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Simulations of the thermodynamics and kinetics of NH$_3$ at the RuO$_2$ (110) surface

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Abstract

Ruthenium(IV)oxide (RuO$_2$) is a material used for various purposes. It acts as a catalytic agent in several reactions, for example oxidation of carbon monoxide. Furthermore, it is used as gate material in gas sensors. In this work theoretical and computational studies were made on adsorbed molecules on RuO$_2$ (110) surface, in order to follow the chemistry on the molecular level. Density functional theory calculations of the reactions on the surface have been performed. The calculated reaction and activation energies have been used as input for thermodynamic and kinetics calculations. A surface phase diagram was calculated, presenting the equilibrium composition of the surface at different temperature and gas compositions. The kinetics results are in line with the experimental studies of gas sensors, where water has been produced on the surface, and hydrogen is found at the surface which is responsible for the sensor response.

Keywords
catalysis, ruthenium dioxide, thermodynamics, kinetics, sensor, surface
1 Introduction

Ruthenium(IV)oxide (RuO$_2$) is found to be a material of unique redox and catalytically properties. The high electronic conductivity[1], high thermal stability (up to ~800 °C) and high chemical corrosion resistance [2] makes RuO$_2$ suitable for a variety of applications. For example in CO oxidation RuO$_2$ acts as a catalyst [3]. It is further used in fuel cell electrodes [4] and in construction of thin- and thick-film resistors [5, 6].

RuO$_2$ is used as gate material in sensors for detection of hydrogen containing gases [7, 8]. The mechanism of the sensor starts with the adsorption of gas molecules on the catalytically active RuO$_2$ surface. After dissociation, hydrogen atoms are transferred to an insulator. The hydrogen atoms are trapped in the interface between the oxide and the insulator, which gives rise to an electrical potential. It is found that three phase boundaries between gas, conductor and insulator is required to get a response from ammonia[9, 10]. The use of RuO$_2$ nanoparticles as gate material increases the number of three phase boundaries, and hence the sensor becomes more sensitive[7].

Under normal pressure conditions, the most stable crystal structure of RuO$_2$ is rutile, which is also the most stable crystal structure of TiO$_2$.[1] RuO$_2$ and TiO$_2$ have many similarities but RuO$_2$ is more catalytically active than TiO$_2$ due to its ability to change oxidation number. It has been found that the RuO$_2$ (110) surface is catalytically active.[3] On the RuO$_2$ (110) surface (Figure 1) there are the one-fold coordinately unsaturated Ru atoms (Ru$^{\text{cus}}$), the bridging O atoms (O$^{\text{br}}$), and the three-coordinated oxygen (O$^{\text{p}}$) in the same plane as the Ru$^{\text{cus}}$ atoms. In the catalytic reaction of CO oxidation for example, the CO molecules adsorb to the Ru$^{\text{cus}}$ forming CO$_2$ with O$^{\text{br}}$ [11]. This process reduces the surface, leaving a vacancy at the O$^{\text{br}}$ position. This vacancy is recovered by molecular oxygen. The O$^{\text{p}}$ atoms are strongly bound to the RuO$_2$ bulk, and are hence less likely to be involved in the catalytic reactions.
Ruthenium dioxide has been studied experimentally with LEED [12], TDS[13, 14], HREELS [13], STM[3], and theoretically with DFT calculations [11, 15-22] and kinetic Monte Carlo (KMC) [23, 24]. The absorption of different gas molecules such as carbon dioxide, hydrogen, ammonia, oxygen and water has been studied.

Desorption studies of ammonia on the RuO$_2$ (110) surface [13] have shown that chemisorbed ammonia does not dissociate on the stoichiometric RuO$_2$ (110). However, on an oxygen rich surface NO, N$_2$ and H$_2$O is produced. However, no NO$_2$ or N$_2$O were detected. Water desorbs from the surface even in the absence of NH$_3$, which is found to be due to that hydrogen atoms, which are discovered on the surface even at UHV (ultra high vacuum).[25]

Hydrogen absorbs both as a dihydrogen at the Ru$^{\text{cus}}$ sites and dissociated as dihydride and monohydride species at the O$^{\text{br}}$ sites. Upon heating the physisorbed dihydrogen molecules desorbs at 95 K, and chemisorbed hydrogen desorbs at 260 K. [26] At higher temperatures (400 K) hydrogen is desorbed as water. [13, 26].

