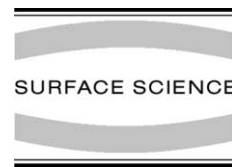




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The chemisorption of H₂O and CO₂ on TiO₂ surfaces: studies with MIES and UPS (HeI/II)

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Abstract

The interaction of H₂O and CO₂ with bare and alkali (Li, Na, K, Cs) pre-covered TiO₂ surfaces was investigated (130 and 300 K). Metastable impact electron spectroscopy and ultraviolet photoelectron spectroscopy (HeI and II) spectra were collected in situ during the exposure procedure. For H₂O at 130 K on bare TiO₂ an eventual initial dissociative adsorption at defect sites is followed by molecular adsorption up to multi-layer adsorption. The interaction of H₂O with the alkali pre-covered surfaces (130 and 300 K) leads to the formation of hydroxyl groups. At 130 K the formation of a mixed layer consisting of alkali atoms and OH species is followed by molecular adsorption on top of this layer. Annealing experiments show that the first layer remains intact when the second layer forms. For CO₂ no chemisorption takes place on the bare surface. However, the alkali pre-covered surface was found to be highly reactive under CO₂ exposure. The formation of carbonate (CO₃) species is observed. Both for H₂O and CO₂ electron transfer between the alkali atoms and the molecules plays a decisive role in the chemisorption process. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Metastable induced electron spectroscopy (MIES); Photoelectron spectroscopy; Water; Carbon dioxide; Titanium oxide

1. Introduction

The promoting role of alkali atoms in heterogeneous catalysis is well established [1–3]. This, together with the central role of metal oxides as substrate systems underlines, the interest in the study of alkali/metal oxides interfaces as well as in the reaction of small molecules with metal oxides. Rutile TiO₂ is one of the best studied metal oxides

as far as its interaction with alkali atoms is concerned.

For many oxides it has been found that water dissociates upon contact with the surface, forming various types of hydroxyl groups. Despite a great deal of investigations, the mechanism of the water–oxide interaction still appears to be poorly understood [4]. As compared to water, the number of studies on the CO₂ interaction with TiO₂ is scarce [5–9]. It is however known that sub-monolayer quantities of alkali atoms enhance the reactivity of TiO₂ towards CO₂ dramatically. The formation of a carbonate-like species is suggested. At room temperature (RT) both water and CO₂ react weakly (if at all) with near-ideal titania surfaces.

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Even at temperatures as low as 130 K only water physisorbs molecularly, whereas no changes in the spectra are observed if titania is exposed to CO₂.

We have studied the alkali-assisted chemisorption of water and CO₂, as hydroxyl and carbonate species, respectively, with titania at RT. In order to characterize the surface-adsorbed species, we use metastable impact electron spectroscopy (MIES) in combination with ultraviolet photoelectron spectroscopy (UPS). We show that the chemisorption process is initiated by the transfer of the alkali valence electron to the molecules. For both water and CO₂ we propose a chemisorption mechanism which successfully describes the experimental observations.

2. Experimental remarks

The experiments were carried out in an ultra-high vacuum system (base pressure $< 2 \times 10^{-10}$ Torr) equipped with low energy electron diffraction, X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS), Auger electron spectroscopy, and MIES, and is described in detail elsewhere [10–12]. In MIES metastable helium atoms ($2^3S/2^1S$) are utilized to eject electrons from the substrate surface. Since the metastable helium atoms approach the surface with thermal kinetic energy (below 100 meV), this technique is non-destructive and highly surface sensitive. For a more detailed introduction in MIES and its various applications in molecular and surface spectroscopy see the recent review from Harada et al. [13]. A cold cathode He gas discharge source serves both as the source for an intense metastable He beam for MIES ($\text{He}^*(2^3S/2^1S)$ with 19.8/20.6 eV excitation energy) and as a HeI photon source for UPS (HeI with 21.2 eV). The contributions to the electron spectra from metastables and photons within the beam are separated by means of a time-of-flight technique. The energy scales in the figures are adjusted in such a way that electrons emitted from the Fermi level, denoted by E_F , i.e. electrons with the maximal kinetic energy, show up at the fixed energy $E_B = 0$ eV. The position of E_F is determined from MIES spectra for alkali-titania [14]. In the MIES spectra E_F is positioned at

19.8 eV by choosing a suitable bias potential; the low-energy cutoff in the spectra gives directly the surface work function, irrespective of the actual interaction process which leads to the production of electrons. Alkali atoms were dosed employing carefully outgassed commercial dispenser sources (SAES Getters). The dispensers operate at a rate of 0.05 ML/min, typically. (1ML corresponds to the saturation coverage at RT.) The procedure for the calibration of the Na coverage is described elsewhere [14]. During the co-adsorption the vapor pressures are 5×10^{-9} Torr, typically.

