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Structure-function relationship for alumina supported platinum during formation of ammonia from nitrogen oxide and hydrogen in presence of oxygen

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We study the structure-function relationship of alumina supported platinum during formation of ammonia from nitrogen oxide and dihydrogen by employing *in situ* X-ray absorption and Fourier transformed infrared spectroscopy. Particular focus is directed towards the effect of oxygen on the reaction as a model system for emerging technologies for passive selective catalytic reduction of nitrogen oxides. The suppressed formation of ammonia observed as the feed becomes net-oxidizing is accompanied by a considerable increase in the oxidation state of platinum as well as formation of surface nitrates and loss of NH-containing surface species. In the presence of (excess) oxygen, the ammonia formation is proposed to be limited by weak interaction between nitrogen oxide and the oxidized platinum surface. This leads to slow dissociation rate of nitrogen oxide and thus low abundance of atomic nitrogen surface species that can react with adsorbed hydrogen species. In this case the consumption of hydrogen through the competing water formation reaction and decomposition/oxidation of ammonia are of less importance for the net ammonia formation.

In the field of catalysis for emission control, the formation of ammonia (NH₃) from nitrogen oxides (NO_x) in the exhausts

from combustion processes has thus far solely been regarded as a detrimental side reaction, e.g. during operation of three-way and NO_x storage and reduction (NSR) catalysts, that demands sophisticated modification of the catalyst to be suppressed. This view, however, is about to change as emerging techniques such as passive selective catalytic reduction (passive-SCR) of NO_x presently attracts increasingly more interest. The basic idea behind passive-SCR is to react part of the undesired NO_x with hydrogen-containing compounds present in the exhaust to form ammonia, which in turn is stored and used as a reducing agent for the remaining NO_x in a down-stream positioned SCR catalyst^{1,2}. Thereby, an on-board supply of NH₃ is provided, eliminating obstacles associated with external storage of a suitable reductant, for example urea as is currently used in heavy-duty NH₃-SCR applications^{3,4}. Since passive-SCR is a new concept, basic understanding of governing surface reactions and catalytic materials for formation of NH₃ is of vital importance when exploring competitive catalyst technologies. On the fundamental level, producing ammonia from NO_x through heterogeneous catalytic processes involves fascinating surface chemistry that is not yet well understood. This communication contributes to the fundamental knowledge about the catalytically active phase and how its oxidation state influences the likelihood of specific elementary steps participating in the overall ammonia formation reaction.

Two prominent catalytic routes for NH₃ formation using nitric oxide (NO) have been reported, namely the direct reaction of NO with dihydrogen (H₂) and hydrolysis of surface-bound isocyanate groups⁵. Due to fuel economy benefits of combustion in excess oxygen in automotive applications, it is essential to study the effect of oxygen (O₂) concentration on these reaction routes. Through kinetic measurements in continuous flow reactors, we

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have shown that the ability for ammonia formation over alumina supported platinum (Pt/Al₂O₃) is severely impeded as the feed becomes net-oxidizing⁶. Similarly, DiGulio *et al.*² studied the effect of transient air-to-fuel ratio on the formation of NH₃ over three-way catalysts, where it was reported that NH₃ is formed in significant quantities in exhaust gas compositions representative of rich operation. However, upon increased air-to-fuel ratio of the feed, the activity for NH₃ formation decreases and becomes entirely suppressed even before lean conditions are completely established. To elucidate the origin of this suppression we employ *in situ* X-ray absorption spectroscopy (XAS) and *in situ* Fourier transformed infrared (FTIR) spectroscopy to study a Pt/Al₂O₃ catalyst during reaction conditions. The chosen feed gas composition is the simplest model gas, consisting of NO, H₂, carrier Ar and different levels of O₂ as to avoid an overly complex reaction network.

The Pt/Al₂O₃ model catalyst used was prepared by incipient wetness impregnation to a nominal metal content of 1 wt.%, as previously described by Adams *et al.*⁶. In addition to previous characterization⁶ we herein provide scanning transmission electron microscopy (STEM) imaging of the sample *ex situ*, giving a more direct complementary measurement of the dispersed Pt particles. To prepare the STEM specimen, a small amount of the sample was dispersed in ethanol in an ultrasonic bath for 20 seconds whereafter one drop of the dispersed sample was deposited onto a lacey carbon copper grid. Images were recorded at different magnifications ranging from 36 × 36 to 294 × 294 nm using a Technai T20 G2 microscope (FEI). Representative STEM images of the Pt/Al₂O₃ sample are displayed in Figure 1. Well-ordered Pt particles with an approximate size of 30 nm evenly distributed throughout the Al₂O₃ matrix can be observed.

