (U. Maryland)

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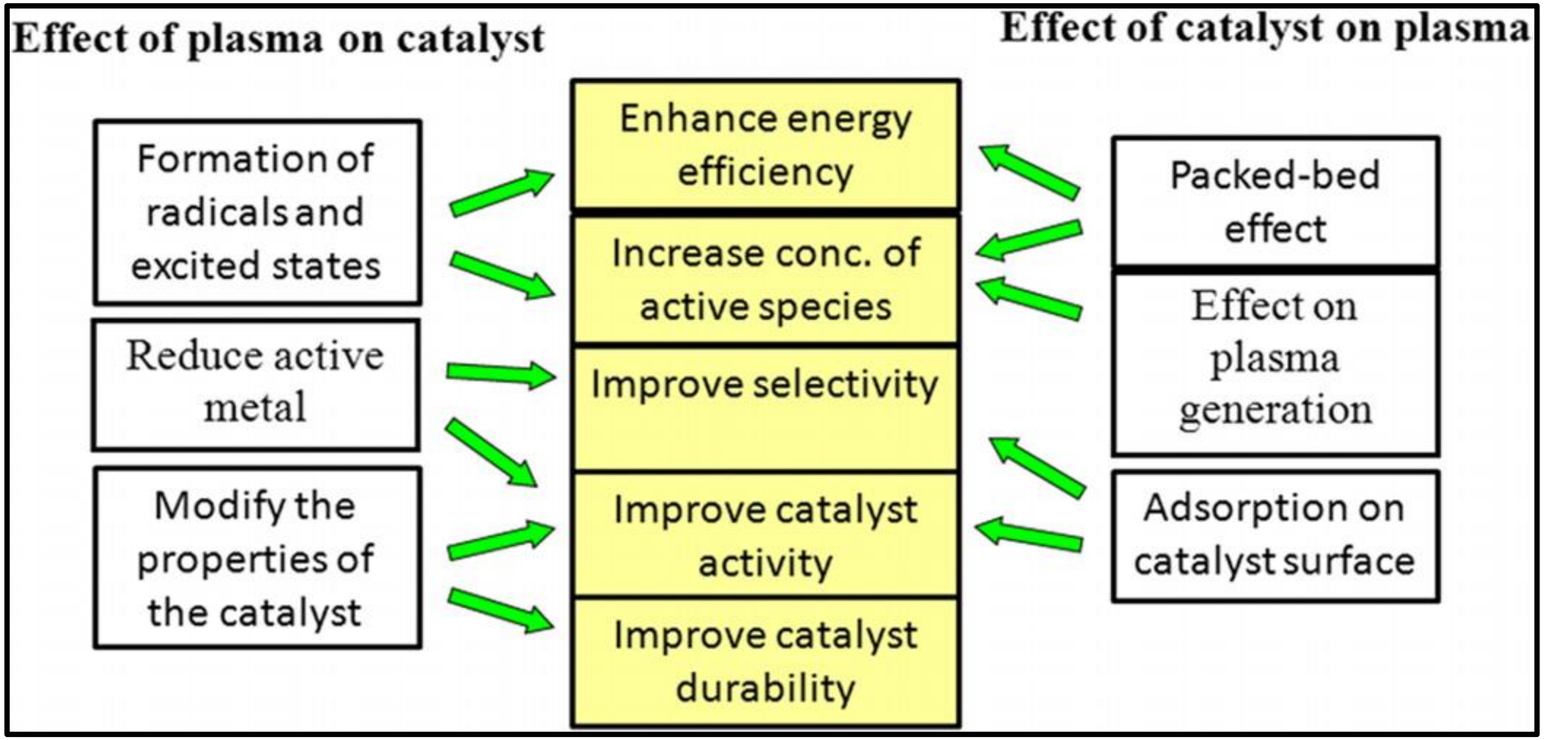
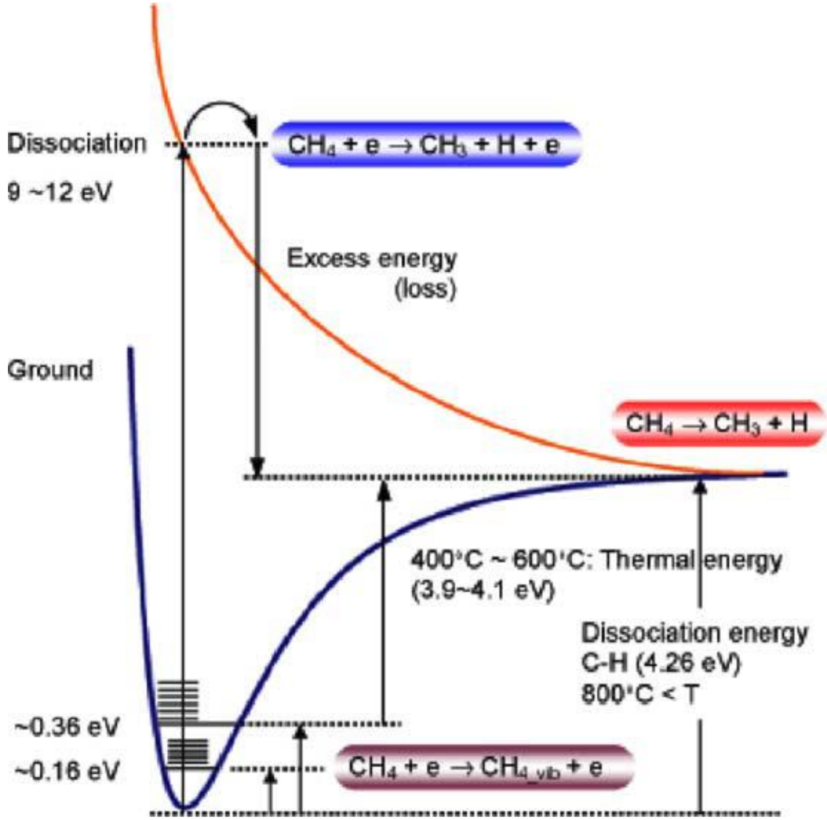
SUPPORTING INFORMATION



