First Principles Analysis of H2O Adsorption on the (110) Surfaces of SnO2, TiO2 and Their Solid Solutions

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Abstract: Both associative and dissociative H2O adsorption on SnO2(110), TiO2(110), and Ti-enriched Sn1-xTixO2(110) surfaces have been investigated at low (1/12 monolayer (ML)) and high coverage (1 ML) by density functional theory calculations using the Gaussian and plane waves formalism. The use of a large supercell allowed the simulation at low symmetry levels. On SnO2(110), dissociative adsorption was favored at all coverages and was accompanied by stable associative H2O configurations. Increasing the coverage from 1/12 to 1 ML stabilized the (associatively or dissociatively) adsorbed H2O on SnO2(110) because of the formation of intermolecular H bonds. In contrast, on TiO2(110), the adsorption of isolated H2O groups (1/12 ML) was more stable than at high coverage, and the favored adsorption changed from dissociative to associative with increasing coverage. For dissociative H2O adsorption on Ti-enriched Sn1-xTixO2(110) surfaces with Ti atoms preferably located on 6-fold-coordinated surface sites, the analysis of the Wannier centers showed a polarization of electrons surrounding bridging O atoms that were bound simultaneously to 6-fold-coordinated Sn and Ti surface atoms. This polarization suggested the formation of an additional bond between the 6-fold-coordinated Ti-6c and bridging O atoms that had to be broken upon H2O adsorption. As a result, the H2O adsorption energy initially decreased, with increasing surface Ti content reaching a minimum at 25% Ti for 1/12 ML. This behavior was even more accentuated at high H2O coverage (1 ML) with the adsorption energy decreasing rapidly from 145.2 to 101.6 kJ/mol with the surface Ti content increasing from 0 to 33%. A global minimum of binding energies at both low and high coverage was found between 25 and 33% surface Ti content, which may explain the minimal cross-sensitivity to humidity previously reported for Sn1-xTixO2 gas sensors. Above 12.5% surface Ti content, the binding energy decreased with increasing coverage, suggesting that the partial desorption of H2O is facilitated at a high fractional coverage.

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First Principles Analysis of H$_2$O Adsorption on the (110) Surfaces of SnO$_2$, TiO$_2$ and their Solid Solutions

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ABSTRACT

Associative and dissociative H$_2$O adsorption on SnO$_2$(110), TiO$_2$(110) and Ti-enriched Sn$_{1-x}$Ti$_x$O$_2$(110) surfaces have been investigated at low (1/12 monolayer (ML)) and high coverage (1 ML) by density functional theory calculations using the Gaussian and plane waves formalism. The use of a large supercell allowed the simulation at low symmetry levels. On SnO$_2$(110) dissociative adsorption was favored at all coverages accompanied by stable associative H$_2$O configurations. Increasing the coverage from 1/12 to 1 ML stabilized the (associatively or dissociatively) adsorbed H$_2$O on SnO$_2$(110) due to the formation of intermolecular H-bonds. In contrast, on TiO$_2$(110), adsorption of isolated H$_2$O groups (1/12ML) was more stable than at high coverage and favored adsorption changed from dissociative to associative with increasing coverage.

For dissociative H$_2$O adsorption on Ti-enriched Sn$_{1-x}$Ti$_x$O$_2$(110) surfaces with Ti atoms preferably located on six-fold coordinated surface sites, analysis of the Wannier centers showed a polarization of electrons surrounding bridging O atoms that were bound simultaneously to six-fold coordinated Sn and Ti surface atoms. This polarization suggested the formation of an additional bond between the six-fold coordinated Ti$_{6c}$ and bridging O atoms that had to be broken upon H$_2$O adsorption. As a result, the H$_2$O adsorption energy initially decreased with increasing surface Ti-content reaching a minimum at 25 % Ti for 1/12 ML. This behavior was even more accentuated at high H$_2$O coverage (1ML) with the adsorption energy decreasing rapidly from 145.2 to 101.6 kJ/mol with Ti content increasing from 0 to 33 %. A global minimum of binding energies at both low and high coverage was found between 25 and 33 % surface Ti-content which may explain the minimal cross-sensitivity to humidity previously reported for Sn$_{1-x}$Ti$_x$O$_2$ gas sensors. Above 12.5 % surface Ti-content, the binding energy decreased with increasing coverage suggesting that partial desorption of H$_2$O is facilitated at high fractional coverage.
INTRODUCTION

The semiconducting nature of many metal oxides makes them interesting materials for numerous industrial and economical important applications. Wide band gap semiconducting metal oxides such as SnO$_2$ and TiO$_2$ are used, for example, in solar cells$^{1,2}$, photocatalysis$^{3,4}$ and as chemoresistive portable gas sensors$^5$. Since the pioneering work of Fujishima and Honda$^3$ in 1972 on photoinduced decomposition of H$_2$O on TiO$_2$, intensive research has been done to optimize the photocatalytic behavior of TiO$_2$ for hydrogen production from H$_2$O or hydrocarbons and for degradation of organic pollutants$^{6,7}$. The main advantages of TiO$_2$-based materials in this area are their high stability, low costs and high photoactivity$^{8,9}$. Considerable improvement of TiO$_2$ was achieved by substitutional or interstitial doping with anionic species, in particular nitrogen$^{4,10}$. Doping with cationic metal atoms such as Pt$^{11}$ and Sn$^{12,13}$ has also shown to improve the photocatalytic behavior.

The performance of TiO$_2$-based photocatalysts used in gas-solid phase reactions varies significantly with the relative humidity$^{14-16}$. At low H$_2$O content, degradation of pollutants is enhanced by an increased number of hydroxyl groups on the surface$^{14}$. However, for higher water content the H$_2$O species are competing with the actual reactants$^{14,15}$, reducing the reaction rates as it has been shown for trichloroethylene$^{15}$ and $m$-xylene$^{17}$. Furthermore, H$_2$O species adsorbed on the TiO$_2$ surface decrease the upward band bending. This facilitates the recombination of electron and holes and reduces the photocatalytic activity$^{9,16}$. Thus it is an important task to control the water adsorption properties on TiO$_2$-based catalysts in order to optimize their photocatalytic activity.

Another interesting field for semiconducting metal oxides is their use as chemoresistive gas sensors$^{18}$. Their ability to change conductivity when gaseous molecules are reacting with the surface makes them particularly applicable for such devices$^{19,20}$. Solid state gas sensors made of metal oxide nanoparticles are currently utilized for process safety control, environmental monitoring and homeland security$^{21,22}$. They have been applied to human breath analysis to estimate the blood alcohol content of drunk drivers$^{23}$ and more recently for the detection and monitoring of breath markers for several diseases such as lung cancer$^{24}$ or diabetes$^{25}$. Tin oxide (SnO$_2$) is the most widely used metal oxide for chemoresistive gas sensors$^{26}$. Its sensitivity and selectivity depend also on the exposed facets of the rutile crystal structure$^{27}$. Han et al.$^{28}$ synthesized SnO$_2$ particles with different morphology and found that octahedral particles with
exposed high-energy (221) facets show highest gas-sensing performance towards ethanol.
However, the gas sensing performances reported in this article are rather poor compared to those found in other studies with exposed low-index SnO$_2$ facets such as (110), (101) and (100).$^{29}$ Furthermore, such high-index (221) facets have a higher surface energy$^{28}$ and thus are more difficult to produce than spontaneously growing low-index facets.$^{30}$

High sensitivity and selectivity is in particular important for chemoresistive gas sensors used in non-invasive medical diagnostics (breath analysis) since the breath consists of more than 1000 volatile compounds and has a high relative humidity (r.h.).$^{31}$ This is particularly problematic as water vapor increases the electrical conductivity of the metal oxide upon reaction with its surface and thus results in an unreliable sensor response.$^{32,33}$ High cross-sensitivity to humidity is a major drawback of SnO$_2$, one of the most studied and widely used gas sensing metal oxides, sensitive to several relevant analytes such as CO, NO$_x$, H$_2$ and ethanol.$^{26}$ In fact, the reaction between water vapor and the SnO$_2$ surface leads to remarkable changes (up to 85%) in its sensor response.$^{32,33}$ Even for more selective sensing oxides such as WO$_3$, water vapor is a common problem$^{34}$ that limits its applicability to non-invasive medical diagnostics by breath analysis.