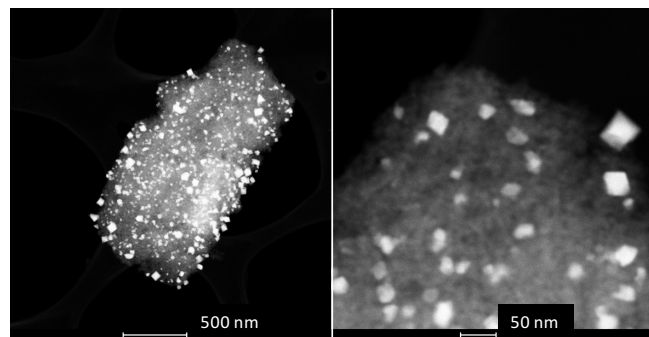


Fig. 1 STEM imaging of the model Pt/Al₂O₃ catalyst

To study changes in the platinum phase during reaction conditions, *in situ* transmission XAS measurements were performed at beamline i811 at the MAX IV Laboratory, Sweden, using an *in situ* environment reaction cell described in detail by Zhang *et al.*⁷. The Pt L_{III} edge of the Pt/Al₂O₃ sample was measured at 350 °C during exposure to different feed compositions, controlled by separate mass flow controllers (Bronkhorst Hi-Tech LOW-ΔP-FLOW) providing a well-defined flow of reactants (500 ppm NO, 1500 ppm H₂ and Ar_{bal}, F_{tot} = 50 ml/min). Subsequently, the O₂ concentration was adjusted to correspond to the stoichiometric numbers (S) of the feed(s) investigated previously⁶. The align-

ment, averaging, background subtraction and normalization of the Pt L_{III} edge spectra were performed using the Athena software package⁸. Energy scales were calibrated using simultaneously acquired reference spectra from a Pt foil, the first inflection point of the edge being defined as E₀ = 11564 eV. Equivalent sweeps were then averaged and normalized using a linear fit to the pre-edge in the E₀ range of -150 to -50 eV and a third order polynomial to fit the post-edge over the E₀ range of +35 to +1000 eV. Figure 2a shows the obtained *in situ* X-ray absorption spectra as function of the stoichiometric number of the feed and a clear absorption edge, typical of Pt L_{III} can be observed at 11560 eV. It is clearly seen that the intensity of the white-line increases as the stoichiometric number (and thus oxygen content) of the feed is increased, as compared to the reduced sample in the absence of oxygen (black dotted lines in Figure 2a). This represents an increased oxidation state of platinum within the sample as the feed becomes increasingly oxidizing. Figure 2b displays the Fourier transformed Extended X-ray absorption fine structure (EXAFS) spectra obtained using the k-points 3 to 12 with a k-weight factor of 1.2. The trend of decreasing peaks at 2.2 and 3.0 Å, and increasing peak at 1.4 Å, indicates a decrease in the Pt-Pt component and increase in the Pt-O component, respectively. This is representative of a physical change within the sample, being increasingly oxidized as the stoichiometric number is increased, and not merely in the surface coverage of oxygen.

