

MULTISCALE MODELING OF BIFUNCTIONAL CATALYSTS FOR THE WATER-GAS SHIFT REACTION

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Summary

Precious metal nanoparticles supported on reducible oxides are known to exhibit excellent activity and selectivity for the water-gas shift (WGS) reaction which is a key step in fuel processing to maximize hydrogen yield and for providing clean hydrogen. In this paper, we explain the role of the three-phase boundary (TPB) of a gas-phase, a reducible oxide surface, and a noble metal cluster in determining the unique activity and selectivity of TiO₂ and CeO₂ supported Pt and Au catalysts for the WGS reaction. Furthermore, we illustrate a new highly efficient and accurate computational strategy for these systems.

Keywords

Rational design of catalysts; Computational catalysis; Reaction Path Analysis; Hydrogen production.

Introduction

For heterogeneously catalyzed reactions with more than one key surface intermediate, it is likely that multiphase catalysts have a significant advantage over conventional monophase catalysts since each phase can potentially be adjusted independently to activate a key reaction step. At the same time, our understanding of bifunctional multiphase systems is relatively poor. It is the objective of this paper to significantly enhance our molecular understanding of heterogeneous catalysis at the three-phase boundary (TPB) of a gas-phase, a reducible oxide surface, and a noble metal cluster. In particular, we intend to illustrate the specific role of the TPB in determining the activity and selectivity of TiO₂ and CeO₂ supported Pt and Au catalysts for the water-gas shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$).

The heterogeneously catalyzed WGS reaction is a key step in fuel processing to provide clean hydrogen and maximize hydrogen yield. In addition, the WGS reaction or its reverse is directly or indirectly relevant to several industrial catalytic technologies, such as methanol synthesis, methanol steam reforming for hydrogen production, ammonia synthesis, coal gasification, and catalytic combustion. The significance of this reaction in numerous industrial processes, especially its application to hydrogen fuel cells, has sparked an enormous interest in finding improved WGS catalysts. Such heterogeneous catalysts should combine both high activity and structural stability in air and in cyclic operation; these are stringent requirements not met by the commercially available low-temperature WGS catalysts. As an alternative, noble metals such as Au, Pt, or Pd on oxide supports such as

CeO₂, ZrO₂, and TiO₂ have been reported to be promising WGS catalysts. Recent experimental studies suggest that supported bimetallic catalysts such as Au-Pt, Pt-Re, Ir-Pt, etc. display even better activity and selectivity for WGS reactions than the monometallic catalysts. Despite numerous studies, the nature and function of the noble metal, oxide support, and TPB in determining the activity and selectivity for the WGS reaction is still unclear.

We report here the results of density functional theory (DFT) calculations for a large number of elementary processes of the WGS on TiO₂ and CeO₂ supported Pt and Au catalysts that permit understanding the origin of the unique catalytic activity of the TPB of oxide supported metal catalysts for the WGS.

Computational Methodology

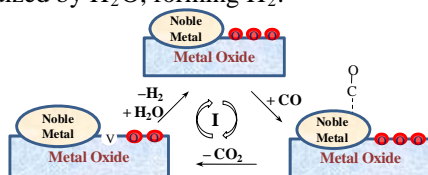
Our overall strategy for obtaining a deeper understanding of the unique activity of the TPB of noble metal clusters supported on reducible oxide supports starts with the development of a reasonably accurate computational strategy for these systems. In particular, we are required to use computational methods that are significantly more accurate than pure DFT functionals for estimating reaction barriers and interactions with reduced oxides (owing to the significant delocalization error of standard DFT for these systems), and that are significantly more accurate than standard hybrid DFT methods for calculating the interaction within metal clusters (owing to static correlation problems). At the same time, these methods have to still be affordable. Recently, Grimme and co-workers developed such a technique with the

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double-hybrid density functionals (DHDF). In particular, they showed that the computationally efficient B2PLYP technique with at least triple- ζ quality atomic orbital basis sets has an accuracy that is competitive with the computationally very expensive coupled-cluster methods for transition metal complexes and noble metal clusters such as Au₈. As a result, our computational strategy consists of (i) performing periodic slab calculations using the periodic DFT code VASP and pure density functionals to build and validate a periodic electrostatic embedded cluster (PEEC) model and (ii) performing embedded cluster model calculations using the B2PLYP functional and the PEEC functionality as implemented in the TURBOMOLE 6.0 package to investigate various reaction pathways. To calculate reaction barriers, transition states have to be located. This task has been done with our own highly efficient transition state search algorithms.