3. Results and discussion

3.1. Water

MIES results (supplemented by HeI and HeII data) collected for bare TiO₂(1 1 0) at 300 and 130 K are published elsewhere [10,11,14,15] (see also Fig. 1 bottom). The spectra show two structures, labeled Auger neutralization (AN) and Auger de-excitation (AD). They are caused by the processes resonance ionization, followed by AN, and AD of He^* probe atoms, involving the O2p electrons of the titania valence band. The spectra collected under exposure to water at 130 K show that molecular physisorption dominates. An eventual dissociative adsorption at surface defects cannot be excluded, however. The respective OH species do however not account for more than 5% of the total water induced signal [11].

The situation changes drastically, even at RT, when water and alkali atoms are co-adsorbed. Fig. 1 shows the MIES results for the (Na–water) co-adsorption, as described in Section 2, on TiO₂ at RT. Under the assumption that the Na sticking coefficient is not altered by the water co-adsorption, the Na coverage is 0.5 ML after about 10 spectra; at this point the work function has dropped to its minimum value. The insert shows the region between E_F and $E_B = 4$ eV. Results for the other studied alkalis (Li, K, Cs) are qualitatively similar [10]. In the early stage of alkali exposure no adsorption of water takes place: the spectral features still result from AD and AN of He^* involving oxygen 2p electrons of the titania valence band.

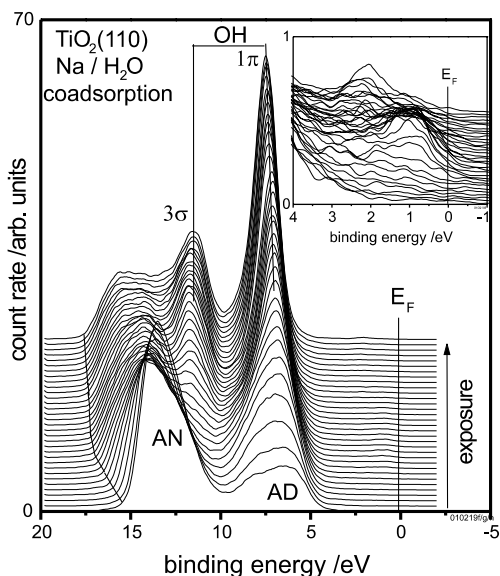


Fig. 1. MIES spectra for co-adsorption of Na and water at RT on $\text{TiO}_2(110)$ (see text for the acronyms employed in the figure); Na dispenser: 0.05 ML/min; H_2O pressure: 5×10^{-9} Torr.

The adsorption of Na is however manifested by the decrease of the work function as is evident from the shift of the cut-off of the spectra at low kinetic energies. This is the exposure range where the alkali adsorbs ionically, thereby transferring its valence electron to the surface. At larger exposures the initially observed work function decrease levels off, and two water-induced features labeled 1π and 3σ , appear. They originate from the ionization of the 1π and 3σ MOs of OH [16]. In addition, weak intensity is seen at binding energies between zero and about 4 eV that we attribute to the presence of the alkali s-electron at the alkali core.

Our interpretation is as follows: the charge transfer from the Na atom to the surface is incomplete at larger exposures. Instead, Na 3s-charge density is transferred to adjacent water molecules, which, as a consequence, dissociate. The beginning of OH formation coincides with the build up of a small peak at E_F as shown in the insert of Fig. 1. Features close to E_F are typical for alkali atoms that are surrounded by s-charge density [13,14]. The shift of the feature close to E_F for higher coverages is typical for alkali atoms surrounded by

water or OH. However, these details are beyond the scope of this publication and will be discussed elsewhere [10]. The resulting (Na–OH) complex bonds to the surface comparatively strongly, as can be shown by heating experiments. When the Na supply is stopped, but the surface held at 130 K is still exposed to water, adsorption takes place in molecular form, underlining the importance of a direct (Na–water) interaction, connected with electron exchange, for the dissociation of water. The details of these experiments are not shown here, but can be found in a forthcoming publication.