The understanding of the cross-sensitivity mechanism of gas sensing metal oxides to humidity is still in progress. As a result, there is a necessity for further research on the H$_2$O adsorption on wide band gap semiconducting metal oxides that overlaps with the interest to optimize such materials for photocatalysis. For adsorption of H$_2$O on SnO$_2$ and the resulting increase in electrical conductivity, three main paths have been proposed.$^{33}$ In the first mechanism, it is suggested that H$_2$O dissociates in an H atom and OH group that react further with the metal oxide surface. The OH group (terminal OH) binds to a surface metal atom, whereas the H atom binds to a rooted O atom resulting in a rooted OH group. The latter is then donating an electron to the conduction band$^{35}$ according to:

$$\text{H}_2\text{O}_{\text{gas}} + \text{Sn}^{\delta+} + \text{O}^\delta \rightarrow (\text{Sn}^{\delta+} - \text{OH}^\delta) + (\text{OH})^\delta + e^- \quad (1)$$

The asterisk indicates the active sites of the metal oxide surface, whereas (Sn$^{\delta+}$ - OH$^{\delta}$) is referred to an isolated (terminal) hydroxyl group and (OH)$^\delta$ to a rooted OH group. Since the rooted O is normally in the (2-) state it can become ionized and function as an electron donor.

The second mechanism considers the formation of oxygen vacancies. In this mechanism, the rooted OH group reacts further and binds to a neighboring Sn atom producing an oxygen vacancy. This vacancy donates by ionization two electrons to the conduction band of the
The third mechanism is described as an indirect process where pre-adsorbed species are changing the electron affinity of the surface. This could be for instance the reaction of the adsorbed hydroxyl group or the hydrogen atom bond to rooted O which are acting as active sites on the surface and possibly react with acid or basic groups.

Recently, it has been shown that altering the SnO\textsubscript{2} structure by introduction of impurities results in a drastic stabilization of the sensor response in the presence of varying water vapor content. Doping of SnO\textsubscript{2} nanoparticles with low Ti-content (4.6 at\%) decreased the cross-sensitivity to r.h. remarkably while maintaining high sensitivity towards the tested analyte (ethanol). At the optimal doping content, a residual cross-sensitivity to r.h. of ca. 15\% was measurable increasing the r.h. from 0 (dry air) to 20\%. Further increase of the r.h. did not have any effect on the sensor signal. This approach was particularly convenient as both metal oxides (SnO\textsubscript{2} and TiO\textsubscript{2}) share a rutile crystal phase and their co-synthesis at high temperature (>2000K) promoted the formation of a substitutional solid solution without any segregation up to 80 at\% of Ti.

The two metal oxides, SnO\textsubscript{2} and TiO\textsubscript{2}, have noticeable differences in electronic and adsorption properties due to the fact that Ti is a transition metal and Sn is a group IV element. In terms of sensitivity and conductivity, TiO\textsubscript{2} is inferior to SnO\textsubscript{2}. Nevertheless, it has a higher thermodynamic stability and less cross-sensitivity to humidity than SnO\textsubscript{2}. Experimentally studied Sn\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{2} nanoparticles combined the advantages of both metal oxides but the fundamental understanding of the H\textsubscript{2}O interaction with their surface is still sought for.

In this regard, theoretical investigation of the Sn\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{2} system represents a unique opportunity to achieve a better understanding of the mechanisms controlling the adsorption properties of H\textsubscript{2}O on wide band gap semiconducting metal oxides for application in gas sensing and photocatalysis. Among computational methods, density functional theory (DFT) is a quantum mechanical method that is widely used to describe catalytic processes mainly on crystal metal surfaces. Furthermore, it has been proven to be an appropriate method for the calculation of metal oxide surfaces. In fact, DFT has been applied to evaluate the stability of stoichiometric pure SnO\textsubscript{2} and TiO\textsubscript{2} surfaces showing that for both crystals the (110) surface is the most favored. Moreover, the Sn\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{2} bulk system has been studied by DFT confirming the experimentally measured variation from Vegard’s law for the rutile lattice parameters. Adsorption properties of H\textsubscript{2}O on the pure SnO\textsubscript{2} and TiO\textsubscript{2}(110) surfaces have been studied extensively by DFT. It has been shown that H\textsubscript{2}O tends to dissociate spontaneously on the
SnO$_2$(110) surface at high coverages, indicating that dissociative adsorption is favored over associative one.$^{48,49}$ In contrast for TiO$_2$, associative adsorption is favored over dissociative adsorption at full coverage$^{50}$ while dissociative adsorption becomes favorable at low coverage.$^{51}$

In this study, we have used DFT calculations with Gaussian plane wave (GPW) basis sets$^{52,53}$ to investigate the H$_2$O adsorption properties on Sn$_{1-x}$Ti$_x$O$_2$ solid solutions. The GPW approach allows the simulation of large systems with good computational efficiency. First, the binding energies and geometrical properties for dissociative and associative H$_2$O adsorption were computed on the pure SnO$_2$ and TiO$_2$ surfaces at high and low H$_2$O coverages to verify the consistence with previous works. The dissociative adsorption energy was then evaluated for Sn$_{1-x}$Ti$_x$O$_2$ solid solutions as a function of the Ti-content providing an explanation for the minimal cross-sensitivity to humidity observed for gas sensors made of such solid solutions.

