Catalytic Oxidation of Ammonia on RuO₂(110) Surfaces: Mechanism and Selectivity

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The selective oxidation of ammonia to either N_2 or NO on $RuO_2(110)$ single-crystal surfaces was investigated by a combination of vibrational spectroscopy (HREELS), thermal desorption spectroscopy (TDS) and steadystate rate measurements under continuous flow conditions. The stoichiometric $RuO_2(110)$ surface exposes coordinatively unsaturated (cus) Ru atoms onto which adsorption of NH₃ (NH₃-cus) or dissociative adsorption of oxygen (O-cus) may occur. In the absence of O-cus, ammonia desorbs completely thermally without any reaction. However, interaction between NH₃-cus and O-cus starts already at 90 K by hydrogen abstraction and hydrogenation to OH-cus, leading eventually to N-cus and H₂O. The N-cus species recombine either with each other to N₂ or with neighboring O-cus leading to strongly held NO-cus which desorbs around 500 K. The latter reaction is favored by higher concentrations of O-cus. Under steady-state flow condition with constant NH₃ partial pressure and varying O₂ pressure, the rate for N₂ formation takes off first, passes through a maximum and then decreases again, whereas that for NO production exhibits an S-shape and rises continuously. In this way at 530 K almost 100% selectivity for NO formation (with fairly high reaction probability for NH₃) is reached.

1. Introduction

The catalytic oxidation of ammonia to NO, the so-called Ostwald process, is an important industrial process for the production of nitric acid.^{1,2} On the other hand, an alternate route of ammonia oxidation leading to nitrogen and water has become of increasing interest in connection with the removal of ammonia from waste streams (see ref 3 and references therein). This is a particularly obvious example for the relevance of selectivity in heterogeneous catalysis. This term denotes the ratio of the rate for production of the desired product over the sums of the rates for all reaction channels. As emphasized recently by Somorjai:4 "The focus of catalysis research in the 21st century should be on achieving 100% selectivity for the desired product". In contrast to catalytic activity (i.e., the productivity per site and second), our knowledge about the factors affecting selectivity is still rather limited. According to the just given definition, research on this phenomena should concentrate on the rates (under steady-state flow conditions) and their control by the various external parameters. For the example to be presented here this latter factor is revealed to be particularly important: Whereas with low relative O₂ concentrations N₂ is the main reaction product, the selectivity toward NO formation increases continuously with the proportion of oxygen and reaches eventually nearly 100%. The study was performed with a welldefined RuO₂(110) single-crystal surface as model system, and both the reaction mechanism and the question of selectivity could be clarified on an atomic scale.

Recently, the RuO₂(110) surface, prepared by exposing Ru-(0001) to high doses of O₂ at elevated sample temperatures,^{5–7} has been found to exhibit high catalytic activity for CO oxidation.^{5,6,8} The stoichiometric RuO₂(110) surface is schematically shown in Figure 1 together with the relevant adsorbed



Figure 1. Ball-and-stick model of the stoichiometric $\text{RuO}_2(110)$ surface in perspective view together with adsorbed NH₃ and O atoms (O-cus).

species to be discussed below. It is characterized by two different, coordinatively unsaturated surface atoms organized in rows along [001]: (i) 2-fold coordinated oxygen atoms (O-bridge) and (ii) 5-fold coordinated Ru atoms (Ru-cus). Additional oxygen atoms may be adsorbed by further exposure to O₂ on top of Ru-cus, called O-cus in the following. A maximum coverage of about 80% of the Ru-cus atoms may thus be achieved.^{9,10} The O-cus species is weakly bound on the surface and desorbs at temperatures as low as 400–500 K. Therefore, this species is expected to be very reactive as verified, e.g., by CO oxidation,^{6,8} carbonate formation,^{10,11} and ethylene oxidation.¹²

In the present work the interaction of ammonia with the stoichiometric and oxygen-rich $RuO_2(110)$ surfaces is studied in detail using thermal desorption spectroscopy (TDS) and high-resolution electron energy-loss spectroscopy (HREELS). At the stoichiometric surface NH₃ chemisorbs molecularly on Ru-cus, as also sketched in Figure 1, and desorbs molecularly again. In the presence of O-cus, however, high catalytic activity for NH₃ oxidation is observed, leading either to NO or N₂, whereby the product selectivity is controlled by the O-cus coverage. Identification of the reaction intermediates enables formulation of the reaction mechanism which is verified in steady-state rate measurements under flow conditions.

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2. Experimental Section

The experiments were performed in an ultrahigh vacuum (UHV) apparatus consisting of two chambers separated by a valve. The base pressure was 2×10^{-11} mbar. The upper chamber was used for sample preparation and contained a quadrupole mass spectrometer for TDS and for reaction rate measurements, as well as facilities for low-energy electron diffraction (LEED), gas dosing, and surface cleaning by Ar ion sputtering. The lower chamber housed a HREEL spectrometer (Delta 0.5, SPECS). Spectra were taken in specular geometry at an angle of incidence of 55° with respect to the surface normal. The primary electron energy was set to 3 eV and the energy resolution was better than 2.5 meV.

The substrate, a Ru(0001) single crystal, was clamped between two Ta wires. A NiCr-Ni thermocouple was spotwelded to the back of the Ru crystal. The sample temperature could be varied between 85 and ~1300 K by combining cooling with liquid nitrogen and heating by radiation or by combined radiation and electron bombardment from the backside of the sample. The RuO₂(110) surface was prepared in-situ following a procedure described in preceding publications.^{5,6} In brief, the Ru crystal was cleaned by applying repeated sputtering and annealing cycles. The oxide film was then grown epitaxially by exposing the clean Ru(0001) surface to about 10⁷ langmuir of O₂ (1 langmuir = 1.33×10^{-6} mbars) at 700 K using a gas shower. The preparation could be repeated after restoring the original Ru(0001) surface by sputtering and annealing cycles.

