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COMMUNICATION

The CatMath: an online predictive platform for thermal + electrocatalysis

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Abstract The catalytic volcano activity models are the quantified and visualized tools of the *Sabatier* principle for heterogeneous catalysis, which can depict the intrinsic activity optima and trends of a catalytic reaction as a function of the reaction descriptors, i.e., the bonding strengths of key reaction species. These models can be derived by microkinetic modeling and/or free energy changes in combination with the scaling relations among the reaction intermediates. Herein, we introduce the CatMath—an online platform for generating a variety of common and industrially important thermal + electrocatalysis. With the CatMath, users can request the volcano models for available reactions and analyze their materials of interests as potential catalysts. Besides, the CatMath provides the function of the online generation of Surface Pourbaix Diagram for surface state analysis under electrocatalytic conditions, which is an essential step before analyzing the activity of an electrocatalytic surface. All the model generation and analysis processes are realized by cloud computing via a user-friendly interface.

Keywords CatMath, catalysis, volcano activity plots, Surface Pourbaix Diagrams, online platform

1 Introduction

Catalysis is playing an irreplaceable role in developing a sustainable future [1]. Heterogeneous thermal catalysis currently serves as a critical facilitator in modern industrial processes, while electrocatalysis may play a prominent role in the future since it can be in principle powered by green electricity. Nevertheless, the understanding and design of a cost-effective catalyst represent a formidable challenge. The majority of successful catalyst discoveries have historically relied on a time- and resource-consuming trial-and-error process.

Back in the 1920s, the *Sabatier* principle was proposed, which revolutionized how scientists evaluated the performance of a catalyst [2]: A good heterogeneous catalyst should neither bind the adsorbate too strongly, nor too weakly, to reach the optimal activity (Fig. 1). In the 2000s, Jens K. Nørskov [3], a pioneer of modern catalysis theory development, successfully quantified and visualized the Sabatier principle by volcano activity models coupling the identified scaling relations and microkinetic modeling based upon density functional theory (DFT) calculations [4–6]. This type of models can depict the intrinsic activity optima and trends of a catalytic reaction as a function of the reaction descriptors, i.e., the bonding strengths of key reaction species, which can reduce the high-dimension catalytic problem into one- or two-dimension. Over the past two decades, tremendous follow-up works have corroborated that as long as it is judiciously derived (e.g., with rational computational methods and parameters, well-defined mechanism, and precise linear scaling relations), a catalytic volcano model can be precisely developed and can exhibit strong concordance with experimental measurements [7–16]. Therefore, when designing an active catalytic site, one can only provide the information about the bonding strength of the key adsorbate(s) over the site, and the model can predict the corresponding activity in the form of turnover frequency (TOF), $G_{\max}$ (i.e., the maximum free energy needs to be overcome along the favorable reaction pathway), current density, or overpotential [10,17,18]. This offers a substantial

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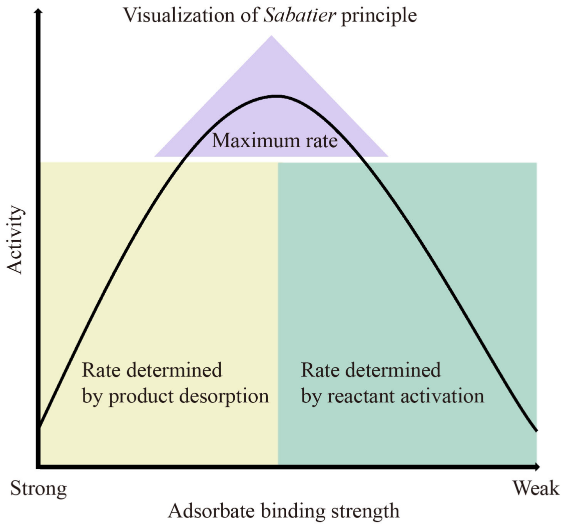

Fig. 1 Schematic illustration of the *Sabatier* principle for understanding heterogeneous catalysis.

advantage for researchers by obviating the need for a resource-intensive experimental trial-and-error process, thereby enabling a more streamlined approach to catalyst design [1].

Nonetheless, a significant challenge arises in that many of these volcano activity models are derived via a complicated process, which could be a hard task for beginners in catalysis theory research and experimentalists. Although there are some available packages for microkinetic modeling, e.g., the CatMap package [19], these tools often necessitate a degree of proficiency in programming languages (e.g., Python), thereby requiring users to undergo preliminary training prior to effective utilization. This significantly impedes the broad adoption of a systematic approach to catalyst design and understanding, in both pre- and post-experimental investigations.