**METHODS**

**Computational Details.** The simulations performed in this investigation were based on DFT as implemented in the CP2K program package, a suite of programs aimed at performing efficient electronic structure calculations and molecular dynamics at different levels of theory.$^{54}$ Rutile type metal oxides can be simulated with good agreement to experimental results using exchange-correlation potentials with general gradient approximation (GGA).$^{41}$ The electronic structure calculations employ the Gaussian and plane wave (GPW) formalism.$^{52,53}$ Interaction of valence electrons with frozen atomic cores was described using norm conserving, dual-space type pseudopotentials.$^{55}$ For Sn and Ti metal atoms, 4 and 12 electrons were explicitly considered, respectively, in the valence shell. A double-zeta valence plus polarization (DZVP) basis set, optimized according to the Mol-Opt method$^{56}$ has been adopted for the metal atoms and hydrogen and a triple-zeta valence plus polarization for oxygen. For auxiliary PW expansion of the charge density, the energy cutoff has been set at 400 Ry. Exchange-correlation potentials were modeled using the Perdew-Burke-Ernzerhof (PBE) functional.$^{57}$

The size of the simulation domain is a critical parameter in real space calculations. It defines the accuracy of the density, the accuracy of the physical system and the computational time frame needed. The optimal compromise between physical accuracy and resource allocation for the present investigation was found to be a supercell of 720 atoms. The rutile primitive cell has been repeated 3 and 4 times along the x and y directions, respectively. Along the z-direction, the cell
has been repeated 10 times, in order to form a slab of ten metal atom layers. All simulations were performed with periodic boundary conditions. Determination of the optimal lattice parameters \( a \), \( c \) and \( u \) has been carried out by self-consistent wave function calculations for different lattice values until the convergence in the total energy was lower than \( 10^{-3} \) eV per metal atom of the super cell. The cell parameters for Sn\(_{1-x}\)Ti\(_x\)O\(_2\) solid solutions were optimized with Ti atoms distributed in the bulk. The optimized parameters can be found elsewhere.\(^{58}\) The simulations with Ti-surface distribution were performed using the parameters optimized for bulk calculations. To simulate the surface, 10 Å of vacuum were added along the z-direction in order to avoid any interaction of the cluster with its periodic image. Three metal atom layers on the top and the bottom of the slab were allowed to relax in all dimensions while four layers were fixed to simulate the bulk corresponding to the simulation domain used previously\(^{58}\) investigating the stability of Sn\(_{1-x}\)Ti\(_x\)O\(_2\)(110) surfaces.

The adsorption of \( \text{H}_2\text{O} \) was simulated on one of the exposed surfaces of the slab. It is supposed that placing adsorbates on both sides gives more accurate results since possible dipoles are eliminated.\(^{59}\) However, calculations with adsorbates on both sides showed a difference in binding energy of less than 3.5 kJ/mol. Thus, it was concluded that precise values of the binding energy are yielded also when simulating adsorption only on one surface. The \( \text{H}_2\text{O} \) binding energies \( (E_B) \) were calculated according to:

\[
E_B = \frac{E_{\text{slab}+n\text{H}_2\text{O}} - (E_{\text{slab}} + n \cdot E_{\text{H}_2\text{O},g})}{n}
\]  

(2)

where \( n \) gives the number of adsorbed species on the described surface and \( E_{\text{slab}+n\text{H}_2\text{O}} \) denotes the energy of the surface slab plus \( n \) adsorbates. The energy of an isolated \( \text{H}_2\text{O} \) molecule \( (E_{\text{H}_2\text{O},g}) \) was calculated in a periodically repeated cell of 20 Å. Here, the surface plane consisted of 12 unit cells meaning that full \( \text{H}_2\text{O} \) coverage (1 ML) corresponds to 12 adsorbed \( \text{H}_2\text{O} \) groups.

Surface metal atoms (Fig. 1) bound to five or six neighboring O atoms were named as Me\(_{5c}\) or Me\(_{6c}\), respectively. Rooted O atoms that are located in the surface layer were denoted as O\(_r\), whereas bridging O atoms are denoted as O\(_{br}\) (Fig. 1). The O atoms where \( \text{H}_2\text{O} \) was associatively adsorbed were denoted as O\(_{\text{H}_2\text{O}}\).
RESULTS AND DISCUSSION

On pure SnO$_2$ and TiO$_2$, associative and dissociative chemisorption of water at different coverages was simulated. For associative adsorption, the bonds of the water molecule were preserved and the H$_2$O molecule was placed perpendicular to the surface with the oxygen atom (O$_{H2O}$) bound to a fivefold coordinated metal atom site.\textsuperscript{44,50} In contrast, for dissociative adsorption, one H atom was separated from the H$_2$O molecule (Fig. 1). The OH group was bound to a five-fold coordinated (5c) metal atom (Me$_{5c}$), resulting in a terminal OH group (OH$_{term}$), and the separated H atom was bound to a bridging O (O$_{br}$), resulting in a rooted OH group (OH$_{root}$). This mechanism was proposed previously for dissociative H$_2$O adsorption on rutile (110) surfaces.\textsuperscript{48,50,60} For dissociative H$_2$O adsorption, the interaction between surface OH groups plays an important role. In the following, the distance between the H atom of an OH$_{root}$ group and the O atom of an OH$_{term}$ group is denoted as $d_{root}$ and the distance between H and O atom of two adjacent terminal groups as $d_{term}$ (Fig. 1a).

Adsorption on SnO$_2$(110)

\textit{Isolated Adsorption (1/12 ML).} Associative adsorption of an isolated H$_2$O molecule (1/12 ML) was found to be stable in a perpendicular configuration (Fig. 2a,b). The distance between Sn$_{5c}$ and O$_{H2O}$ was 2.28 Å. Additionally to the perpendicular configuration, the H$_2$O molecule was initially placed parallel to the surface (not shown). In this case, however, the H$_2$O molecule dissociated spontaneously. In the dissociated configuration, the Sn$_{5c}$-OH$_{term}$ (Fig.1b) bond length was remarkably smaller (2.02 Å) indicating a stronger bond. This Sn$_{5c}$-OH$_{term}$ bond length was equal to that between Sn$_{6c}$ and O$_{br}$ of the clean SnO$_2$(110) slab\textsuperscript{58} suggesting similar characteristics to the Sn-O bonds.

The distance between H atoms of an associatively adsorbed H$_2$O molecule and O$_{br}$ was 2.86 Å (Fig. 2a). For dissociative adsorption, smaller intermolecular distances were found: The H atom of the OH$_{root}$ group and the O atom of the OH$_{term}$ had a distance ($d_{root}$) of 2.36 Å (Fig. 2d). This indicated the presence of additional attractive interactions for dissociative adsorption. It was further observed that the H atom of the OH$_{term}$ group pointed towards the nearest O$_{br}$ atom (opposite of the OH$_{root}$ group, 3.11 Å, Fig. 2d). Thus, approaching of the two OH groups as it was observed at higher coverages (1.94 Å\textsuperscript{44}) was prevented.

The binding energy of associatively adsorbed H$_2$O was 98.8 kJ/mol, whereas for dissociative adsorption it was significantly larger amounting to 135.2 kJ/mol. Based on these results, it is
concluded that at low coverage H$_2$O tends to dissociate on the SnO$_2$(110) surface. The stabilization of dissociated H$_2$O can be explained by attractive interactions between the OH groups and a stronger bond between Sn$_{5c}$ and the O of the OH$_{term}$ group.

**High coverage adsorption (1 ML)**

*Structural properties.* For associatively adsorbed H$_2$O, the initial configuration was perpendicular to the surface as set for the isolated H$_2$O adsorption (1/12 ML). However, at this high coverage the H$_2$O molecules bent towards the surface resulting in a parallel associative adsorption configuration (Fig. 3a). This is in contrast to what was observed (see discussion above) for isolated H$_2$O molecules which spontaneously dissociated when initially positioned in a parallel configuration. As a result, at high coverage, the distance between an H atom and an O$_{br}$ atom was reduced to 1.42-1.88 Å (Fig. 3a) due to this bending of the molecules towards the surface. It is suggested that these H-bonds are stabilizing the H$_2$O on the surface at high coverage. The intermolecular distance between two H$_2$O molecules was 2.49 Å (Fig. 3a) indicating additional attractive interactions that are not present for isolated H$_2$O. The latter presumably affected the electron density around the H pointing to the O$_{br}$ atom hindering the dissociation of an H atom as it was observed for isolated H$_2$O. The distance between the O$_{H_2O}$ atom and the Sn$_{5c}$ atom (Sn$_{5c}$-O$_{H_2O}$) was larger for 1 ML associative adsorption (2.39 Å) than at low coverage (2.28 Å) indicating weaker bonds.