Prior to each experiment, impurities such as H_2O or CO were desorbed and the surface ordering was improved by heating the sample to 700 K for 1 min. The chemical cleanliness of the surface and the surface order were controlled by standard techniques. The following gases were admitted to the surface: NH₃ (purity 99.98%, Linde), ND₃ (minimum 99 atom % for D, Campro), ${}^{16}O_2$ (purity 99.998%, Messer Griesheim), ${}^{18}O_2$, (minimum 99 atom % ${}^{18}O_2$, Isotec) and C¹⁶O (purity 99.997%, Messer Griesheim).

Steady-state rate measurements were performed by operating the upper chamber as a continuous-flow reactor. A tube of a diameter of 5 mm attached to our mass spectrometer, which reached about 0.5 mm to one side of our sample and about 3 mm to the other side. By this arrangement we basically collected reaction products coming directly from the sample surface and also provided, by the tilt of the sample with respect to the axis of the mass spectrometer, access of ambient molecules to the sample surface. By this arrangement, reactions other than from the front surface of the sample did not play a role. The later conclusion was also tested by additional experiments.

Reactants (NH₃ and O₂) were introduced through separate leak valves and were continuously pumped off together with the reaction products by a turbomolecular pump. The partial pressures of the products p_i were transformed into the respective rates of formation through

$$r_{\rm i} = p_{\rm i} N_{\rm o} V / \tau_{\rm A} R T_{\rm g} \, (\text{molecules/s}) \tag{1}$$

where N_0 is Avogadro's number, V is the volume of the reactor, τ_A is the residence time in the reactor as evaluated from the effective pumping speed, R is the gas constant, and T_g is the gas temperature. As will be shown, catalytic reaction under the chosen conditions proceeds predominantly on the Ru-cus sites. The RuO₂(110) single-crystal surface exhibits 5 × 10¹⁴ Ru-cus sites/cm², so that with the known surface area (0.3 cm²) the absolute rate values evaluated according to eq 1 can be



Figure 2. Thermal desorption spectra of NH_3 (mass 17) for various NH_3 exposures at 90 K on the stoichiometric $RuO_2(110)$ surface. The heating rate was 3 K s⁻¹. The exposure is given in units of langmuir.

transformed into turnover frequencies, i.e., number of reactive events per active site and second.

3. Results and Discussion

3.1. Adsorption of NH₃ on the Stoichiometric RuO₂(110) Surface. Figure 2 shows the NH₃ TD spectra recorded after exposing the stoichiometric RuO₂(110) surface to varying amounts of NH₃ at 90 K. At low exposures only one desorption peak is observed at around 460 K (denoted as α_1 -NH₃). As the coverage is increased, the α_1 state shifts to lower temperatures and is saturated at an exposure of 0.2 langmuir, whereas a broad feature centered at about 355 K evolves (denoted as α_2 -NH₃). After further exposure new desorption peaks appear at lower temperatures: β -NH₃ at 170 K and γ -NH₃ at 130 K. The latter is not saturated with increasing NH₃ exposure, indicating its origin from multilayer desorption. In analogy to the data for NH₃ on Ru single-crystal surfaces,¹³⁻¹⁵ α -NH₃ and β -NH₃ are attributed to the desorption from the first and second monolayer, respectively.

Interestingly, compared with the data for Ru single-crystal surfaces,^{13–15} both α -NH₃ states are shifted upward by about 100 K, which indicates that the ammonia monolayer is more strongly bound on the RuO₂(110) than on the Ru(0001) surface. This finding can be rationalized by the existence of electronegative O-bridge atoms on RuO₂(110), causing some electron deficiency at the Ru-cus atoms, which then interact more strongly with the N lone pair of ammonia. By assuming a preexponential of 10^{-13} s, activation energies of 32 and 43 kJ mol⁻¹ for the desorption of multilayer and second-layer ammonia result, respectively. The latter value is again higher than with elemental Ru and has presumably to be attributed to additional hydrogen bonding between the second-layer NH₃ and O-bridge, as further suggested below from the HREEL spectra.

To check for ammonia oxidation, we have performed TDS measurements at mass 18 (H₂O), 28 (N₂), and 30 (NO). No desorption of NO is detected. The TD spectrum of N₂ exhibits only a weak peak at 160 K which is associated with the adsorption of molecular nitrogen obtained most likely due to decomposition of NH₃ in the dosing line as reported in the literature.^{14,16} These results clearly demonstrate that ammonia undergoes only molecular desorption and oxidation does not take place on the stoichiometric RuO₂(110) surface.

Spurious amounts of H_2O are observed in the temperature range 500–700 K, indicative for the recombination of OHbridge.¹⁷ The formation of the OH-bridge is not due to interaction with NH₃ but rather to the interaction of hydrogen from the residual gas with the O-bridge, because the peak



Figure 3. HREEL spectra for various NH₃ exposures on the stoichiometric RuO₂(110) surface at 90 K. All spectra were recorded at 90 K in specular geometry with an incidence angle of 55° with respect to the surface normal and with a primary energy of 3 eV. The factors ×100 and ×400 are relative to the elastic intensity. The exposure is given in units of langmuir.

intensity is independent of NH₃ exposure. From our recent measurements^{10–12,18} it is known that adsorption of hydrogen from the residual gas cannot be prevented for the reactive RuO₂-(110) surface even at a background pressure of 2×10^{-11} mbar. In addition, there is a weak H₂O desorption peak at 420 K that is attributed to adsorption on Ru-cus from the residual gas atmosphere.¹⁹

Figure 3 shows a series of HREEL spectra recorded after NH₃ exposure at 90 K. The stoichiometric RuO₂(110) surface is characterized by an intense band at 69 meV from the O-bridge stretching mode against the surface,⁹ and phonon contributions at 12 and 45 meV. After an exposure of 0.02 langmuir of NH₃ the spectrum exhibits a new peak at 149 meV, which becomes more intense and shifts slightly downward in energy with increasing NH₃ exposure. This feature is attributed to the NH₃ umbrella mode δ_s (NH₃) and indicative for molecular adsorption. After an exposure of 0.1 langmuir, additional NH₃-related modes appear at 199, 403, and 418 meV arising from the asymmetric deformation mode δ_a (NH₃), the symmetric stretching mode δ_a (NH₃), respectively. Beyond 0.2 langmuir exposure the surface is saturated with ammonia in the first monolayer.

