

Evidences of the origin of N₂O in the high-temperature NH₃ oxidation over Pt–Rh gauze

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Transient isotopic experiments reveal that the mechanism of N₂O formation in the high-temperature NH₃ oxidation over Pt–Rh gauze involves the reaction of adsorbed ammonia intermediate species (NH_x) and NO.

Ammonia is oxidized over Pt–Rh alloy gauzes at 1073–1223 K to form NO as the first step in the industrial production of nitric acid, a process that has been in large-scale for over 80 years. The reaction typically yields 95–97% of NO and only 3–5% of by-products (N₂O and N₂).¹ Academic interest in the reaction lies in the challenge of elucidating details of the reaction mechanism and kinetics. However, despite numerous studies, there is still much uncertainty, particularly concerning the origin(s) of the reaction products.² Surface science techniques in ultra-high vacuum (UHV) and in general low-pressure studies provided new insights into elementary reaction steps of ammonia oxidation leading to NO and N₂ over Pt single crystals.^{3–9} However the robustness of this approach for achieving an accurate mechanistic description of the overall process is questionable, since N₂O was never detected as a product in UHV studies with model surfaces and thus its formation was not discussed. Accordingly, the reaction has been considered as biphasic in mechanistic terms,⁹ yielding NO and N₂. This result has remained a puzzle for scientists in academic and industrial environments, since N₂O is formed in NH₃ burners. In fact, nitric acid production is the largest single source of N₂O in the chemical industry (400 kton per year). Due to the environmental impact of N₂O, producers have come under pressure to develop and implement abatement technology.² Therefore understanding of the origin of N₂O is of great fundamental and practical relevance.

Herein, for the first time, we provide experimental evidences on the mechanism of N₂O formation in the high-temperature NH₃ oxidation over a commercial Pt–Rh alloy gauze. To this end, the Temporal Analysis of Products (TAP),¹⁰ a transient pulse technique, has been applied. A 28 mm² piece of Pt–Rh gauze catalyst (95%Pt–5%Rh, K. A. Rasmussen, 1024 mesh per cm² and wire diameter of 76 μm) was placed between two layers of quartz-sand in the isothermal zone of the TAP reactor (quartz, 6 mm i.d.). Prior to the experiments, the sample was pretreated in pure O₂ at 1273 K and ambient pressure for 2 h. Then the catalyst was exposed to vacuum (*ca.* 10^{–5} Pa) and transient experiments with ¹⁵NH₃, O₂, and NO were carried out. Pulses containing a small amount of reactants diluted by an inert gas (~10¹⁶ molecules per pulse, <50 nmol of reactant) were independently dosed in the reactor *via* two high-speed valves. The conversion of ammonia upon reaction with O₂ or NO was studied at 973–1073 K using sequential pulse experiments, *i.e.* applying a certain time delay (Δ*t*) between the two pulses. During pulsing, the peak pressure inside the TAP reactor was below 200 Pa. Isotopically labelled ¹⁵NH₃ and ¹⁵NO were used in sequential pulsing with ¹⁴NO and ¹⁴NH₃, respectively, in order to discriminate between N₂O and CO₂ in mass spectrometry analysis. It is well known that the surface of commercial Pt-gauzes is covered by substantial amounts of carbon.¹¹ Carbon deposits are oxidized to CO₂ during O₂ pulsing in the TAP reactor at 1023 K (even after pretreatment in pure O₂ at 1273 K).

The normalised transient responses of selected reactants and products during sequential pulsing of ¹⁶O₂–¹⁵NH₃ and ¹⁵NH₃–¹⁴NO at Δ*t* = 0.1 s are shown in Figs. 1 and 2, respectively. For the sake of conciseness, we concentrate here on aspects relevant to N₂O

formation. As shown in Fig. 1, the concentration of oxygen dramatically decreases at the time of the ammonia pulse at 0.1 s. The strong decrease of the O₂ signal reveals that adsorbed oxygen species formed during the O₂ pulse react with ¹⁵NH₃ yielding ¹⁵NO, ¹⁵N₂, ¹⁵N₂O, H₂, and H₂O. The shape of the NO and N₂O responses is very narrow, and strongly differs from that of N₂, which is broader and shifted to longer times. The amount of N₂O formed decreased upon increasing temperature in the range of 973–1073 K (not shown), in good agreement with steady-state results at industrial conditions.² Surprisingly N₂O was not detected at time delays between oxygen and ammonia pulses >0.1 s, while the profiles of the other products were very similar (discussed later). *A priori*, from this result, one may conceive N₂O as a primary product of ammonia oxidation, *i.e.* originating from the direct reaction between NH₃ and O₂. This pathway has been concluded for NO formation.^{3–9} For nitrous oxide, this hypothesis can be overruled by analysing the transient responses of N₂O during sequential pulsing of ¹⁵NH₃ and ¹⁴NO. In these experiments, N₂O was observed at the time of the NO pulse (Fig. 2). The main N₂O isotope produced was ¹⁵N¹⁴NO (Fig. 3), which results from the N-pairing reaction