3.2. Carbon dioxide

At clean titania the CO_2 uptake is virtually zero, even at 130 K. It was found that sub-monolayers of Na atoms enhance the reactivity dramatically at RT [5,6,8]. The formation of a carbonate species was found. In order to understand the chemisorption mechanism we have studied the co-adsorption of alkali atoms (Li, Na, K, Cs) and CO_2 at $\text{TiO}_2(110)$ under in situ control of MIES (and UPS). The results for K and Cs at RT are already published elsewhere [5]. Fig. 2 shows the MIES results for Na and CO_2 co-adsorption obtained at RT: as for water, no chemisorption of CO_2 takes place in the early stage of alkali adsorption, and only the features AN and AD, typical for the clean TiO_2 substrate, are seen. The insert shows the region between E_F and $E_B = 4$ eV. On the other hand, the work function decrease signals Na adsorption. In this exposure range the Na 3s electron is fully transferred to the surface (see Section 3.1). When the work function starts to saturate, the electron transfer becomes incomplete, and three CO_2 -induced features show up at 6.4; 11.0; 13.2 eV. The identification of the features follows from our earlier results dealing with the interaction of CO_2 with MgO and CaO surfaces [17,18]. The features are due to the ionization of a CO_3^{2-} species, and are assigned to the MOs ($1a_2'$; $1e''$, $4e'$) (6.1 eV), ($3e'$; $1a_2''$) (11 eV) and ($4a'$) (13.2 eV). As for water, weak intensity is seen at the larger exposures at binding energies between zero and 4 eV. When the Na supply is stopped, no additional CO_2 is adsorbed anymore.

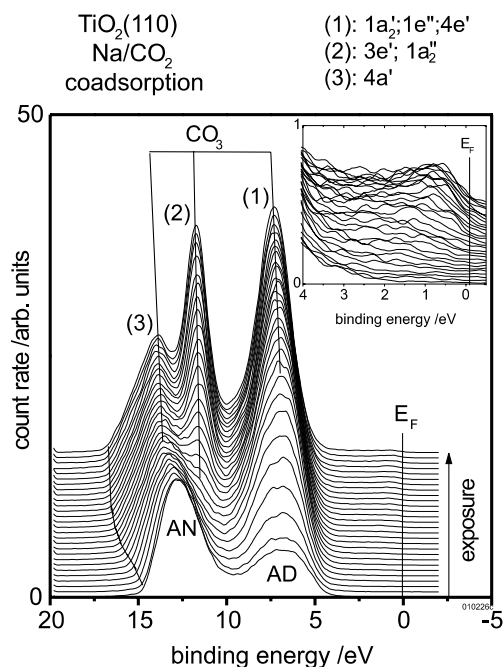


Fig. 2. MIES spectra for co-adsorption of Na and CO₂ at RT on TiO₂(110) (see text for the acronyms employed in the figure); Na dispenser: 0.05 ML/min; CO₂ pressure: 5×10^{-9} Torr.

Experiments with Li, K and Cs show an equivalent behavior and, at last in case of K, no difference could be observed for 300 and 130 K.

In the simplest model, able to account for the present results, only one CO₂ molecule is involved in the chemisorption process: the chemisorption complex results from the CO₂ interaction with O²⁻ surface ions. At the bare titania surface, the interaction potential between CO₂ and O²⁻ possesses a barrier along the reaction co-ordinate which prevents the formation of a stable (CO₂/O²⁻) complex at all temperatures. Obviously, alkali co-adsorption removes the kinematic barrier in the following way: transfer of Na 3s-charge density takes place to the CO₂ adsorbate, presumably into the 2π_u MO. As a consequence, a bent CO₂^{δ-} species is formed. The (sp³)-hybridized CO₃ species is due to chemisorption of the CO₂^{δ-} species at surface oxygen ions. A similar mechanism was proposed in order to explain the different reactivity of MgO and CaO with respect to CO₂ [19,20]. At metal surfaces, the formation of CO₂⁻-like com-

plexes by alkali atom co-adsorption is quite common and is discussed at length in Refs. [1,3]. Carbonate-like species may be formed by the CO₂⁻ interaction with neutral CO₂. This mechanism may also contribute to CO₂ chemisorption.

4. Summary

The interaction of water and carbon dioxide with TiO₂ surfaces was studied with MIES and UPS (HeI and II) at RT and 130 K. At the clean surface water adsorbs molecularly at 130 K and forms amorphous water multi-layers whereby hydrogen bonding between adjacent water molecules is important. No CO₂-induced changes in the electronic structure are apparent, even at 130 K.

The interaction of water and alkali atoms on TiO₂ produces hydroxyl groups, both at RT and 130 K, which are probably part of (Na–OH) complexes. MIES proves that OH formation is correlated with transfer of alkali valence charge density to the water molecules offered to the surface.

Carbonate (CO₃) formation occurs when CO₂ interacts with alkali atoms on titania, both at RT and 130 K. As MIES shows, CO₃ formation is again correlated with transfer of alkali charge density to the CO₂ molecule, facilitating the CO₃ formation via the formation of a CO₂^{δ-} precursor.

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