For dissociative adsorption, the d$_{root}$ distance (Fig. 1a) was remarkably smaller at high coverage (1.80 Å, Fig. 4a) than at low coverage (2.36 Å) indicating enhanced H-bonds. At high coverage, the H atom of OH$_{term}$ groups was attracted by the O atom of a neighboring OH$_{term}$ group. In contrast, at low coverage, the H atom of the OH$_{term}$ group was attracted by an adjacent O$_{br}$ (3.11 Å, Fig. 2d) atom leading to a larger d$_{root}$ distance.

Moreover, the neighboring OH$_{term}$ groups showed additional attractive interactions between the H and O atom of two adjacent groups that was not possible for isolated H$_2$O adsorption. The distance between these H and O atoms (d$_{term}$) was 2.49 Å. The bond length between Sn$_{5c}$ atoms and an OH$_{term}$ group (Sn$_{5c}$-OH$_{term}$, Fig. 1b) was similar for both high (2.06 Å) and low (2.02 Å) coverage indicating same bond characteristics for both coverages. These values were close to the bond length between Sn$_{6c}$ and O$_{br}$ (2.02 Å) of the clean SnO$_2$(110) surface.$^{58}$

Additional to pure associative and dissociative configurations, a stable state was found in a mixed configuration where half of the molecules dissociated and the other half was adsorbed
associatively (Fig. 3b). This configuration resembles the one found for partial H₂O dissociation on Ru(0001) where a hexagonal pattern was formed. On SnO₂, the Sn₅c-OH₂O bond length was with 2.25 Å similar to that (2.28 Å) for isolated H₂O adsorption suggesting similar bond characteristics. The bond length between Sn₅c and the dissociated OH₄term groups (2.09 Å) was close to that for pure dissociative adsorption at high (2.06 Å) coverage and isolated H₂O (2.02 Å). The complete geometrical properties are reported in Figure 3b.

**Stability.** Pure associative adsorption of H₂O at 1 ML had a binding energy of 112 kJ/mol (Fig, 3a, Table 1). The same binding energy (113 kJ/mol) was computed in a previous study using a smaller unit cell with the PBE exchange-correlation functional. However, in the latter, artificial constraints were introduced for the relaxation to prevent spontaneous dissociation of the H₂O molecules. Figure 3a shows that the H₂O molecules bound to the left and the middle column of Sn₅c atoms pointed towards the Obr atom on their left side, whereas the H₂O molecules of the last column pointed towards the Obr atom on their right side resulting in an asymmetric configuration. Previous DFT studies applying the planewaves approach showed that molecular H₂O on rutile (110) SnO₂ is neither stable for a complete nor half a monolayer coverage of H₂O. There, water molecules placed initially above a fivefold coordinated Sn atom dissociated spontaneously into OH and H. However, the unit cells used in those studies had a surface about three times smaller than that used here. The use of smaller cells restricts the possible configurations of adsorbates and their periodic repetition leads to more symmetric arrangements of adsorbed species. To understand the destabilizing effect of higher orientation symmetry (all H₂O molecules pointing into the same direction), the water molecules of the third column (Fig. 3a) were artificially placed so that they pointed all into the same direction. This led to dissociation of half the H₂O molecules (Fig. 3b) resulting in a mixed associative and dissociative adsorption state with a binding energy of 137.8 kJ/mol (Table 1). An associative configuration was found in previous studies using a smaller unit cell but required the utilization of the hybrid functional B3LYP. This was attributed to the larger H-bond length in hybrid DFT calculations such as B3LYP (than in plain ones) that inhibited the formation of covalent bonds and thus H₂O dissociation. However, the results presented here demonstrate that spontaneous dissociation of H₂O on SnO₂(110) is not only affected by the functional used but also by constraints resulting from the use of a small unit cell with periodic boundary conditions which lead to unreasonably high symmetry configurations. Here, for the first time, a stable state for associative adsorption configuration was established in a more asymmetric configuration.
using a standard exchange-correlation potential (PBE). Such associative adsorption is consistent with experiments showing the presence H₂O molecules on the SnO₂(110) surface. This suggests that restrictions of the system size have to be considered as potential sources of errors in DFT calculations.

Pure dissociative adsorption at 1 ML H₂O resulted in a binding energy of 145.2 kJ/mol. Again, this was in very good agreement with previous results reporting a value of 141 kJ/mol. It was significantly more stable than associative adsorption (112 kJ/mol) (Table 1), similarly to that observed for isolated H₂O adsorption. For all coverages simulated in this study, on SnO₂, the binding energies of dissociative H₂O (135.2-145.2 kJ/mol) adsorption were higher than that of associative H₂O adsorption (98.8-112.0 kJ/mol) demonstrating that H₂O molecules preferably adsorb dissociatively on SnO₂(110) independent of the coverage.

The analysis of the geometry suggested the presence of intermolecular H-bonds at high H₂O coverage for both associative and dissociative adsorption. These H-bonds stabilized the adsorbates and resulted in higher binding energies at high coverage. In contrast, H-bonding was previously considered to play only a marginal role for H₂O adsorption on SnO₂. Furthermore, the higher binding energies at high coverage indicate that on SnO₂ adsorption of H₂O is enhanced with increasing water content. For the use of SnO₂ as a gas sensor, this means that the higher the relative humidity the more H₂O is adsorbed. Consequently, the conductivity and response of SnO₂ gas sensors depend on the relative humidity also at relatively high humidity concentration.

**Adsorption on TiO₂(110)**

*Isolated Adsorption (1/12 ML).* On TiO₂, in contrast to SnO₂, associatively adsorbed H₂O was stable both in configurations perpendicular (not shown, cf. Fig. 2a,b) and parallel (Fig. 5a,b) to the surface. The bond length between Ti₅c and O₉H₂O was similar for both configurations (2.25 Å and 2.26 Å) and close to that on SnO₂ (2.28 Å). Despite the smaller lattice parameters of TiO₂ (a = 4.64 Å and c = 2.98 Å), the perpendicular H-O₉ distance (2.87 Å) was similar to that on SnO₂ (2.86 Å). This suggests that the H-O interaction is hardly affected by the dimension of the lattice or by the metal atom type (Sn or Ti).

For dissociatively adsorbed H₂O, the Ti₅c-OH₉term distance (1.82 Å, Fig. 5c) was remarkably smaller than for associative adsorption and, as observed for SnO₂, close to the Ti₆c-Obr distance of the clean TiO₂(110) surface (1.83 Å). For dissociation of the H₂O molecule, droot (Fig. 5c) of 2.30 Å was found.
The perpendicular configuration (92.0 kJ/mol) of an H$_2$O molecule was slightly more stable than the parallel one (89.5 kJ/mol, Table 2). Dissociation was, similar to SnO$_2$, favored over both types of associative configurations with a binding energy of 99.4 kJ/mol (Table 2).