The reaction mechanism of the oxidation of ammonia was studied by Seitsonen et al. by DFT calculations. Their calculations show that the first deprotonation of NH$_3$ is activated with an energy barrier of 73 kJ/mol. Desorption of NO is proposed to be the rate-determining step with a 191 kJ/mol barrier. The activation energy of the diffusion of hydrogen atoms along the O$^{\text{br}}$ was calculated to be as high as 240 kJ/mol, while the diffusion of hydrogen along oxygen on Ru$^{\text{cus}}$ sites was only 21 kJ/mol. [27] The bonding energy of adsorbed ammonia has also been studied by DFT methods [22]. The high binding energy of NH$_x$ on RuO$_2$ compared to metal surfaces, could be explained by the hydrogen bonds between NH$_x$ and O$^{\text{br}}$, and the additional $\pi$-bonds formed when NH$_x$ dissociated. [22]
In a KMC study based on DFT by Hong et al. [23] the catalytic mechanism of the oxidation of NH$_3$ to NO and N$_2$ on the surface of RuO$_2$ was studied. Further, Pogodin and López recently simulated oxygen absorption on a RuO$_2$(110) surface by KMC[24]. They proposed a two-step absorption reaction of oxygen to the surface and the results are in line with experimental programmed temperature desorption spectra.

In this work the reactions of hydrogen, oxygen, ammonia on the RuO$_2$ (110) surface has been studied by computational methods in order to get more insight into the chemical reactions involved in sensors. Optimised structures and reaction paths with energy barriers was found from quantum chemical calculations. The thermodynamic equilibrium distributions at the surface under various conditions were found by minimising the Gibbs free energy. Calculations of the surface reaction kinetics was carried out from the barrier free energies.

2 Methods

The RuO$_2$(110) surface is herein represented by a cluster model, motivated by the fact that nanoparticles of RuO$_2$ as gate material in sensor devices have been studied experimentally.[7] In Supplementary Materials (section S1), a few calculations on a periodic model is also presented for reference. The cluster model was chosen over the periodic since it, besides being appropriate for nanoparticle studies, facilitated the large amount of computations performed in this study. For the cases in Table S1 it can be seen that two different models give at least comparable results. Both models were built from a bulk unit cell of the rutile structure[28].
The prepared cluster consisted of 15 Ru atoms and 26 oxygen atoms, truncated by 8 hydroxyl groups (Figure 1). On the (110) surface of this cluster there were two one-fold coordinatively unsaturated Ru sites (Ru\textsuperscript{cus} or *) and four under-coordinated bridging oxygen sites (O\textsubscript{br} or #). The cluster was made in two layers, for stabilisation of the surface. The hydroxyl ligands were arranged so that the structure was stabilised by hydrogen bonds. A test using more layers (Table S2) gave that the use of two layers was sufficient for adsorption energy studies.

Geometry optimisations (i.e. total energy minimization with respect to the nuclear coordinates) were performed generally in the singlet spin state including a vibration analysis. Energies of higher spin states were calculated from single-point calculations for the singlet geometries.

The geometry optimisations of the cluster were performed in Gaussian09 rev D01 [29]. The B3LYP functional [30, 31] with dispersion correction [32, 33] was used in conjunction with the basis set CEP-31G with pseudopotentials on the heavy atoms [34, 35]. The method was validated by performing single point calculations at higher levels of theory. The adsorption energy of ammonia with the B3LYP method described above was -195 kJ/mol (singlet spin states). The MP2 method with same basis set (767 basis functions) gave an adsorption energy of -181 kJ/mol, while $\Delta_{\text{ads}}E = -180$ using MP2 with the LANL2DZ basis set (667 basis functions). The MP2/SDD method, with 957 basis functions was the highest level of theory tested, which gave an adsorption energy of -185 kJ/mol. The agreement between the method used and the higher methods is in this case thus fair. (i.e. an over-estimation of the adsorption energy of ammonia by 5%).
The method was further evaluated by computing the formation enthalpies of NH\textsubscript{3}(g), NO(g) and H\textsubscript{2}O(g), where the computed values (-83, 88 and -189 kJ/mol) can be compared to the experimental (-46, 90 and -242 kJ/mol) [36]. The deviations for NH\textsubscript{3} and H\textsubscript{2}O are due mainly to shortcomings of the basis set: if the basis is augmented to a near-complete set (6-311++G(3df3pd))[37] values closer to the experimental are obtained (-53, 88 and -227 kJ/mol).

The reaction paths have been followed by approximate screening of different possibilities. Transition states were found by scanning bond distances. The transition state structures were then optimised as saddle points, using the same algorithm as for the local minima geometry optimisations. The products and reactants of each reaction step are found by following the reaction coordinate.