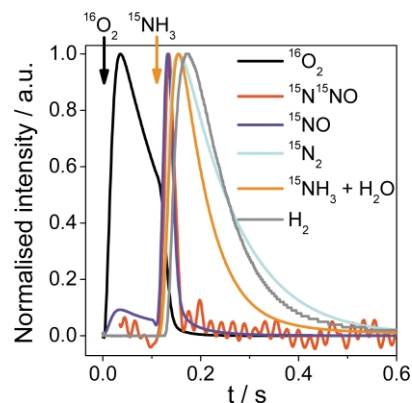


Fig. 1 Transient responses during sequential pulsing of ¹⁶O₂ and ¹⁵NH₃ (Δ*t* = 0.1 s) over Pt–Rh gauze at 1023 K. Pulse size of ¹⁶O₂ and ¹⁵NH₃: 1.6·10¹⁶ and 2.4·10¹⁶ molecules, respectively.

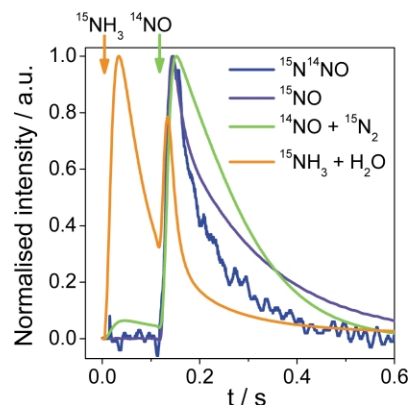


Fig. 2 Transient responses during sequential pulsing of ¹⁵NH₃ and ¹⁴NO (Δ*t* = 0.1 s) over Pt–Rh gauze at 1023 K. Pulse size of ¹⁵NH₃ and ¹⁴NO: 2.2·10¹⁶ and 3.0·10¹⁶ molecules, respectively.

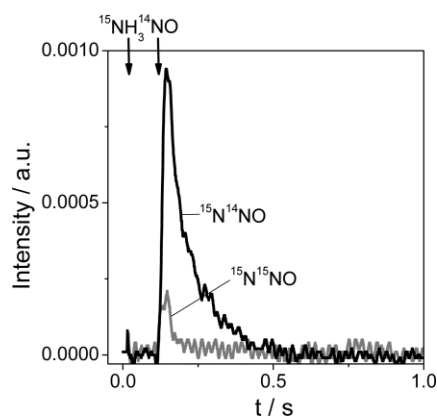


Fig. 3 Transient responses of $^{15}\text{N}^{14}\text{NO}$ and $^{15}\text{N}^{15}\text{NO}$ during sequential pulsing of $^{15}\text{NH}_3$ and ^{14}NO ($\Delta t = 0.1$ s) over Pt–Rh gauze at 1023 K. Pulse sizes as in caption of Fig. 2.

between $^{15}\text{NH}_3$ and ^{14}NO . The same result was obtained when $^{14}\text{NH}_3$ and ^{15}NO were sequentially pulsed. $^{15}\text{N}^{15}\text{NO}$ is formed in much smaller amounts and stems from the reaction between $^{15}\text{NH}_3$ in the first pulse and ^{15}NO eventually formed in the pulse of ^{14}NO (see Fig. 2). ^{15}NO is produced at the time of the $^{15}\text{NH}_3$ pulse and rapidly reacts with remaining ammonia species, producing the limited amount of $^{15}\text{N}^{15}\text{NO}$ observed. N_2O formation from ^{14}NO would yield $^{14}\text{N}^{14}\text{NO}$, but this mass cannot be detached from that of CO_2 in mass spectrometry. The irrelevance of this route for N_2O formation was confirmed by performing single pulse experiments with ^{15}NO at 1023 K, yielding only nitrogen as $^{15}\text{N}^{15}\text{N}$. The implication of the Pt–Rh gauze in originating N_2O was further substantiated by performing simultaneous pulsing ($\Delta t = 0$ s) of $^{15}\text{NH}_3$ and ^{14}NO at 1073 K in the TAP reactor filled with quartz sand. In this experiment, no N_2O was observed, so other potential contributions towards N_2O production, like homogeneous or heterogeneous processes on the reactor wall can be categorically excluded. Concluding, N_2O formation during the high-temperature ammonia oxidation over Pt–Rh alloy catalyst is mainly a product of the secondary reaction between ammonia and nitric oxide.