The HREEL spectra exhibit additional features at 25, 57, 76, and 83 meV, which cannot be attributed to the frustrated translational and rotational modes of chemisorbed ammonia. This conclusion is supported by the isotope substitution experiment with ND₃. New peaks are observed at 112.5, 145, 295, and 312.5 meV, which display the expected isotope shifts with respect to NH₃. However, the peaks at 25, 57, 76, 83, and 433 meV remain unchanged, which means that they originate not from NH₃. Actually, they are indicative for a water-like species (H₂O-bridge) formed through interaction of hydrogen with O-bridge.¹⁷ The lack of the D₂O-related modes in the HREEL spectrum of ND₃ demonstrate that hydrogen originates from the background instead from surface reaction of NH₃, in line with the TDS results.

Increasing the NH_3 exposure to 0.3 langmuir leads to the buildup of the second layer, characterized by a new peak at 150 meV for the umbrella mode and an intense loss at 54 meV for a librational mode. Exposure to 2 langmuirs of NH_3 causes the formation of multilayers. By comparison with literature data, the observed features can be assigned to the frustrated translation perpendicular to the surface (30 meV), librations (51, 57 meV), symmetrical and asymmetrical deformations (153, 203 meV), as well as the symmetrical and asymmetrical N–H stretching modes (405, 422 meV). Hydrogen bonds are formed between NH₃ molecules in the multilayer as reflected by the broadening of the symmetrical stretching mode at 405 meV.

To determine the adsorption site of ammonia, we have performed the following experiment: The Ru-cus atoms were first capped by CO-cus through exposure to 1 langmuir of CO at 90 K, giving rise to the ν (Ru–CO) mode at 38 and the ν -(C–O) mode at 262 meV (Figure 4).⁵ When this surface was further exposed to 0.2 langmuir of NH₃ at 90 K, no monolayer ammonia but only second-layer type ammonia was detected with vibrational losses at 47, 53, 133, 201 and 420 meV. This conclusion is supported by the corresponding TD spectrum shown in the insert exhibiting merely the β -state. This demonstrates that NH₃ chemisorbs at Ru-cus and also suggests that the second-layer ammonia can interact with the coordinatively unsaturated O-bridge atoms presumably via NH···O hydrogen bonds.

To further confirm the presented picture with the stoichiometric RuO₂(110) surface, the sample was exposed to 2 langmuirs of NH3 at 90 K, and subsequently annealed to different temperatures. The corresponding HREEL spectra are shown in Figure 5. After annealing at 140 K, ammonia adsorbed in multilayers beyond the second layer has been desorbed. The two umbrella modes $\delta_s(NH_3)$ at 145 and 151 meV are indicative for bilayer ammonia, with two intense losses at 30 and 54 meV for the frustrated translational and librational modes, respectively. Annealing to 210 K leads to desorption of the secondlayer ammonia, and the spectrum exhibits now the vibrational features of (monolayer) ammonia chemisorbed on Ru-cus. The asymmetrical deformation mode $\delta_{as}(NH_3)$ shifts to 196 meV. Chemisorbed NH₃ remains unaffected in its molecular state during further annealing and desorbs completely upon heating to 470 K.

In this experiment—apart from the spectral features characteristic for adsorbed ammonia—no other surface species could be identified. Thus, the appearance of two desorption states (α_1 and α_2) in TDS has to be attributed to the repulsive interaction between chemisorbed ammonia molecules. Finally, we note that the H₂O-bridge related losses were detected again at 27, 58, 76, 84, and 434 meV due to spurious adsorption of hydrogen from the residual gas. After heating to 470 K, the decomposition



Figure 4. HREEL spectra recorded after the stoichiometric $RuO_2(110)$ surface was exposed to (a) 1 langmuir of CO at 90 K and then (b) 0.2 langmuir of NH_3 at 90 K. The corresponding TD spectrum of NH_3 (mass 17) is shown in the inset. Parameters are as for Figure 3.



Figure 5. HREEL spectra recorded after exposing the stoichiometric $RuO_2(110)$ surface to 2 langmuirs of NH_3 at 90 K and subsequently annealed to the indicated temperatures. Parameters as for Figure 3.

of the H_2O -bridge species has taken place, as indicated by the appearance of OH related peaks at 54 and 446 meV.

In summary, on the stoichiometric $\text{RuO}_2(110)$ surface NH_3 chemisorbs molecularly on Ru-cus and desorbs completely below 500 K. Compared to the Ru surfaces, ammonia is more strongly bound to the $\text{RuO}_2(110)$ surface due to the enhanced electron donation from the N lone pair of NH_3 to the Ru-cus atoms of the substrate. The relatively high desorption barrier for the second-layer ammonia is attributed to additional hydrogen bond interaction with O-bridge atoms. There is no indication for dissociation followed by further reaction.

3.2. Interaction of Ammonia with the Oxygen-Rich RuO₂-(**110**) **Surface.** Oxygen-rich $\text{RuO}_2(110)$ surfaces were prepared by exposing the stoichiometric $\text{RuO}_2(110)$ surface to O₂ at room temperature. The maximum coverage of O-cus is achieved for an exposure of 1 langmuir, which corresponds to 80% of Rucus sites being occupied by O atoms.⁹ Afterward the sample was cooled to 90 K and then exposed to 0.2 langmuir of NH₃. The resulting TD spectra for NH₃, N₂, NO, and H₂O are reproduced in Figures 6a–d, respectively. No other N-containing products such as N₂O and NO₂ were detected for all O-coverages.

