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Transient studies on the effect of oxygen on the high-temperature NO reduction by NH_3 over Pt–Rh gauze

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Abstract

The effect of oxygen on the activity and selectivity of the NO reduction by NH_3 over Pt–Rh (95–5 wt.%) alloy gauze at 1023–1073 K has been investigated. To this end, the Temporal Analysis of Products (TAP) reactor in combination with isotopic tracers was applied. Single pulse experiments evidenced the rapid activation of NH_3 over the catalyst surface covered by adsorbed oxygen. Contrarily, NO requires an essentially reduced surface in order to be dissociated. Adsorbed oxygen species in the O_2-pretreated gauze accelerate the reaction of NH_3 with NO with respect to the as-received gauze. N_2 was the main reaction product and traces of N_2O were comparatively formed ($N_2O/N_2 \sim 10^{-3}$). Pulsing of an equimolar O_2–$^{15}NH_3$–NO mixture over the Pt–Rh gauze mainly produces ^{15}NO, while the formation of N_2 is largely suppressed. The selectivity to ^{15}NO and N_2O in the ternary O_2–$^{15}NH_3$–NO system diminished upon decreasing the $O_2/(^{15}NH_3 + NO)$ ratio, in favor of N_2. This ratio was qualitatively varied by changing the time delay between O_2 and $^{15}NH_3$–NO in sequential pulse experiments. Our results indicate that the NH_3 oxidation by O_2 to NO is much faster than the NO reduction by NH_3 at similar concentrations of oxygen and nitric oxide. This explains the low production of N_2 and N_2O in ammonia burners within nitric acid manufacture.

Keywords: NH_3 oxidation; NO reduction; Oxygen; Platinum; Rhodium; Gauze; Mechanism; Transient experiments; TAP reactor

1. Introduction

Recent studies using the Temporal Analysis of Products (TAP) reactor have provided valuable mechanistic insights into NO, N_2O, and N_2 formation in the high-temperature ammonia oxidation over commercial Pt and Pt–Rh alloy gauzes [1–3]. Selectivity-directing factors towards these reaction products were derived from the investigation of NH_3–O_2 and NH_3–NO interactions at 973–1173 K. The application of pulses within the molecular diffusion regime (ca. 10^{16} molecules/pulse) in combination with isotopic tracers was essential to unravel the origins of the various products in this complex reaction network [1–3]. It was concluded that secondary reactions involving NO and NH_3 are the main cause for the occurrence of loss reactions in ammonia burners, yielding the undesired N_2O and N_2 products. The mechanism and kinetics of the NO reduction by NH_3 in the absence of O_2 have been investigated over platinum catalysts of different nature, including single crystals (Pt(1 0 0) [4,5] or stepped Pt 12(1 1 l) × (l 1 1) [6]), polycrystalline Pt wire [7,8] and foils [9–11], as well as supported Pt catalysts [12–14], at different molar feed NH_3/NO ratios (1–9), pressures (0.1–1000 Pa), and temperatures (473–873 K), using batch and flow reactors, as well as surface science techniques in ultra-high vacuum (UHV). N_2 (mainly) and N_2O were found as the reaction products, with a typical increase in the N_2/N_2O ratio upon increasing the temperature and/or the feed NH_3 concentration [7].

Several works [2,15–17] have concluded the importance of oxygen species adsorbed on platinum for NH_3 dehydrogenation (Eq. (1)), leading to highly reactive NH_x intermediates. Simplistically, the ultimately formed N atom by abstraction of three hydrogen atoms from the ammonia molecule can be

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converted to NO, N_2 and N_2O according to Eqs. (2)–(4). Attending to the important role of oxygen in generating NH_x species, its influence in the NO reduction with NH_3 can be anticipated. As stressed by several authors, the low temperature NH_3-SCR of NO_x over Pt/Al_2O_3 [18], polycrystalline Pt foil [10], and Pt(1 0 0) single crystal surface [19] is influenced by O_2 in the feed. For example, Katona et al. [10] reported a 10-fold higher reaction rate between NH_3 and NO in the presence of O_2 at 623 K, although the effect of oxygen on the selectivity towards N_2 and N_2O was not specified.

$$NH_{3,ads} + (3-x)O_{ads} \rightarrow NH_{x,ads} + (3-x)OH_{ads} \quad (1)$$

$$N_{ads} + O_{ads} \rightarrow NO \quad (2)$$

$$N_{ads} + N_{ads} \rightarrow N_2 \quad (3)$$

$$N_{ads} + NO_{ads} \rightarrow N_2O \quad (4)$$

This manuscript attempts to investigate the influence of oxygen on the activity and selectivity of commercial Pt–Rh alloy gauze in the reduction of NO by NH_3 at 1023–1073 K, i.e. relevant temperatures of industrial ammonia burners. To this end, the individual interactions of NH_3 and NO as well as the combined interactions of NH_3–NO and O_2–NH_3–NO over the as-received and O_2-pretreated Pt–Rh gauzes have been investigated in the TAP reactor using isotopic tracers.