Figure 3a shows the measured concentrations of different gas phase species in the effluent stream at each feed composition obtained during previous continuous flow reactor experiments⁶. As N₂ could not be directly measured, a nitrogen balance was used to calculate the formed amounts of N₂ according to the following equation: $[N_2] = [\frac{1}{2}NO]_{inlet} - [N_2O + \frac{1}{2}NH_3 + \frac{1}{2}NO + \frac{1}{2}NO_2]_{outlet}$. Further, Figure 3b shows the white-line area obtained by integrating the absorbance in the energy interval 11560 - 11573 eV for each spectrum presented in Figure 2a. This panel also shows the Pt-Pt and Pt-O coordination number obtained from the EXAFS fitting. When S < 1, it is likely that most of the O₂ present in the feed is reduced by H₂ to form H₂O. However, when the feed becomes net-oxidizing, i.e., the O₂ concentration exceeds that required for total oxidation of H₂, the proportion of platinum oxides in the sample rapidly increases. As the formation of water from H₂ and O₂ over Pt occurs via a Langmuir-Hinshelwood mechanism⁹ whereby O₂ must be surface-bound and dissociated before reaction with surface-bound H, this indicates that as we move from rich to lean conditions a transition from a surface covered with chemisorbed hydrogen and oxygen to a surface covered by oxide occurs. This is reflected in the spectroscopic data in Figure 3b; although a small increase in white-line area (WLA) is observed upon increasing the stoichiometric value of the feed whilst maintaining it as net-reducing (S < 1), no change is observed in the Pt-O component of the EXAFS region, indicative of an adsorbed surface layer of oxygen atoms. However, as discussed previously, the large increase in WLA and Pt-O component of the EXAFS region when the feed is net-oxidizing indicates a structural change within the sample as a result of the excess availability of oxygen in the feed and complete conversion of the hydrogen reductant. A secondary effect of the oxidation of H₂ to H₂O (rel-

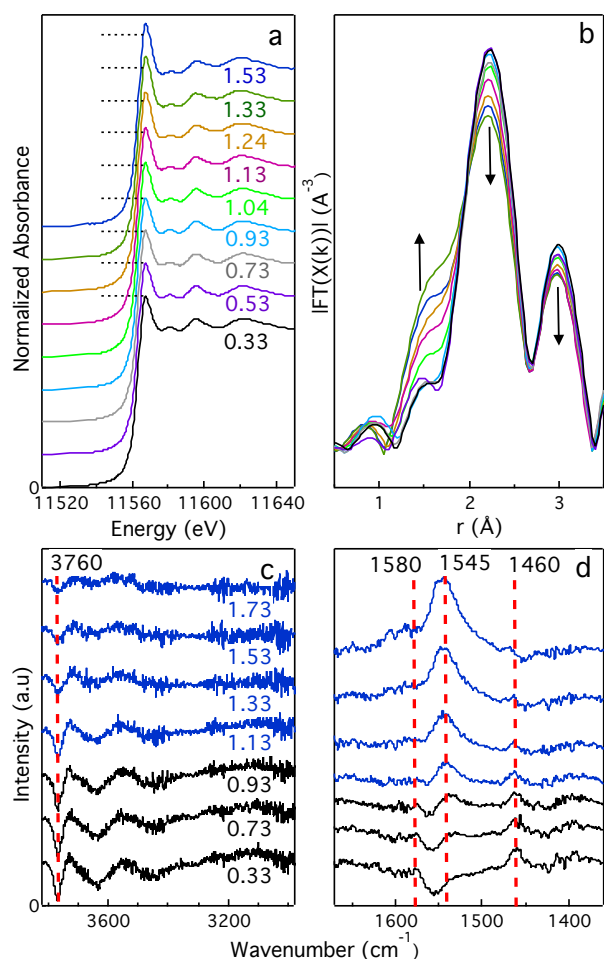


Fig. 2 *In situ* spectroscopic data obtained during exposure of Pt/Al₂O₃ to NO and H₂ at varying S-value of the feed (displayed on spectra). a) X-ray absorption spectra of the Pt L_{III} edge at 11.56 keV. The dotted lines indicate the relative height of the white-line for the reduced sample, b) Fourier transformed EXAFS spectra showing the Pt-O component at 1.5 Å and the Pt-Pt component at 2.2 and 3 Å, c) infrared spectra in the wavenumber region 3820-2980 cm⁻¹ and d) infrared spectra in the wavenumber region 1670-1350 cm⁻¹.

evant to all stoichiometric values above 0.33) is the lower surface abundance of hydrogen, resulting in lower NH₃ formation rates for two reasons; not only is hydrogen clearly required for the direct reaction with N ad-atoms to form NH₃, but it is also able to facilitate the dissociation of adsorbed NO for further reaction¹⁰⁻¹².

