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Selectivity-directing factors of ammonia oxidation over PGM gauzes in the Temporal Analysis of Products reactor: Secondary interactions of NH₃ and NO

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Abstract

Factors that direct the selectivity of ammonia oxidation for NO were determined previously (J. Catal. 227 (2004) 90) by the investigation of primary NH₃–O₂ interactions over pure Pt and Pt–Rh (95–5) alloy gauzes at 973–1173 K in the temporal analysis of products (TAP) reactor. A solid mechanistic understanding of the processes leading to by-products (N₂O and N₂) requires an analysis of secondary NH₃–NO interactions, which we investigated in the TAP reactor with isotopically labeled molecules. Our experiments under transient vacuum conditions indicate that these secondary processes determine the reaction selectivity for N₂O and N₂ in high-temperature ammonia oxidation over noble metal catalysts. Adsorbed oxygen species initiate the reaction of ammonia with nitric oxide. N₂O originates from the coupling of ammonia intermediates (NH_x) and nitric oxide. Different reaction pathways leading to N₂ have been identified, including primary (NH₃ oxidation) and secondary (NH_x and H-assisted NO reduction) processes. The relative contributions of these routes depend on the surface coverage of nitrogen and hydrogen-containing species. A reaction scheme accounting for our experimental observations has been proposed, giving rise to an improved mechanistic description of the complex processes in ammonia burners. © 2004 Elsevier Inc. All rights reserved.

Keywords: NH₃ oxidation; NO reduction; Platinum; Rhodium; Gauze; Selectivity; N₂O; N₂; Mechanism; Transient experiments; TAP reactor; Isotopes

1. Introduction

Our previous study using the Temporal Analysis of Products (TAP) technique [1] has provided valuable insight into the mechanism of high-temperature NH₃ oxidation over platinum group metal (PGM) catalysts. The analysis of primary interactions between ammonia and oxygen elucidated the process of ammonia activation over Pt and Pt–Rh gauzes and the factors determining the reaction selectivity for NO. Importantly, these results indicated that not only the coverage but also the nature of oxygen species adsorbed to the metal sites are important for obtain-

* Corresponding authors. E-mail address: javier.perez.ramirez@yara.com (J. Pérez-Ramírez). ing a high NO selectivity. The formation of N_2O and N_2 was also discussed in [1], but specific reaction pathways leading to these by-products could not be fully assessed merely through the study of the primary interaction of NH_3 and O_2 .

Since both N_2O and N_2 molecules contain two nitrogen atoms, one can anticipate that these reaction products should largely originate from the recombination of N-containing surface intermediates of NH₃ and/or NO, as a result of decomposition or coupling reactions involving one or both species. In this sense, studies in the TAP reactor indicated the high activity of reduced and oxidized PGM gauzes for the direct decomposition of NO and NH₃, respectively, and the rapid reaction between NO and NH₃ [1,2]. Accordingly, a solid understanding of the complex reaction network involved in ammonia oxidation in industrial burners requires

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an in-depth analysis of secondary interactions between the desired reaction product (NO) and the reactant (NH₃).

The mechanism and kinetics of NO reduction by NH₃ in the absence of oxygen (Eqs. (1)-(2)) have been investigated over platinum catalysts of different natures, including single crystals (Pt(100) [3,4] or stepped Pt $12(111) \times (111)$ [5]), polycrystalline Pt wire [6,7] and foils [8-10], and supported Pt catalysts [11–13]. The process is highly exothermic and has typically shown an oscillatory kinetics, presenting analogies with the NO– H_2 reaction over platinum surfaces [4,14]. The mechanism of these (isothermal) spontaneous oscillations has been studied at different molar feed NH₃/NO ratios (1-9) in a wide range of pressures (0.1-1000 Pa) and temperatures (473-873 K) with batch and flow methods and ultrahigh vacuum (UHV) techniques. N2 and N2O were found as the reaction products, with a typical increase in the N_2/N_2O ratio with increasing temperature and/or increasing concentration of NH₃ in the feed [6].

$$6\text{NO} + 2\text{NH}_3 \rightarrow 5\text{N}_2 + 6\text{H}_2\text{O}$$
$$\Delta H^{\text{o}} = -452 \text{ kJ mol}_{\text{NH}_3}^{-1} \tag{1}$$

$$8NO + 2NH_3 \to 5N_2O + 3H_2O \Delta H^o = -473 \text{ kJ mol}_{NH_3}^{-1}$$
(2)

Otto et al. [11] studied the catalytic reduction of nitric oxide with ammonia by circulating mixtures of ¹⁵NH₃, ¹⁴NO, and Ar in a gradientless batch reactor over Pt/Al2O3 at pressures of 0.025-40 kPa and temperatures of 473-523 K. The proposed reaction mechanism is given in Eqs. (3)-(9), where * denotes an active site. It was basically concluded that N₂ is predominantly formed via interaction of adsorbed NO and the ammonia intermediate NH_2 (Eq. (5)). N_2O formation involved the interaction of two NO molecules with chemisorbed hydrogen (obtained from the dissociative chemisorption of NH₃, Eq. (3)), leading to nitroxyl species (HNO) as a reaction intermediate (Eqs. (7)-(8)). Andrussow claimed that this intermediate plays a central role in the mechanism of ammonia oxidation [15], although this has been never observed experimentally. Eqs. (6) and (9) were considered to be minor paths for N2O and N2 formation, respectively.

$$\mathrm{NH}_3 + 2^* \leftrightarrow \mathrm{NH}_2^* + \mathrm{H}^*,\tag{3}$$

$$NO + * \leftrightarrow NO^*,$$
 (4)

$$NO^* + NH_2^* \to N_2 + H_2O + 2^*, \tag{5}$$

$$NO^* + NH_2^* \to N_2O + 2H^*, \tag{6}$$

$$\mathrm{H}^* + \mathrm{NO}^* \to \mathrm{HNO}^* + ^*, \tag{7}$$

 $2HNO^* \to N_2O + H_2O + 2^*,$ (8)

$$2HNO^* + 2H^* \to N_2 + 2H_2O + 4^*.$$
(9)

More recent studies of the NO–NH₃ reaction over polycrystalline Pt foils up to 623 K by Katona et al. [9,10] have supported the reaction scheme proposed by Otto et al. [11] and the relative importance of the steps leading to N_2O and N_2 . These investigations concluded that N_2O formation depends mostly on the relative coverage of NO and explicitly excluded the pathway involving the reaction between NO and NH_2 species (Eq. (6)).

