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Reaction mechanism of ammonia oxidation over $RuO_2(1\ 1\ 0)$: A combined theory/experiment approach

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ABSTRACT

Combining state-of-the-art density functional theory (DFT) calculations with high resolution core level shift spectroscopy experiments we explored the reaction mechanism of the ammonia oxidation reaction over $RuO_2(1 \ 1 \ 0)$. The high catalytic activity of $RuO_2(1 \ 1 \ 0)$ is traced to the low activation energies for the successive hydrogen abstractions of ammonia by on-top O (less than 73 kJ/mol) and the low activation barrier for the recombination of adsorbed O and N (77 kJ/mol) to form adsorbed NO. The NO desorption is activated by 121 kJ/mol and represents therefore the rate determining step in the ammonia oxidation reaction over $RuO_2(1 \ 1 \ 0)$.

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The oxidation of ammonia to NO is the first step in the industrial synthesis of nitric acid (cf. Eq. (1)). In general, the oxidation reaction of ammonia is catalyzed over Rh stabilized Pt gauzes at temperatures as high as 1000–1200 K with great efficiency and selectivity [1]. This reaction is known as the Ostwald process and its microscopic reaction steps have been studied quite thoroughly [2–4]:

$$2NH_{3} + \frac{5}{2}O_{2} \underset{1000 \text{ K}-1200 \text{ K}}{\overset{\text{Pt}}{\Longrightarrow}} 2NO + 3H_{2}O. \tag{1}$$

There are two major shortcomings in the Ostwald process: Firstly, the Pt gauzes must be replaced routinely every 6– 10 months since Pt is corroded by the formation of volatile PtO_2 under these harsh reaction conditions [5]. Secondly, the reaction temperature is very high so that the resulting water steam is extremely corrosive and technically difficult to handle.

Alternative NH₃ oxidation catalysts consist of transition metal oxides [6,7], which allow operation at lower temperatures and which produce less N₂O than commercial Pt gauzes. The main disadvantages of oxide catalysts are the requirement of using leaner NH₃/air mixtures of <10% of NH₃, which may be mitigated by using micro reactors, and the higher flow resistance. Very recently, it was

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demonstrated that RuO_2 is an efficient and selective oxidation catalyst for ammonia, running at a temperature as low as 550 K [8].

In this communication we report on a combined theory/experiment approach exploring the microscopic reaction steps in the oxidation of ammonia over $RuO_2(1\ 1\ 0)$; we have applied this intimate interplay of theory and experiments in model catalysis routinely and successfully over the past 15 years [9]. In the exhaustive density functional theory (DFT) calculations [10] we modelled the surface with five tri-layers of $RuO_2(1\ 1\ 0)$. Consecutive $RuO_2(1\ 1\ 0)$ slabs were separated by a vacuum region of 16 Å (supercell approach). The reaction coordinate was taken to be the distance between the reacting H atom of NH_x , x = 1, 2, 3 and the under-coordinated O atom. The transition state of each reaction pathway and the corresponding activation barrier were searched with a constrained minimization technique.

These DFT calculations are corroborated by high resolution core level shift spectroscopy (HRCLS) experiments performed at the beam line I311 at MAXII in Lund, Sweden [11]. The photon energies for the measurements of the N1s core levels were chosen to be 665 eV in order to enhance the surface sensitivity without facing a too intense background in the spectra by secondary electrons; the total energy resolutions of N1s spectra was set to be 180 meV. All HRCL spectra were recorded at a sample temperature of 100 K. The experimental HRCL spectra were decomposed into a small number of Donjiac–Sunjic profiles convoluted with Gaussian



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Fig. 1. (A) Ball and stick model of the clean $RuO_2(1 \ 1 \ 0)$ surface. Large balls represent oxygen, and small balls represent ruthenium atoms of $RuO_2(1 \ 1 \ 0)$. The bridge-bonded oxygen atoms O_{br} and Ru_{cus} atoms are indicated. Both surface species are one-fold under coordinated with respect to bulk-coordination. O_{3f} indicates 3-fold (bulk-coordinated) surface O atoms. (B) The adsorption of oxygen onto the stoichiometric $RuO_2(1 \ 1 \ 0)$ surface proceeds via the on-top positions above the Ru_{cus} atoms. O_{ot} indicates on-top adsorbed O atoms.



