

Toward Computational Design of Photocatalysts for deNO_x Reaction through High-dimensional Reaction Potential Surface

Studying selectivity and activity of NO₂ and water reactions on a series of metal oxides surface

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In Short

- Studying catalytic mechanism for denoxification, especially the selectivity and activity of NO₂ and H₂O reaction on a series of catalytic semiconductor oxides (we forced on TiO₂ firstly) with scaling relations under dark condition and illumination condition
- Identifying the role of photo generated carries in NO₂ and H₂O reactions under illumination condition
- Applying slabcc (total energy correction) and scpc (self-consistent potential correction) methods for periodic charged system to correct the effect of background charge

To date, applying TiO₂ in deNO_x has been widely studied and it is reported that TiO₂ is a promising NO_x removal material due to the strong oxidation ability and low cost. It's interesting to find that NO₂ and H₂O reaction on TiO₂ has divergent behaviors under dark condition and photo condition[1]. However, the reaction mechanisms is quite complex (see in **Figure 1c** and haven't been understood clearly and further studies are needed. Both the understanding of the reaction mechanisms for the deNO_x photocatalytic processes and the design of relevant catalysts with higher activity and specific selectivity, have become one of the most urgent topics currently.

Herein, we applied the method developed by Jens K. Norskov and his co-workers into our project and we can effectively identify the activity of active sites and catalysts through this method [2–4]. It suggested that a roughly linear scaling relationship among the energies of key reaction intermediates is essential for rationalizing trends in catalytic activity across different catalysts. In general, the activity over different catalysts can be evaluated by the volcano curve, based on the relevant descriptor (adsorption energies of key intermedeates).

Objectives

The aim of this project is to study catalytic mechanisms for denoxification, more specifically the NO₂

+ H₂O reaction, both under dark conditions and under illumination with over-the-band-gap light, on the surface of a series of catalytic metal oxides (TiO₂, RuO₂, SnO₂, and CeO₂), in order to predict catalytic activity and selectivity trends. Instead of just assuming pathways, the investigation will be based on a full reaction network, establishing a high-dimensional reaction potential surface on the basis of correlating the adsorption energies of intermediates over different active sites[5]. The adsorption and reaction energies, as well as energy barriers will be calculated by advanced techniques, applying a modified Lany-Zunger correction scheme to DFT-GGA (which rectifies the underestimation of the band gap and the delocalization tendency both in the bulk and on the surface)[6], and a self-consistent potential correction (to counteract the artifacts arising from a periodically repeated charge on the surface) [lit7]. The energy data will be collected on all the possible reaction species, including adsorption energies for intermediates (Eg: N*, NO*, O*, H*, OH*, OOH*) and adsorbed molecules (Eg: NO₂*, H₂O*, H₂O₂*, HONO*, HNO₃*). Based on the thermodynamic properties of the elementary reaction steps (energy of reaction and of activation), the reaction network can then be built, corresponding to the chosen descriptors, which are usually the adsorption energies of key adsorbates. The catalytic mechanisms can then be derived from the full reaction network with an optimal pathway-searching algorithm[5], in case of different surfaces of various oxides, thereby contributing to catalyst design (seen in **Figure 1b**).

An accurate high-dimensional reaction potential surface, named reaction phase diagram (RPD) for simplicity in this project, will be built by considering both reaction free energies and activation barriers, which will be displayed as a Bronsted Evans Polanyi relationship (BEP). A reasonable activity trend can be then obtained with the optimized catalytic mechanisms in different phases. In addition, microkinetic modelling will be conducted towards the accurate prediction of reaction rates. A general understanding of reaction mechanism and pathways over a given catalyst (e.g. for our starting material TiO₂) can be obtained based on the catalytic trends from high-dimensional RPD. The break-down of scaling relations shows a possibility for improving catalytic activity, which is also the motivation to build two- (or higher-) dimensional reaction potential surfaces (seen in **Figure 1d**). Moreover, besides the adsorption energies, the correlations between

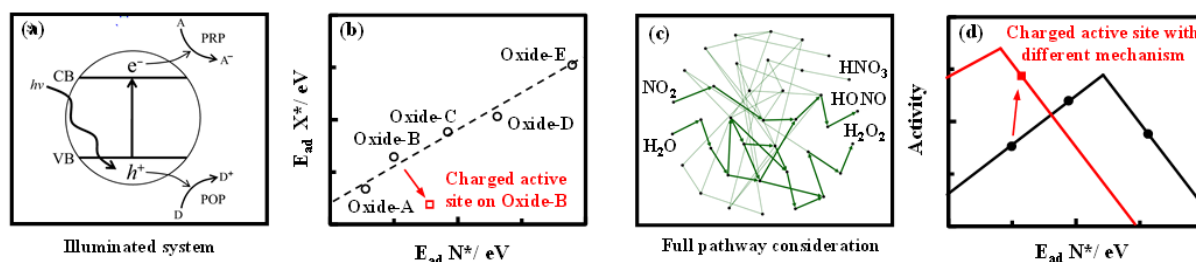


Figure 1: (a) Scheme of photo-oxidation/reduction processes (POP/PRP) upon photo-generation of an electron-hole pair in a semiconductor, with acceptor (A) and donor (D) molecules in the vicinity of the surface. (b) The breaking of scaling relation based on the charged system in photocatalysis. (c) All possible reaction species and elementary steps in NO₂ conversion. One of the possible reaction pathways to products observed in photocatalytic experiments. (d) Activity trend with the consideration of all possible reaction mechanisms.

activity and activation barriers, stability, and local charge/field effects can all be established, so will be applied as the second dimension toward a more extended description of the catalytic processes. Different catalytic mechanisms will be described by using varying descriptors. To put it short, the 2D RPD will be further developed to search for new catalytic materials.

The summarize, project aims at building and analyzing full reaction networks (instead of just assuming certain pathways as it was usual so far), based on calculated thermodynamic data. The conceptual novelty is, on the one hand, the application of appropriate corrections, recently developed by the German participant, for the gap- and localization-error of GGA-DFT for surfaces, and for the artifacts arising due to the periodic repetition of charge. To our knowledge, no such calculations have as yet been published. On the other hand, the analysis of the full reaction network will be carried out by an optimization algorithm developed and recently published by the Chinese participant. This new strategy will be applied for a series of catalysts/sites to study photocatalytic denoxification.

Modeling charge assisted surface reactions

Adding a localized charge to a periodic model leads to an infinite Coulomb-energy, due to the electrostatic interaction between the repeated images. To avoid that, in all electronic structure codes used for modelling periodic systems with a net charge, an evenly distributed (so called jellium) countercharge is added, to keep the repeated supercell electronically neutral. Considering the different localization of the charge and countercharge, however, the repeated charges cause a spurious electrostatic potential, which affects the energy of the calculated one-electron states and shifts the total energy. Therefore, we will apply our recently developed method for total

energy correction[6] and potential correction[7] in charged system.

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More Information

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Project Partners

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