Vibrational normal-mode calculations within the harmonic approximation using analytical second derivatives with respect to positions were performed in order to verify the imaginary frequency of the transition state, and to estimate the Gibbs free energy of local minima as well as of transition states at various temperatures.[38]

![Cluster model of the RuO\textsubscript{2} (110) surface. Ru atoms are given in magenta, O atoms in pink and H atoms in white colour.](image)

**Figure 1.** Cluster model of the RuO\textsubscript{2} (110) surface. Ru atoms are given in magenta, O atoms in pink and H atoms in white colour.
2.1 Thermodynamics

In the first step, the Gibbs free energy ($G_i$) of each molecular specimen was computed from the quantum-chemical energy and vibrational spectrum of its optimised structure.[38] In the second step, the total Gibbs free energy of the system was minimised with respect to the distribution of the species in order to obtain the thermodynamically most stable (i.e. the equilibrium) composition of the system:

$$\min_{n_i} \Delta G(n_i) = \sum_i \mu_i n_i$$

with the boundary conditions:

$$B \cdot \bar{n} = \bar{b}_0$$  \hspace{1cm} (2)

and

$$0 \leq \{n_i\} \leq \infty$$  \hspace{1cm} (3)

where $n_i$ and $\mu_i$ are the amount of molecule $i$ and the chemical potential of molecule $i$, respectively. $B$ is a matrix containing the stoichiometric content of the molecules, $\bar{n}$ is the column vector of $n_i$ and $\bar{b}_0$ is a column vector with the total amounts of each atom type in the system. $\mu_i$ is dependent of the composition of the system and was given by:

$$\mu_i = \mu_i^0 + RT \ln(p_i/p^0)$$  \hspace{1cm} (4)

for gaseous species and

$$\mu_i = \mu_i^0 + RT \ln(\theta_i)$$  \hspace{1cm} (5)
for surface species, where the Gibbs free energies $G_i$ obtained from the quantum-chemical calculations are used for $\mu_i^0$, $p_i$ is the partial pressure of gas $i$, $p^0$ is the standard pressure of 1 bar and $T$ is the temperature. $\theta_i$ is the coverage ratio of molecule $i$, i.e. number of surface species of type $i$ divided by the number of sites. In Supplementary Materials the case when surface species are assumed not to mix is investigated (section S3), which amount to setting $\mu_i = \mu_i^0$. In the calculations the number of sites were set to be limited to 1% of the initial total amount of gas. The calculations were performed in MATLAB, using the nonlinear equation system solver fmincon. [39]

### 2.2 Kinetics

The chemical reaction rate equations were set up for each elementary reaction step in the reaction mechanism, which constitutes a system of coupled differential equations. Numerical integration of the equations enabled changes in the amount of each molecular specie to be followed over time. In a bimolecular reaction step the reaction rate of adsorption of molecule $AB$ depend on the amount of free sites available on the surface ($n_{\text{free}}$) and the amount of gas phase specie $AB$ ($n_{AB}$) [40]:

$$
\frac{dn_{AB}}{dt} = k_{\text{ads}_{AB}} n_{\text{free}} n_{AB}
$$

(6)

The rate constants of reactions between gaseous molecules and adsorbed states are dependent on the number of times a gas molecule hits the surface and an approximately temperature independent sticking coefficient $S_0$ and the temperature dependent Boltzmann distribution of the Gibbs free energy adsorption barrier. When molar amounts of each species are used, $k_{\text{ads}}$ for molecule $AB$ can be written:

$$
k_{\text{ads}_{AB}} = \frac{A_{\text{surf}} N_A}{V_{\text{gas}}} \sqrt{\frac{RT}{2\pi M_{AB}}} S_0 \exp \left( - \frac{\Delta G^+_{\text{ads}_{AB}}}{RT} \right),
$$

(7)
where $A_{surf}$ is the area of each surface site ($A_{surf}$ was measured from the Ru-Ru atom distances in the optimised structure to be 9.435 Å²), $V_{gas}$ is the total ambient gas volume (set to 1 dm³), $M_{AB}$ is the molar mass of the gas molecule and $N_A$ is Avogadro’s number. The adsorption processes are in most cases exergonic. In such case the $\Delta G_{ads}^\pm$ are approximated to be negligible, and the sticking coefficient $S_0$ was set to 1. The surface reaction rates, are dependent of the product of the absorption ratios of all reactants in that particular reaction step. For example for the reaction step of $A + B \rightleftharpoons C + D$ the forward surface reaction rate is:

$$\frac{dn_{C^*}}{dt} = k_{surf} n_{A^*} n_{B^*} ,$$

(8)

where the rate constants of the surface reactions are related to the Gibbs energy of activation by the Eyring–Polanyi equation [41]:

$$k_{surf} = \frac{k_B T}{h} \left( \frac{N_A}{N_{sites}} \right)^{order-1} \exp \left( -\frac{\Delta G^\pm}{RT} \right)$$

(9)

where $k_B$ is the Boltzmann constant, $h$ is the Planck constant, $\Delta G^\pm$ is the activation free energy of the reaction and $T$ is the temperature. A factor $(N_A/N_{sites})^{order-1}$ is included in the pre-factor for reaction steps of higher order than two since the amounts are given in mol units. All $\Delta G^\pm$ values were calculated from Gibbs free energy of the transition state ($G^\dagger$) and the sum of the reactant Gibbs free energies:

$$\Delta G^\pm = G^\dagger - \sum_{reactants} G_i ,$$

(10)

where all Gibbs free energies were obtained from the DFT computations.