Fig. 2. Illustration of the microscopic reaction steps in the oxidation of NH_3 over $RuO_2(1 \ 1 \ 0)$. The activation energies (red) are determined by DFT calculations and are given in kJ/mol. $-H_{diff}$ means that the abstracted H from NH_x is removed from its direct neighborhood by diffusion along the various O species on the surface.

distributions [12]. The assignment of experimental N1s features to specific chemical entities on the $RuO_2(1\ 1\ 0)$ surface is based on DFT-calculated core level shifts which were calculated by removing half of an electron from the core orbital and performing a self-consistent calculation of the electronic structure [13]. Thus the screening effects ("final state") of the hole are included. The energy is obtained as the energy difference between the Kohn-Sham eigenvalue of the core state and the Fermi energy.

The RuO₂(1 1 0) offers two distinct catalytically active sites with which molecules from the gas phase can interact, i.e. the undercoordinated Ru atoms (Ru_{cus}) and the under-coordinated bridging O atoms (O_{br}) (cf. Fig. 1A). For the stoichiometric RuO₂(1 1 0) surface, DFT calculations show that ammonia adsorbs initially ontop of the Ru_{cus} sites with its lone pair pointing towards the Ru_{cus} atom. The adsorbed NH₃ molecule forms a hydrogen bond to the adjacent O_{br} species. The adsorption energy of NH₃ is 150 kJ/mol at low coverages and 113 kJ/mol for high coverages in very good agreement with a recent DFT study [14]. The hydrogen transfer from NH₃ to the O_{br} species is endothermic by 39 kJ/mol with an activation barrier of 73 kJ/mol. The H-atoms can practically not diffuse along the bridging O rows due to the high diffusion barrier of 240 kJ/mol. Therefore, if no on-top O atoms are present on the surface then the shifted H atom of adsorbed NH₃ is localized at the adjacent bridging O position. The equilibrium of $NH_3(ad) \rightarrow$ $NH_2(ad) + O_{br} - H$ on the stoichiometric $RuO_2(110)$ surface is exceedingly on the NH₃ side for temperatures below 500 K, consistent with corresponding experiments in Ref. [8].

Under typical reaction conditions, ammonia oxidation proceeds in oxygen excess where most of cus sites are occupied by on-top O atoms (cf. Fig. 1B). With DFT calculations we studied therefore the reaction pathway of cus adsorbed NH₃ on RuO₂(110) with both on-top O and bridging O species in its direct neighborhood to which H-atoms of NH₃ can be transferred. In Fig. 2, the various microscopic reaction steps are compiled including the respective energy barriers ΔE_{act} (red) and total adsorption energies (black). The adsorption energy of NH₃ on O pre-covered RuO₂(110) is 165 kJ/mol, again in good agreement with a very recent DFT study [14]. The hydrogen abstraction from NH_3 to O_{br} is activated by 65 kJ/mol, while that to the on-top O is activated by 73 kJ/mol. The activation barrier for the first H abstraction is already quite low if one compares this value with a recently found value on Pt(100) (120 kJ/mol) [4]. The found activation energies on RuO₂ suggest that at 90 K dissociation of NH₃ is not favorable in contrast to conclusions drawn from recent HREELS experiments [8]. This first dehydrogenation step of NH₃ on RuO₂(110) imposes the highest activation barrier among the H stripping reactions of NH₃ similar to the case of methane activation [15]. The next dehydrogenation step from the amine NH₂ to NH is activated by only 29 kJ/ mol independent of whether the hydrogen atom shifts to the next bridging O or to the on-top O atom.