Gland and Korchak [5] investigated the NH₃–NO interactions over a clean stepped platinum single crystal at pressures of 10^{-6} Pa and proposed the conversion of HNO to N₂ according to Eqs. (10)–(11) instead of Eq. (8), since N₂O was not observed under their UHV conditions. By combining the mechanisms in [5,11] and excluding Eqs. (6) and (9), Takoudis and Schmidt [6] described the global kinetics of Eqs. (1)–(2) with a single Langmuir–Hinshelwood model, which was said to be valid for UHV and high-pressure conditions.

$$HNO^* + H^* \to N^* + H_2O + *,$$
 (10)

$$2N^* \to N_2 + 2^*. \tag{11}$$

It should be pointed out that the absence of N₂O in [5] has frequently been experienced in other UHV studies dealing with the NH₃–NO reaction over Pt(100) in the temperature range of 300–700 K [3,16]. As reasoned in [1], the low peak pressure applied in high and ultrahigh vacuum experiments may represent an important limitation for N₂O analysis and thus for gaining mechanistic insights into the formation of this essential by-product in NH₃ oxidation or the reduction of NO by NH₃.

Based on the above analysis, it can be concluded that the reduction of NO by NH_3 has not been studied over noble metal gauzes at relevant temperatures of industrial ammonia burners. In this work we have investigated the mechanism of this reaction over Pt and Pt–Rh gauzes in the TAP reactor using isotopic tracers. The intrinsic features of the TAP reactor make it possible to study the highly exothermic processes in Eqs. (1)–(2) under isothermal conditions, as previously demonstrated for ammonia oxidation [1]. It is shown that secondary NH_3 –NO interactions chiefly contribute to the loss reactions in ammonia burners, yielding N_2O and N_2 . Reaction pathways leading to these undesired products have been elucidated.

2. Experimental

The commercial gauzes used in this study, knitted pure Pt and woven Pt–Rh (95–5 wt%) alloy, and the experimental procedures during TAP experiments were described in [1]. Briefly, a single piece of gauze catalyst (ca. 30 mm²) was placed between two layers of quartz particles (sieve fraction $250–350\,\mu\text{m}$) in the isothermal zone of the TAP microreactor (6 mm i.d.). The amount of Pt and Pt–Rh gauzes used was 110 and 25 mg, respectively. Prior to the experiments, the samples were pretreated in pure O₂ at 1273 K and ambient pressure for 2 h. Then the catalysts were exposed to vacuum conditions (10^{-5} Pa) and transient studies of the NH₃–NO reaction were performed by means of single and sequential pulse experiments.

Single pulsing was carried out at 1073 K with mixtures of ¹⁴NH₃:¹⁴NO:Xe = 1:1:1, ¹⁵NH₃:¹⁴NO:Xe = 1:1:1, and ¹⁵NO:Ne = 1:1. In sequential pulse (pump-probe) experiments, mixtures of ¹⁴NO:Ne = 1:1 and ¹⁴NH₃:Xe = 1:1 (or ¹⁵NH₃:Xe = 1:1) were independently introduced into the reactor via two high-speed pulse valves, with a time delay (Δt) of 0.1–2 s between the two pulses at 1023 or 1073 K. The pulse size was varied from ca. 10¹⁴ to 10¹⁶ molecules to study the reaction in Knudsen and molecular diffusion regimes, respectively.

In the experiments, Ne (4.5), Xe (4.0), O₂ (4.5), ¹⁴NO (2.5), ¹⁴NH₃ (2.5), ¹⁵NH₃ (99.9% atoms of ¹⁵N), and ¹⁵NO (99.5% atoms of ¹⁵N) were used without additional purification. Isotopically labeled ammonia and nitric oxide were purchased from ISOTEC. Transient responses were monitored at atomic mass units (AMUs) related to reactants, reaction products, and inert gases at the reactor outlet with a quadruple mass spectrometer (Hiden Analytical). The following AMUs were analyzed: 132 (Xe), 46 (¹⁴NO₂, ¹⁵N¹⁵NO), 45 (¹⁵N¹⁴NO), 44 (¹⁴N¹⁴NO, CO₂), 32 (O₂), 31 (¹⁵NO, H¹⁴NO), 30 (¹⁴N¹⁴NO, ¹⁴NO, ¹⁵N¹⁵N), 29 (15N14N), 28 (14N14NO, 14N14N), 20 (Ne), 18 (H₂O, $^{15}NH_3$), 17 ($^{14}NH_3$, $^{15}NH_3$, H₂O, OH), 16 (O₂, H₂O, ¹⁴NH₃, ¹⁵NH₃), 15 (¹⁴NH₃, ¹⁵NO, ¹⁵NH₃, ¹⁵N¹⁵N), and 2 (H₂). For each AMU, pulses were repeated 10 times and averaged to improve the signal-to-noise ratio. The concentration of feed components and reaction products was determined from the respective AMUs with the use of standard fragmentation patterns and sensitivity factors. Because of overlap of the various masses of ¹⁵NH₃ with other species in the MS analysis, the degree of ¹⁵NH₃ conversion was calculated from the N-balance.