Besides, because electrochemical conditions will induce water activation or generation (which would lead to the formation of HO*/O*/H* or anion vacancy on the surface), analyzing the electrochemistry-induced surface state (i.e., the coverage of an electrocatalyst under electrochemical conditions) is essential [20]. In an electrochemical environment, various phenomena may occur, including the poisoning of reactive sites, alterations in the surface's electronic structure, or the generation of new active sites. These transformations yield a mechanistic understanding that diverges significantly from the analysis of activity over a stoichiometric pristine surface. However, this is an often-dismissed process in electrocatalyst design and understanding. To provide a more precise understanding of an electrocatalyst, Surface Pourbaix Diagram analysis [21,22] is an important tool to theoretically probe the surface state under electrocatalytic conditions, before the analysis of the activity [14,23].

Motivated by the current stage, we developed a user-friendly online platform for volcano activity model development—the CatMath[1]—to provide the catalyst community with the predictive volcano activity models of industrially significant thermal + electrocatalysis and electrocatalytic Surface Pourbaix Diagrams. All the model generation processes are based on cloud computing, and thus users are not required to implement a special package for model generation. This online platform is dynamically updated by the Hao Li Laboratory (the Digital Catalysis Laboratory, DigCat), which currently contains the volcano activity models of six thermal catalysis (four 1D and three 2D volcano models), and eight electrocatalysis (seven 1D and five 2D volcano models). Specifically, the thermal catalysis contained in the current version of CatMath includes CO oxidation, ethylene epoxidation, nitrite reduction, Hg oxidation, and NO oxidation, while the available electrocatalysis includes hydrogen evolution, oxygen evolution, oxygen reduction, CO_2 reduction, water oxidation, and electrolytic propylene epoxidation. The scaling relations behind each model and the applied energy references of each binding energy can be found on the CatMath website. Details of the reaction models are listed in Table 1.

2 Results and discussion

The illustration of the main interface of CatMath in the current version is shown in Fig. 2. From the interface, users can use the "Surface Pourbaix Diagrams" module to generate a Surface Pourbaix Diagram based on their calculated energetic values (Fig. 2(a)). The "Catalytic Volcano Models" module can be used to access the available catalytic reactions included in the up-to-date version (Fig. 2(b)).

Some examples of the CatMath are also presented here as shown in Fig. 3. For the Surface Pourbaix Diagrams module, we used $ZnCr_2O_4$ as a typical example (Fig. 3(a)). In terms of the Catalytic Volcano Models, herein, we take the ethylene epoxidation and CO_2 reduction reaction (CO_2RR) as the examples of thermal catalysis and electrocatalysis, respectively (Figs. 3(b) and 3(c)). Users can use the built-in drop-down menu to choose the reaction, set the required and optional parameters (e.g., temperature, pressure, and applied potential), and submit requests to the cloud. After cloud computing, the volcano model can be generated (Figs. 3(b) and 3(c)), respectively for ethylene epoxidation and CO_2RR. Meanwhile, for those reactions involving significant selectivity competition, their selectivity plots can also be displayed. A video showing how the CatMath

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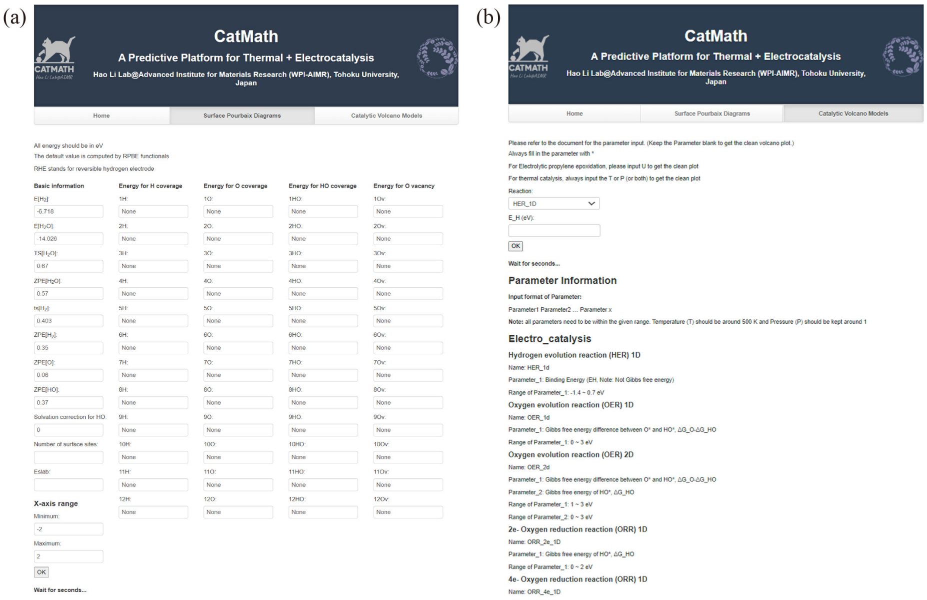
[1] The up-to-date URL of CatMath can be found in: doi.org/10.50974/0002000003