The heterogeneous nature of the reaction steps leading to N_2O can be elegantly demonstrated by comparing the formation of $^{15}\text{N}^{14}\text{NO}$ at different time delays between the $^{15}\text{NH}_3$ and ^{14}NO pulses. Fig. 4 shows a decreased formation of N_2O (at the time of the NO pulse) upon increasing the time delay between $^{15}\text{NH}_3$ and NO. Particularly significant is the decrease observed between 0.1 and 1 s. This result indicates the preferential N_2O formation over catalyst surface covered by adsorbed NH_x species. At this stage, the influence of the oxygen species formed during the Pt–Rh gauze pretreatment in O_2 (see Experimental) in N_2O formation cannot be completely ascertained. What is clear is that adsorbed O-species are

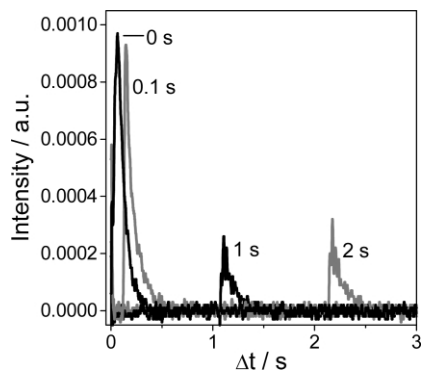


Fig. 4 Transient responses of $^{15}\text{N}^{14}\text{NO}$ during sequential pulsing of $^{15}\text{NH}_3$ and ^{14}NO over Pt–Rh gauze at 1023 K at different time delays (Δt , in seconds). Pulse sizes as in caption of Fig. 2.

essential to activate ammonia by oxidative dehydrogenation, leading to reactive NH_x fragments on the catalyst surface.^{8,9,12} This can also be concluded from the strong decrease of the O_2 signal at the time of the $^{15}\text{NH}_3$ pulse in Fig. 1. The structure of the preferred NH_x intermediate has been subject of controversy and remains unsolved. Both NH_{ads} and $\text{NH}_{2,\text{ads}}$ species were found as intermediates in the ammonia oxidation reaction on the Pt(111) and Pt(100) surfaces.^{8,9,13}

The isotopic TAP technique applied here has proven a unique experimental approach for deriving mechanistic insights into N_2O formation during the high-temperature ammonia oxidation, a highly exothermic reaction. The small size of the pulses, in the nmol range, enables an excellent control of temperature (estimated within 2 K at 1073 K). Operation under these conditions minimizes the presence of heat and mass transport limitations and prevents typical phenomena like ignition, extinction, hysteresis, and oscillations, which are extremely problematic in kinetic investigations with steady-state flow techniques.^{14,15} Compared to UHV techniques, the TAP approach presents two advantages: it uses a real catalyst specimen instead of a model surface and much higher peak pressures can be achieved. The ‘invisibility’ of N_2O in previous UHV studies might be related to the fact that the concentration of N_2O is below the detection limit of the analytical unit, as a consequence of the extremely low reactant peak pressures (typically 10^{-5} – 10^{-7} Pa), which are apparently suitable for a proper analysis of NO and N_2 but insufficient for N_2O . This can be related to the kinetics of products formation and its dependence with respect to the partial pressures of NH_3 and NO and requires a more detailed assessment.

The above evidence enables us to conclude that N_2O originates from the pairing of adsorbed ammonia intermediate species and nitric oxide. This result contributes to unravelling an important mechanistic feature of a classical reaction in one of the most traditional processes in modern chemical industry. The reaction pathway leading to N_2O is detrimental from two points of view, since it involves the loss of reactant (NH_3) and desired product (NO). The origin of N_2O should be obviously situated in a region of the catalytic burner where NO is formed and some NH_3 remains unconverted, *i.e.* in the very first gauzes of the pack. This valuable information establishes the essential basis to design strategies for preventing or minimizing this undesired by-product in nitric acid production.

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