

Sulfuric Acid Decomposition Reaction: Atomic-Scale Mechanisms of Deactivation of Supported Transition Metal Particles Catalysts

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Introduction

Production of hydrogen by the splitting of water at lower temperatures than required for direct thermal decomposition can be achieved by a series of particular chemical reactions [1]. Among the high number of proposed thermochemical water-splitting cycles, the sulfur-based group that employs the catalytic decomposition of sulfuric acid into SO_2 and O_2 [2] is of considerable interest.

Research work performed at the Idaho National Laboratory [3] has found that all the catalytic systems studied to date that consist of metal particles on oxide substrate deactivate with time on stream. To develop an understanding of the factors that cause catalyst deactivation, we performed DFT-based first-principles calculations and computer simulations for transition metal (TM) particles on γ -alumina catalytic systems.

Materials and Methods

Calculations were performed on 5-layer-thick $\gamma\text{-Al}_2\text{O}_3$ (110) periodic slabs separated by vacuum layers. The adsorbates (metal particles) and the top surface layers were fully relaxed, keeping the bottom layer fixed. For simulation of processes on larger clusters, quasi-one-dimensional periodic rod-like structures containing a well-defined boundary between the cluster and the substrate were used. The calculations were based on the generalized gradient approximation (GGA) for exchange and correlation, and plane waves. We used ultrasoft scalar relativistic pseudopotentials and the VASP codes. The minimum reaction paths for the decomposition reactions were found using the nudged-elastic-band (NEB) method.

Results and Discussion

We found that the catalyst decline is defined by several factors, namely:

(i) The necessity of detaching oxygen atoms from the SO_n ($n = 1,2,3$) sulfur-containing species. These species can attach to both the alumina substrate and the transition metal cluster (Figs. 1, left panels). However, the reaction of breaking the S-O bond at the substrate is endothermic (and takes about 1.5 eV per bond) while at the cluster it is exothermic (with energy gain of about 0.5 eV per bond). It explains why the presence of transition metal clusters at the surface support improves the catalytic performance (Fig. 1, right panel);

(ii) The ability of the cluster to “clean” itself, i.e., to eliminate the atomic and molecular oxygen from its surface, in order to regain the catalytically active sites and to continue the process. We found that the clusters of all the considered transition metals (Pd, Pt, Rh, and Ir) are efficient in this process if they are larger than 2-3 nm because stable oxides do not form at relatively flat areas of the cluster (smaller clusters get poisoned by oxygen);

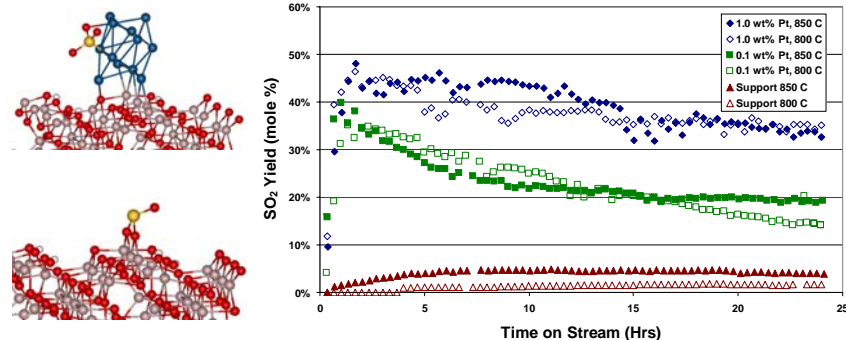


Figure 1. Attachment of SO_3 to the Pt cluster and to the alumina substrate (left panels); experimental SO_2 yield curves for the pure alumina substrate (brown) and for the substrate with Pt clusters (blue and green; right panel).

(iii) The ability of the cluster to keep its size to avoid sublimation and sintering (that reduces the number of low-coordinated catalytically active sites at the surface of the cluster). It is likely that the Ostwald ripening mechanism plays an important role in catalyst deactivation. We found that the sintering of Rh and Ir clusters is significantly suppressed in comparison with the sintering of Pd and Pt clusters of the same size (the individual atoms at the surface of Rh and Ir clusters have a tendency to have higher coordination number, i.e., the detachment of individual atoms from the surface is less likely).

Summarizing, the deactivation of the TM-cluster/ γ -alumina catalytic system is defined by at least three different factors including the mechanism of O-atoms detachment from the SO_n species, the TM-cluster dynamic oxidation mechanism, and the clusters sintering. We suggest a powerful methodology for comparative analysis of TM clusters that is based on first-principles calculations and computer modeling.

Significance

Thermochemical water-splitting cycles consist of a series of chemical reactions to produce hydrogen from water without the need of fossil fuels. The work reported in this contribution refers to the applicability of TM particles supported on alumina for the sulfuric acid decomposition reaction, which is the common reaction in all sulfur-based thermochemical water-splitting cycles.

References

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