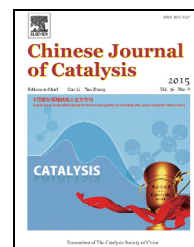


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Article (Special Issue for Excellent Research Work in Recognition of Scientists Who Are in Catalysis Field in China)

Catalyst screening: Refinement of the origin of the volcano curve and its implication in heterogeneous catalysis

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ABSTRACT

Understanding the overall catalytic activity trend for rational catalyst design is one of the core goals in heterogeneous catalysis. In the past two decades, the development of density functional theory (DFT) and surface kinetics make it feasible to theoretically evaluate and predict the catalytic activity variation of catalysts within a descriptor-based framework. Thereinto, the concept of the volcano curve, which reveals the general activity trend, usually constitutes the basic foundation of catalyst screening. However, although it is a widely accepted concept in heterogeneous catalysis, its origin lacks a clear physical picture and definite interpretation. Herein, starting with a brief review of the development of the catalyst screening framework, we use a two-step kinetic model to refine and clarify the origin of the volcano curve with a full analytical analysis by integrating the surface kinetics and the results of first-principles calculations. It is mathematically demonstrated that the volcano curve is an essential property in catalysis, which results from the self-poisoning effect accompanying the catalytic adsorption process. Specifically, when adsorption is strong, it is the rapid decrease of surface free sites rather than the augmentation of energy barriers that inhibits the overall reaction rate and results in the volcano curve. Some interesting points and implications in assisting catalyst screening are also discussed based on the kinetic derivation. Moreover, recent applications of the volcano curve for catalyst design in two important photoelectrocatalytic processes (the hydrogen evolution reaction and dye-sensitized solar cells) are also briefly discussed.

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1. Introduction

Rational design/screening of catalysts has long been an important target in heterogeneous catalysis [1–3], since the traditional trial-and-error method is inadequate to meet the demands of the rapid development of the catalyst industry. However, the lack of understanding of the catalytic mechanism at the atomic level greatly limits the efficient design of heteroge-

neous catalysts. Fortunately, the popularization of density functional theory (DFT) tools in the past two decades and surface reaction kinetics allows us to theoretically evaluate a catalyst's activity and thus facilitates the overall searching process [1]. Among that, the volcano curve, which was introduced by Balandin [4,5], plays a key role in current descriptor-based catalyst screening framework [6]. Empirically, a volcano-shaped curve (first ascending and then descending) can

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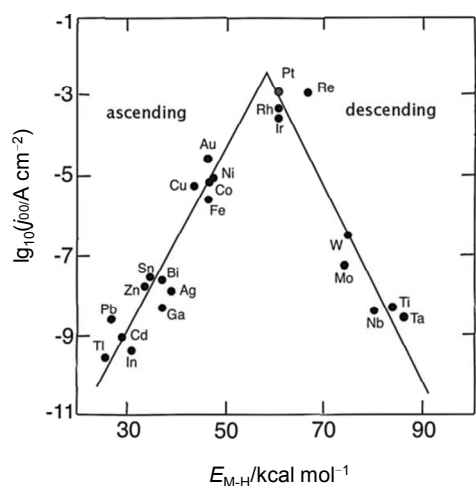
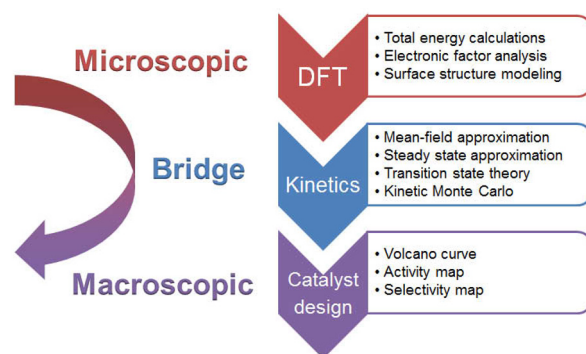


Fig. 1. Trasatti's volcano curve for the hydrogen evolution reaction in acid solutions. $\log(j_{000})$ denotes the exchange current density while E_{M-H} denotes the energy of hydride formation. Original Fig. in Ref. [8], Copyright 1972, Elsevier. Adapted from Ref. [11]. Copyright 2014, Beilstein-Institut.

usually be obtained upon examining the variation of the catalytic activity for a certain reaction with the position of the transition metals in the periodic table [6,7].