In addition to limited hydrogen availability, it is also apparent that an inverse relationship between platinum oxide formation and NH₃ generation exists. This suggests that, for NH₃ formation to take place, platinum must be present in the reduced form. It is well known that adsorption of O₂ and NO on noble metal sites is a competitive process¹³. At high temperatures, the adsorption of O₂ is preferred due to its rapid dissociation upon adsorption whereas the rate of NO desorption from the catalyst surface is considerable. As the oxygen content in the feed is increased, a subsequent increase in platinum oxides of the sample is observed, indicating that adsorption of oxygen is preferred even at an in-

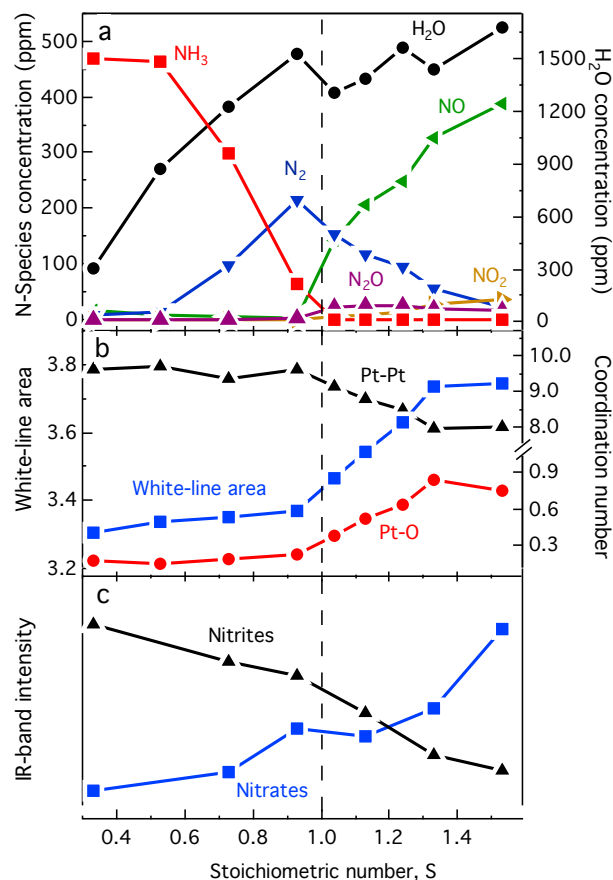


Fig. 3 a) Gas phase products in the effluent stream during exposure of Pt/Al₂O₃ to NO and H₂ versus the stoichiometric number of the feed, b) evolution of the corresponding white-line area of the XANES spectra and Pt-Pt and Pt-O coordination number obtained from fitting of EXAFS data and c) evolution of the corresponding surface nitrates and nitrites obtained by integrating the infrared peaks positioned between 1500-1560 and 1450-1475 cm⁻¹, respectively.

intermediate temperature of 350 °C but also that the presence of excess oxygen facilitates the formation of platinum oxides. As the concentration of O₂ present in the feed is increased and the competitive adsorption of NO becomes more challenging, it is indeed not surprising that the amount of NO that remains unreacted over the catalyst increases. The cause for this is two-fold. Due to the rapid desorption of NO from the catalyst surface at elevated temperatures the probability of interaction, and thus reaction, with other surface species is low. Further, as the dissociative adsorption of NO is preferred over reduced platinum sites¹⁴, the oxide formation limits the extent of NO dissociation due to weak interaction with the platinum oxide.

In order to confirm this statement, density functional theory was used, as implemented in GPAW¹⁵⁻¹⁷, which uses a real space grid of the projector-augmented wave. The ground-state structure calculations were performed using a plane-wave basis of 450 eV, and a real-space grid distance of 0.18 Å. A 6x6x1 Monkhorst-Pack¹⁸ sampling was used for the integration of the Brillouin zone, together with a temperature of 0.1 eV to smear the electronic Fermi distribution. The exchange and correlation func-

