Molecular Dynamics Simulations of Ammonia Adsorbed on Titanium Dioxide (Rutile) Surfaces

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Molecularly adsorbed ammonia on the (110) surface of TiO_2 (rutile) is studied by realistic molecular dynamics (MD) simulations. The simulations are carried out in the submonolayer region at a temperature of 300 K. The orientational space accessed by adsorbed molecules strongly depends on the adsorption site and the specific structure of the substrate. This provides a simple explanation for the experimentally observed transition from solid-like to liquid-like behaviour at a coverage of 0.6 to 0.7 monolayers.

1 Introduction.

Due to it's importance in catalysis and photolysis [1] TiO_2 (rutile and anatase) surfaces and surface reactions are widely studied. The adsorption of small polar molecules is the subject of numerous publications [2-5].

Depending on the adsorbed molecular species and the defect concentration of the TiO_2 substrate a wide variety of adsorption types occurs. While water dissociates on both perfect and defective rutile surfaces [2], ammonia is adsorbed molecularly [3]. Accordingly, the obtained isosteric heat of adsorption of ammonia is much smaller than for water with an estimated value of 65 kJ $mole^{-1}$ [4].

Recent NMR investigations of deuterated ammonia adsorbed on microcrystalline rutile revealed an unusual transformation of the observed ^2H spectra as a function of coverage [5]. The solid-state 'Pake' spectrum that occures at low degrees of coverage is superimposed by a liquid-like motionally averaged singulett at a value of 0.7 monolayers and higher. Boddenberg and Niepmann assumed that the specific structure of the substrate, mainly the (110) surface, in conjuntion with the high lateral repulsive interaction of molecules adsorbed on neighbouring sites are causing this transition.

According to MEED measurements, the structure of the thermodynamically most stable (110) surface of rutile is bulk-like terminated and not-reconstructed, no relaxtion of the surface near Ti-atoms is observed [6]. In contrast to this, the (100) surface shows a (1×3) reconstruction which transforms to (1×5) and (1×7) reconstructions during

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high temperature annealing. The (100) surface tries to gain surface energy by forming (110) microfacets which grow at high temperature conditions [7]. There is evidence that almost 80% of the total surface of microcrystalline rutile is covered by the (110) surface [8]. Consequently the ideal (110) surface should represent the real system well and be used as a model-substrate for our molecular dynamics simulations.

The aim of our simulations is to model realistically the environment that interacts with the adsorbed ammonia molecules and thus explaines 'naturally' the experimentally observed behaviour. In this contribution we focus mainly on the interaction potential and structural properties.

2 The model potential

Fig. 1b shows a view on the TiO_2 (rutile) (110) surface. The surface consist of linear rows of Ti-sites with distance of 2.96 Å. The rows are seperated by linear walls of oxygen-atoms. The spacing between two rows is 6.49 Å. For simplicity the surface is treated as a rigid lattice where each ion is regarded as an interaction site. The interaction potential is parametrized in Lennard-Jones (LJ) and electrostatic terms.

NH_3-NH_3 interaction

The ammonia intermolecular potential is described by a five center site-site model, proposed by Impey and Klein [9] and refined by Cheng and Steele [10] (d_{NH} = 1.0124 Å, d_{HH} = 1.6243 Å). Each of the nuclei is a LJ-center (Table 1). The hydrogen atoms carry partial charges of $q_H = 0.485$ e, while the fourth charge $q_C = -3q_H$ is shifted from the nitrogen by distance d_{NC} = 0.156 Å along the C_3-axis towards the center of mass.

NH_3-TiO_2 interaction

The electrostatic part of the substrate-adsorbent interaction is calculated via a Fourier-representation of the charge density in order to compute the potential efficiently and to avoid cut-off effects [11,12]. The electrostatic potential at a position $\vec{r} = (x, y, z)$ outside an infinite two-dimensional x,y-plane of periodically repeated unit cells is given by

$$\Phi(\vec{r}) = \frac{2\pi}{A}\sum_{j=1}^{N}\sum_{\vec{k}_{l,m}} q_j \frac{\exp\left(-\left|\vec{k}_{l,m}\right||z-z_j|\right)}{\left|\vec{k}_{l,m}\right|}\cos\left(\vec{k}_{l,m}(\vec{u}-\vec{u}_j)\right) - \frac{2\pi}{A}\sum_{j=1}^{N} q_j|z-z_j| \qquad (1)$$

A is the area of the two-dimensional rectangular unit cell. $\vec{u} = (x, y)$ describes the location above a unit cell, while $\vec{u}_j = (x_j, y_j)$ is the corresponding position of the point

charge q_j in the plane. $\vec{k}_{l,m}$ are reciprocal lattice vectors, according to

$$\vec{k}_{l,m} = (l/a, m/b) \tag{2}$$

a and b are the lattice constants of the two-dimensional lattice. The summation has to be carried out over all reciprocal lattice vectors except $l = m = 0$. In practice this sum converges rapidly so that the number of vectors can be kept small. In our simulation, we used 144 vectors for the first layer, 40 vectors for the next three layers and 4 vectors for the last two layers (see Fig. 1a). This setup leads to an accuracy of about 0.1 percent compared to an infinite lattice.