Desorbing NH₃ shows up in two desorption peaks at about 430 and 190 K corresponding to chemisorbed molecules in the first (α) and second (β) layer in agreement with the findings for the stoichiometric surface as discussed above. The amount of chemisorbed NH₃ is significantly decreased compared with the stoichiometric RuO₂(110) surface. This may have two reasons: On the O-rich surface fewer unoccupied Ru-cus sites are available for NH₃ chemisorption. Even more important,



Figure 6. TD spectra recorded after exposing 0.2 langmuir of NH₃ to RuO₂(110) surfaces with various preexposures to O₂ at 90 K. The data are for the following species: (a) NH₃ (mass 16), (b) N₂ (mass 28), (c) NO (mass 30), and (d) H₂O (mass 18). The heating rate was 3 K s⁻¹. The exposures are given in units of langmuir.

however, adsorbed NH₃ will react with neighboring O-cus atoms, as will become evident later. No desorption of first-layer NH₃ is observed after an exposure of 0.5 langmuir of O₂ at 300 K, although even ~35% Ru-cus sites are still unoccupied. (Note that the weak feature at 400 K is due to the cracking of H₂Ocus, as discussed below.) Instead NH₃ molecules come increasingly off from second-layer type sites (β). If compared with the stoichiometric RuO₂(110) surface, the desorption peak of the second-layer ammonia shifts upward to 190 K, indicating stronger interaction with the underlying layer, most likely due to additional NH•••O hydrogen-bond attraction.

The observation of N₂ (Figure 6b) and NO (Figure 6c) desorption together with the absence of the O₂ from O-cus recombination confirms that surface reaction of adsorbed ammonia has taken place. The high temperature of the N₂ peak at about 420 K suggests that it originates from N atom recombination whereas the weak broad peak in the temperature range 140–240 K is attributed to spurious effects from coadsorbed molecular species. On the other hand, NO is desorbed at 505 K as a result of recombination between adsorbed N and O. The peak temperature is consistent with the data for NO adsorption on Ru-cus.¹⁸ This means that the NO release into the gas phase is desorption- instead of reaction-limited. NO formation proceeds indeed already at lower temperatures, as will be confirmed by the HREELS data below.

The occurrence of surface reactions is further manifested by the observation of an H_2O peak at 400 K (Figure 6d), which is characteristic for H_2O adsorbed on the Ru-cus sites.¹⁹ From the

much higher intensity—as compared with the TD spectra from the stoichiometric surface—it is concluded that this H₂O-cus is produced through ammonia oxidation even if it might contain some contribution from the interaction of O-cus with the background hydrogen. At lower O-cus coverage a weak H₂O peak in the temperature range between 530 and 700 K is detected caused by recombination of OH-bridge formed via reaction of O-bridge with background H₂.¹⁷ However, at saturation only the desorption of H₂O-cus is observed which clearly confirms that O-cus instead of O-bridge serve as the active species for ammonia oxidation.

Detailed inspection of the TDS data indicate that for a given NH₃ exposure the amounts of N₂ and NO desorbing depend on the O-cus coverage: At low O-cus coverage the formation of N₂ is observed, whereas with increasing O-cus concentration the N₂ production is suppressed and instead the NO production increases. To quantitatively analyze the dependence of reaction products on the O-cus coverage, the amounts of N₂ and NO released were determined by normalizing the desorption peaks with those obtained after saturation of N₂ at 90 K and NO at 300 K.¹⁸ The results are shown in Figure 7 and will be reflected also by the steady-state kinetic data to be presented below. Obviously, low O-cus coverage favors N₂ production, which takes place via the following overall reaction:

$$2NH_3 + 3O \rightarrow N_2 + 3H_2O \tag{2}$$

whereas for high O-cus coverage NO is preferentially formed



Figure 7. Integrated amounts of N_2 and NO in units of monolayers released in the experiments underlying Figure 6 as a function of the O-cus coverage.

according to

$$2NH_3 + 5O \rightarrow 2NO + 3H_2O \tag{3}$$

If one assumes optimum occupation of the cus sites, we can estimate the maximum amount of N_2 formed according to route (2), taking into account the overall stoichiometry. It is reached at an O-cus coverage of 0.6 monolayer, leading to formation of 0.2 monolayer of N_2 . From our experiments a maximum N_2 amount of 0.15 monolayer is achieved at an O-cus coverage of 0.66 monolayer, accompanied by 0.05 monolayer of NO. From these numbers we can derive the total amount of O-cus reacted with NH₃ according to both routes under these conditions as 0.52 monolayer. The remaining amount of 0.14 monolayer of O-cus is most likely consumed by reaction with hydrogen from the residual gas to H₂O, because no O₂ desorption is observed in the TD spectra.

At O-cus saturation the amount of N_2 is decreased to only 0.03 monolayer, whereas NO becomes the main product according to route (3) with a maximum of 0.21 monolayer. At saturation of O-cus about 20% Ru-cus sites are still available for NH_3 adsorption, which would allow a maximum NO production of 0.2 monolayer in good agreement with the experimental value.

HREELS experiments provided further insight into the reaction mechanism. First, the O-saturated $RuO_2(110)$ surface

was prepared by exposing the stoichiometric surface to 1 langmuir of O_2 at room temperature, corresponding to an O-cus coverage of about 80%. The sample was then exposed to 0.2 langmuir of NH₃ at 90 K, and subsequently annealed to the temperatures indicated in Figure 8. The respective HREEL spectra were measured at 90 K. To unambiguously identify the reaction intermediates and products, in addition to HREEL spectra, obtained after exposing the ¹⁸O-saturated RuO₂(110) surface to 0.2 langmuir of ND₃ at 90 K, were recorded and are presented in Figure 9. The observed vibrational energies, mode assignments, and isotope shifts are summarized in Table 1.