For the desorption reactions, equation 9 was used for the calculation of the rate constant, but using the $\Delta G_{des}^\pm$ instead of $\Delta G^\pm$, where:

$$\Delta G_{des}^\pm = G_{gas} + G_{surface} - G_{ads,gas}$$

(11)

The rate of formation of each molecule was calculated from the reaction rates of all reaction steps that the molecule participates in. The kinetics simulations were performed in MATLAB, using their built-in module for reaction rates SimBiology.[39]
3 Results and discussion

3.1 The RuO$_2$ cluster

The geometry of the cluster model of the RuO$_2$ (110) surface shown in Figure 1 was geometry minimised at different spin states. The relative energies are given in Table 1. Single point calculations performed at higher spin states showed that the quintet had the lowest energy, followed by the triplet. However, when geometry optimisations were performed on the higher spin states, it appeared that the triplet was slightly more stable than the quintet. Even though the triplet and quintet states are much lower in energy than the singlets it was technically difficult to optimise the transition state geometries using Gaussian09’s transition-state search routines. Hence, the absorption energies are calculated from the optimised structures while the reaction path was followed for the singlet states, and higher spin states were included from single-point calculations. Hence the quintet state of the free cluster was used as lowest energy reference for the thermodynamic and kinetic simulations.
Table 1. Relative energy of the RuO$_2$ cluster with the singlet as reference.

<table>
<thead>
<tr>
<th>Spin state</th>
<th>$\Delta E / \text{kJ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Optimised</td>
</tr>
<tr>
<td>Singlet</td>
<td>0</td>
</tr>
<tr>
<td>Triplet</td>
<td>-193</td>
</tr>
<tr>
<td>Quintet</td>
<td>-189</td>
</tr>
</tbody>
</table>

$^a$ The energies at the higher spin states are obtained from single-point calculations on the singlet structure.

3.2 Adsorption on the ruthenia surface

In Table 2 adsorption energies and adsorption free energies are given for the gases involved in this study. The structures are shown in Figure 2. From the energetic point of view, the gas molecules adsorb more easily to the under-coordinated ruthenium atom (*). However, oxygen and hydrogen can also adsorb to the O$^{\text{br}}$-atoms on the surface (#).

Table 2. Adsorption energies ($\Delta E_{ads}$) and Gibbs free adsorption energies ($\Delta G_{ads}$) relative to gaseous molecules.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta E_{ads}$ / kJ mol$^{-1}$</th>
<th>$\Delta G_{ads}$ / kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Optimised$^c$</td>
<td>Single-point$^d$</td>
</tr>
<tr>
<td>O$_2$* (phys)$^a$</td>
<td>-43</td>
<td>-156$^e$</td>
</tr>
<tr>
<td>O$_2$* (chem)$^b$</td>
<td>-55</td>
<td>+18</td>
</tr>
<tr>
<td><em>O-O</em></td>
<td>-48</td>
<td>+64</td>
</tr>
<tr>
<td>O*</td>
<td>-246</td>
<td>-228</td>
</tr>
<tr>
<td>NH$_3$*</td>
<td>-217</td>
<td>-180</td>
</tr>
<tr>
<td>H$_2$* (phys)$^a$</td>
<td>-22</td>
<td>-39</td>
</tr>
<tr>
<td>H$_2$O*</td>
<td>-145</td>
<td>-133</td>
</tr>
<tr>
<td>N$_2$*</td>
<td>-46</td>
<td>-76</td>
</tr>
<tr>
<td>N*</td>
<td>-463</td>
<td>-591</td>
</tr>
<tr>
<td>NO*</td>
<td>-332</td>
<td>-266</td>
</tr>
</tbody>
</table>

$^a$ Physisorbed
$^b$ Chemisorbed monodentate O$_2$ (to distinguish it from physisorbed O$_2$). Generally the species are chemisorbed.
$^c$ Energies were calculated from the lowest energy spin state of optimised adsorbed species
$^d$ Energies were calculated from single-point calculations of the singlet state geometry
$^e$ Single-point calculations were based on the triplet spin state geometry.
Figure 2. Structures of adsorbed species and reaction intermediates. Ru atoms are given in magenta, O atoms in pink, N atoms in cyan and H atoms white colour. Some important optimised distances are given for each structure. The notation of the indexes of the bond distances are: atom type followed by position. An atom in position 1 is the closest to the spectator, and in position 2 the farthest as shown in the first structure.
In the calculations of the adsorption energies in Table 2 the lowest energy spin states of the gases were used, e.g. triplet dioxygen, singlet water and doublet NO. When O$_2$ reacts with the surface, oxygen first physisorbs in a monodentate mode to a Ru$^{\text{cus}}$ site (O$_2^*$(phys)) with a Ru$^{\text{cus}}$ – O interaction distance of 2.55 Å. A triplet spin state is the lowest energy state when oxygen reacts with the cluster. The chemisorption of O$_2$ is exothermic from the optimised structures with $\Delta E_{\text{ads}} = -55$ kJ/mol. The length of the Ru-O bond is then 1.93 Å. Whether the molecule is classified as physisorbed or chemisorbed is here determined by the bond distance. The oxygen-oxygen bond distance in the physisorbed state does not change significantly in comparison to that in the gaseous molecule (1.27 Å), whereas when oxygen is chemisorbed, the O-O bond length increases to 1.35 Å.