**High Coverage Adsorption (1 ML)**

**Structural Properties.** For 1 ML associatively adsorbed H$_2$O, the distance between the H atom and O$_{br}$ was with 2.11 Å (Fig. 3c) remarkably larger than that on SnO$_2$ (1.42-1.88 Å, Fig. 3a) regardless of the smaller lattice parameters of TiO$_2$. This suggests, that H-bonds between adsorbates and surface are less pronounced on TiO$_2$. The Ti$_{5c}$-O$_{H2O}$ distance was larger at high coverage (2.40 Å) than for both perpendicular (2.25 Å) and parallel (2.25 Å, Fig. 5a) configuration at low coverage as observed for SnO$_2$. This indicates that at high coverage, the Ti-O bond is weaker. The distance between H and O$_{H2O}$ was smaller (2.15 Å, Fig. 3c) on TiO$_2$ than on SnO$_2$ (2.49 Å, Fig. 3a) in agreement with the smaller lattice parameters of TiO$_2$.

For dissociative adsorption, d$_{oot}$ at high coverage (2.37 Å, Fig. 5d) was larger than for isolated adsorption (2.30 Å, Fig. 5d), indicating repulsive intermolecular interactions. Thus, on TiO$_2$, no stabilization but rather marginal destabilization was established at high coverage for dissociative H$_2$O adsorption. In agreement with the different lattice parameters, d$_{term}$ was smaller on TiO$_2$ (2.16 Å, Fig. 4d) than on SnO$_2$ (2.49 Å, Fig. 4a). The Ti$_{5c}$-OH$_{term}$ distance at high coverage (1.87 Å, Table 4) was similar to that (1.82 Å) for isolated adsorption and close to the Ti$_{6c}$-O$_{br}$ distance of the clean TiO$_2$ (110) surface (1.83 Å).$^{58}$

**Stability.** At 1 ML, associative H$_2$O adsorption on TiO$_2$ (Fig. 3c) resulted in a binding energy of 78.7 kJ/mol (Table 2). Similar values (83-95.5 kJ/mol) were reported previously for associative H$_2$O adsorption on TiO$_2$ at high coverage.$^{49,50}$ Dissociatively adsorbed H$_2$O (Fig. 4d) was found to be less stable with a binding energy of 60.3 kJ/mol. This is again in reasonable agreement with previous studies (66-87.9 kJ/mol).$^{49,50,63}$ Partially dissociated H$_2$O (75.4 kJ/mol, not shown) was slightly less stable than pure associative and dissociative adsorption. This is in contrast to SnO$_2$ where partial dissociation of H$_2$O (Fig. 3b) was found to be favored over pure associative adsorption and is in agreement with the observed stabilization effect of H-bonds.

For both associative and dissociative adsorption, the binding energy at high coverage (78.7 kJ/mol and 60.3 kJ/mol, respectively) was lower than at low coverage (92.0 kJ/mol and 99.4 kJ/mol, respectively) suggesting the presence of repulsive interactions between adsorbed species. This is in contrast to SnO$_2$, where H$_2$O was more stable at high coverage. There the
stabilizing effect was attributed to the formation of H-bonds between H and O \( (1.42-1.88 \, \text{Å}, \) Fig. 3a) for associative adsorption and between OH\(_{\text{term}}\) and OH\(_{\text{root}}\) groups (\( d_{\text{root}}(1 \, \text{ML}) = 1.80 \, \text{Å} \)) for dissociative adsorption. Both distances (2.11 and 2.37 Å, respectively) were larger on TiO\(_2\), indicating a lack of intermolecular attraction. As a result, on TiO\(_2\), the binding energy decreased with increasing H\(_2\)O coverage. In other words, on TiO\(_2\), H\(_2\)O adsorption is facilitated at low H\(_2\)O content in contrast to SnO\(_2\). This implies that the saturation coverage is dependent on the temperature and can be reached already at a low relative humidity at a certain temperature. Furthermore, a larger spread between high and low coverage binding energy was observed compared to SnO\(_2\).

On the TiO\(_2\)(110) surface, the binding energies showed that, for isolated adsorption, the H\(_2\)O molecules preferred to dissociate whereas associative adsorption was favored at high coverage. Thus, the preferred adsorption mechanism changed with the coverage. There has been discrepancy about the favored adsorption mechanism on TiO\(_2\) (110) in the literature previously.\(^{43,50,51,63,64}\) Some DFT studies\(^{43,51}\) using the plane-waves formalism and the revised PBE exchange-correlation functional revealed that the dissociative mechanisms is favored at low coverages (\( \theta \leq 0.5 \, \text{ML} \)), whereas others\(^{63}\) using the PW91 functional stated that associative adsorption is favored for coverage \( \leq 1 \, \text{ML} \). Experimental studies using TPD, however, determined a tail of the desorption peak extending to higher temperatures (100 °C) which was attributed to hydroxyl groups.\(^{65}\) This confirmed the presence of dissociated H\(_2\)O at low coverages. On the other hand, at high H\(_2\)O doses (high coverage), molecular species were detected\(^{65,66}\) which supports the higher binding energy of associative adsorption at 1 ML found in this study. Furthermore, TPD analysis\(^{65,66}\) at lower H\(_2\)O doses showed a shift of the H\(_2\)O desorption peak to higher temperatures. This indicates a higher desorption energy at lower H\(_2\)O coverage which can be attributed to less dipole-dipole repulsion between adsorbed species in agreement with our findings.

**Adsorption on Sn\(_{1-x}\)Ti\(_x\)O\(_2\)(110)**

On Sn\(_{1-x}\)Ti\(_x\)O\(_2\) solid solutions dissociative H\(_2\)O adsorption was investigated for isolated species (1/12 ML) and full (1 ML) coverage. It has been shown previously that Ti is preferably distributed in the surface layer of Sn\(_{1-x}\)Ti\(_x\)O\(_2\) solid solutions,\(^{58}\) more specific on six-fold coordinated (6c) surface sites.\(^{58,67}\) Therefore, here, H\(_2\)O adsorption mechanisms were investigated on Sn\(_{1-x}\)Ti\(_x\)O\(_2\) (110) surfaces with Ti atoms located exclusively on 6c-sites up to a surface Ti-
content of 50 % where all 6c sites were occupied by Ti. For higher surface Ti-content, up to 100 %, Ti atoms were distributed additionally on 5c sites. The binding energy shown in Figure 7 represents an average value for the different binding sites at a specific surface Ti-content.

**Isolated Adsorption (1/12 ML)**

**Structural Properties.** Adsorption of isolated H$_2$O groups was investigated on all possible surface sites at each Ti-content. Accordingly, Table 3 summarizes the results averaged on all possible sites. The Me$_{5c}$-OH$_{term}$ bond length hardly changed compared to that on pure SnO$_2$ (2.02 Å) and TiO$_2$ (1.82 Å). In contrast, the average d$_{root}$ distance increased from 2.36 to 2.50 Å with increasing surface Ti-content from 0 to 100 % and was always larger than that observed for pure TiO$_2$ (2.30 Å). The increase of d$_{root}$ indicated reduced interactions and could possibly lead to weaker bond strength. The large scatter at 67% surface Ti-content resulted from a high level of irregular surface restructuring.