- **Schematic representation of the way in which plasma catalysis involves both effects of the plasma on the catalyst and the catalyst on the plasma.[1]**

[1] S. Samukawa *et al., J. Phys. D Appl. Phys.* 45 (2012).

SUPPORTING INFORMATION

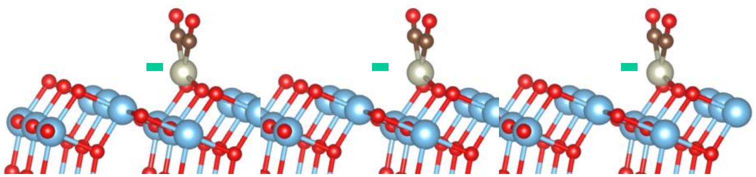


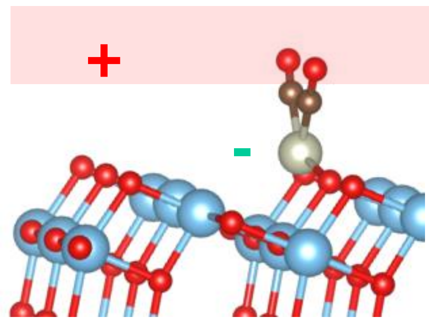
- **Methane activation by thermal energy, electron impact, and their combined effect.[1]**

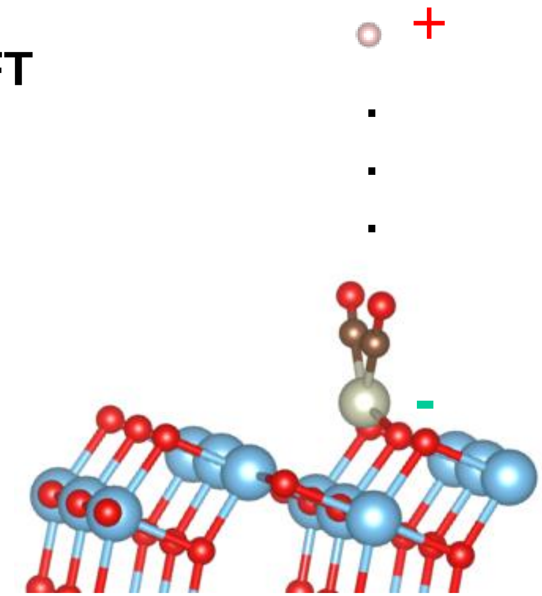
[1] T. Nozaki *et al., Catal. Today* 89, 57 (2004).
[2] T. Nozaki *et al., Catal. Today* 89, 67 (2004).
[3] T. Nozaki and K. Okazaki, *Catal. Today* 211 (2013).
[4] S. Nave *et al., J. Phys. Chem. A* 118 (2014).

SUPPORTING INFORMATION

Treatment of Charged Surfaces in DFT







- **Modeling just the negative charge will cause problems for periodic systems.**
- **Repeated charges build up across the periodic boundaries and diverge.**

- **Traditional method of diffuse background charge not appropriate for heterogeneous surface.**
- **More appropriate for solvated ions surrounded by uniform distribution of counterions.**

- **Using a gas phase counterion (H^+) in the supercell fixes these issues and models the electric field present.**