2. Experimental

The commercial woven Pt–Rh alloy gauze (95–5 wt.%) used in this study, and the description of the Temporal Analysis of Products reactor for mechanistic investigations of NH_3–O_2 and NH_3–NO interactions over noble metal gauzes were described in [2,3]. Briefly, a single piece of the gauze catalyst (ca. 30 mm^2, weighing 25 mg) was placed between two layers of quartz particles (sieve fraction 250–350 μm) in the isothermal zone of the TAP microreactor (6 mm i.d.). Prior to the transient experiments, the as-received gauze was pretreated in a flow of pure O_2 at 1273 K and ambient pressure for 2 h. In some cases, the O_2-pretreated gauze was also subjected to $^{18}O_2$ pulsing (20 nmol $^{18}O_2$ in total) at the corresponding reaction temperature. Mixtures of $^{14}NH_3$:Ne = 1:1, ^{14}NO:Ne = 1:1, and $^{15}NH_3$:^{14}NO:Ne = 1:1:1 were individually pulsed over the as-received and O_2-pretreated Pt–Rh gauze samples in the temperature range of 1023–1173 K. Additionally, pump-probe experiments were performed over the O_2-pretreated gauze at 1023 and 1073 K by pulsing mixtures of O_2:Xe = 1:1 (pump) and $^{15}NH_3$:^{14}NO:Ne = 1:1:1 (probe) at different time delays (Δt) in the range of Δt = 0–0.5 s. The pulse size was in the range of 10^{14}–10^{16} molecules.

In the experiments, Xe (4.0), Ne (4.5), $^{16}O_2$ (4.6), $^{18}O_2$ (98% atoms of ^{18}O), ^{14}NO (2.5), $^{14}NH_3$ (2.5) and $^{15}NH_3$ (99.9% atoms of ^{15}N) were used without additional purification. Isotopically labeled oxygen and ammonia were purchased from ISOTEC. Along the manuscript, the ^{18}O and ^{15}N labels in reactants and products are explicitly mentioned when unambiguous distinction with the non-labeled atoms is not possible. By default, N and O refer to non-labeled ^{14}N and ^{16}O. Transient responses were monitored at atomic mass units (AMUs) related to reactants, reaction products, and inert gases at the reactor outlet using a quadruple mass spectrometer (Hiden Analytical). The following AMUs were analyzed: 132 (Xe), 46 ($^{14}NO_2$, $^{15}N^{15}NO$), 45 ($^{15}N^{14}NO$), 44 ($^{14}N^{14}NO$, CO_2), 36 ($^{18}O_2$), 34 ($^{18}O^{16}O$), 32 ($N^{18}O$, O_2), 31 (^{15}NO, $H^{14}NO$), 30 ($^{14}N^{14}NO$, ^{14}NO, $^{15}N^{15}N$), 29 ($^{15}N^{14}N$), 28 ($^{14}N^{14}NO$, $^{14}N^{14}N$), 20 (Ne), 18 (H_2O, $^{15}NH_3$), 17 ($^{14}NH_3$, $^{15}NH_3$, H_2O, OH), 15 ($^{14}NH_3$, ^{15}NO, $^{15}NH_3$, $^{15}N^{15}N$), and 2 (H_2). 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 using standard fragmentation patterns and sensitivity factors. The mole fraction (y) of N-containing components at the reactor outlet was determined by Eq. (5), where $n(i)$ represents the moles of $^{15}NH_3$, ^{14}NO, ^{15}NO, $^{14}N^{15}NO$, $^{15}N^{15}NO$, $^{14}N^{15}N$, and $^{14}N^{14}N$ at the reactor outlet and j is the number of N-containing components.

$$y_i(\%) = \frac{n_i}{\sum_{i=1}^{j} n_j} \times 100 \quad (5)$$

3. Results and discussion

3.1. Activation of NH_3 and NO

The influence of oxygen pretreatment on the activation of ammonia was studied by single pulsing of NH_3 in Knudsen diffusion regime over the as-received and O_2-pretreated Pt–Rh gauzes. In these experiments, N_2 was the main N-containing reaction product, while only traces of NO were detected. The transient responses of NO, N_2, and NH_3 at 1073 K are shown in Fig. 1. Attending to the intensities of the N_2 signal, it can be concluded that the amount of N_2 formed and therefore the degree of NH_3 conversion is ca. 10 times higher over the O_2-pretreated Pt–Rh gauze than over the as-received Pt–Rh gauze. This unequivocally indicates the higher activity of the oxidized gauze for ammonia conversion to nitrogen as compared with the essentially reduced surface of the as-received gauze. The efficient activation of ammonia in the presence of oxygen species has been demonstrated in previous works over Pt(1 1 1) single crystal [15], hex-R and (1 × 1) faces of the Pt(1 0 0) crystal [16], Pt sponge [17], as well as Pt and Pt–Rh gauzes [2] using UHV, ambient, and transient vacuum techniques in a wide range of temperatures. The preferential formation of N_2 and very low NO production upon NH_3 pulsing over O_2-pretreated Pt–Rh gauze can be explained by the quantity and quality of the adsorbed oxygen species [2]. In single NH_3 pulse experiments, the relative