In ref [15] the binding energy of oxygen bonded to Ru$^{\text{cus}}$ was found to be 309 kJ/mol with respect to triplet O (g). Our cluster model gives the corresponding binding energy 246 kJ/mol ($E_{\text{bond}} = -\Delta E_{\text{ads}}$ in Table 2). Nitrogen binds much harder, with a binding energy of 463 kJ/mol.

The adsorption of ammonia is an exothermic process with $\Delta E_{\text{ads}} = -217$ kJ/mol. Nitrogen gas adsorbs to the surface with an energy gain of 46 kJ/mol, while NO adsorbs very strongly to the surface with $\Delta E_{\text{ads}} = -332$ kJ/mol. Hydrogen adsorbs with $\Delta E_{\text{ads}} = -22$ kJ/mol, and water with $\Delta E_{\text{ads}} = -145$ kJ/mol.

### 3.3 Dissociation on the surface

The reactions on the ruthenia surface was studied with the aim of understanding the molecular mechanisms and the sensor response.

The reaction free energy of dissociation of O$_2$ from the bidentate mode was $-92$ kJ/mol with an energy barrier of 20 kJ/mol.
Ammonia does not dissociate spontaneously on the stoichiometric surface according to experiments [13]. This can partly be explained by an endergonic first dissociation step ($\Delta G = +99$ kJ/mol), with a forward barrier of $\Delta G_r^\ddagger = 121$ kJ/mol, and a backward barrier of only $\Delta G_r^\ddagger = 22$ kJ/mol:

$$\text{NH}_3^* + \# \rightleftharpoons \text{NH}_2^* + \text{H}^#$$

However, Seitsonen et al. [27] concluded that the main reason for the observation of no ammonia dissociation is the high barrier of the $\text{H}^#$-proton transport, which blocks further dissociation of ammonia. Wang et al. [13] have shown that dissociation of ammonia is possible when co-adsorbed with oxygen. Water, NO (g) and N$_2$ (g) was then detected as products. This has also been shown by simulations.[19]

Simultaneous adsorption of ammonia and oxygen at the surface was studied to find out the reaction path for the formation of nitrogen and nitrogen oxide. In our cluster model only two Ru$^{\text{III}}$ sites (*) and four O$^{\text{IV}}$ sites (#) were included, which leads to a limited set of adsorption possibilities. Hence, the reaction mechanism model was divided into three parts.

The first part is the co-adsorption of oxygen and ammonia. The chemisorption of oxygen and ammonia separately was discussed above. The adsorption free energy of $\frac{1}{2} \text{O}_2$ at a clean cluster is $-38$ kJ/mol, while next to an already adsorbed NH$_3$ it is $-13$ kJ/mol. Ammonia adsorbs with an adsorption free energy of $-160$ kJ/mol, and next to an oxygen atom on the cluster the adsorption free energy is $-135$ kJ/mol. Hence, in total the adsorption free energy of $\frac{1}{2} \text{O}_2$ and NH$_3$ is $-173$ kJ/mol.

The second part is the dissociation of ammonia on the surface and desorption of water, which is studied by three different mechanisms. The Gibbs free energy chart of this part is shown in Figure 3. The free energies given in Figure 3 are calculated from the single-point calculations of the singlet state structures, but it can be noted that the use of the higher spin states at large shift the energy profiles relative those of the singlets by similar amounts, why computed distributions and rates should not be severely influenced by this approximation.
Figure 3. Gibbs free energy reaction plot of the dissociation of NH$_3$ on an oxygen-rich RuO$_2$(110) surface at 298 K. The optimised structures with cluster in the singlet spin state are shown in black, with the optimised transition state structures located at the top of the arcs. Single point energies are plotted in blue (triplet) and red (quintet). Dashed lines indicate adsorption/desorption steps.

