

# Adsorbate-adsorbate interactions in metal surface: DFT and ab initio thermodynamic studies of pressure- and temperature-dependant impact of alkalis on surface reactions of electronegative adsorbates

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## Introduction

Understanding adsorbate-adsorbate interactions on surfaces is critical for the development of predictive theories of heterogeneous catalysis.[1] We will present a very general and physically transparent framework, grounded in DFT calculations, to analyze adsorbate-adsorbate interactions on surfaces. This framework allows us to distinguish between electro-static, electro-dynamic, and electronic mechanisms of adsorbate-adsorbate interactions on surface. A fairly simple procedure was developed to calculate independently the different contributions to the adsorbate-adsorbate interaction energies.

This model was utilized to examine the effect of Cs adsorbates on the O<sub>2</sub> dissociation reaction on Ag(111). The studies revealed that the main mode by which Cs affects the dissociation of O<sub>2</sub> on Ag(111), in the limit of low Cs and oxygen surface concentration, is through the Cs-induced polarization of the Ag-O bond. This interaction stabilizes the transition state involved in the dissociation of O<sub>2</sub>, therefore lowering the activation barrier. The mechanisms can be generalized to systems involving electronegative and electropositive adsorbates on metal surfaces.

Ab initio thermodynamic simulations were employed to study how a working state of an alkali promoter and of the promoted catalytic material changes as a function of external conditions, i.e., pressure and temperature of reactants. In this context, we have examined possible formation of Cs-oxide complexes and the formation of sub-surface oxygen as a function of the chemical potential of gas-phase O<sub>2</sub> (pressure and temperature). We find that the nature of adsorbate-adsorbate interactions can be affected significantly by external conditions.

## Materials and Methods

We performed the DFT calculations with the Dacapo pseudo-potentials plane wave code [www.fysik.dtu.dk/CAMPOS]. The density of valence electrons was determined self-consistently by iterative diagonalization of Kohn-Sham Hamiltonians. The plane wave basis set used to describe the one-electron states was cut off at 350 eV. An electronic temperature ( $k_B T$ ) of 0.1 was used during calculations with the final results extrapolated to 0 K. The forces were minimized to 0.05 eV/Å.

DFT calculations are used to calculate electronic energies of various reaction intermediates on electrode surface. The energies obtained from DFT calculations were suitably corrected for the effect of temperature and pressure.

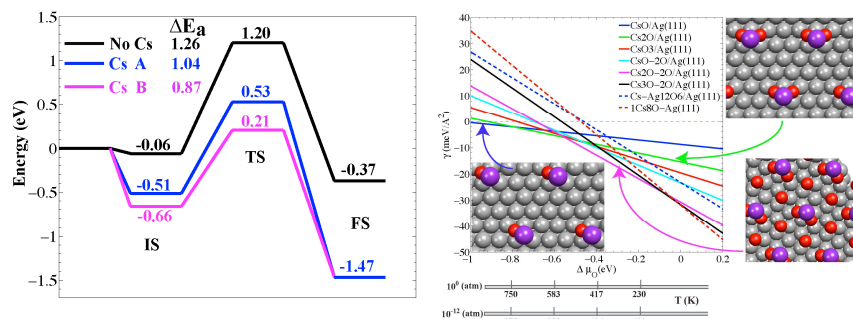
## Results and Discussion

Figure 1(a) shows the DFT calculated potential energy surface for the dissociation of O<sub>2</sub> on unpromoted and Cs-promoted Ag(111) surface. The energies were calculated in the limit of low surface concentration of oxygen and Cs. The calculation shows that the activation barrier is significantly lower for the promoted surface. A detailed analysis of adsorbate-adsorbate interactions was performed establishing that the main reason for the Cs-induced

lowering in the activation barrier is a strong polarization of Ag-O bonds due to high electric fields induced on the Ag(111) surface as a consequence of the adsorption of Cs.

Ab-initio thermodynamic analysis was performed to investigate the effect of elevated O<sub>2</sub> pressure and temperature. These studies showed that the surface concentration of oxygen is increased for Cs-promoted Ag compared to the unpromoted Ag surface for identical external conditions. The main reason for this is an attractive Cs-O interaction which leads to the formation of the CsOx complexes on the Ag(111) surfaces. This is illustrated in Figure 1(b) where the surface energy of various Cs/O configurations on Ag(111) was calculated using DFT calculations.

We find that these complexes can also affect the dissociation of O<sub>2</sub>. We will discuss the mechanism of interaction between the CsOx complexes and various states of oxygen molecule involved in the dissociation of O<sub>2</sub> on Ag(111) (i.e., initial, transition, and final state). We will also discuss the impact of alkali promoters on the oxidation state of Ag under steady-state oxidizing and reducing conditions.



**Figure 1.** (a) DFT calculated activation barriers for the dissociation of O<sub>2</sub> on Ag(111) for unpromoted Ag(111), and for Cs-promoted Ag(111) with Cs atoms far from the O<sub>2</sub> adsorption site (blue line), and close to the Cs adsorption site (red line) (b) Surface free energy is calculated for various Cs/O structures on Ag(111) as a function of gas phase chemical potential of oxygen. Temperature and O<sub>2</sub> pressure scale is also included. The most favorable structures are those that have the lowest surface energy under relevant conditions.

## Significance

We have extended the DFT calculation to include the effect of pressure and temperature. We conclude that the nature of adsorbate-adsorbate interactions can be affected significantly by external conditions.

## References

1. S. Linic, M.A. Barteau, *Journal of the American Chemical Society*, **2004**, 126, 8086.