**Electronic structure.** For the representation of isolated H$_2$O adsorption, only a section of the surface is shown (Fig. 6) since surface configurations were relevant only in the vicinity of the adsorbate. To describe the adsorption properties, the centers of the Wannier functions were determined before (Fig. 6, left side) and after (Fig. 6, right side) H$_2$O adsorption. Green spheres in Figure 6 visualize the position of the Wannier centers around O$_{br}$ atoms.

On pure SnO$_2$(110) (Fig. 6a), four Wannier centers were close to O$_{6c}$, two of which pointed towards the adjacent Sn$_{6c}$ atoms (in [001] direction). The other two were oriented out of the surface in [110] direction indicating two free electron pairs. Upon dissociative H$_2$O adsorption, one of these free electron pairs was transformed into a bond with the H atom (Fig. 6a, right side). When some Sn$_{6c}$ atoms were substituted with Ti atoms some O$_{br}$ were bound to both metal atom types (Fig. 6b) resulting in a reorientation of the Wannier centers. In this situation, one center pointed to the Sn$_{6c}$ atom while two centers pointed to the Ti$_{6c}$ atom suggesting the formation of an additional bond between O$_{br}$ and Ti$_{6c}$. In other words, the O$_{br}$ atom formed a total of three bonds to the adjacent metal atoms and had one free electron pair. For the O$_{br}$-H bond formation, here, one of the O$_{br}$-Ti$_{6c}$ bonds (Fig. 6b, right side) had to be broken. The required energy for this step was reflected in a lower binding energy of H$_2$O (Fig. 7) on such surfaces. Regarding the reverse step this means that less energy, e.g. a lower temperature, is needed to remove H$_2$O from the Sn$_{1-x}$Ti$_x$O$_2$ surfaces.

At surface Ti-contents $>$25 %, two or more Ti$_{6c}$ atoms can be adjacent to each other (Fig. 6c).
In these cases, the neighboring Ti$_{6c}$ equally polarized the electrons (Wannier centers) of the enclosed O$_{br}$ atom resulting in a single O$_{br}$-Ti$_{6c}$ bond each (Fig. 6c) and a total of two bonds of the O$_{br}$ atom. A correlation was found between the H$_2$O binding energy and the bonds formed by O$_{br}$. For this, the fraction of O$_{br}$ atoms forming a total of three bonds to adjacent Me$_{6c}$ atoms was analyzed as a function of the surface Ti-content (Fig. 7, circles). It was maximal at 25 % surface Ti-content. The converse behavior was observed for the average binding energy. The average binding energy of all possible adsorption sites on the surface decreased (Fig. 7, diamonds) since the number of O$_{br}$ with three bonds increased with the surface Ti-content up to 25 % (Fig. 7, circles). However, further increase of the surface Ti-content decreased the number of O$_{br}$ with three bonds and thus the average binding energy increased.

At surface Ti-contents between 25 and 50 % (Fig. 6c) an additional effect was observed leading to an increase of the binding energy. When the H atom was bound to an O$_{br}$ site between Sn$_{5c}$ and Ti$_{6c}$, i.e. with three bonds, one Ti-O$_{br}$ bond was broken. However, this change in the electronic structure led to a shift of all connected Ti$_{6c}$ atoms in [001] direction closer to the O$_{br}$ atoms (Fig. 6c, right side). This induced the formation of additional Ti$_{6c}$-O$_{br}$ which was reflected in an increased binding energy (by ca. 10 kJ/mol) on such sites.

Higher surface Ti-contents (50-100 %) increased the surface reconstruction and formation of additional Ti$_{6c}$-O$_{br}$ and Ti$_{5c}$-O$_{r}$ bonds on the surface. Here, the H$_2$O adsorption led to enhanced rearrangements of the geometrical and electronic structure dependent on the local environment of the active site. Decrease of the symmetry of the surface with increasing surface Ti-content was reflected in an increased range of binding energies for different surface sites (Fig. 9). This made it difficult to draw a general conclusion for surface Ti-contents >50 %. However, it is assumed that, in the case of low coverage, H$_2$O species adsorb on the energetically most favorable site. Thus, the highest binding energy for each Ti-content is relevant for the determination of the adsorption characteristics. As a result, a global minimum of the H$_2$O binding energy for isolated adsorption (1/12 ML) was found at a surface Ti-content of 25 % suggesting that, for this Ti-content, the temperature needed to desorb small amounts of H$_2$O species from the surface is lowest.

**High Coverage Adsorption (1 ML)**

*Structural Properties.* At high coverage, d$_{root}$ increased drastically from 1.86 to 2.49 Å when increasing the surface Ti-content from 0 to 33 %. This demonstrated a loss of H-bonds between
adjacent OH groups that were observed on pure SnO$_2$. Further increase of the Ti-content hardly had any effect (2.41±0.1 Å) on $d_{\text{root}}$. It was close to that on pure TiO$_2$ (2.37 Å) indicating that $d_{\text{root}}$ was rather determined by the surface composition than by the lattice parameters. In contrast, only marginal changes were observed for the $d_{\text{term}}$ and the Sn$_{5c}$-OH and Ti$_{5c}$-OH bond length. A slight decrease of $d_{\text{term}}$ from 2.49 to 2.41 Å (Table 4) was observed with increasing surface Ti-content, consistent with the decreasing lattice parameters.\textsuperscript{58} The influence of the lattice parameters was as well reflected in the drop (0.25 Å) of $d_{\text{term}}$ between 100% surface Ti-content, corresponding to 20% total Ti-content (2.41 Å), and pure TiO$_2$ (2.16 Å). When Ti atoms were introduced in the surface layer (17-67%), Sn$_{5c}$-OH$_{\text{term}}$ decreased from 2.06 Å for pure SnO$_2$ to 2.03 Å (Table 4). The Ti$_{5c}$-OH bond length, on the other hand, was equivalent to that on pure TiO$_2$ (1.87 Å) indicating that the characteristic of this bond is determined by the chemical nature of the Me$_{5c}$ atom rather than the surrounding atoms.

**Stability.** The binding energy at high coverage (1 ML) decreased rapidly from 145.2 to 101.6 kJ/mol with increasing surface Ti-content from 0 to 33 %. Further increase of the surface Ti-content up to 100 % had only marginal effect (±3.4 kJ/mol) (Fig. 8, diamonds, Fig. 9, filled diamonds). The behavior of the binding energy correlated well with $d_{\text{root}}$ (Fig. 8, circles): a decrease in the binding energy was related to an increase in the H-O distance. This verifies the stabilization of adsorbed species by intermolecular H-bonds which can be quantified by $d_{\text{root}}$. For 100 % surface Ti-content, the binding energy (101.8 kJ/mol) was still remarkably higher than that on pure TiO$_2$ (60.3 kJ/mol). This suggests that the underlying SnO$_2$ crystal contributes considerably to the adsorption properties.

