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Insight into chemical reactions in catalysis

The chemical reaction lies at the very heart of chemistry. In spite of its paramount importance, an understanding of chemical reactions still falls short of the chemists' expectation. Microscopically, chemical reactions are constituted by *atomic movements* on a typical time scale of several hundreds of *picosecond* (10^{-12} s). It has been a formidable task for chemists to track down a reaction process in experiment, as both the high spatial and temporal resolutions are required. On the other hand, there are no such problems in the 'virtual laboratory'. With highly accurate ab initio methods such as density functional theory, chemical reactions can be studied in detail on powerful computers.

My thesis focused on the basic principles that govern reactions, in particular catalytic process. By developing and applying ab initio quantum mechanical calculations with the aid of massively parallel supercomputers, my research geared towards elucidating reaction mechanisms, predicting the fundamental properties of chemical reactions and designing new catalysts and materials. The catalytic reactions that I was most concerned with were those of relevance to *heterogeneous catalysis*. It is a field of tremendous economic incentives, which represents 20~30% of global GNP annually. Furthermore, the big challenges that human beings are facing, such as finding the new energy sources and dealing with the environmental problems, are all intimately associated with heterogeneous catalysis. Below I highlight two contributions of my Ph.D work in this field.

New framework for predicting reaction barriers on metal surfaces

Predicting energy barriers of chemical reactions is a fundamental goal in chemistry. It

has long believed that the design of new catalysts will be much facilitated if the barrier can be simply estimated. Traditional tools in chemistry such as Marcus Theory and its more qualitative pre-version, Bronsted-Evans-Polanyi Principle, often do not work well in explaining the reactivity in heterogeneous catalysis, because the bonding between the molecule and the surface is complex and the reaction involving surface atoms is extremely difficult to study. Therefore, an understanding of the barrier to surface reactions remains one of the greatest challenges to chemists.

With the aim to build a framework to understand catalytic reactions on surfaces, we systematically studied many elementary dissociation and association reactions on transition metals. By comparing the same dissociation reaction on different metal surfaces, we found that the barrier of a dissociation reaction is linearly dependent on its final state chemisorption energy. The linear relationship has a slope being close to -1 (Fig. 1). In order to explain this result, we derived the following equation: $E_a^{dis} = E_a^{ass} + E_{bond} - E_{FS}$; where E_a^{dis} is the dissociation barrier, E_a^{ass} is the barrier of the reverse reaction (association), E_{bond} is the bond strength of the breaking bond, which is constant for a reaction, and E_{FS} is the total chemisorption energy of dissociation products. The equation is exact. It was discovered that the change of E_a^{ass} is much smaller (one order of magnitude) than that of E_{FS} with the variation of the metal substrate. Therefore, E_a^{dis} is mainly determined by E_{FS} . This energetic feature is in accord with our observation that the transition states of dissociation reactions on metal surfaces are very *late* (like the final states). The result has been used to explain many experimental observations.

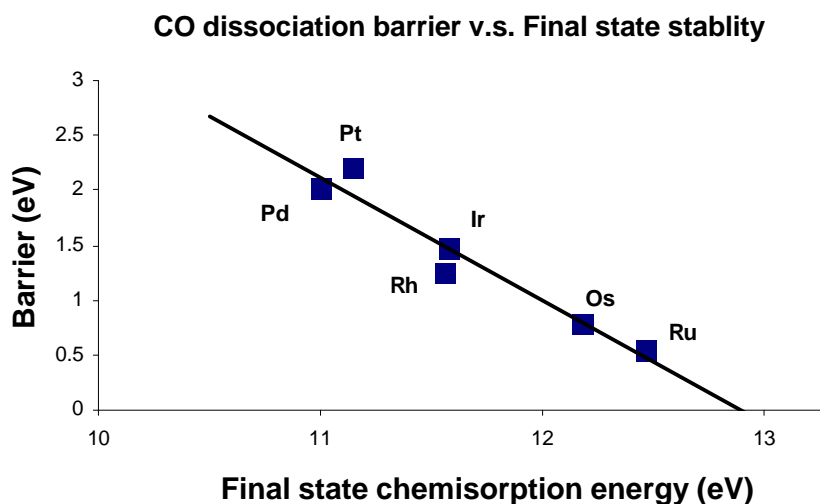


Fig. 1 Linear dependency of dissociation barrier on final state stability

Through further studies on association reactions, we found that they can be divided into two classes according to their transition state structures. In the reactions of class I, the two

reactants bond with the same surface atom to achieve the transition state. In such a structure, there is a bonding competition between the two reactants, which adds an extra energy cost to the barrier. In contrast, this bonding competition effect is absent in the class II reactions because the reactants in the transition state do not bond with the same metal atom directly. We also obtained some simple rules for estimating the barriers for these reactions. In addition to their differences in energetics, these two classes of reactions have distinct preference in their reaction sites. Class I reactions prefer to occur on surface defects such as steps, but such preference is not present in class II. These results provide important insights into a fundamental question in catalysis, namely where do reactions occur on surfaces? We believe that the knowledge gleaned from these fundamental studies will facilitate the optimization of existing catalyst and the design of new ones in the future.

Synergetic effect: why are noble metals not noble?

It is known that the real catalysts used in industry contain multi-components and most commonly, they consist of metals dispersed on metal oxides. The multi-component catalyst can often dramatically boost the catalytic performance. Therefore, to gain insight into the synergetic effect between metals and metal oxides is a natural step to extend our work on metals. In recent years gold-based catalysts are found to exhibit unusually high catalytic ability for many reactions. For example, CO oxidation on TiO₂-supported Au is observed at a temperature as low as 200 K. This is very surprising considering that neither gold (the most inert metal) nor the oxides are good catalysts for the reaction. Because of this, gold-based catalysts are often quoted as a textbook example for the synergetic effect. Using density functional theory calculations, we systematically studied CO oxidation on many different unsupported Au surfaces as well as a Au/TiO₂ system. Through exhaustive searching for the pathways of O₂ dissociation on a series of Au surfaces, including small Au particles, we demonstrated that O₂ dissociation on unsupported Au possesses a high barrier and is thus difficult at low temperatures. This rules out the possibility of a long-suspected mechanism involving O₂ dissociation.

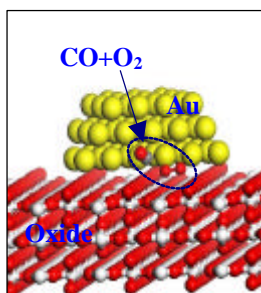


Fig. 2 CO oxidation on Au/oxide

By further including TiO_2 into the Au system, we discovered the physical origin of the synergetic effect. It was found that O_2 can adsorb much stronger at the Au/ TiO_2 interface than that on pure Au, causing an increase in the concentration of O_2 on the catalyst. More importantly, our calculations showed that the oxide can induce a significant electron transfer from the Au to the 2π anti-bonding states of O_2 that sit at the interface between the metal and the oxide, which causes the O_2 to be highly negatively charged. Such electron transfer not only enhances the binding of O_2 on the catalyst but also activates the O_2 . This results in a facile bi-molecular pathway ($\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}$) leading to CO_2 formation (Fig. 2). The synergetic effect identified is believed to be general in heterogeneous catalysis.

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