3. Results

3.1. Sequential pulsing of ^{14}NO and $^{14}NH_3$ in the Knudsen diffusion regime

Fig. 1 shows representative normalized transient responses during sequential pulsing of NH3 and NO over Pt-Rh gauze and of NO and NH3 over Pt gauze at 1073 K in the Knudsen diffusion regime (ca. 10¹⁴ molecules per pulse). These experiments make it possible to analyze the effect of adsorbed species formed during the first pulse on the primary heterogeneous steps of activation of gas-phase molecules in the second pulse. In this case, normalization of the responses is convenient for a proper comparison of pulse shapes. The results show clear mechanistic analogies between Pt and Pt-Rh gauzes in NO-NH₃ interactions. N₂, H_2 , and H_2O were the only reaction products over the noble metal gauzes and were not influenced by the order in which the reactant gases were pulsed. Formation of N₂ and H₂O was observed in both the ammonia and nitric oxide pulses. This suggests two independent reaction pathways leading to these products, involving (i) oxidation of two NH3 mole-



Pt

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Fig. 1. Transient responses during sequential pulsing of ¹⁴NO and ¹⁴NH₃ over Pt gauze ($\Delta t = 0.2$ s) and ¹⁴NH₃ and ¹⁴NO over Pt–Rh gauze ($\Delta t = 0.5$ s) at 1073 K. Pulse size of ¹⁴NO and ¹⁴NH₃ ~ 10¹⁴ molecules.

cules in the ammonia pulse and (ii) reduction of two NO molecules in the nitric oxide pulse. H_2 was detected in the ammonia pulse only.

Fig. 2 shows the sharp decrease in the concentration of gas-phase H₂ at the time of the NO pulse during sequential pulsing of NH₃ and NO at $\Delta t = 0.2$ (Pt gauze) and 0.5 s (Pt-Rh gauze). This feature indicates that hydrogen-containing species adsorbed to the gauze surface, from which H₂ is formed, effectively catalyze the reduction of NO to N₂ and H_2O . The reduction of NO by H_2 at low temperatures (300– 700 K) over Pt-supported catalysts in the presence of O₂ was originally reported by Jones et al. [17]. As clearly shown in Fig. 3, the H₂ yield in the NH₃ pulse drops to zero with decreasing time delay between the NH₃ and NO pulses from $\Delta t = 0.5$ s to 0 s. The latter case, when ammonia and nitric oxide were simultaneously pulsed, corresponds with the highest degree of NO conversion (42%, Fig. 3 and Table 1). These results indicate the high activity of Pt and Pt-Rh gauzes for the NO reduction by NH₃ to N₂ under the vacuum conditions in the TAP reactor. This is in agreement with pre-

Table 1
Performance of noble metal gauzes and SiO ₂ particles in NO reduction by NH ₃ at 1073 H

Sample	Diffusion regime	$X(^{14}NO)^{a}(\%)$	$Y(^{15}N^{14}NO)(\%)$	$Y(^{15}NO)(\%)$	$Y(^{15}N^{14}N)^{b}$ (%)	$Y(^{14}N^{14}N)(\%)$	$Y(H_2)(\%)$
Pt gauze	Knudsen	57	n.d. ^c	4	15	42	n.d. ^c
	Molecular	65	0.3	4	20	48	n.d.
Pt-Rh gauze	Knudsen	42	n.d.	6	10	31	n.d.
	Molecular	48	0.2	6	13	35	n.d.
SiO ₂ spheres	Molecular	2	n.d.	n.d.	1	1.5	n.d.

Conditions: single pulsing of a mixture ${}^{15}NH_3$: ${}^{14}NO$: Xe = 1:1:1, ${}^{15}NH_3$ pulse size $\sim 10^{14}$ molecules (Knudsen diffusion regime) and $\sim 10^{16}$ molecules (molecular diffusion regime).

^a $X(^{14}NO) = Y(^{15}N^{14}N) + Y(^{14}N^{14}N).$

^b $Y(^{15}N^{14}N) = N(^{15}N^{14}N)/N^{o}(NO) = N(^{15}N^{14}N)/N^{o}(^{15}NH_3)$, where N^{o} is the number of reactant molecules in the feed and N the number of product molecules at the reactor outlet.

^c Not detected.



Fig. 2. Participation of hydrogen-containing species in NO reduction during sequential pulsing of $^{14}\rm NH_3$ and $^{14}\rm NO$ over Pt gauze ($\Delta t=0.2$ s) and Pt–Rh gauze ($\Delta t=0.5$ s) at 1073 K. Pulse sizes of $^{14}\rm NO$ and $^{14}\rm NH_3 \sim 10^{14}$ molecules.

vious ultrahigh vacuum [3–5], vacuum [6–9], and ambient pressure [11] studies over different Pt specimens (see Introduction).

Sequential pulse experiments in Fig. 1 also show that the concentration of gas-phase NO strongly decreases at the time of the NH₃ pulse over the Pt gauze. This indirectly indicates the reversible dissociation of NO into N and O atoms on the reduced catalyst surface. The resulting oxygen species are essential for NH₃ conversion into N₂, H₂O, and H₂. No conclusion can be drawn about N₂O formation from the experiments in Fig. 1, where nonlabeled molecules and a low peak pressure (Knudsen diffusion regime) were applied.



Fig. 3. NO conversion and H₂ yield vs time delay during sequential pulsing of $^{14}NH_3$ and ^{14}NO over Pt–Rh gauze at 1073 K. Pulse sizes of ^{14}NO and $^{14}NH_3 \sim 10^{14}$ molecules.

This is further assessed in Sections 3.2 and 3.3 by means of single and sequential pulse experiments with $^{15}NH_3$ and ^{14}NO in the molecular diffusion regime.