In Figure 3 the Gibbs free energies of three different mechanisms are shown:

\[ \text{NH}_3^* + \text{O}^* \rightleftharpoons \text{NH}_2^* + \text{OH}^* \rightleftharpoons \text{NH}_2^* + \text{OH}^* \rightleftharpoons \text{N}^* + \text{H}_2\text{O}^* + \text{H}^\# \]  \hspace{1cm} (1)

\[ \text{NH}_3^* + \text{O}^* \rightleftharpoons \text{NH}_2^* + \text{OH}^* \rightleftharpoons \text{NH}^* + \text{OH}^* + \text{H}^\# \rightleftharpoons \text{N}^* + \text{H}_2\text{O}^* + \text{H}^\# \]  \hspace{1cm} (2)

\[ \text{NH}_3^* + \text{O}^* \rightleftharpoons \text{NH}_2^* + \text{O}^* + \text{H}^\# \rightleftharpoons \text{NH}^* + \text{OH}^* + \text{H}^\# \rightleftharpoons \text{N}^* + \text{H}_2\text{O}^* + \text{H}^\# \]  \hspace{1cm} (3)
In mechanism 1, the first proton transfer step has an activation free energy of 78 kJ/mol (singlet 114 kJ/mol) followed by an OH rotation (OH* ⇌ OH*\textsuperscript{r}) step, which is barrierless at higher spin state (singlet 9 kJ/mol). The third and rate-determining step is a concerted proton transfer step with an activation free energy of 137 kJ/mol (singlet 119 kJ/mol). The transition state structure is stabilised by pairing of two electrons to a triplet state. Mechanism 2 has the same first step as mechanism 1. The second step is the rate-determining step – a proton transfer from NH\textsubscript{2}* to the O\textsuperscript{br} position (\#), with a singlet activation energy of 87 kJ/mol. At higher spin states the transition state is lower in free energy than the product, and the energy difference is 85 kJ/mol. By this step two unpaired electrons are paired, and the quintet is converted into a triplet. The last step has a low barrier of 10 kJ/mol (singlet: 23 kJ/mol) and is a proton transfer from NH* to OH* to form the H\textsubscript{2}O*. However, the backward second step competes with the third step (singlet 7 kJ/mol, and no barrier at higher spin states).

In mechanism 3 the first step is an uphill reaction with a free energy difference of 58 kJ/mol (singlet activation free energy: 115 kJ/mol), the second step is the proton transfer from NH\textsubscript{2}* to O* with an activation free energy of 96 kJ/mol (singlet. 46 kJ/mol). The last step is equal to the last step in mechanism 2, and here the reverse second step competes to the third step with an activation free energy of only 12 kJ/mol (singlet: 5 kJ/mol).

The proton transfer to O\textsuperscript{br} is the rate-determining step in all of the three mechanisms. One can imagine that there might be another mechanism, where O\textsuperscript{br} is not involved at all. In such a mechanism all protons could be transferred to two neighbouring O* instead. The cluster used in this work is however too small to study this mechanism.

The third part of the overall process is the association and desorption of adsorbed NO and N\textsubscript{2}. HREEL spectral results have shown that nitrogen oxide, nitrogen and water is formed on the surface due to the oxygen coverage.[13] The overall reactions can simply be written:

\[2 \text{NH}_3 + 3 \text{O} \rightleftharpoons \text{N}_2 + 3 \text{H}_2\text{O}\]

\[2 \text{NH}_3 + 5 \text{O} \rightleftharpoons 2 \text{NO} + 3 \text{H}_2\text{O}\]
Those experiments also showed the existence of intermediate NH₂* at 90 K, but no NH* or N*, which indicates that they are consumed very fast.

Figure 4. Potential Gibbs energy surface of the association and desorption of NO on the RuO₂(110) surface at 298 K. The optimised structures in the doublet spin state are shown in black, with the optimised transition state structures located at the top of the arcs. Single point energies are plotted in magenta (quartets). Dashed lines indicate desorption steps.

In Figure 4 the free energies of the reaction steps for formation of NO (g) are shown. The association of NO on the surface has a low barrier (ΔG‡ = 28 kJ/mol). Here desorption of NO is found to be the rate-determining step with a Δ_{des}G = +280 kJ/mol. If there is a spin state change involved in the desorption process from doublet NO* to doublet NO (g) and quintet cluster, the free energy of desorption is Δ_{des}G = +215 kJ/mol. The computed desorption energy is over-estimated in comparison to desorption experiments (129 kJ/mol)[42]. NO has been found on the surface above 320 K, desorbing at 505 K. [13] It is difficult to pinpoint exactly why the computed desorption energy is too large but we note that the desorption energy from the periodic GGA computations (Table S1) is significantly lower for this particular molecule.
Figure 5. Potential Gibbs energy surface of the association and desorption of N\textsubscript{2} on the RuO\textsubscript{2}(110) surface at 298 K. The optimised structures in the singlet spin state are shown in black, with the optimised transition state structures located at the top of the arcs. Single point energies are plotted in blue (triplets) and red (quintets). Dashed lines indicate desorption steps.