The O-saturated surface is characterized in Figure 8 by the peak at 103 meV (99 meV for ¹⁸O-cus in Figure 9), which is assigned to the stretching mode of O-cus against Ru. After exposure of 0.2 langmuir of NH₃ at 90 K, additional modes occur that are characteristic for bilayers of adsorbed ammonia in which the second-layer NH₃ is weakly bonded to NH₃ molecules underneath and/or to oxygen species (O-bridge and O-cus) with hydrogen bonds. On the basis of isotope substitution experiments (see Figure 9) these spectral features are assigned to the frustrated translation mode (28 meV), the frustrated rotation modes (40, 58 meV), the umbrella mode (151 meV), the asymmetric deformation modes (199 meV, first-layer NH₃; 207 meV, second-layer NH₃), and the symmetric (404 meV) and asymmetric (420 meV) stretching modes, respectively.

According to our previous investigation of NH and NH₂ species on Ru single-crystal surfaces,^{14,20} the peaks observed at 172 and 186 meV are characteristic for NH₂ as reaction intermediate and are assigned to the rocking and scissoring mode of this intermediate, respectively. The observation of NH₂ together with the finding that the O-cus peak shifts slightly to 101 meV and loses significantly in intensity reveals that ammonia oxidation starts to occur at temperatures as low as 90 K. This conclusion is further supported by the detection of a small amount of H₂O-cus, monitored by the O–H stretching mode at 436 meV and the libration mode at 113 meV.¹⁹

By warming the sample to 200 K (see Figure 8), we observe new losses at 61, 110, 127, and 446 meV, which are indicative for H₂O-cus,¹⁹ accompanied by a further decrease of the O-cus peak intensity at 101 meV. In addition, the peaks attributed to



Figure 8. HREEL spectra recorded after exposing the O-cus saturated $RuO_2(110)$ surface (prepared by dosing 1 langmuir of O_2 at room temperature) to 0.2 langmuir of NH_3 at 90 K and subsequent annealing to the indicated temperatures. Parameters as for Figure 3.



Figure 9. HREEL spectra recorded after exposing the ¹⁸O-saturated RuO₂(110) surface (prepared by dosing 1 langmuir of ¹⁸O₂ at room temperature) to 0.2 langmuir of ND₃ at 90 K and subsequent annealing to the indicated temperatures. Parameters as for Figure 3.

TABLE 1: Mode Assignments, Vibrational Energies in Units of meV, and Isotope Shifts for Different Species during NH₃ (ND₃) Oxidation at the ¹⁶O (¹⁸O)-Saturated RuO₂(110) Surface^{*a*}

species	TII	T⊥	R	$\delta_{ m s}$	δ_{a}	$\nu_{ m s}$	$ u_{\mathrm{a}} $
NH ₃				154	199	404	420
ND_3				117	144	292	311
				(1.32)	(1.38)	(1.38)	(1.35)
NH_2			172	186			
ND_2			127	140			
			(1.35)	(1.33)			
$H_2^{10}O$	15	61	98	192		436	446
	28		110				
D 180	14	50	127	1.42		212	207
$D_2^{10}O$	14	39 (1.02)	/5	(1.24)		$\frac{512}{(1.40)}$	$\frac{327}{(1.26)}$
	(1.07)	(1.05)	(1.54)	(1.54)		(1.40)	(1.30)
	(104)		(1.34)				
	(1.04)		94				
			(1.35)				
¹⁶ OH		52	(1.00)				
18OD		50					
		(1.04)					
$N^{16}O$						231	
$N^{18}O$						226	
						(1.02)	

^{*a*} T, translational mode; || and \perp to the surface plane; R, librational mode; δ_s and δ_a symmetric and asymmetric deformation modes; ν_s and ν_a , symmetric and asymmetric stretching modes.

the NH₃ bilayer are no longer observed in accordance with the desorption of the second-layer NH₃ (Figure 6a); the spectrum displays now the δ_s (NH₃) mode at 154 meV and the δ_a (NH₃) mode at 199 meV for NH₃ chemisorbed on Ru-cus. Interestingly, compared with the stoichiometric RuO₂(110) surface, the δ_s -(NH₃) mode shifts upward by 10 meV on the O-rich surface. This finding is attributed to a change of the charge at the surface: ²¹ A more positive charge at the surface leads to a higher mode frequency. On the O-rich RuO₂(110} surface the electron density of the substrate is reduced by the electronegative O-cus adatoms leading to a more positive charge at the unoccupied Ru-cus sites.

After heating to 250 K, the HREEL spectrum changes again: (i) The NH_2 related modes vanish, which reveals that NH_2 is not stable at higher temperatures. (ii) H_2O -cus related losses gain in intensity and are well resolved. On the basis of

isotope-substitution experiments (see Figure 9) these are attributed to the frustrated translations parallel to the surface (14 and 28 meV), the frustrated translation perpendicular to the surface (61 meV), the frustrated rotation modes (110 and 127 meV), the scissoring mode (192 meV), and the symmetric (436 meV) and asymmetric (446 meV) stretching modes, respectively. (iii) A weak peak at 225 meV is attributed to the internal N-Ostretching mode indicative for the formation of NO on Ru-cus¹⁸ and supported by the expected isotope shift for N¹⁸O to 221 meV.

Furthermore, a weak feature at 52 meV is resolved, which exhibits an isotope shift of 1.04 for ND₃. By comparison with the Ru–OH_{bridge} stretching mode, observed at 64 meV,¹⁷ it is suggested that this peak arises from an OH group at Ru-cus as a reaction intermediate of NH₃ oxidation. On Ru single-crystal surfaces^{14,15,20,22} the Ru–N stretching mode has been detected in the energy region between 50 and 80 meV. With the present system unfortunately no clear assignment can be made due to overlap with various other spectral features. The NH group, which might be formed during NH₃ oxidation and exhibits—according to our reassignment^{14,20}—a characteristic bending mode in the 80–90 meV energy region, can also not be identified.