3.2. Single pulsing of ¹⁴NO and ¹⁵NH₃: Knudsen vs molecular diffusion regimes

The influence of the diffusion regime and peak pressure in the TAP reactor on the reaction of ammonia with nitric oxide over the Pt and Pt-Rh gauzes at 1073 K has been evaluated. To this end, an equimolar mixture of ¹⁵NH₃ and ¹⁴NO was pulsed in Knudsen diffusion (pulse size $\sim 10^{14}$ molecules, peak pressure \sim 5 Pa) and molecular diffusion (pulse size $\sim 10^{16}$ molecules, peak pressure ~ 200 Pa) regimes. The transient responses of the reactants and N-containing products are displayed in Fig. 4. Table 1 quantifies the corresponding catalytic performance. As shown in the figure, the mechanism of the high-temperature reduction of NO by NH₃ appears to be similar in general terms over the knitted Pt and woven Pt-Rh alloy gauzes, as concluded in our previous study dedicated to primary O_2 -NH₃ interactions [1]. The higher NO conversion over the knitted Pt gauze in Table 1 is due to the higher amount of Pt gauze used in the



Fig. 4. Transient responses during single pulsing of a 15 NH₃: 14 NO:Xe = 1:1:1 mixture over Pt and Pt–Rh gauzes at 1073 K under (a) Knudsen diffusion regime (pulse size of 15 NH₃ $\sim 10^{14}$ molecules) and (b) molecular diffusion regime (pulse size of 15 NH₃ $\sim 10^{16}$ molecules). The order of the profiles and the associated labels shown in (a) for Pt gauze are the same for all the figures.

experiments (4 times as much) compared with the woven Pt–Rh gauze (see Section 2).

Regardless of the diffusion regime, labeled nitric oxide (15 NO) and molecular nitrogen were identified as reaction products. Two nitrogen isotopes can be discerned: $^{15}N^{14}N$ and $^{14}N^{14}N$. Identification of the other possible nitrogen isotope, $^{15}N^{15}N$, in this specific experiment is complicated, since it overlaps with the reactant ^{14}NO in MS analysis (AMU 30). To this end, the sequential pulse experiments in Section 3.3 are required. The diffusion regime has only a slight influence on the NH₃–NO interactions, indicating a negligible contribution of gas-phase processes (excluded under Knudsen diffusion) to the overall performance. In fact, the conversion of ^{14}NO over quartz particles during TAP experiments in the molecular diffusion regime was only 2% at 1073 K (see Table 1).

As indicated in Section 3.1, Fig. 4a shows that N₂O formation was not observed at the low peak pressures characteristic of the Knudsen diffusion regime. This agrees with the reported absence of N₂O in previous investigations of the NH₃–NO reaction under UHV conditions [3–5,16]. All of these studies were performed at T < 873 K, and hence a direct comparison with the present results cannot be established. N₂O has typically been observed in low amounts as a reaction product of the NO reduction by NH_3 below 1073 K in high-pressure studies [6,7]. As a matter of fact, formation of nitrous oxide as $^{15}N^{14}NO$ can be clearly identified when the pulse experiments were performed in the molecular diffusion regime, that is, with higher peak pressures (Fig. 4b). The relatively low intensity of the N₂O signal in Fig. 4 indicates, once more, that concentrations of this by-product are very low compared with N₂.

The formation of ${}^{14}N^{14}NO$ from two ${}^{14}NO$ molecules (as suggested by Otto et al. [11] in Eqs. (7) and (8) at 523 K cannot be decoupled from CO₂ in mass spectrometry (both have an AMU of 44). It is well known that the surface of commercial PGM gauzes is covered by substantial amounts of carbon [18], and part of the carbon remains even after pretreatment in O₂ flow at 1273 K. As a consequence, a small but significant amount of CO₂ originates from the oxidation of carbon by O₂ or, in this case, NO. This aspect was extensively discussed in [1] and indeed motivated us to apply isotopic tracers to elegantly discriminate between N₂O and CO₂ in MS analysis.

As expected, single pulsing of a ${}^{15}\text{NH}_3$ - ${}^{14}\text{NO}$ mixture in the TAP microreactor filled with quartz particles (i.e., without gauze) did not induce N₂O formation in the temperature range investigated. Accordingly, it can safely be concluded



Fig. 5. Transient responses of $^{15}\mathrm{N}^{14}\mathrm{NO}$ and $^{15}\mathrm{N}^{15}\mathrm{NO}$ formed during sequential pulsing of $^{15}\mathrm{NH}_3$ and $^{14}\mathrm{NO}$ over Pt–Rh gauze at 1023 K. Pulse sizes of $^{15}\mathrm{NH}_3$ and $^{14}\mathrm{NO}\sim2.2\times10^{16}$ and 3.0×10^{16} molecules, respectively.

that the N₂O observed in the experiments at higher peak pressures originates from the heterogeneous reaction of NH₃ and NO over the noble metal gauzes. The absence of nitrous oxide in ammonia-nitric oxide interactions in the Knudsen regime can be attributed to the detection limit of analysis in relation to the low amount of N₂O formed. This also explains the unsuccessful identification of this by-product in UHV studies of NH₃ oxidation and NO reduction by NH₃ over platinum surfaces, since typical pressures in UHV experiments (10^{-6} – 10^{-7} Pa) are several orders of magnitude lower by a factor of 10^6 than the peak pressure in the TAP reactor under the Knudsen diffusion region.

3.3. Sequential pulsing of ^{14}NO and $^{15}NH_3$ in the molecular diffusion regime

To gain additional insights into the mechanism of N₂O and N₂ formation during the reduction of nitric oxide by ammonia, ¹⁵NH₃ and ¹⁴NO were sequentially pulsed over Pt-Rh gauze at different time delays in the range of $\Delta t =$ 0.1-2 s. As shown in Fig. 5, N₂O was observed at the time of the NO pulse. The main N₂O isotope produced was ¹⁵N¹⁴NO, which clearly originates from the reaction between ${}^{15}NH_3$ and ${}^{14}NO$. ${}^{15}N^{15}NO$ is formed in much smaller amounts (${}^{14}N^{15}NO/{}^{15}NO \sim 8$). The latter isotope is not a primary reaction product, that is, it is not formed by direct ¹⁵NH₃ oxidation. Rather it stems from the reaction between ¹⁵NH₃ in the first pulse and ¹⁵NO formed in the pulse of ¹⁴NO. As shown in Section 3.1 and in previous single-pulse experiments [1], NO can oxidize the reduced noble metal gauze, and the deposited oxygen can eventually react with a surface ${}^{15}\text{NH}_x$ intermediate, leading to ${}^{15}\text{NO}$. Again, N₂O formation from ¹⁴NO would yield ¹⁴N¹⁴NO, but this mass cannot be decoupled from that of CO₂ in mass spectrometry. However, the irrelevance of this route for N2O formation was indirectly concluded from single-pulse exper-



Fig. 6. Transient responses of ${}^{15}N{}^{14}NO$ formed during sequential pulsing of ${}^{15}NH_3$ and ${}^{14}NO$ over Pt–Rh gauze at 1023 K at different time delays (Δt , in seconds). Pulse sizes as in caption of Fig. 5.