The last H transfer step from NH to N proceeds even without any noticeable activation barrier so that the imide species is likely to be instable on the $RuO_2(1 \ 1 \ 0)$ surface. Altogether these calculated activation barriers suggest that as soon as the first hydrogen

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Fig. 3. High resolution core level shift spectra of N1s, explaining the oxidation of ammonia to NO. The intensities are given in arbitrary units, but the same units are used in all panel. (a) N1s spectrum when 0.4 L of NH₃ is exposed to the stoichiometric RuO₂(1 1 0) surface at 100 K. (b). The stoichiometric RuO₂(1 1 0) surface was exposed to 2.5 L of O₂ at room temperature followed by dosing 0.5 L of NH₃ at 100 K and then annealed to various temperatures: (b₁) 250 K, (b₂) 300 K, (b₃) 350 K, and (b₄) 400 K.

is transferred from an ammonia molecule to the on-top oxygen covered catalyst surface the further H abstraction proceeds automatically. Therefore reaction intermediates in the form of NH_x , x < 3 are of transient nature and accordingly difficult to detect with spectroscopy.

The N1s spectrum in Fig. 3a of NH_3 adsorbed on the stoichiometric $RuO_2(1\ 1\ 0)$ surface shows three signals at 398.4, 400.5 and 403.5 eV which are assigned to adsorbed NH_3 in the first ($NH_3(1)$), second ($NH_3(2)$) and multi-layer ($NH_3(3)$), respectively. These assignments are based on thermal desorption spectra of NH_3 [8]. Only for NH_3 of the first layer ($NH_3(1)$), ammonia adsorbs on-top of the Ru_{cus} sites.

The DFT-based reaction mechanism of ammonia oxidation is nicely reconciled with the experimental N1s spectra shown in Fig. 3b. The $RuO_2(1\ 1\ 0)$ surface was exposed to 2.0 L of oxygen at room temperature (0.8 monolayer of on-top O) and subsequently exposed to 0.5 L of NH₃ at 100 K. The N1s spectra are shown in Fig. 2b₁, indicating two spectral features at 398.8 and 400.5 eV. The N1s at 398.8 eV is assigned to NH₃ adsorbed on Ru_{cus} , the other to NH₃ adsorbed in the second layer, H-bonded to the ontop O. Experimental and calculated N1s core level shifts are compiled and assigned to specific N-containing surface species in Table 1.

Upon annealing the surface to 250 K, a single peak remains at 398.9 eV, i.e. on-top adsorbed NH3(1) in proximity to on-top O. Part of the NH₃ has already desorbed from the $RuO_2(1 \ 1 \ 0)$ surface, a process which continues upon annealing to 300 K. Further annealing to 350 K transforms part of the NH₃-related emission into an additional emission at 397.4 eV and a small signal at 400.3 eV. The N1s emission at 397.4 eV is assigned to adsorbed N, while that at 400.3 eV is ascribed to adsorbed NO. The assignment of the experimental N1s emissions to particular NH_x species and NO is based on DFT calculations. Taking the adsorbed $NH_3(1)$ species in the first layer as the reference, DFT calculations determine that the N1s core levels of NH₂ and NH are shifted by 3.0 and 2.9 eV to lower binding energies, respectively. None of these features are seen in the experimental N1s core level spectra consistent with the above determined reaction barriers. A recent HREELS study is partly consistent with this finding in that a NH species could not be identified during the oxidation of ammonia, while a NH₂ surface species was proposed [8]. The calculated N1s core level of a naked N atom adsorbed on Rucus atom is shifted by 1.7 eV to lower binding energy in good agreement with the experiment (−1.4 eV).