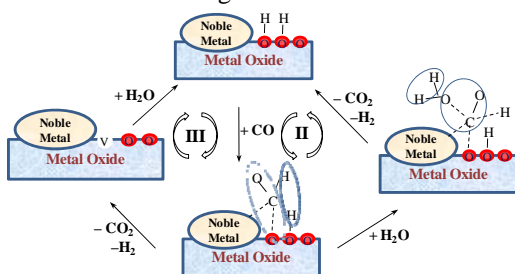
Reaction Pathways

Based on experimental and computational studies, five different reaction pathways have been proposed in the literature for the WGS reaction on oxide supported noble metals. And, all reaction pathways described in the following have been studied using our theoretical approach with various metal cluster sizes. The first pathway is a classical redox mechanism (Scheme 1). In this mechanism, CO adsorbs on the metal and reacts with oxygen from the support surface, forming CO₂ and reducing the oxide support surface. The reduced surface is then oxidized by H₂O, forming H₂.



Scheme 1. Classical redox route

In another well-known associative mechanism, the reaction proceeds through surface hydroxyl groups which react with CO and form surface formates. The decomposition of formate species is suggested to be facilitated by the presence of water in the gas phase and its rate determining (route II in Scheme 2). No surface oxygen atoms are exchanged in this reaction mechanism.

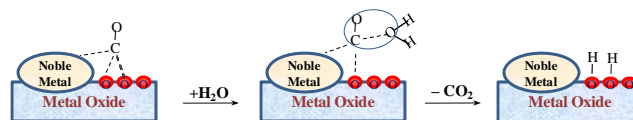


Scheme 2. (II) Associative formate route (III) Associative formate with redox regeneration route

Alternatively, a direct dissociation of the formate intermediate with the formation of H₂ and CO₂ could lead to the formation of a vacant site on the surface (route III in

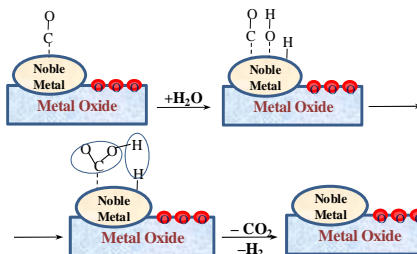
Scheme 2). The vacant site further reacts with water to form hydroxyl groups which completes the catalytic cycle.

A fourth possibility is the participation of carbonate and bicarbonate intermediate complexes instead of formate complexes. This reaction sequence is known as the carbonate route (Scheme 3).



Scheme 3. Carbonate route

Finally, several groups proposed a carboxyl (COOH) mechanism. This reaction pathway is most likely dominant for noble metals supported on irreducible Al₂O₃. The mechanism involves (i) the dissociative adsorption of water (possibly on the supported metal cluster), (ii) the reaction of CO and OH to form COOH intermediates, and (iii) the decomposition of COOH (Scheme 4).



Scheme 4. Carboxyl route

Overall, we observe that the presence of metal clusters (Au and Pt) improves the reducibility of the oxide surface; a key reaction step in various mechanisms. Furthermore, both positively and negative charged metal clusters significantly improve the reducibility of the oxide. And finally, for various elementary reactions on oxide and metal surfaces that possess relatively large reaction barriers, reaction pathways with significantly reduced activation energies could be found at the TPB. As a result, the WGS reaction at the TPB is significantly facilitated to reactions on oxide or metal surfaces due to (i) indirect electronic effects where one phase affects the electronic structure and consequently reaction rate and equilibrium constant for various elementary reactions on the other phase, and (ii) direct effects where elementary reactions can shuttle to whatever phase that facilitates a specific elementary reaction. Reaction barriers for changing phases are found to be very low.