Fig. 7. Transient responses of N₂-isotopes formed during sequential pulsing of $^{15}\rm NH_3$ and $^{14}\rm NO~(\Delta t=0.5~s)$ over Pt–Rh gauze at 1023 K. Pulse sizes as in caption of Fig. 5.

iments on ¹⁵NO over PGM gauzes at 1023 K, yielding only ¹⁵N¹⁵N as the reaction product (not shown). Our previous paper [1] also reported that single pulsing of ¹⁴NO over reduced PGM gauzes yielded only ¹⁴N¹⁴N, and the N₂/O₂ ratio at the reactor outlet was > 2, indicating oxidation of the catalyst surface by NO.

The heterogeneous nature of the reaction steps leading to N₂O can be conclusively demonstrated by comparing the formation of the main isotope ¹⁵N¹⁴NO at different time delays between the ¹⁵NH₃ and ¹⁴NO pulses. Fig. 6 nicely shows the decreased formation of nitrous oxide (always at the time of the NO pulse) with increasing time delay between ammonia and nitric oxide pulses. Particularly significant is the decrease observed between $\Delta t = 0.1$ and 1 s. In view of this result, formation of nitrous oxide is highly dependent on the surface coverage by reactive NH_x intermediates, which couple with NO, yielding N₂O.

Sequential pulse experiments with ¹⁵NH₃ and ¹⁴NO have revealed the formation of three nitrogen isotopes: ¹⁵N¹⁵N, ¹⁵N¹⁴N, and ¹⁴N¹⁴N. As shown in Fig. 7 for the experiment



Fig. 8. Distribution of isotopically labelled N-atoms in N₂ molecules vs time delay during sequential pulsing of 15 NH₃ and 14 NO over Pt–Rh gauze at 1023 K. Pulse size as in caption of Fig. 5.



Fig. 9. Ratio of ${}^{15}N{}^{14}N{}^{14}N{}^{14}N$ vs time delay during sequential pulsing of ${}^{15}NH_3$ and ${}^{14}NO$ over Pt–Rh gauze at 1023 K. Pulse sizes as in caption of Fig. 5.

at $\Delta t = 0.5$ s and 1023 K, the simple isotopes ${}^{15}N{}^{15}N$ and ${}^{14}N{}^{14}N$ were formed at the time of the ${}^{15}NH_3$ and ${}^{14}NO$ pulses, respectively. However, the mixed ${}^{15}N{}^{14}N$ isotope is formed in both pulses. It should be mentioned here that the small amount of ${}^{14}N{}^{14}N$ at the time of the ammonia pulse is due to the presence of impurities in the ${}^{15}NH_3$ source.

The distribution of nitrogen isotopes as a function of the time delay is shown in Fig. 8. The yield of the mixed nitrogen isotope was determined by the sum of the ¹⁵N¹⁴N yield in each pulse. The ¹⁵N¹⁴N yield at $\Delta t = 0$ s (simultaneous pulsing of ¹⁵NH₃ and ¹⁴NO) is relatively high (25%) and strongly decreasing at longer time delays. The decrease in ¹⁴N¹⁴N yield with time delay follows a trend similar to that of ¹⁵N¹⁴N, whereas an opposite behavior is observed for ¹⁵N¹⁵N. The dependences of the distributions of N₂ isotopes presented in Fig. 8 can be associated with the relative coverage of N-species on the catalyst surface. This coverage can be tuned by the application of different time delays between the ¹⁵NH₃ and ¹⁴NO pulses. Furthermore, the time

delay can also be related to the ratio of ¹⁵NH₃/¹⁴NO in the NO pulse, which is 1 at $\Delta t = 0$ s and 0 at $\Delta t = 2$ s. This can be qualitatively associated with the NH₃/NO ratio at different locations of the gauze pack in the ammonia burner (see Section 4.3). The absence of ${}^{15}N{}^{15}N$ at $\Delta t = 0$ s indicates that N₂ formation from two ¹⁵NH₃ molecules is inhibited in the presence of ¹⁴NO. In contrast, the high relative yield of ¹⁴N¹⁴N and ¹⁵N¹⁴N at $\Delta t = 0$ s is related to the high activity of the PGM gauzes for ¹⁴NO reduction by H and ${}^{15}NH_x$ species, respectively. The decreased yield of these two isotopes with an increased time delay is directly related to the decreased coverage of intermediate surface species resulting from ammonia activation, which are essential for NO reduction to N₂. Fig. 9 shows that the ratio of $^{15}N^{14}N/^{14}N^{14}N$ in the product gas decreases with an increased time delay between the ¹⁵NH₃ and ¹⁴NO pulses. This indicates that the coupling of NO and NH₃ leading to mixed nitrogen isotope prevails over direct NO reduction with an increased NH_3/NO ratio. The yield of ${}^{15}N^{15}N$ in Fig. 8, which is formed in the ¹⁵NH₃ pulse (see Fig. 7), is significant at $\Delta t \ge 0.5$ s and stems from the oxidation of NH₃ by O-species. Such oxygen species may originate from the dissociation of nitric oxide in the ¹⁴NO pulse or the high-temperature pretreatment of the gauzes in O₂ (discussed later).