Table 1 Summary of the current available catalytic reactions in CatMath[a)]

Reaction name	Model type	Descriptor	Parameter
Electrocatalysis			
Hydrogen evolution reaction	1D	E_H	E_H
Oxygen evolution reaction	1D	$\Delta G_O - \Delta G_{HO}$	$\Delta G_O - \Delta G_{HO}$
	2D	$\Delta G_O - \Delta G_{HO}$, ΔG_{HO}	$\Delta G_O - \Delta G_{HO}$, ΔG_{HO}
Oxygen reduction reaction	$2e^-$, 1D	ΔG_{HO}	ΔG_{HO}
	$4e^-$, 1D	ΔG_{HO}	ΔG_{HO}
	2D	E_{HO}, E_{HOO}	E_{HO}, E_{HOO}
	2D	E_{HO}, E_{HO}	E_{HO}, E_{HO}
CO_2 reduction reaction	HCOOH, 2D	ΔG_{HCOOH}, ΔG_{OCHO}	ΔG_{HCOOH}, ΔG_{OCHO}
	CO, 2D	ΔG_{CO}, ΔG_{COOH}	ΔG_{CO}, ΔG_{COOH}
Water oxidation reaction	Thermal dynamic, 1D Kinetic, 1D	ΔG_{HO}	ΔG_{HO}
Electrolytic propylene epoxidation	1D	E_O	U (*), E_O
Thermal catalysis			
CO oxidation	2D	E_{CO}, E_O	T (*), E_{CO}, E_O
Ethylene epoxidation	Activity, 1D Selectivity, 1D	E_O	T (*), P (*), E_O
Nitrite reduction	NH_3, 2D	E_N, E_{NH_3}	E_N, E_{NH_3}
	N_2, 2D	E_N, E_{N_2}	E_N, E_{N_2}
Hg oxidation	1D	E_O	T (*), P (*), E_O
NO oxidation	1D	E_O	T (*), P (*), E_O

a) All energetics (E for binding energy and ΔG for Gibbs free energy) are in eV; the potential (U) is in V. The required parameters are marked by *.



(a)

All energy should be in eV

The default value is computed by RPBE functionals

RHE stands for reversible hydrogen electrode

Basic information	Energy for H coverage	Energy for O coverage	Energy for HO coverage	Energy for O vacancy
E[H_2]: -6.718	1H: None	1O: None	1HO: None	1Ov: None
E[H_2O]: -14.026	2H: None	2O: None	2HO: None	2Ov: None
TS[H_2O]: 0.67	3H: None	3O: None	3HO: None	3Ov: None
ZPE[H_2O]: 0.57	4H: None	4O: None	4HO: None	4Ov: None
ts[H_2]: 0.403	5H: None	5O: None	5HO: None	5Ov: None
ZPE[H_2]: 0.35	6H: None	6O: None	6HO: None	6Ov: None
ZPE[O]: 0.06	7H: None	7O: None	7HO: None	7Ov: None
ZPE[HO]: 0.37	8H: None	8O: None	8HO: None	8Ov: None
Solvation correction for HO: 0	9H: None	9O: None	9HO: None	9Ov: None
Number of surface sites:	10H: None	10O: None	10HO: None	10Ov: None
Eslab:	11H: None	11O: None	11HO: None	11Ov: None
	12H: None	12O: None	12HO: None	12Ov: None

X-axis range

Minimum: -2

Maximum: 2

Wait for seconds...

(b)

Please refer to the document for the parameter input. (Keep the Parameter blank to get the clean volcano plot.)

Always fill in the parameter with *

For Electrolytic propylene epoxidation, please input U to get the clean plot

For thermal catalysis, always input the T or P (or both) to get the clean plot

Reaction: HER_1D

E_H (eV):

Wait for seconds...