In summary, a minimum of the adsorption binding energy of isolated dissociatively adsorbed H$_2$O was evidenced for a surface Ti-content of 25%. This minimum is attributed to the maximum number of O$_{\text{br}}$ atoms with three bonds to neighboring Me$_{6c}$ atoms which had to be broken upon H$_2$O adsorption. Furthermore, the high coverage binding energy dropped rapidly from 145.2 to 101.6 kJ/mol with increased surface Ti-content from 0 to 33 %. Higher surface Ti-contents had almost no effect on the high coverage binding energy of H$_2$O. This led to an overall minimum of all binding energies between 25 and 33 % surface Ti-content. A qualitatively similar minimum was found experimentally at a total (surface + bulk) Ti-content of 4.6 % for the cross-sensitivity to humidity of FSP-made Sn$_{1-x}$Ti$_x$O$_2$ nanoparticles. However, no explanation could be given yet for this behavior.\textsuperscript{5} Assuming that all Ti atoms are distributed on the particle surface and the particles have an average size between 9 and 11 nm, the surface Ti-content of such particles is
approximately 24 to 29 % and thus in good agreement with the computed surface Ti-content for
the minimum of the H\textsubscript{2}O binding energy. This suggests that dissociative H\textsubscript{2}O adsorption plays a
key role in the cross-sensitivity mechanisms to humidity of SnO\textsubscript{2}-based gas sensors. Furthermore,
it supports the proposed homolytic dissociation of water on SnO\textsubscript{2} that leads to an increase in its
conductivity.\textsuperscript{32,33,35} It has been shown previously that Sn-doping of TiO\textsubscript{2} catalysts leads to
enhanced photoactivity\textsuperscript{13} which was partly attributed to the decrease of the band gap.\textsuperscript{13,68} The
results of the present study suggest additionally that the dependency of the catalytic activity on
the relative humidity can be minimized for an optimal Sn:Ti ratio.

Moreover, the rapid decrease of the 1 ML binding energy caused adsorbed H\textsubscript{2}O to be more
stable at low coverage (Fig. 9, open diamonds) than at high coverage (Fig. 9, filled diamonds).
Already at a surface Ti-content of 33 %, repulsive interactions between adsorbed species were
more pronounced than attractive ones (H-bonds). The amount of adsorbed H\textsubscript{2}O is not only
dependent on the relative humidity but also on the process conditions such as temperature. This
gives a possible explanation for the remaining minimal cross-sensitivity (15 %) of FSP-made Sn\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{2}
nanoparticles that was shown experimentally.\textsuperscript{5} In fact, there, the working temperature of
the gas sensor (320 °C) was most probably high enough to overcome the binding energy at full
coverage. However, due to the increased binding energy at low coverages, trace amounts of H\textsubscript{2}O
remained on the surface leading to a variation of the sensor signal measured in dry air and thus to
a small cross-sensitivity residual.

Furthermore, the difference between H\textsubscript{2}O binding energy at high and low coverage became
larger with increasing surface Ti-content due to the drop of the binding energy at 1 ML and the
rise of the one at 1/12 ML for surface Ti-contents >25 % (Fig. 9). Assuming a linear dependency
of the binding energy on the coverage, it is suggested that controlling of the amount of adsorbed
H\textsubscript{2}O species by the temperature is facilitated when the difference between low and high coverage
binding energy gets larger.

Finally it should be stressed that our theoretical study of H\textsubscript{2}O adsorption on TiO\textsubscript{2}, SnO\textsubscript{2} and
Sn\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{2} surfaces and its impact on the cross-sensitivity of gas sensors only holds rigorously for
equilibrated systems. However, it may also reflect the tendencies to be expected under dynamic
conditions and therefore help in the interpretation of the relation between water adsorption and its
impact on the cross-sensitivity.
CONCLUSIONS

The binding energy of dissociatively and associatively adsorbed H2O was calculated on pure SnO2(110) and TiO2(110) at high coverage (1 ML) and for isolated species (1/12 ML). On pure SnO2, a stable configuration was found for 1 ML associatively adsorbed H2O using plain DFT calculations in agreement with experiments. This was possible by the simulation of a larger unit which reduced the level of symmetry. In agreement with previous calculations, dissociative adsorption is shown to be the favored mechanism for all coverages. Independent of the adsorption mechanism, the formation of H-bonds was observed on SnO2, leading to a higher binding energy at high coverage compared to that at low coverage.

On TiO2, the favored adsorption mechanism changed with coverage. Isolated H2O groups tended to dissociate, while at high coverage, associative adsorption was favored. For both adsorption mechanisms, the binding energy at low coverage was higher than at high coverage. These finding are in agreement with TPD experiments which show a shift of H2O desorption to higher temperatures at low doses.

On Sn1-xTiₓO₂(110) with homogeneous surface Ti distribution, the binding energies for dissociative adsorption were determined at high and low coverages. Analysis of the Wannier centers at low coverage suggested the formation of additional bonds between Ti6c and bridging O_br atoms. These have to be broken upon H2O adsorption resulting in a decrease of the binding energy up to a surface Ti-content of 25 %. At higher Ti-contents, less additional Ti6c-O_br bond formation was observed due to the effect of neighboring Ti6c atoms. This caused again an increase of the low coverage binding energy at Ti-contents >25 %.

The binding energy at high coverage on Sn1-xTiₓO₂(110) decreased rapidly with increasing surface Ti-content up to 33 %. This is attributed to the loss of H-bonds indicated by a larger distance between neighboring OH groups (d_MOH). Higher surface Ti-contents had hardly any effect on the binding energy. Already at 12.5 % surface Ti-content, H2O adsorption at low coverage was more stable than at high coverage. In this case it is suggested that the amount of adsorbed H2O can be controlled by process parameters such as temperature.

Considering both high and low coverage binding energies, a global minimum was found between 25 and 33 % surface Ti-content. This minimum in binding energy gives a possible explanation to the previously observed minimum in cross-sensitivity to humidity of Sn1-xTiₓO₂ nanoparticle-based gas sensors. Furthermore, it supports the proposed interaction mechanism between SnO2 and H2O vapor based on the homolytic dissociation of H2O on Sn5c.
and $O_{br}$ atoms.

The results of this study show that already small amounts of Ti on the SnO$_2$(110) surface significantly change the H$_2$O adsorption behavior and that first-principles calculations can aid in designing mixed metal oxides with specific H$_2$O adsorption characteristics. Controlling the H$_2$O adsorption and reaction mechanism on the desired metal oxides can improve the performance of such materials both in the fields of gas sensors as well as photocatalysis.

ACKNOWLEDGMENT

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REFERENCES


Table 1: Dissociative and associative H$_2$O binding energies at 1 ML and 1/12 ML coverage on SnO$_2$. All values are given in kJ/mol.

<table>
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<th>associative (kJ/mol)</th>
<th>mixed adsorption</th>
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<td>1/12 ML</td>
<td>135.2</td>
<td>98.8</td>
<td>-</td>
</tr>
<tr>
<td>1 ML</td>
<td>145.2</td>
<td>112.0</td>
<td>137.8</td>
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<td>reference</td>
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<td>113$^{a,49}$</td>
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</table>

$^a$ use of artificial constraints to obtain only associative H$_2$O adsorption
Table 2: Dissociative and associative H$_2$O binding energies at 1 ML and 1/12 ML coverage on TiO$_2$. All values are given in kJ/mol.