4. Discussion

4.1. Importance of the diffusion regime and the use of isotopes

Two combined experimental aspects are considered to be essential for deriving relevant factors that direct selectivity in the NH₃-NO reaction for N₂O and N₂ in the TAP reactor: (i) the application of high pressures and (ii) isotopically labeled molecules. Experiments in the Knudsen diffusion regime (peak pressure of ca. 5 Pa at 1073 K) gave insights into N2 formation, although N2O was not observed as a reaction product. This result parallels those of previous surface science studies carried out at temperatures up to 823 K with molecular beams in ultrahigh vacuum, where N2O was not observed in the reaction of NH_3 with O_2 [19,20] or with NO [3–5,16]. In contrast, studies of the NH₃–NO reaction over platinum-based catalysts at total pressures in the range of 0.1-1000 Pa and temperatures up to 823 K observed N₂O as a product along with N₂ [6-9,11,21]. In fact, hightemperature ammonia oxidation over PGM gauzes within nitric acid manufacture is the largest source of nitrous oxide in the chemical industry (400 kilotons of N₂O per year), even though the N_2O selectivity (1–2%) is significantly lower compared with the N_2 selectivity (up to 4%) [22].

The "invisibility" of N_2O in (ultra)low-pressure studies can be related to detection constraints on the analytical methods as a consequence of the intrinsically low concentrations of N_2O formed. The low pressure is apparently suitable for a proper analysis of N₂, which is formed in a considerably higher proportion. It should be stressed that the pressure in UHV studies is up to 9 orders of magnitude lower than that in TAP experiments in the Knudsen diffusion regime. TAP experiments with the molecular diffusion regime (peak pressure of ca. 200 Pa at 1073 K, i.e., two orders of magnitude higher than in the Knudsen diffusion regime, ca. 5 Pa) have conclusively determined that N₂O is formed in the NH₃–NO reaction, and it was observed in the previously investigated NH₃–O₂ reaction [1]. Any homogeneous process leading to N₂O can be excluded based on the absence of N₂O during blank experiments in the TAP reactor without the gauzes, with NH₃–NO mixtures and large pulse sizes (Table 1).

The second essential aspect to unraveling the mechanism of secondary NH₃–NO interactions yielding N₂O and N₂ consists is the use of isotopes in the TAP reactor. This is vital for two reasons: (i) to discriminate between N₂O and CO₂ in MS analysis in mass spectrometry and (ii) to trace the origin of reaction products by the distinction of the N-label in the reactants (¹⁵NH₃ and ¹⁴NO). As revealed by the use of isotopes, similar amounts of N₂O and CO₂ were formed in our TAP experiments during pulsing of NH₃–O₂ mixtures [1].

4.2. N_2 formation

It has to be emphasized that the TAP technique, despite its high time resolution, does not provide mechanistic information on the level of elementary reaction steps. Our approach in the previous section was to provide a few relatively elementary steps from which a basic perception of the reaction mechanism could be obtained. Such an approach would, of course, be possible, but it is considered to be merely speculative.

Sequential pulse experiments with isotopes have revealed that three N₂ isotopes, ¹⁵N¹⁵N, ¹⁴N¹⁴N, and ¹⁵N¹⁴N, were formed in the reaction of ¹⁵NH₃ with ¹⁴NO over the Pt and Pt–Rh gauzes. Based on our sequential ¹⁵NH₃–¹⁴NO pulse experiments in Figs. 7 and 8, the reaction pathways in Eqs. (12)–(15) leading to the various N₂ isotopes can be established. In these reaction steps, "s" denotes an active site, and "s– \Box " represents an adsorbed species:

$$2s^{-15}NH_x + 2s^{-}O \rightarrow {}^{15}N^{15}N + 2s^{-}H_xO + 2s, \qquad (12)$$

$$s^{-15}NH_x + s^{-14}NO \rightarrow {}^{15}N^{14}N + s^{-}H_xO + s,$$
 (13)

$$s^{-15}NH_x + 2s^{-14}NO \rightarrow {}^{14}N^{14}N + s^{-}H_xO + s^{-15}N + s^{-}O,$$
 (14)

$$2s-H + 2s^{-14}NO \rightarrow {}^{14}N^{14}N + 2s-OH + 2s.$$
(15)

 N_2 formation involves not only the conversion of two NO or two NH₃ molecules, leading to the simple isotopes, but also the coupling of nitrogen atoms in the reactants, yielding the mixed isotope. These three species were observed in previous isotopic UHV studies (10^{-6} mbar) conducted over Pt(100) at 300–750 K [3,16] with isotopically labeled nitric oxide (^{15}NO) and nonlabeled ammonia ($^{14}NH_3$). These

investigations concluded that the largest contribution to the total nitrogen production arose from the mixed ¹⁴N¹⁵N isotope, suggesting the importance of the interaction between adsorbed ¹⁵NO and ¹⁴NH₃ species. In a related work, van Tol et al. [21] investigated the oscillatory behavior of the NO–NH₃ reaction over Pt(100) at low pressures (1×10^{-6} to 4×10^{-5} mbar) at 420-485 K with ¹⁵NH₃ and ¹⁴NO. In this case, ¹⁴N¹⁴N and ¹⁵N¹⁴N were formed in comparable amounts, whereas the concentration of ¹⁵N¹⁵N was reported to be very low. This agrees well with our findings that N₂ formation from two NH₃ molecules does not occur when NH₃ and NO are simultaneously pulsed over the PGM gauzes (see Fig. 8).