Figure 5 shows the free energies for the association and desorption of N\textsubscript{2}. The rate-determining step is here the association of two N* (For the triplet state $\Delta G^\ddagger = 69$ kJ/mol), and the desorption process has a barrier of only 8 kJ/mol (from the triplet optimised structures).
3.4 Hydrogen dissociation on the surface

The dissociation of hydrogen on the RuO$_2$ (110) surface (H$_2^\#$(phys)) may be either homolytical to the same surface site type, or heterolytical to two different site types. In this work the under-coordinated species O$^{br}$ and Ru$^{cus}$ were studied as such sites. The homolytical dissociation of hydrogen on the Ru$^{cus}$ position (2H*) has a high reaction barrier ($\Delta G^\ddagger = 318$ kJ/mol), and the reaction free energy is also high ($\Delta_{diss}G = +258$ kJ/mol). The heterolytical dissociation to cus and br positions (H*H$^\#$) is much more favourable but still endergonic with $\Delta_{diss}G = +47$ kJ/mol) and a free energy barrier of 71 kJ/mol. The homolytic dissociation to O$^{br}$ has a dissociation energy of -30 kJ/mol when water-like species are formed (H$_2^\#$ in Figure 6), and $\Delta_{diss}G = -142$ kJ/mol when hydrogen is dissociated to two different oxygen atoms (2H$^\#_n$) – a reaction with a barrier of 163 kJ/mol.
Figure 6. Structures of hydrogen adsorbed at the surface with some important distances. The numbers to the right are the $\Delta_{\text{diss}}G$ given in kJ/mol. The same colours and notations are used as in Figure 2.

3.5 Thermodynamic equilibrium distributions

The equilibrium distributions of the different species were calculated from the thermodynamic simulations, where the temperature and the ratio of O$_2$ and NH$_3$ were scanned at constant pressure. The gases were held in excess over the surface positions. The resulting surface phase diagram is shown in Figure 7 where the fraction of NH$_3$/O$_2$ content is plotted on the x-axis and the temperature on the y-axis. The input data is taken from the optimised singlet or doublet states, or from the single point calculation of higher triplet and quintet spin states if they are lower in energy. Gibbs free energy corrections were taken from the vibrational analysis of the singlet structures.
With a NH$_3$/O$_2$ ratio below 0.55 oxygen was found to be physisorbed to the surface in combination with NO chemisorbed at the Ru$^{cua}$s positions. Ammonia has then mainly been dissociated into water vapour, nitrogen gas and NO*. At lower temperatures a small amount of NO$_2^*$ is formed. At a NH$_3$/O$_2$ ratio around 0.55 a water peak is found. In this region the water vapour pressure is high, and hence it readsorbs to the surface. Above a NH$_3$/O$_2$ ratio around 0.55, hydrogen is found at the O$^{br}$ position. These hydrogen atoms originate from the dissociated ammonia. At low temperatures ammonia is also found adsorbed to the surface. Above 0.55 NH$_3$/O$_2$ ratio all oxygen is in the gas state, either as molecular oxygen or water vapour. At temperatures above 500 K, gas-phase ammonia dissociates into hydrogen and nitrogen. There are differences in the geometrical position of the adsorbed hydrogen atoms depending on the temperature. Hydrogens predominantly appear next to each other, in agreement with the dissociation free energies in Figure 6. These energies are however based on that the lowest single-point energy, which is the quintet state of the 2H$^*_n$ structure. If the energies of the optimised singlets or the single-point triplets were compared instead, the 2H$^*_o$ structure is most stable of the three 2H$^*$ structures.
Figure 7. Surface phase diagram for different compositions of NH$_3$ and O$_2$ in the temperature range 200-600 K. Species below 1% are not reported. In the mono-coloured areas, only one form is found (>99%). Striped areas indicate co-existing forms, where the dominant form is represented by the broadest stripes.
Since the best sensor response for RuO$_2$ as a gate material was found at 200 °C (473 K) and atmospheric pressure [7], thermodynamic calculations were performed at these conditions. The initial atomic content corresponded to synthetic air (19.8 % O$_2$ and 79.2 % N$_2$) with 1000 ppm H$_2$ or NH$_3$. The results show that at equilibrium in principle all the hydrogen atoms were found in water vapour, and some as adsorbed water. The nitrogen atoms from NH$_3$ and some from N$_2$ were converted into NO*. The amount of NO* formed was proportional to the amount of surface sites included in the model. Oxygen atoms from O$_2$ were also found on the surface as physisorbed O$_2$ or in NO*. The distributions of the various species at different temperatures for the experimental initial composition are shown in Figure 8. In this calculation the number of sites are limiting, and hence there are a lot of N$_2$ left in the gas phase. If the amounts of the gases were limiting instead, the resulting composition will be almost independent of temperature and the following reactions will occur to completion:

\[
5 \text{N}_2 + \text{O}_2 \rightarrow 3 \text{N}_2^* + 2 \text{NO}^* \\
2 \text{NH}_3 \rightarrow \text{N}_2^* + 6 \text{H}^* 
\]
Figure 8. Thermodynamic equilibrium composition in the temperature range 200-600 K. The initial conditions are 0.1% NH₃, 21.0% O₂, 79.9% N₂ at 1 bar pressure.
3.6 Kinetics