tional was approximated by the Perdew-Burke-Ernzerhof (PBE) formula¹⁹. Activation energies are evaluated with the nudged-elastic band method²⁰ with at least eight images between the initial and the final state. The Pt (111) surface was modeled by a 3x3 slab with five atomic layers. The adsorbates were placed on one side of the slab, with oxygen coverage increasing up to 4/9 monolayers. The entire structure was relaxed until the maximal forces were less than 0.02 eV Å⁻¹. The surface oxide structure of Pt was modeled as PtO₂-trilayer supported on four layers of Pt. The trilayer structure has been observed experimentally under oxidizing conditions²¹. The obtained first-principles results are in full agreement with the statement by Martinez *et al*, showing that with increased oxidation of Pt, the overall interaction with NO decreases. In Figure 4a, the energy of adsorbed and dissociated NO on Pt(111) is shown together with the activation energy, as oxygen coverage is increased from a clean surface up to 4/9 monolayers. There is a destabilization of adsorbed NO, from -1.92 eV at no oxygen coverage to -1.14 eV at 4/9 monolayer. This is associated with an increase in the activation energy, changing from 0.25 eV to 0.96 eV with respect to NO in the gas-phase. A similar destabilization occurs for dissociated NO, where the change is from -1.07 eV to 0.22 eV. For the ammonia formation reaction, the fact that dissociated NO already becomes energetically unstable at an oxygen coverage of 1/3 monolayer effectively hinders any reaction. As for the surface oxide, the first-principles results show no interaction for adsorbed NO (~ 0.0 eV) and dissociated NO is unstable with spontaneous formation of NO using surface oxygen if needed.

The slight increase in NO₂ formation upon exposure to net-oxidizing conditions can also be explained by the limited NO dissociation effect. As NO dissociation decreases, the formation of NO₂ from NO and O ad-atoms becomes more favorable (although NO oxidation over Pt is also reported to suffer from oxygen poisoning²²). Reaction of surface-bound N with NO produces low amounts of N₂O during lean conditions, indicating that although less probable, NO dissociation still occurs but to a lesser extent. Indeed, with regards to the direct dissociation of NO on noble metals, Balint *et al.*²³ report that platinum is susceptible to self-poisoning by strongly adsorbed oxygen in the absence of a suitable reductant. As all H₂ is oxidized to H₂O during net-oxidizing conditions, the availability of reductant in these reaction environments is negligible. Thus, it can be assumed that oxygen poisoning of the catalyst by minor amounts of dissociated NO takes effect during the collection of these data points and one should be aware that chemisorbed oxygen as well as oxygen storage by the alumina support can contribute to the white-line area. As NO dissociation requires the presence of reduced metal sites, it is assumed that not all platinum sites are present in the form of oxides, implying that the surface of the sample is inhomogeneous during the course of the reaction. This observation has been reported previously by Becker *et al.* whilst studying the oxidation state of platinum during methane oxidation over Pt/Al₂O₃²⁴. Conversely to the effect upon NO dissociation observed in the present work, the authors reported that the mixed composition of platinum oxides and chemisorbed oxygen is beneficial for methane dissociation.

To investigate the evolution of surface species during ammonia formation, *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was carried out using a Biorad FTS6000 spectrometer equipped with a Harrick Praying Mantis diffuse reflectance accessory and a Harrick high-temperature reaction chamber mounted with KBr windows. The feed gas composition was controlled in the same manner as for the *in situ* XAS experiments. The effect of varying O₂ concentration was investigated at 350 °C by following the evolution of surface species during NH₃ formation. Figure 2c displays the *in situ* DRIFT spectra in the region where adsorbed OH and NH_x groups would be expected (3000 - 3800 cm⁻¹). Specifically, it is observed that, as the O₂ content of the feed is increased, the negative intensity of the peak at 3760 cm⁻¹ decreases. This peak is indicative of a loss of free OH groups due to their hydrogen-bonding with adsorbed NH₃. Thus, it can be concluded that as the O₂ content increases, the amount of physisorbed NH₃ on the sample decreases. The decreasing intensity of the 3000 - 3300 cm⁻¹ NH stretching region as the S-value increases also indicates a reduction in the amount of adsorbed NH-containing surface species such as NH₃ and NH₄⁺.

Figure 2d displays the *in situ* DRIFTS spectra obtained in the range of 1330 to 1700 cm⁻¹. In this region, it is typical for nitrate species to be observed. It can be seen that as stepwise changes are made from low to high S-value, (bottom to top spectra), the intensity of the sharp peak present at 1545 cm⁻¹ increases and the shoulder present at 1580 cm⁻¹ broadens. These peaks represent the asymmetric NO₂ stretch of unidentate nitrate species and the N=O stretch of chelating bidentate nitrates bound to alumina, respectively. As we discuss the formation of nitrates, it is worth noting that, when net-oxidizing feed compositions were previously tested kinetically⁶, NO₂ was formed over Pt/Al₂O₃ in low amounts (maximum 40 ppm). However, for S<1 no NO₂ formation was observed. The intensity of the peak corresponding to linearly bound nitrite species (1460 cm⁻¹) decreases as the feed becomes increasingly oxidizing. The peaks representative of adsorbed nitrate and nitrite species are integrated and displayed as a function of the stoichiometric number of the feed in Figure 3c.