Upon further annealing to 320 K, the following changes are observed: (i) The NH3-related peaks disappear nearly completely, indicating that chemisorbed NH₃ has been reacted off. NH₃ desorption from the (chemisorbed) α -state can, however, be ruled out on the basis of the TDS results (see Figure 6a). (ii) The H₂O-cus related peaks grow. An additional loss is resolved at 98 meV and assigned to a libration mode of H₂O-cus, as supported by the isotope shift of 1.34. (iii) The NO stretching band shifts upward to 231 meV and gains in intensity. Its blue shift by 6 meV-with respect to the value found at 250 K-is associated with the disappearance of the NH₃ species. At lower temperature the electron density of the substrate is increased due to electron donation from the N lone pair of the chemisorbed ammonia to the surface. As a consequence, electron backdonation from the surface to the antibonding $2\pi^*$ orbital of coadsorbed NO is enhanced, resulting in weakening of the internal N-O bond.



Figure 10. HREEL spectra recorded after exposing the $RuO_2(110)$ surface partly covered by O-cus (prepared by dosing 0.3 langmuir of O_2 at room temperature) to 0.2 langmuir of NH_3 at 90 K and subsequent annealing to the indicated temperatures. Parameters as for Figure 3.

Heating to 400 K leads to the disappearance of the H_2O -cus related modes, whereas the NO-cus mode at 231 meV becomes the leading one (note the change in the sensitivity factor); i.e., the main amount of NO-cus is produced only when the H_2O -cus species desorbs completely at 400 K. Besides NO, the spectrum does not exhibit other N-containing products, in good agreement with the TDS results. By annealing to 530 K, NO disappears due to the desorption of NO at 510 K (Figure 6c), and the spectrum (not shown) displays again the dominant peak at 69 meV characteristic for the stoichiometric RuO₂(110) surface.

The preferential reaction of ammonia to N_2 and H_2O at low O-cus coverage becomes evident from the HREEL data reproduced in Figure 10. A surface partially (i.e., to about 40%) covered by O-cus was prepared by dosing 0.3 langmuir of O_2 at room temperature.¹⁰ Subsequent exposure to 0.2 langmuir of NH₃ at 90 K causes the appearance of new peaks at 152, 199, 406, and 420 meV due to NH₃-cus. Simultaneously, the O-cus related feature at 103 meV is strongly reduced in intensity, indicating that NH₃ oxidation starts already at these low temperatures. This conclusion is further supported by the observation of the intermediate species NH₂ (186 meV) and OH (52 meV) as well as of the product H₂O-cus (112, 433, and 445 meV). (In addition, a small amount of H₂O-bridge is also formed as indicated by the scissoring mode at 221 meV originating from interaction with hydrogen from residual gas.)

Upon annealing to 320 K, O-cus is transformed into H_2O cus (61, 98, 107, 128, 433, and 446), whereas there are NH_3 species left on the surface (152 and 199 meV), in line with the observation of NH_3 desorption in TDS (Figure 6a). At this temperature, the weak feature observed at 225 meV cannot be attributed to the H_2O -bridge any more, because the H_2O -bridge is not stable and dissociated completely to OH-bridge at 320.¹⁷ We attribute therefore this peak to minor amounts of NO-cus formed.

Further annealing to 400 K leads to several changes: (i) The H₂O-cus related losses vanish completely due to the desorption of H₂O-cus. (ii) The new losses at 54 and 446 meV are assigned to OH-bridge formed via the decomposition of the H₂O-bridge.¹⁷ (iii) The umbrella mode of NH₃ is observed at 147 meV with

a red shift by 5 meV, reflecting the change of the electron density at the surface when H₂O-cus is desorbed. Most importantly, the NO stretching mode at 225 meV remains unchanged with very small intensity during heating to 400 K, which reveals that at low O-cus coverage NO formation is almost negligible. This points indirectly to N₂ being the main reaction product formed by recombination of the two neighboring N-cus species, as supported by the TDS results. The release of N₂ into the gas phase is limited by this recombination step, because adsorbed N₂ leaves the surface below 200 K.¹⁸

3.3. Steady-State Reaction Kinetics. The results presented so far demonstrated that with the stoichiometric $RuO_2(110)$ surface NH_3 undergoes simply adsorption and desorption, whereas in the presence of excess oxygen (occupying Ru-cus sites) reaction to both N_2 and NO may take place. From these N_2 comes off the surface around 420 K (by recombination of N-cus), whereas NO is released (desorption-limited) at about 500 K. Therefore steady-state rate measurements were only performed above the latter temperature.

The reaction rate r (=turnover frequency) will depend on three parameters, the temperature T and the partial pressures of NH₃ and O₂, $p(NH_3)$ and $p(O_2)$, respectively. Figure 11a shows the results from experiments with fixed T = 530 K and $p(NH_3)$ = 1 × 10⁻⁷ mbar as a function of $p(O_2)$. For $p(O_2) = 0$; i.e., without occupation of the Ru-cus sites by O-atoms, $r_{\rm NO}$ as well as r_{N_2} vanish, confirming the previous conclusions whereafter both, NH₃ and O, have to be adsorbed on Ru-cus to undergo catalytic reaction. With increasing $p(O_2)$ first r_{N_2} rises, passes through a maximum and then decreases again, whereas $r_{\rm NO}$ has a sigmoid shape and rises continuously. With $p(NH_3) = 10^{-7}$ mbar the impact frequency of an incoming NH₃ molecule onto a Ru-cus site will be about 0.1 s^{-1} , and from Figure 11a one can read the value of the turnover frequency for NO formation to be 0.025 s⁻¹ at $p(O_2) = 2 \times 10^{-6}$ mbar, so that we may conclude that for the highest O2 pressure applied in this experiment (2 \times 10⁻⁶ mbar) an ammonia molecule has a probability of about 25% to be transformed into NO.

The switching of the dominant reaction product from N_2 to NO with increasing O_2 pressure becomes even more evident when the kinetic data of Figure 11a are transformed into



Figure 11. (a) Steady-state rates of N₂ and NO formation (expressed as turnover frequencies) for a constant NH₃ partial pressure, $p(NH_3) = 1 \times 10^{-7}$ mbar, as a function of O₂ partial pressure $p(O_2)$ at T = 530 K. (b) Steady-state selectivities for N₂ and NO formation resulting from the data of the Figure 11a.