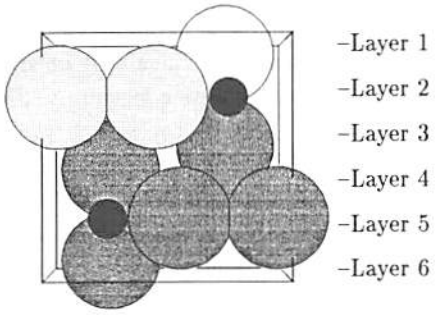

Fig. 1a

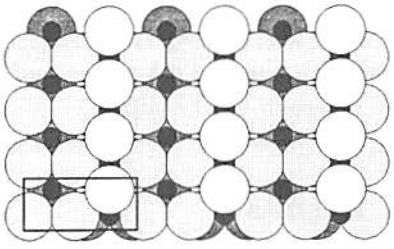

Fig. 1b

Fig. 1a: MD 'surface' unit cell of rutile with layers orientated parallel to the (110) plane . Fig. 1b: 'On top' view of the (110) surface. Black spheres denote Ti-sites, white/grey spheres denote oxygen-sites. Rectangular frame indicates the unit cell, as chosen for Fig. 3.

The Lennard-Jones interaction is calculated via real-space summation due to slow convergence of the corresponding Fourier-sum [13]. A cluster of 5×9 'surface' unit-cells (according to Fig. 1a) is used in this manner. The LJ Parameters describing the TiO_2-NH_3 interaction are taken from a TiO_2-model proposed by Matsui and Akaogi [14] applying the Lorentz-Berthelot combination rules (see Table 1).

	N-N	H-H	Ti-N	Ti-H	O-N	O-H
σ/Å	3.32	2.25	2.64	2.11	3.10	2.57
(ϵ/k_B)/K	36.4	21.1	106.0	80.7	80.7	61.5

Table 1: Lennard-Jones parameters for the site-site interaction potentials.

With these parameters, the experimental adsorption energy is overestimated by far. A value of about 65 kJ mole^{-1} is found experimentally [4] while the model yields an

adsorption energy of 163 kJ mole^{-1}. Therefore the point charges in the surface were scaled to $q_{Ti} = 0.852\ e$ and $q_O = 0.426\ e$. Although this procedure is purely empirical, a decreased effective charge at the substrate surface, however, is reported for various systems [15].

3 Molecular dynamics simulations

The simulations were carried out in the (N,V,E)–ensemble for different degrees of coverage at a temperature of 300 K. The integration of the equations of motion was performed using a quaternion–leapfrog algorithm [16] with a time step of 1 fs. A system size of 200 adsorbed molecules was chosen for all simulations. two–dimensional periodic boundary conditions were applied. The ammonia–ammonia interactions were calculated up to a spherical cut off of 15.0 Å. After equilibration times of 50 ps simulation runs up to 250 ps were recorded and analyzed.

4 Results

To describe the structure of the adsorption layers, we calculate density profiles as a function of distance from the surface and residence probabilities within the unit cell in order to localize the favoured positions of adsorption. As it can be seen from Fig. 2 up to a degree of coverage of about 0.7 monolayers the molecules are adsorbed at a close distance to the surface. At higher coverage additional molecules form a second layer while the density in the first layer increases more slowly. Fig. 3a shows that the molecules in the first layer are highly correlated to the position of the exposed coordinatively unsaturated Ti–sites in the surface. The second–layer adsorption, however, is much less localized as can be seen from the broader residence probabilities in Fig. 3b. Nevertheless, the molecules are adsorbed preferently on the oxygen–walls with two distinct maxima on both sides above the oxygen–oxygen bridge position.

Due to the less strong interaction with the surface, the orientational distribution of the molecules in the second layer is more isotropic than in the first layer. As an example, in Fig. 4 the distribution of the angle θ_{C3} between the the C_3 symmetry–axis and a vector normal to the surface is depicted for two degrees of coverage. The first layer behaviour depends weakly on the degree of coverage, while the second layer molecules show a signifcantly broader distribution. The molecules in first layer are orientated mainly with their symmetry axis perpendicular to the surface and the nitrogen atoms looking towards the surface.