Further increase of the temperature to 400 K leads to a substantial increase of the NO-related N1s feature at 400.3 eV at the expense of the NH₃ emission. This assignment is based on DFT calculations which determine for on-top adsorbed NO an N1s shift of 1.2 eV to higher binding energies w.r.t. NH₃(1). Obviously, only above 350 K neighboring N and O are able to recombine on the RuO₂(1 1 0) surface to form adsorbed NO consistent with recent HREELS experiments [8]. The abstracted H-atoms migrates then along the on-top O-segments with an activation energy of 0.22 eV; this process is called $-H_{diff}$ in Fig. 2.

According to our DFT calculations, the most active O species in the recombination of N and O to form NO is the on-top O species with an activation energy of 77 kJ/mol. This activation barrier is slightly too low to be compatible with a reaction temperature of about 350–400 K as observed in Fig. $2b_4$). However, 400 K is just the temperature where water desorbs from the RuO₂(1 1 0) surface [16,17]. Therefore, we conclude that the NO production is hindered by O_{ot}–H groups in the direct vicinity of N. Only when the O_{ot}–H groups recombine to form water that desorbs at 400 K, nitrogen can react with the remaining O_{ot} on the surface to form NO. Fully consistent with this proposed reaction scheme a recent HREELS study indicated that the majority of NO is produced only when

Table 1

N1s core level binding energies determined by HRCLS. Corresponding N1s core level shifts are compared to DFT-calculated ones with having the N1s of NH₃(1) as reference.

Experimental N1s core level energy (eV)	Experimental N1s core level shift (eV)	Assignment based ()	DFT-calculated N1s core level shifts (eV)
398.4	-0.4	NH ₃ adsorbed on Ru _{cus} : first layer (TDS) [8]	-
400.5	1.7	NH ₃ second layer (TDS) [8]	-
403.5	4.7	NH ₃ third layer (TDS) [8]	-
398.8	0.0	NH_3 adsorbed on-top of Ru_{cus} with on-top O	0
		neighbor	
397.4	-1.4	N adsorbed on-top of Ru _{cus} (DFT)	-1.7
400.3	1.5	NO adsorbed on-top Ru _{cus} (DFT)	1.2
-	-	NH ₂ adsorbed on-top Ru _{cus} (DFT)	-3.0
-	-	NH adsorbed on-top Ru _{cus} (DFT)	-2.9

the H_2O species desorbs at 400 K [8]. The resulting NO molecule is quite strongly adsorbed on the surface by 191 kJ/mol so that desorption of NO molecules takes place only above 500 K as recently observed in temperature programmed reaction [8]. Slightly lower values for the NO adsorption energies were calculated in a recent DFT study by Hong et al. [18].

In conclusion, the high activity of $RuO_2(1 \ 1 \ 0)$ in the ammonia oxidation towards NO is due to low activation energies for the successive hydrogen abstractions. The highest energy barrier among the successive H abstraction is encountered with the first dehydrogenation step (73 kJ/mol), resulting in a reaction temperature of about 300 K to 350 K. The association step of adsorbed N and O on the RuO₂(1 1 0) is activated by 77 kJ/mol which is slightly too low to be reconciled with a required temperature of 350-400 K as suggested by Fig. 2b₄). Therefore, we suggest that OH groups in the vicinity of the adsorbed N inhibit the association of N and O to form NO. The desorption of NO is the rate determining step for the overall reaction process of NH₃ oxidation due to an adsorption energy of 191 kJ/mol, requiring a reaction temperature of 500 K to prevent product poisoning of the catalyst by NO. Whether these results are also relevant to practical RuO₂-based catalysts exposing various surface orientations will be the subject of forthcoming paper where we will present ammonia oxidation experiments of a RuO₂ powder catalyst in a flow reactor [19]. For the catalyzed CO oxidation reaction, at least, it has been shown that the studies on the $(1 \ 1 \ 0)$ orientation of RuO₂ are equally relevant to other surface orientations of RuO₂ [20].

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