

# Water activation on Rh: DFT study on the influence of surface coordination and pre-adsorbed oxygen

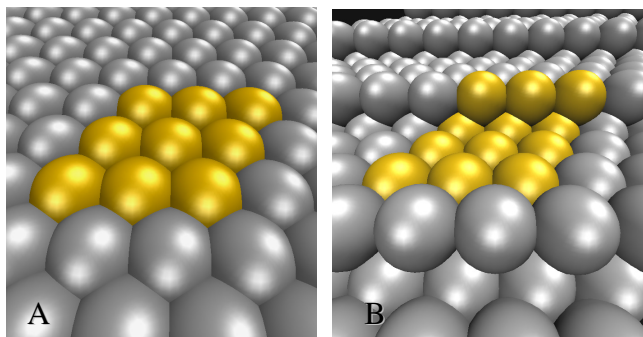
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## Introduction

For methane steam reforming important catalytic steps are the activation of methane and water as well as the recombination of carbon and oxygen to carbon monoxide. C-H dissociation of  $\text{CH}_4$  is structure sensitive and proceeds through lower barriers over low coordinated surface atoms (kinks and steps) than on terrace sites [1,2]. For CO recombination there is a preference for stepped surfaces [2]. Next to the importance of coordinative saturation of the surface atoms, the presence of atomic oxygen to facilitate these reaction steps has been noted [3].

## Materials and Methods

Periodical DFT calculations are performed on Rhodium planar (Figure 1A) and stepped surfaces (Figure 1B), where the activation of water is studied in presence or absence of pre-adsorbed atomic oxygen. VASP [4] is used for the DFT calculations, with the PW91 functional and energy cutoff of 400 eV.



**Figure 1.** The two surfaces calculated, the planar Rhodium surface (A) and the stepped surface (B). The unit cell is highlighted in gold.

## Results and Discussion

Here we investigate the role of atomic oxygen species in the elementary reactions steps of methane steam reforming by rhodium. Specifically, the sensitivity of water activation to the coordination of the rhodium surface atoms is studied. To this end, water activation on stepped Rh(221) and flat Rh(111) are compared. For the former surface, it is shown that water preferentially adsorbs on the bridge position between a step site and its lower lying neighbour on the terrace. The resulting hydroxyl group is adsorbed on the bridge position between two step atoms, while the hydrogen ends up on the lower terrace in a hollow site. The activation energy is calculated to be 65 kJ/mol. On a terrace site of the Rh(111) surface the preferred adsorption site is found to be the atop site, with the OH bonds parallel to the surface. The dissociation barrier of water dissociation is 60 kJ/mol with the resulting hydroxyl and hydrogen fragments being adsorbed in a hollow site.

In the second set of calculations water dissociation on the surfaces is studied in the presence of oxygen atom. Oxygen is able to accept a hydrogen atom. On the Rh(221) surface the oxygen is adsorbed on the lower terrace. After dissociation, the hydroxyl will be adsorbed in a hollow site on the lower terrace while the other hydroxyl will be on the edge of the step. This reaction proceeds with a barrier of only 25 kJ/mol. On the flat surface the oxygen atom in the hollow site moves towards the bridge position close to the water molecule ( $E_{\text{act}} = 40$  kJ/mol). After dissociation both hydroxyl groups are in hollow positions. Also this barrier is substantially lower than the one earlier reported [3]. The reaction appears to follow that of  $\text{NH}_3$  dissociation in the presence of oxygen [5].

## Significance

We conclude that water dissociation is not likely to be rate limiting in methane steam reforming. The results however show that surface oxygen facilitates bond dissociation reactions. We are now investigating the role of atomic oxygen species in the dissociation of CH species on Rh which proceeds through a high barrier [6].

## References

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