Figure 1 shows a typical volcano curve, which was firstly drawn by Trasatti for the hydrogen evolution reaction (HER) [8]. It is clear that the optimal metal catalyst for the HER is located near the peak of the volcano curve. Scientifically, the volcano curve can serve as a comprehensive basis for understanding the catalytic activities of different catalysts or active sites; technically, it is useful guide in high-throughput screening or design of excellent catalysts [9,10].

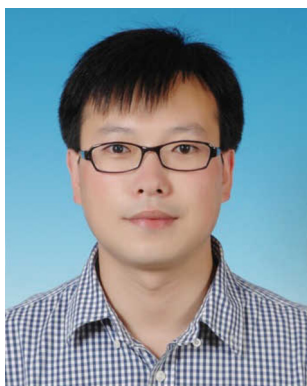
This concept, however, did not prevail until the last 10 to 20 years, possibly owing to the lack of understanding about the reaction mechanism at the microscopic level, including the key thermodynamic and kinetic reaction information. Fortunately, the use of DFT calculations and quantum chemical softwares with massively parallel computing techniques facilitates the accumulation of relevant information. Firstly, DFT calculations have become a powerful tool to investigate catalytic processes [12,13]. The binding energies of intermediates, reaction barriers, surface structures, and so on can be routinely obtained



Scheme 1. Illustration of the hierarchical relation among DFT calculations, kinetics, and catalyst design/screening.

with reasonable accuracy. However, some challenges still remain, such as the *ab initio* simulation of liquid–solid interfaces and proper consideration of the inherent errors in DFT [14,15]. Secondly, with the necessary energies obtained by DFT calculations, kinetic analysis has been increasingly used to assess the performance of catalysts and determine the key rate-limiting factor [7,16]. In short, the kinetics serves as a bridge between the macroscopic behavior of catalysts and the microscopic reaction pathways. Scheme 1 illustrates the hierarchical relation among DFT calculations, kinetics, and catalyst design/screening. Nørskov et al. theoretically calculated the rate of ammonium synthesis using the above framework, and the results were within a factor of 3 to 20 of the experimental rate [17]. Their result quantitatively demonstrated the feasibility and reliability of catalyst screening using DFT calculations and kinetics. With these developments, the volcano curve has become the main tool in descriptor-based catalyst screening. Typically, the adsorption energy (or other related parameters) should be located near the peak position of the volcano curve. Such an idea has been successfully applied to many catalytic systems, and has shown to be a simple but powerful approach to assist the theoretical design of catalysts.

The Brønsted-Evans-Polanyi (BEP) relation is a convenient tool to qualitatively analyze the volcano curve for certain catalytic reactions [6,18–24]. There is generally a universal linear relationship between the reaction barrier E_a and the reaction enthalpy ΔH . Based on the BEP relation, Nørskov et al. made a significant advance in obtaining the volcano curves of a series



Haifeng Wang (East China University of Science and Technology) received the **Rising Star Award in 2014**, which was presented by The Catalysis Society of China. Dr. Hai-Feng Wang studied chemistry at East China University of Science and Technology (ECUST) and received Ph.D. degree in 2012. During 2008 to 2010, he did research work in Queen's University Belfast sponsored by China Scholarship Council. After graduation, he joined the Centre for Computational Chemistry in ECUST as an associate professor. His research interests lie in (1) the first principle simulations of heterogeneous catalysts, aiming to clarify the electronic structure and reaction mechanism on gas-solid and liquid-solid interface; (2) developing efficient models for assessment of catalytic activity and rational screening of catalysts; (3) simulation and design of novel electrocatalysts and photocatalysts for renewable energy conversion and solar cells. Currently, he has published more than 30 papers on international peer-reviewed journals, including *Nat. Commun.*, *Angew. Chem. Int. Ed.*, *J. Catal.* and so on.

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