Parameter Information

Input format of Parameter:

Parameter1 Parameter2 ... Parameter x

Note: all parameters need to be within the given range. Temperature (T) should be around 500 K and Pressure (P) should be kept around 1

Electro_catalysis

Hydrogen evolution reaction (HER) 1D

Name: HER_1d

Parameter_1: Binding Energy (EH, Note: Not Gibbs free energy)

Range of Parameter_1: -1.4 ~ 0.7 eV

Oxygen evolution reaction (OER) 1D

Name: OER_1d

Parameter_1: Gibbs free energy difference between O* and HO*, ΔG_O-ΔG_HO

Range of Parameter_1: 0 ~ 3 eV

Oxygen evolution reaction (OER) 2D

Name: OER_2d

Parameter_1: Gibbs free energy difference between O* and HO*, ΔG_O-ΔG_HO

Parameter_2: Gibbs free energy of HO*, ΔG_HO

Range of Parameter_1: 1 ~ 3 eV

Range of Parameter_2: 0 ~ 3 eV

2e- Oxygen reduction reaction (ORR) 1D

Name: ORR_2e_1D

Parameter_1: Gibbs free energy of HO*, ΔG_HO

Range of Parameter_1: 0 ~ 2 eV

4e- Oxygen reduction reaction (ORR) 1D

Name: ORR_4e_1D

Fig. 2 The user interface of CatMath in the currently available version: (a) the Surface Pourbaix Diagrams module and (b) the Catalytic Volcano Models module.

works can be found in the Electronic Supplementary Material (video).

3 Conclusions

Herein, we have developed an online predictive platform through cloud computing, for analyzing thermal + electrocatalysis (namely, the CatMath). This platform is dynamically updated. We expect that this user-friendly tool can provide researchers with a convenient way to understand the reaction trend of a catalysis and make fast prediction on their materials of interest as a potential catalyst.

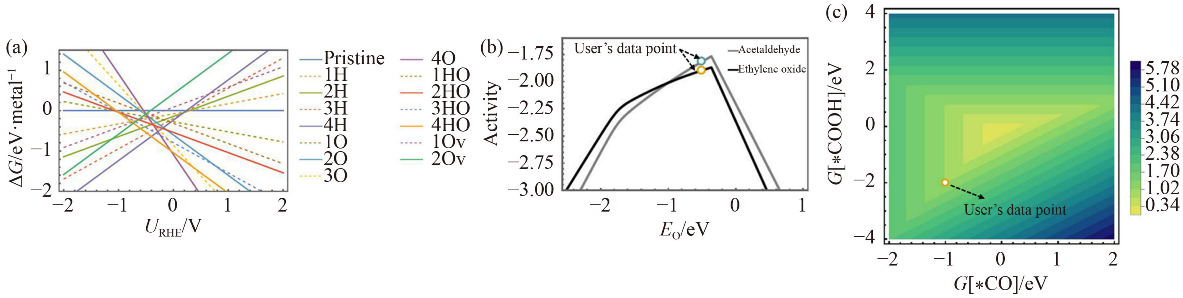


Fig. 3 Examples of the generated Surface Pourbaix Diagram for $ZnCr_2O_4$ (a) with a solvation correction value of −0.15 eV, volcano activity model for (b) thermal catalysis and (c) electrocatalysis. Note: The fonts on the images have been adjusted by the journal based on the publication requirement.

Competing interests The authors declare that they have no competing interests.