Upon consideration of both the growth in platinum oxides and adsorbed nitrates observed as the feed becomes net-oxidizing, a number of reaction mechanisms may be proposed. Firstly we propose that as the O₂ content exceeds the concentration required to oxidize all available H₂ to H₂O, NO oxidation will occur on the oxidized platinum surface. These oxidized NO species will subsequently spillover to the support and interact with available oxygen groups of the Al₂O₃ support to adsorb as a nitrate. Simultaneously, the large excess of O₂ is able to saturate the active platinum phase, forming platinum oxides. In this hypothesis, the two trends described, *i.e.* increased nitrate formation and platinum oxide formation, are mutually exclusive. In other words, one mechanism does not depend on the other. One could, however, surmise that these two observations are indeed related. We propose that for S > 1 conditions, as the alumina surface becomes saturated by nitrite groups, interaction between these groups and nearby platinum oxide species occurs, thus forming weak surface nitrate species bridged between Pt and the alumina support.

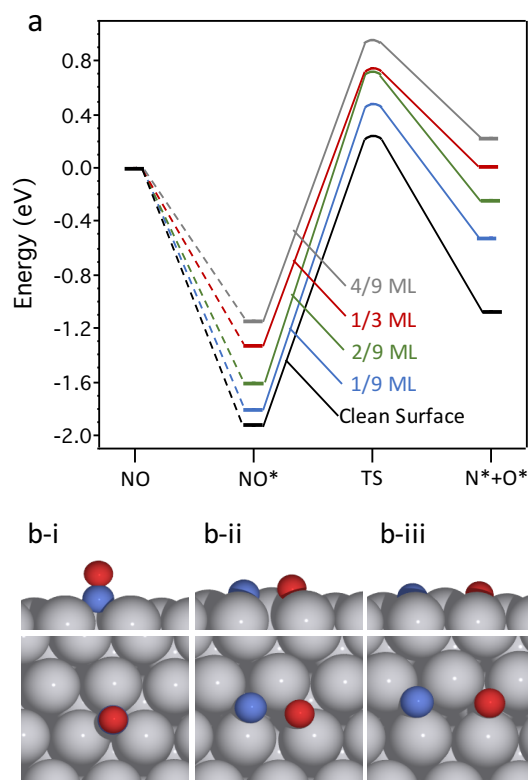


Fig. 4 a) The energy profile of NO adsorption and dissociation of Pt(111) as the coverage of oxygen increases up to 4/9 monolayer. The different coverages are indicated in the figure. b) The initial (i), transition state (ii) and final structure (iii) are shown in top- and side-view for NO dissociation on a clean Pt(111) surface.

This mechanistic proposition supports the observation of nitrate storage on Pt/Al₂O₃ by Clayton *et al.*²⁵. Their study shows that the storage capacity of Pt/Al₂O₃ at temperatures above 250 °C is roughly half that of a Pt/Ba/Al₂O₃ NSR catalyst. Although barium is generally considered to be the main component for NO_x storage in these systems, Fridell *et al.* have concluded that a noble metal is required in the formulation of Ba/Al₂O₃ based catalysts in order for nitrate storage to take place²⁶, further suggesting that platinum plays a role in the NO_x storage mechanism. The proposed mechanism also supports the observations made by Bhatia *et al.*²⁷ that the storage of NO₂ on Pt/Al₂O₃ is also responsible for the formation of platinum oxides due to its highly oxidizing nature.

In summary, *in situ* characterisation coupled with flow reactor experiments and density functional theory was performed in order to clarify the structure-function relationship of Pt/Al₂O₃ for the formation of NH₃ from NO and H₂ in the presence of O₂. We report that the oxidation of hydrogen and subsequent formation of platinum oxides in net-oxidizing conditions is the primary cause for the decrease in NH₃ formation. This is due to the inhibition of NO dissociation which occurs preferentially over reduced

platinum sites and is a necessary prerequisite step for reaction of N with H adatoms. Thus we propose NO dissociation as the rate-determining step in the reaction of NO with H₂ in the presence of stoichiometric excess of O₂ (S>1).

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