Figure 12. Data as with Figure 11, but for T = 500 K.

selectivity, namely the rates for N₂ and NO divided by the total rates, respectively, viz. $S_{N_2} = (r_{N_2})/(r_{N_2} + r_{NO})$ and $S_{NO} = (r_{NO})/(r_{N_2} + r_{NO})$. As can be seen from Figure 11b the selectivity for NO production rises from zero to almost 100%, whereas that for N₂ formation, on the other hand, decreases continuously.

Analogous kinetic data for a somewhat lower temperature (500 K) are reproduced in Figure 12a. The qualitative behavior is similar to that of the data of Figure 11. However, the absolute

rates are lower and the selectivity for N_2 formation is favored, whereas that for NO production reaches a maximum value of only about 0.8 (Figure 12b).

No full exploration of the full parameter space (T, p_{O_2} , p_{NH_3}) could be performed. Qualitatively the following conclusions were drawn: At fixed partial pressures of NH₃ and O₂, both the rates and selectivities remain relatively independent of temperature between about 530 and 630 K. Below 530 K the rate for NO formation decreases markedly (because of limiting thermal desorption of NO), whereas that for N₂ production remains still fairly constant. Above 630 K both rates decrease continuously, presumably mainly because the steady-state surface concentrations of the reacting species decrease due to thermal desorption.

However, at higher temperatures another reaction step has to be taken into account: Reaction between NH_3 and the bridge (or even bulk) O atoms of the $RuO_2(110)$ surface is associated with a higher activation energy than that with O-cus, so that these processes will no longer be negligible at higher temperatures. HREELS data demonstrated indeed that the $RuO_2(110)$ surface may even become partly reduced to Ru(0001) (covered by chemisorbed O atoms), which phase is catalytically completely inactive.

4. Discussion

Because the properties of the various surface species have been analyzed already in detail in the preceding section, the following discussion will concentrate on the mechanism and kinetics of the catalytic reactions leading to N_2 or NO, whereby particular emphasis will be put on the phenomenon of catalytic selectivity.

Under technical conditions, oxidation of ammonia by atmospheric oxygen is typically carried out with Pt/Rh gauzes operated at 1100-1200 K providing NO yields of up to 98%.^{1,2} The product selectivity was found to depend mainly on temperature: At low temperatures N2 is the main product, whereas above 850 K NO becomes increasingly dominant. In view of the extremely short contact times ($\sim 10^{-3}$ s) possible surface intermediates were hard to detect and discussions about the reaction mechanism remained largely speculative.²³ This situation remained essentially unchanged in later studies with various metal^{24,25} or oxide²⁴⁻²⁹ surfaces. More recently, surface science experiments provided more insight.30-35 For Pt it was found that the selectivity was not only governed by temperature but also by the composition of the gas phase, in that excess oxygen favors the production of NO (as with the present system).^{33–35} Bradley et al.³⁴ proposed a reaction mechanism consisting of a complex series of steps that contains competition between NO desorption and NO dissociation as essential ingredients. However, so far no reports about the steady-state kinetics and its modeling are available for this type of study with metal surfaces.

With the RuO₂(110) surface the Ru-cus atoms can unequivocally be identified as the active sites for catalytic reaction for the following reasons: (i) NH₃ chemisorbed in the first layer will be attached to Ru-cus. (ii) Reaction will only take place if also O atoms are coadsorbed on Ru-cus. (iii) Only H₂O molecules adsorbed on Ru-cus are detected as reaction products. If H₂O-bridge or OH-bridge groups would have been formed through interaction between NH₃-cus and O-bridge, the corresponding spectral features would be thermally stable up to 600 K,¹⁷ which is not the case. (iv) The NO molecules formed are also adsorbed on Ru-cus.¹⁸ Their formation via O-bridge can be excluded on the basis of the isotope substitution experiments.



Figure 13. Sketch of the $RuO_2(110)$ surface along the Ru-cus atoms (open circles) in [001] direction with O-cus and NH₃-cus adsorbed on neighboring sites, illustrating H-bridge interaction with O-cus as primary reaction step.



Figure 14. Overall scheme for the various surface processes and their characteristic reaction temperatures.

The primary reaction step is illustrated in Figure 13, which shows a cut through the surface in [001] direction along the Ru-cus atoms. NH₃ adsorbed on Ru-cus will desorb unless it interacts with a neighboring O-cus species. That is why no reaction at all is observed with the stoichiometric (i.e., O-cus free) RuO₂(110) surface. However, there exists obviously a fairly strong interaction between an H-atom from NH₃ and a neighboring O-cus atom as sketched by the dotted line. Hydrogen abstraction and formation of OH-cus takes place at temperatures as low as 90 K, as demonstrated by the HREELS data. The further progress of the surface reactions is depicted schematically by Figure 14 whereby no account of the exact stoichiometry is taken for the sake of simplicity.

Although NH_{ad} as a possible further intermediate cannot be ruled out and N_{ad} cannot be directly identified spectroscopically, there is very strong evidence that this species plays the key role in the formation of the reaction products. Depending on the configuration of neighboring adspecies, either recombination with another N_{ad} to N_2 (which then immediately desorbs) or with O_{ad} to adsorbed NO will take place. Thermal activation of these two competing processes is presumably not very different and also affected by desorption of H₂O because these steps all take place in the same temperature range. NO_{ad} can clearly be identified by HRELSS and desorbs only around 500 K, so that at lower temperatures this process will be limiting the overall rate. There is also no indication for dissociation of adsorbed NO at elevated temperatures,¹⁸ which was considered to be the source for N_{ad} in the reaction over Pt surfaces.^{34,35}

Although not all details of this reaction scheme are yet known, it provides a safe framework also for qualitative rationalization of the steady-state rate data. Inspection of Figures 11a and 12a reveals that the reactions to formation of both products take off only if there is continuous admission of O₂ forming O-cus, so that ammonia may become dehydrogenated and N_{ad} is formed. As long as most O-cus is consumed for this process, recombination of N_{ad} with O_{ad} will be suppressed and the formation of N₂ will be dominant. Only with increasing O₂ pressure will NO formation take off. A further increase of the O_{ad} concentration (by further increase of p_{O_2}) will reduce the probability that an N_{ad} species is next to another N_{ad}. Instead,

the probability for recombination to NO will continuously rise while that for N_2 formation drops. This model provides a straightforward rationalization for the observed variations of reactivity and selectivity.