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References

1. Seh Z W, Kibsgaard J, Dickens C F, Chorkendorff I, Nørskov J K, Jaramillo T F. Combining theory and experiment in electrocatalysis: insights into materials design. Science, 2017, 355(6321): eaad4998
2. Medford A J, Vojvodic A, Hummelshøj J S, Voss J, Abild-Pedersen F, Studt F, Bligaard T, Nilsson A, Nørskov J K. From the *Sabatier* principle to a predictive theory of transition-metal heterogeneous catalysis. Journal of Catalysis, 2015, 328: 36–42
3. Medford A J, Moses P G, Jacobsen K W, Peterson A A. A career in catalysis: Jens Kehlet Nørskov. ACS Catalysis, 2022, 12(15): 9679–9689
4. Hammer B, Nørskov J K. Theoretical surface science and catalysis—calculations and concepts. Advances in Catalysis, 2000, 45: 71–129
5. Nørskov J K, Abild-Pedersen F, Studt F, Bligaard T. Density functional theory in surface chemistry and catalysis. Proceedings of the National Academy of Sciences of the United States of America, 2011, 108(3): 937–943
6. Jones G, Bligaard T, Abild-Pedersen F, Nørskov J K. Using scaling relations to understand trends in the catalytic activity of transition metals. Journal of Physics Condensed Matter, 2008, 20(6): 064239
7. Nørskov J K, Bligaard T, Logadottir A, Kitchin J R, Chen J G, Pandelov S, Stimming U. Trends in the exchange current for hydrogen evolution. Journal of the Electrochemical Society, 2005, 152(3): J23–J26
8. Nørskov J K, Rossmeisl J, Logadottir A, Lindqvist L, Kitchin J R, Bligaard T, Jónsson H. Origin of the overpotential for oxygen reduction at a fuel-cell cathode. Journal of Physical Chemistry B, 2004, 108(46): 17886–17892
9. Falsig H, Hvolbæk B, Kristensen I S, Jiang T, Bligaard T, Christensen C H, Nørskov J K. Trends in the catalytic CO oxidation activity of nanoparticles. Angewandte Chemie International Edition, 2008, 47(26): 4835–4839
10. Dickens C F, Kirk C, Nørskov J K. Insights into the electrochemical oxygen evolution reaction with *ab initio* calculations and microkinetic modeling: beyond the limiting potential volcano. Journal of Physical Chemistry C, 2019, 123(31): 18960–18977
11. Hansen H A, Varley J B, Peterson A A, Nørskov J K. Understanding trends in the electrocatalytic activity of metals and enzymes for CO_2 reduction to CO. Journal of Physical Chemistry Letters, 2013, 4(3): 388–392
12. Pan S, Li H, Liu D, Huang R, Pan X, Ren D, Li J, Shakouri M, Zhang Q X, Wang M J, et al. Efficient and stable noble-metal-free catalyst for acidic water oxidation. Nature Communications, 2022, 13(1): 2294
13. Man I C, Su H Y, Calle-Vallejo F, Hansen H A, Martínez J I, Inoglu N G, Kitchin J, Jaramillo T F, Nørskov J K, Rossmeisl J. Universality in oxygen evolution electrocatalysis on oxide surfaces. ChemCatChem, 2011, 3(7): 1159–1165
14. Liu H, Zhang D, Holmes S M, D’Agostino C, Li H. Origin of the superior oxygen reduction activity of zirconium nitride in alkaline media. Chemical Science, 2023, 14(34): 9000–9009
15. Xu H, Zhu L, Nan Y, Xie Y, Cheng D. Revisit the role of metal dopants in enhancing the selectivity of Ag-catalyzed ethylene epoxidation: optimizing oxophilicity of reaction site via cocatalytic mechanism. ACS Catalysis, 2021, 11(6): 3371–3383
16. Liu X, Xiao J, Peng H, Hong X, Chan K, Nørskov J K. Understanding trends in electrochemical carbon dioxide reduction rates. Nature Communications, 2017, 8(1): 15438
17. Nørskov J K, Bligaard T, Rossmeisl J, Christensen C H. Towards the computational design of solid catalysts. Nature Chemistry,

2009, 1(1): 37–46

18. Kelly S R, Kirk C, Chan K, Nørskov J K. Electric field effects in oxygen reduction kinetics: rationalizing pH dependence at the Pt(111), Au(111), and Au(100) Electrodes. Journal of Physical Chemistry C, 2020, 124(27): 14581–14591
19. Medford A J, Shi C, Hoffmann M J, Lausche A C, Fitzgibbon S R, Bligaard T, Nørskov J K. CatMAP: a software package for descriptor-based microkinetic mapping of catalytic trends. Catalysis Letters, 2015, 145(3): 794–807
20. Liu H, Jia X, Cao A, Wei L, D'Agostino C, Li H. The surface states of transition metal X-ides under electrocatalytic conditions. Journal of Chemical Physics, 2023, 158(12): 124705
21. Hansen H A, Rossmeisl J, Nørskov J K. Surface Pourbaix diagrams and oxygen reduction activity of Pt, Ag and Ni(111) surfaces studied by DFT. Physical Chemistry Chemical Physics, 2008, 10(25): 3722–3730
22. Vinogradova O, Krishnamurthy D, Pande V, Viswanathan V. Quantifying confidence in DFT-predicted surface pourbaix diagrams of transition-metal electrode-electrolyte interfaces. Langmuir, 2018, 34(41): 12259–12269
23. Yang W, Jia Z, Zhou B, Wei L, Gao Z, Li H. Surface states of dual-atom catalysts should be considered for analysis of electrocatalytic activity. Communications Chemistry, 2023, 6(1): 6