<table>
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<th>Coverage</th>
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<th>associative</th>
<th>mixed adsorption</th>
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<tr>
<td>1/12 ML</td>
<td>99.4</td>
<td>92.0 (89.5$^a$)</td>
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<tr>
<td>1 ML</td>
<td>60.3</td>
<td>78.7</td>
<td>75.4</td>
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<tr>
<td></td>
<td>66$^{49}$</td>
<td>83$^{49}$</td>
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</tbody>
</table>

$^a$ configuration parallel to surface (Fig. 5a,b)
Table 3: Bond length between Me\textsubscript{5c} atoms and adsorbed OH\textsubscript{term} groups (Me\textsubscript{5c}-OH\textsubscript{term}, Fig. 1b) and distance between OH groups (d\textsubscript{root}, Fig. 1a) for dissociative H\textsubscript{2}O adsorption at 1/12 ML coverage. All distances are given in Å. The increase of the standard deviation of d\textsubscript{root} with the surface Ti-content reflects the irregularity of the surface.

<table>
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<tr>
<th>surf Ti-content [%]</th>
<th>Sn\textsubscript{5c}-OH\textsubscript{term}</th>
<th>Ti\textsubscript{6c}-OH\textsubscript{term}</th>
<th>d\textsubscript{root}</th>
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<td></td>
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<td></td>
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<tr>
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Table 4: Bond length between Me$_{5c}$ atoms and adsorbed OH$_{term}$ groups (Me$_{5c}$-OH$_{term}$, Fig. 1b) and distance between adjacent OH groups $d_{\text{root}}$ and $d_{\text{term}}$ (Fig. 1a) upon dissociative H$_2$O adsorption at 1 ML coverage. All distances are given in Å.

<table>
<thead>
<tr>
<th>surf Ti-content [%]</th>
<th>Sn$<em>{5c}$-OH$</em>{term}$</th>
<th>Ti$<em>{6c}$-OH$</em>{term}$</th>
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<tr>
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<td>100</td>
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<td>2.37</td>
<td>2.16</td>
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Figure 1
Top (a) and cross-sectional (b) schematic illustration of geometrical properties of dissociative H$_2$O adsorption on rutile (110). Large spheres indicate metal atoms (Sn or Ti), small gray spheres indicate O atoms of the (110) surface. Red spheres indicate O atoms of the adsorbing H$_2$O molecule and blue ones H atoms.
Figure 2
Cross-sectional (a,c) and top (b,d) view of stable configurations of isolated H$_2$O adsorbed associatively (a,b) and dissociatively (c,d) on SnO$_2$(110). The Sn-O bond length was remarkably smaller for dissociative adsorption (2.20 Å) than for associative one (2.28 Å) indicating stronger bonds. This was as well reflected in a higher binding energy of dissociative adsorption (Table 1).
Figure 3

Top view of stable configurations for associative adsorption of H\(_2\)O at 1 ML coverage on SnO\(_2\) (a) and TiO\(_2\) (c). On SnO\(_2\), when all molecules pointed into the same direction, H\(_2\)O spontaneously dissociated resulting in a mixed associative/dissociative adsorption state (b). Since the mixed adsorption state (b) also accounts for dissociative adsorption, the obtained energy was higher (137.8 kJ/mol, Table 1) than that for pure associative adsorption (112 kJ/mol). On TiO\(_2\) (c), the H\(_2\)O molecules did not dissociate leading to pure associative adsorption even for a highly symmetric configuration with a binding energy of 78.7 kJ/mol. Sn: dark gray, Ti: cyan, surface O: light gray, O of H\(_2\)O: red, H: blue.
Figure 4

Top view of stable configurations of dissociative H₂O adsorption on SnO₂ (a), TiO₂ (d) and on Sn₁₋ₓTiₓO₂ with surface Ti-contents of 16.7% (b) and 100% (c) at 1 ML coverage. The calculated binding energies were: 145.2 (a), 116.6 (b), 101.8 (c) and 60.3 kJ/mol (d). The inhomogeneity of the Ti-containing surfaces (b,c) led to an asymmetric configuration of dissociatively adsorbed H₂O. Despite their smaller lattice parameters, d-root was larger on the solid solutions and on pure TiO₂ than on pure SnO₂ indicating a loss of H-bonds.
Cross-sectional (a,c) and top (b,d) view of stable configurations of isolated H$_2$O adsorbed associatively (a,b) and dissociatively (c,d) on TiO$_2$(110). A more stable state was found for associative adsorption in a perpendicular configuration similar to the one on SnO$_2$ (Fig. 2a,b). On TiO$_2$, the difference between the Ti-O bond length for associative and dissociative adsorption was even larger than on SnO$_2$, but less visible in the change of binding energy (Table 2).
Figure 6
Top view of a section of the clean surface (left) of SnO$_2$ (a) and Sn$_{1-x}$Ti$_x$O$_2$ solid solutions with 25% (b) and 37.5% (c) surface Ti-content and after adsorption of one H$_2$O molecule (right side). Small spheres around O atoms indicate the center of Wannier functions. The centers important for H$_2$O adsorption are highlighted in green.
Figure 7
Fraction of O\textsubscript{br} atoms on the (110) surface of Sn\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{2} solid solutions that form three bonds to neighboring Sn\textsubscript{6c} or Ti\textsubscript{6c} atoms as a function of the surface Ti-content (diamonds). When all 6c sites were occupied by the same type of metal atom (Sn for 0% and Ti for 50%), O\textsubscript{br} atoms formed two bonds to the neighboring Me\textsubscript{6c} atoms. However, when O\textsubscript{br} was adjacent to an Sn\textsubscript{6c} atom on one side and a Ti\textsubscript{6c} atom on the other one, two bonds were formed to Ti and one to Sn. The number of O\textsubscript{br} with such three bonds had a maximum at 25% surface Ti-content when Sn\textsubscript{6c} and Ti\textsubscript{6c} atoms were alternating. Upon H\textsubscript{2}O adsorption, the third Ti\textsubscript{6c}-O\textsubscript{br} bond had to be broken resulting in an inverse behavior of the H\textsubscript{2}O binding energy (triangles): the binding energy had a minimum at 25% surface Ti-content.
Figure 8

Change of $d_{\text{root}}$ (circles) for 1 ML dissociative H$_2$O adsorption as a function of the surface Ti-content. Already at a surface Ti-content of 33 %, $d_{\text{root}}$ drastically increased from 1.80 to 2.49 Å. At the same time, the H$_2$O binding energy (squares) decreased from 145.2 to 101.6 kJ/mol. This inverted trend suggests the presence of intermolecular H-bonds when $d_{\text{root}}$ is small leading to higher binding energies.
Figure 9
Maximum binding energy of dissociative H$_2$O adsorption on Sn$_{1-x}$Ti$_x$O$_2$(110) surfaces at 1/12 ML (open diamonds) and average binding energy at 1 ML (filled diamonds) coverage as a function of the surface Ti-content. The gray area shows the range of different binding energies that were observed on different adsorption sites for each Ti-content. The 1/12 ML binding energy had a minimum at 25% surface Ti-content attributed to the maximum number of Obr atoms with three bonds to neighboring Me$_6$c atoms (Fig. 7). For higher surface Ti-contents the binding energy increased as well as the range of binding energies observed for each Ti-content. This was caused by a large degree of inhomogeneity of the surface structure. The 1 ML binding energy decreased drastically up to a surface Ti-content of 50%. Higher Ti-contents had hardly any effect on the binding energy.
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