The kinetics calculations were performed on the system to follow the evolution of the species over time. The reaction steps in the kinetic mechanism considered in this work are presented in Table 3. In Figure 9 the initial contents stated are for comparison to the sensor experiment – synthetic air with 0.1% ammonia at 473 K. [7] Nitrogen, oxygen and ammonia adsorbs to the surface very fast. However, only a small amount of the nitrogen gas is adsorbed, which is a result of its lower adsorption energy. Due to the stable physisorbed form of oxygen, its dissociation is slow. Ammonia dissociates on the surface, and desorbs as N$_2$ (g) and water. In Figure 10 the composition after 10 000 seconds is plotted. Water starts to desorb when the temperature is raised above 550 K. Our simulations seems to over-estimate desorption temperatures somewhat, since water was found in experiments already at 473 K.[7] This is in line with the general overestimation of adsorption energies using the present method as discussed in Section 3.3. Further, TD spectra shows that NH$_3$, H$_2$O, N$_2$ and NO all desorbs between 400-500 K [13].

As NH$_3$ dissociates, hydrogen is found on the surface. At lower temperatures the formation of H-O$^\bullet$ (H$^\bullet$) requires longer time, and that is why the amount of H$^\bullet$ is reduced in Figure 10. Hydrogen adsorbed to the surface is an indication of a gas response of the sensor.[8]

In the sensor experiments the highest response was found at around 200 °C with a lower response at higher temperatures,[7] which is interesting to compare to the sharp decrease of adsorbed H at 600 K in Figure 10. At elevated temperatures, oxygen on the surface dissociates and water is formed.[7]
Table 3. Reaction steps considered in kinetics simulations, and the corresponding activation energies (kJ/mol). * denotes Ru\textsuperscript{cvi} site and # denotes a O\textsuperscript{ph} site.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>forward</th>
<th>backward</th>
</tr>
</thead>
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<tr>
<td></td>
<td>$\Delta G_{\text{fwd}}^\ddagger$</td>
<td>$\Delta E_{\text{fwd}}^\ddagger$</td>
</tr>
<tr>
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<td>-</td>
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<tr>
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<td>20</td>
</tr>
<tr>
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<td>-</td>
</tr>
<tr>
<td>$\text{H}_2\text{O} (g) + {^\circ} \rightleftharpoons \text{H}_2\text{O}^*$</td>
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<td>-</td>
</tr>
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<td>105</td>
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<td>26</td>
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<td>154</td>
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<td>0</td>
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<tr>
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<td>153</td>
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Figure 9. Amounts of the molecular species as a function of time from the reaction kinetics simulation of the RuO$_2$(110) surface and an initial gas composition of 78.9% N$_2$, 21.0% O$_2$ and 0.1% NH$_3$ at a pressure of 1 bar and a temperature of 473 K. Surface sites are in excess.
Figure 10. Amounts of the molecular species as a function of temperature from the reaction kinetics simulation of the RuO$_2$(110) surface and an initial gas composition of 78.9% N$_2$, 21.0% O$_2$ and 0.1% NH$_3$ at a pressure of 1 bar. Amounts were plotted as snapshots after 10 000 s at a temperature between 300 and 1200 K.

4 Conclusions

Density functional theory calculations were performed for ammonia on an oxygen-rich RuO$_2$ surface to elucidate the reaction paths and mechanisms for dissociation and formation of NO, N$_2$ and H$_2$O.
These data have been used for thermodynamic equilibrium distribution and kinetic calculations, to compare the composition of the surface at different conditions. The presence of hydrogen adsorbed on the surface as for example HO\textsuperscript{br} species and the transfer of these species to the insulator can be considered to be the origin to the sensor response.[7] Therefore, it is of interest to follow the levels of HO\textsuperscript{br} at different conditions. It was found from the thermodynamics calculations that hydrogen atoms were present at the O\textsuperscript{br} positions at high NH\textsubscript{3} load. Kinetics show that HO\textsuperscript{br} species are also found at lower NH\textsubscript{3} concentrations. When temperature is raised, physisorbed oxygen is dissociated and water is formed from HO\textsuperscript{br}.

The calculations agree with experiment, since at these conditions water was the only gas phase molecule to be produced. The surface was according to the kinetics simulations found to be poisoned by oxygen and (at lower temperatures) nitrogen species, which might reduce the activity of the sensors.

We have devised a multiscale scheme, where thermodynamic data from ab initio calculations were used in calculating phase diagrams and to follow the reaction kinetics. This method will be further used in investigations of currently used sensors.

## 5 Acknowledgements

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