The relevance of the various pathways for N₂ formation depends on the relative coverage of NO, NH_x , and H species on the catalyst surface. It is important to discuss the distribution of N-labels in N2 as a function of the time delay between ¹⁵NH₃ and ¹⁴NO pulses described in Section 3.3 (see Fig. 8). These experiments are extremely valuable to understanding the influence of the NH₃/NO ratio on the above reaction pathways. A short time delay ($\Delta t \rightarrow 0$ s) between NH₃ and NO pulses is associated with a relatively high NH₃/NO ratio in the NO pulse and accordingly with a high surface coverage of NH_x species on the catalyst surface. In contrast, a long time delay time indicates a low NH3/NO ratio in the NO pulse and thus a low coverage of NH_x species in the NO pulse. As shown in Fig. 7, ¹⁵N¹⁵N was the main nitrogen isotope formed (in the ¹⁵NH₃ pulse) during sequential ¹⁵NH₃–¹⁴NO pulsing at $\Delta t = 2$ s. This is explained by the direct oxidation of ammonia to nitrogen by surface oxygen species (Eq. (12)). A decrease in the time delay between the $^{15}\rm NH_3$ and $^{14}\rm NO$ pulses leads to a decreased concentration of $^{15}\rm N^{15}N$ at the expense of $^{14}\rm N^{15}N$ and $^{14}\rm N^{14}N$ formation (Fig. 8). The increased formation of ${}^{14}N{}^{14}N$ and ${}^{14}N{}^{15}N$ is in good agreement with steady-state tests of NO reduction by NH₃ over polycrystalline platinum wire reported by Takoudis and Schmidt [6]. These authors found that the rate of NO decomposition at 1000 K increased with the molar feed NH₃/NO ratio. However, since no isotopically labeled molecules were used in that study, no conclusion about the reaction pathways of nitrogen formation could be drawn. From a chemical point of view, the pathways for N₂ formation with NO participation identified in this study differ in that Eq. (13) involves the coupling of nitrogen atoms in adsorbed NO and NH_x species, whereas Eqs. (14) and (15) involve the reduction of two NO molecules by adsorbed NH_x or H species, respectively. The participation of H-containing species in NO reduction was unequivocally concluded from the results given in Fig. 2. These routes have different dependences on the NH₃/NO ratio, as previously reported in studies conducted over Pt(100) at 425 K and 450 K [3]. The decreased molar 14N15N/14N14N ratio with increasing time delay between the ¹⁵NH₃ and ¹⁴NO pulses in Fig. 9 indicates that Eqs. (14) and (15) are the major route for N_2 at a low NH₃/NO ratio, whereas Eq. (13) becomes more important with an increasing NH₃/NO ratio.

4.3. N₂O formation

As pointed out in the Introduction, low-temperature NH₃-NO studies conducted over Pt/Al₂O₃ found the reaction between adsorbed NH_2 and NO species (Eq. (6)) to play too small a role to explain N₂O formation [11]. This step was discarded because of the absence of H₂ in the product gases, which would have been expected from the spontaneous recombination of reactive adsorbed H atoms. Instead, the main reaction pathway of N₂O formation was suggested to involve the reaction of two NO molecules with chemisorbed hydrogen, via formation of nitroxyl (HNO) as an intermediate species (Eqs. (7) and (8)). Our results were obtained at significantly higher temperature and over PGM gauzes and conclusively show that N₂O formation requires the coupling of N-atoms of adsorbed ¹⁵NH₃ and ¹⁴NO species. Eq. (6), originally suggested by Otto et al. [11], cannot be considered the reaction route for N2O formation, since it implies the formation of two H atoms. These atoms can recombine to yield gas-phase H₂, which was not observed in our experiments when a mixture of NO and NH3 was introduced as a pulse into the reactor (water was the only hydrogen-containing product); this was when the highest N₂O production was found. Taking into account this experimental fact and the importance of oxygen species in the NH3-NO reaction (Section 4.4), Eq. (16) can be suggested as the exclusive route for N₂O formation

$$s^{-15}NH_x + s^{-14}NO + s^{-}O \rightarrow {}^{15}N^{14}NO + s^{-}H_xO + 2s.$$
(16)

This reaction resembles the pathway for ¹⁵N¹⁴N formation in Eq. (13) and suggests increased N₂O formation (relative to N₂ formation) with increased oxygen coverage on the catalyst surface. Accordingly, N₂O would be expected to be the main by-product of high-temperature ammonia oxidation, which is carried out in the presence of excess oxygen (typically 10 vol% NH₃ in air). However, this is not in line with results obtained in our study (Figs. 4-6) and reported in the literature [22-24]. As a matter of fact, N₂ is the main Ncontaining by-product in industrial NH₃ burners (typically $N_2/N_2O \sim 2$). The relatively high N_2/N_2O ratio can be explained we take into account (i) direct N2O decomposition into N2 and O2, which can occur over the oxidized Pt-Rh gauze at high temperatures [25], or (ii) reduction of N₂O by NH_3 into N_2 and H_2O . According to [8], the reaction between NH3 and N2O has to be considered during NO reduction with NH₃ over polycrystalline platinum foil at high temperature.

4.4. Reaction network and loss reactions in the ammonia burner

Based on the results reported here and in our previous paper [1], an improved description of the complex processes occurring during the high-temperature oxidation of ammonia over PGM gauzes has been attained. A simplified scheme

Fig. 10. Reaction network during the high-temperature NH₃ oxidation over noble metal gauzes, as derived from TAP studies here and in [1]. The dashed area includes steps at high oxygen coverages, i.e., more representative of industrial ammonia oxidation. Dashed arrows indicate minor reaction pathways and crosses on certain arrows denote that the corresponding process is inhibited in the presence of oxygen. Two types of adsorbed oxygen species are distinguished (O and O*, see text).

representing the reaction network and product formation as a function of oxygen coverage (θ_0) is considered in Fig. 10. An accurate value for the coverage in the "low" and "high" cases cannot be provided at this stage, but extreme values approaching 0 and 100%, respectively, can be considered for the purpose of this paper. No reaction products were obtained upon interaction of NH3 with the reduced PGM surface ($\theta_0 = 0$). As concluded in previous studies [1,26], the NH₃-O₂ reaction is initiated by the activation of the ammonia molecule by adsorbed oxygen species. These oxygen species induce the consecutive stripping of hydrogen atoms from ammonia according to Eq. (17), yielding reactive NH_{3-y} intermediates (referred to as NH_x here). Recombination of two NH_x fragments is favored at low oxygen coverage, leading to N_2 (Eq. (18)), with formation of insignificant amounts of NO [1]. The above-mentioned formation of N₂ via direct NH₃ oxidation (see ¹⁵N¹⁵N in Figs. 7 and 8) likely originates from the combination of Eqs. (17) and (18). Together with the oxygen coverage, the nature of the adsorbed oxygen species appears to be of vital importance in the NO:N₂ distribution [1]. To this end, O and O* are distinguished in Fig. 10, representing strongly bounded and highly reactive adsorbed oxygen species, respectively. The pathway in Eq. (18) is virtually suppressed under conditions of industrial relevance because of the high oxygen coverage. This is due to the excess oxygen in the feed (molar NH₃/O₂ ratio $\sim 1/2$) and the high affinity of O₂ for dissociative adsorption on a reduced noble metal surface. Formation of N2 from direct NH3 decomposition would oc-