To further substantiate this concept an attempt was made for mathematical modeling. For this purpose the reaction scheme depicted in Figure 14 is approximated by the following steps:

$$O_2 + 2^* \xrightarrow{k_1} 2O_{ad}$$
 (4)

$$\mathrm{NH}_3 + * \xrightarrow{k_2}_{k_{-2}} \mathrm{NH}_{3,\mathrm{ad}}$$
(5)

$$\mathrm{NH}_{3,\mathrm{ad}} + \mathrm{O}_{\mathrm{ad}} \xrightarrow{k_3} \mathrm{N}_{\mathrm{ad}} + \mathrm{H}_2\mathrm{O}^{\uparrow} + * \tag{6}$$

$$N_{ad} + O_{ad} \xrightarrow{k_4} NO^{\uparrow} + 2^*$$
 (7)

$$N_{ad} + N_{ad} \xrightarrow{k_5} N_2 \uparrow + 2*$$
 (8)

* denotes a free Ru-cus site, and the overall surface composition is determined by

$$[O_{ad}] + [NH_{3,ad}] + [N_{ad}] + [*] = 1$$
(9)

The rates for NO and N₂ production are then given by

$$\tau_{\rm NO} = \frac{\mathrm{d}[\mathrm{NO}]}{\mathrm{d}t} = k_4 [\mathrm{N}_{\mathrm{ad}}] [\mathrm{O}_{\mathrm{ad}}] \tag{10}$$

$$\tau_{N_2} = \frac{d[N_2]}{dt} = k_5 [N_{ad}]^2$$
(11)

Under steady-state flow conditions the relevant surface concentrations are determined within the Langmuir-Hinshelwood (mean field) approximation by

$$\frac{d[O_{ad}]}{dt} = k_1 p_{o2} (1 - [O_{ad}] - [N_{ad}] - [NH_{3,ad}])^2 - k_3 [NH_{3,ad}] [O_{ad}] - k_4 [N_{ad}] [O_{ad}] = 0$$
(12)

$$\frac{d[N_{ad}]}{dt} = k_3[NH_{3,ad}][O_{ad}] - k_4[N_{ad}][O_{ad}] - k_5[N_{ad}]^2 = 0$$
(13)

$$\frac{d[\mathrm{NH}_{3,\mathrm{ad}}]}{dt} = k_2 p_{\mathrm{PH}_3} (1 - [\mathrm{O}_{\mathrm{ad}}] - [\mathrm{N}_{\mathrm{ad}}] - [\mathrm{NH}_{3,\mathrm{ad}}]) - k_{-2} [\mathrm{NH}_{3,\mathrm{ad}}] - k_3 [\mathrm{NH}_{3,\mathrm{ad}}] [\mathrm{O}_{\mathrm{ad}}] = 0 \quad (14)$$

This is admittedly a very crude approximation in which all additional surface intermediates are neglected, the stoichiometry is wrong, and the kinetics is described by the Langmuir concept ignoring any interactions between the varying adsorbed species. In addition, the rate constants k_1 to k_5 are not known, so that at best reproduction of the qualitative trends can be expected. On the other hand, solution of the set of equations (10)–(14) is by no means trivial.

As an example for the kind of agreement between experimental results and modeling that can be achieved in this way, Figure 15 shows a fit for the data at 500 K as reproduced in Figure 12. This result was obtained with plausible values for the rate constants k_1 to k_5 (e.g., the initial sticking coefficients for O₂ and NH₃—corresponding to k_1 and k_2 —being close to unity) but is, of course, still associated with ambiguities. The





Figure 15. Experimental data (marked by stars) of Figure 12 in comparison with a fit to the theoretical model with suitable parameters: $k_1 = 1.0, k_2 = 1.2, k_{-2} = 2.4, k_3 = 20, k_4 = 2.0, k_5 = 1.6.$

main purpose was to demonstrate that reasonable modeling can be achieved with the proposed reaction mechanism, which thereby receives further support.

5. Conclusions

The formation of a single reaction product in heterogeneous catalysis is more the exception than the rule, as for example verified with ammonia synthesis or carbon monoxide oxidation. Hence selectivity will be frequently of even higher significance than the overall reactivity. The present work represents, in our opinion, the first example for which this phenomenon could be explored on an atomic level for the resulting kinetics under steady-state flow conditions.

The coordinatively unsaturated (cus) Ru atoms in the RuO2-(110) surface were identified as catalytically active sites onto which either ammonia or oxygen are adsorbed from the gas phase. The concentration of O-atoms adsorbed on these cussites determines both the reactivity and selectivity. Without the presence of this species adsorbed NH3 simply desorbs. However, a neighboring O-cus abstracts readily one of its H-atoms initiating complete dissociation. The resulting adsorbed N-atoms either recombine with each other to N₂ or with O-cus to NO. The selectivity under steady-state conditions is thus determined by the local surface configurations of the adsorbates and thereby

by the relative partial pressures of the reactants. The results also clearly demonstrate the dependence of the selectivity on the external parameters as was also suggested by King et al.^{34,35} for the reaction on Pt surfaces. Almost 100% selectivity for NO formation is reached at 530 K, much lower than the temperatures applied in the technical Ostwald process with platinum-based catalysts (>1100 K). This offers interesting prospects for possible applications.

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