The observed angular distribution suggests a strong influence on the corresponding ^{2}H–NMR spectra. If 'fast motion limit'– theory is applied and the exchange rate between

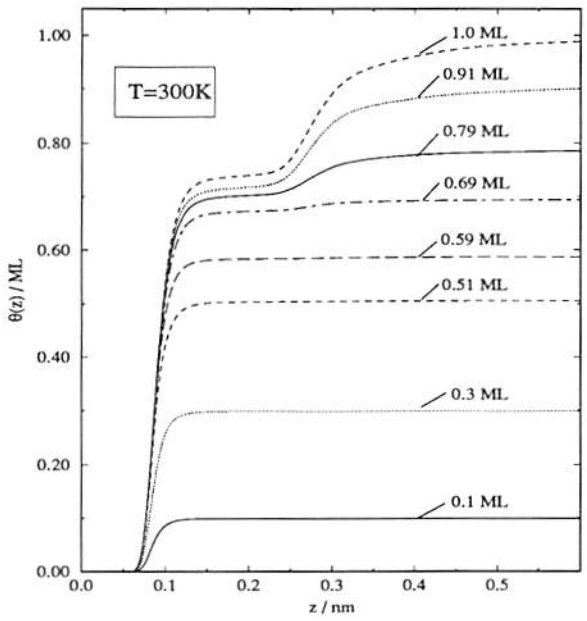

Fig. 2: Integrated profiles of molecular density as a function of distance to the surface for various degrees of coverage. The two steps correspond to the formation of two layers. The formation of the second layer starts at about 0.7 ML coverage

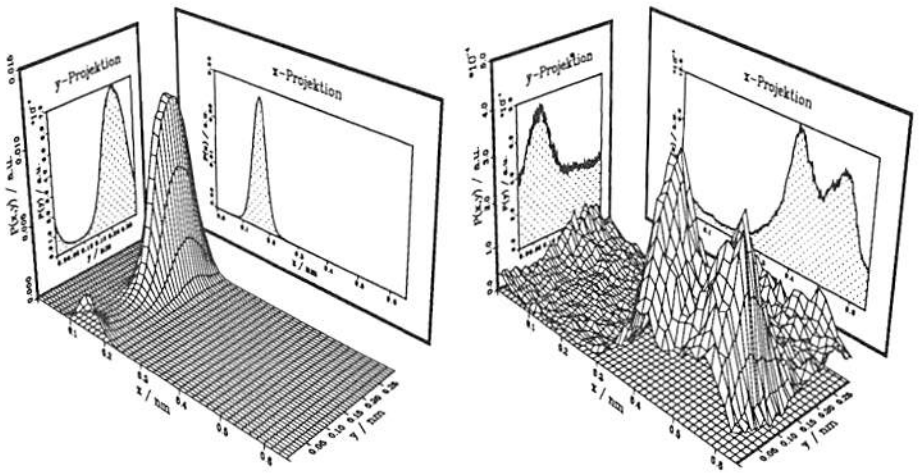

Fig. 3: Probability P(x,y) to find a molecule center of mass at a certain location (x,y) above the surface unit cell. Fig. 3a: First Layer. Fig. 3b: Second layer. The distributions are calculated for T=300K and a coverage of 1.0 ML. The shown graphs are typical for all simulated degrees of coverage. The position of the rectangular unit cell is indicated by the rectangular frame in Fig. 1b.

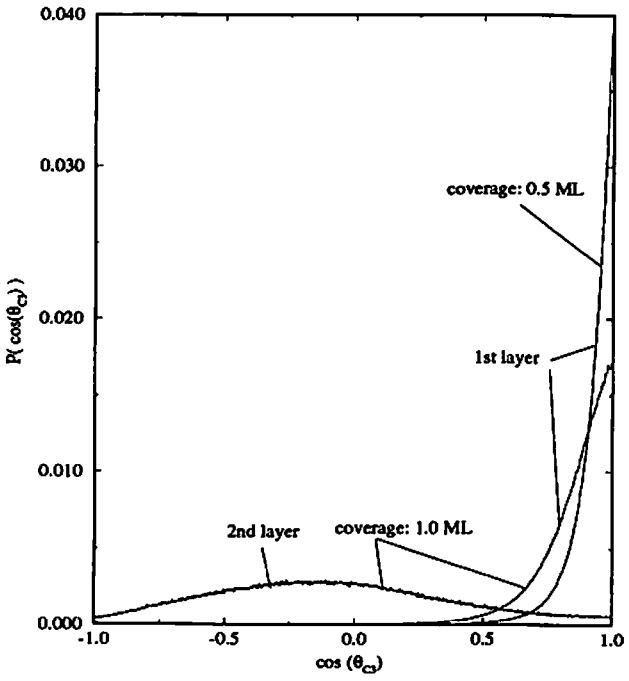

Fig. 4:
Distribution of the angle θ_{C_3} between the C_3 symmetry-axis of the adsorbed ammonia molecules and a vector normal to the TiO_2 (110) plane. The molecules in the first layer are orientated perpendicular, in the second layer more parallel to the (110) surface. The orientational distribution in the second layer is more isotropic.

the two layers is considered to be slow, both layers should lead to two distinguishable spectral forms.

The occurence of second layer molecules at a degree of coverage of 0.6 to 0.7 monolayers coincides with the occurence of a 'liquid-like' singulett in the ^{2}H-NMR spectra. This strongly supports the assumption that the 'liquid-like' singulett found by Boddenberg and Niepmann [5] is caused by weakly bounded molecules adsorbed at oxygen sites.

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