cur only in the presence of a high local NH₃ concentration, giving rise to a low O/NH_x ratio at the surface. N₂ production by this route is expected to be minimal in view of the presence of distributor plates before the gauze pack, which improve the mixing of the ammonia-oxygen mixture and the excess oxygen in the feed gas. As concluded for ammonia oxidation over Pt(100) single crystal at temperatures up to 800 K [27] and in our earlier study [1], a high oxygen coverage increases the selectivity for NO. In this situation, the extraction of H atoms from NH₃ and the recombination of nitrogen and oxygen atoms (Eq. (19)) are accelerated, leading to the most oxidized N-product:

$$s-NH_3 + ys-O \rightarrow s-NH_{3-y} + ys-OH, \tag{17}$$

$$s-NH_x + s-NH_x \rightarrow N_2 + xH_2 + 2s, \tag{18}$$

$$s-N+s-O \to NO+2s. \tag{19}$$

The mechanism of ammonia oxidation is complicated by the occurrence of interactions between NH3 and NO. The results presented here indicate that by-products (N_2 and N_2O) from industrial ammonia burners containing PGM gauze packs are mainly formed by the reduction of NO by NH₃. These secondary reactions are particularly detrimental to the economy of the process, since they involve a loss of reactant and the desired product. In industrial burners, the noble metal gauzes are packed snugly against each other in numbers varying from 4 to 50, depending on the operating pressure; the low-pressure reactor uses fewer gauzes [24]. Obviously, the origin of secondary NH₃–NO interactions should be situated in a region of the catalytic burner where NO and NH₃ coexist, that is, in the very first gauzes of the pack. N₂O formation principally stems from the coupling of adsorbed NO and N atoms resulting from NH₃ (Eq. (16)). However, three different reaction pathways have been identified for N₂ formation, involving two NO molecules, two NH₃ molecules, and one NH₃ molecule and one NO molecule (Eqs. (12)–(15)). The relative importance of these reactions is a function of the NH3/NO ratio, which decreases along the axial coordinate in the gauze pack. Furthermore, nitrogen can be formed from nitrous oxide by the reduction of N2O by NH3 or direct N2O decomposition. The extent of the NH₃-N₂O reaction cannot be assessed from the present study. Under industrial reaction conditions, direct N2O decomposition over PGM gauzes is not expected, in view of the large excess of oxygen in the burner $(O_2/N_2O \sim 70)$, which severely inhibits the reaction [25].

A final aspect to address is the influence of oxygen on the NH₃–NO reaction. This point is relevant since the participation of adsorbed oxygen species in ammonia activation (Eq. (17)) should make them also fundamental to the initiation of the reduction of nitric oxide by ammonia. As stressed by several authors [28], the rate of the NH₃–SCR of NO_x is enhanced by increased partial O₂ pressure in the feed. Katona et al. [9] reported a 10-fold higher reaction rate between NH₃ and NO in the presence of O₂. In our study, oxygen species can be derived from (i) the high-temperature O₂ pretreatment of the as-received gauzes (see Experimental) and/or (ii) the dissociation of NO over reduced metal sites (Eq. (20)). These reduced sites are generated via Eqs. (17)–(19). We have observed a high activity of the H₂-pretreated Pt and Pt–Rh gauzes toward NO conversion to N₂. In contrast, O₂-pretreated Pt and Pt–Rh gauzes are unable to dissociate NO [1]. Therefore, based on this aspect and on the high O₂ content in the burner, direct NO decomposition is not considered an important loss reaction over the noble metal gauzes

$$NO + 2s \rightarrow s - N + s - O. \tag{20}$$

In summary, oxygen species catalyze both the oxidation of NH₃ to NO and the reduction of NO with NH₃ to N₂O and N₂. It is envisaged that the desired reaction is favored over the undesired one at increasing oxygen coverages. In practice, such a situation can be accomplished with a larger excess of oxygen in the feed. In fact, nearly 100% NO selectivity was reported for ammonia oxidation with an O₂/NH₃ ratio ca. 3 [29]. However, this operation would dramatically reduce the lifetime of a gauze pack, since an increase in partial O₂ pressure accelerates platinum loss in the form of volatile PtO₂. Further investigations of the influence of O₂ on the kinetics of the NH₃–NO reaction are required. To this end, TAP studies with the ternary NH₃–O₂–NO system will be undertaken in the near future.

5. Conclusions

The results presented in this paper indicate the importance of secondary NH3-NO interactions for the formation of N2O and N2 by high-temperature ammonia oxidation over PGM gauzes as part of the manufacture of nitric acid. Transient isotopic studies in the temporal analysis of products (TAP) reactor in the molecular diffusion regime with isotopes make it possible to derive valuable information on reaction pathways leading to these undesired by-products. Adsorbed oxygen species catalyze ammonia activation into reactive NH_x and H intermediates, which effectively reduce NO. N₂O was found to be purely a product of the secondary interaction between adsorbed ammonia intermediate species (NH_x) with NO. The absence of N₂O during the NH₃-O₂ and NH₃-NO reactions in the Knudsen diffusion regime (i.e., at a very low peak pressure) is related to the detection limit of mass spectroscopic analysis. This may also explain the invisibility of N₂O in previous UHV studies, where the pressure is much lower than in the TAP reactor. Three different reaction routes of N₂ formation have been established, involving the secondary interaction between NO and NH₃, but also the direct decomposition of NH₃ or NO. The dominant route depends on the surface coverage of N-species, as demonstrated by sequential pulse studies at different time delays. Based on the experimental results presented in this paper and in [1], an improved reaction network for hightemperature NH₃ oxidation has been proposed, taking into account the influence of oxygen coverage on the formation of NO, N₂O, and N₂. This information enables to locate loss reactions in the gauze pack, providing the basis for rational strategies for preventing or minimizing by-product formation in industrial ammonia burners.

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