

Promoting Water Dissociation on TiO₂ (110) Surface: The Key Role of pre-Adsorbed Potassium Atoms.

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Highlights

- K atoms reduce the TiO₂(110) with formation of Ti³⁺ ions located at the subsurface
- The arising K⁺ cations easily move on the surface along the O bridging rows
- Water easily dissociates on the reduced surface
- The resulting OH groups anchors potassium ions to the surface hindering their mobility

1. Introduction

Alkali metals act as promoters of heterogeneous catalysts in a wide range of important chemical process like ammonia synthesis, CO oxidation, the water-gas shift (WGS) reaction or alcohol synthesis. The precise mechanisms behind the alkali promotional effects are not yet fully understood. In principle, an alkali can participate directly in a catalytic process or it can modify the chemical properties of the catalyst components. Recently, it has been shown that the addition of sodium or potassium to WGS ($\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2$) catalysts that contain gold or platinum produces a substantial increase in catalytic activity by inducing the formation of single-site (Pt or Au)-O(OH)_x-(Na or K) species[1]. Active sites that contain only a metal center are formed as a consequence of interactions of the metal with (OH)_x-(Na or K) groups. It is not clear how these groups are formed by the reaction of the alkali with water molecules.

The aim of our study it is to understand and explain the effects of alkalis on the surface chemistry of oxides to increase the catalytic activity. In this work, we have chosen potassium atoms to study water dissociation on titanium oxide surface.

2. Methods

DFT calculations were performed using the plane-wave pseudopotential approach within the projector augmented wave method (PAW) together with the GGA exchange–correlation functional proposed by Perdew et al. (PBE) as implemented in the VASP code. A plane-wave cutoff energy of 400 eV was used. In order to represent adequately the electronic structure of reduced titania, a Hubbard-like U term was added to Ti 3d levels using the rotationally invariant approach proposed by Dudarev et al., in which the Coulomb U and exchange J parameters are combined into a single parameter $U_{\text{eff}} = U - J$. The U_{eff} value for Ti 3d states was of 4.5 eV. The surface was represented by a (4 × 2) supercell model (6 TiO₂ trilayers), where the two lowest TiO₂ trilayers were kept frozen. To build the supercell model, we used optimized lattice parameters for the bulk, $a = 4.669 \text{ \AA}$ and $c = 3.025 \text{ \AA}$.

3. Results and discussion

Potassium single atom deposition on TiO₂(110) gives rise to K⁺ ions and reduction of the substrate with formation of Ti³⁺ species located in the subsurface layer, consistent with the XPS observations[2]. The results predict a large adsorption energy (~ 3.6 eV) with a small barrier (~ 0.25 eV) for diffusion on the oxide surface (Figure 1) therefore potassium species can move easily on the oxide surface along the atoms in the O bridging rows. The most stable adsorption configuration corresponds to a K⁺ ion bonded to two oxygen atoms in an O bridging row of TiO₂(110) as depicted in Figure 2a. Moreover, simulations of different potassium coverages show a decrease of adsorption energy as potassium coverage increases, and point to a limiting value for substrate reduction

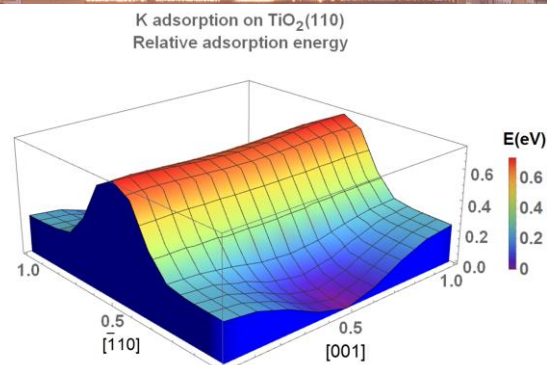


Figure 1. Potential energy surface potassium adsorption on TiO₂(110) surface

When water is adsorbed on this K/TiO₂(110) surface, the presence of alkaline atoms favors the water dissociation stabilizing surface hydroxyl groups. The geometry of the minimum energy structure for water dissociated on the K/TiO₂(110) surface is reported in Figure 2b where formation of a K-OH species is clearly seen, in agreement with STM image, Figure 2c [2]. The presence of resulting OH groups anchors potassium atoms to the surface reducing their mobility [3].

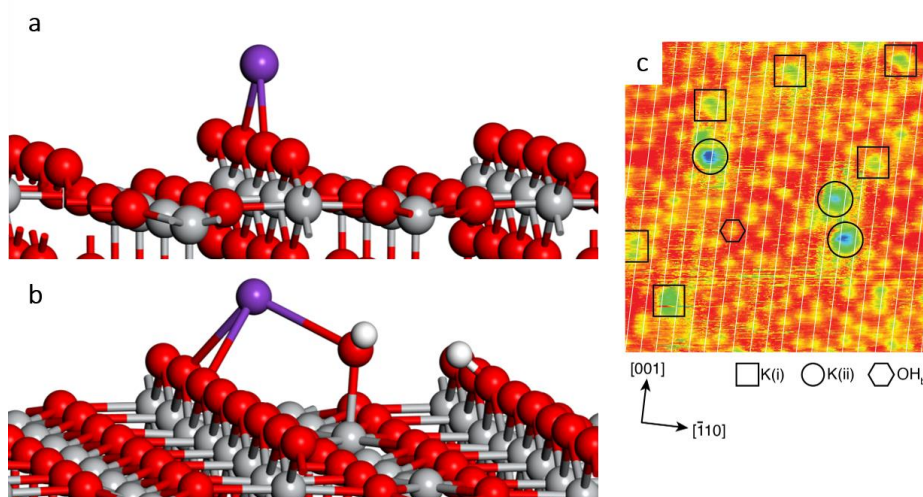


Figure 2. a) Optimized structure of Single potassium adsorption on the TiO₂(110) surface; b) Optimized structure of K-OH species adsorbed on the TiO₂(110) surface; c) STM image (13 × 13 nm², V = +1.78 V, I = 0.10 nA)

4. Conclusions

In summary, our DFT studies of the interaction of K with TiO₂(110) surfaces demonstrate that potassium is ideal for promotional effects because it has the peculiarity of having a strong binding energy and a high mobility on the surface.

For the bare TiO₂ (110) surface, the adsorption of potassium results in reduction of the surface along with the generation of highly mobile K⁺ ions. This reduced surface is able to dissociate water easily, leading to the formation of OH species that anchor the potassium on the surface as K-OH.

References

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Keywords

Potassium, water dissociation, titanium oxide, catalyst