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Mechanistic insights into the formation of N_2O and N_2 in NO reduction by NH_3 over a polycrystalline platinum catalyst

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Abstract

The reaction pathways of N_2 and N_2O formation in the direct decomposition and reduction of NO by NH_3 were investigated over a polycrystalline Pt catalyst between 323 and 973 K by transient experiments using the temporal analysis of products (TAP-2) reactor. The interaction between nitric oxide and ammonia was studied in the sequential pulse mode applying ^{15}NO. Differently labelled nitrogen and nitrous oxide molecules were detected. In both, direct NO decomposition and NH_3–NO interaction, N_2O formation was most marked between 573 and 673 K, whereas N_2 formation dominated at higher temperatures. An unusual interruption of nitrogen formation in the ^{15}NO pulse at 473 K was caused by an inhibiting effect of adsorbed NO species. The detailed analysis of the product distribution at this temperature clearly indicates different reaction pathways leading to the product formation. Nitrogen formation occurs via recombination of nitrogen atoms formed by dissociation of nitric oxide or/and complete dehydrogenation of ammonia. N_2O is formed via recombination of adsorbed NO molecules. Additionally, both products are formed via interactions between adsorbed ammonia fragments and nitric oxide.

Keywords: Mechanism; NO decomposition; NO reduction by NH_3; N_2O formation; ^{15}NO; Pt gauze; Transient experiments; TAP reactor

1. Introduction

The catalytic reduction of nitrogen oxides emissions for environmental protection has been a subject of numerous studies [1]. NO emission from nitric acid plants and stationary power stations is controlled by selective catalytic reduction (SCR) using ammonia or urea. Although metal-oxide catalysts are mostly applied, Pt-based catalysts are also of interest due to their high efficiency in the SCR process under sulphur-free conditions [2]. Moreover, the interaction of NO and NH_3 over Pt catalysts reveals rate oscillations, which gave rise to various detailed mechanistic studies [3–7] aimed at the understanding of the oscillatory behaviour. Besides, the NO–NH_3 interactions play a significant role in side product formation (N_2O and N_2) in the high-temperature ammonia oxidation to nitric oxide [8].

Various mechanistic studies of the interactions between NO and NH_3 on Pt-based catalysts [3–7,9–12] were performed in a broad range of pressures extending from UHV (10^{-7} to 10^{-5} Pa) [5–7,13] over mediate pressures of 10–10^2 Pa [3,10] to ambient pressure [11,12]. The main reaction products were nitrogen and water. N_2O formation was only sporadically observed and discussed. The most informative insights into N_2 and N_2O formation were derived using isotopically labelled molecules (^{15}NO [6] and $^{15}NH_3$ [7,8,14]). The suggested concepts differ in the reaction pathways of product formation. Earlier mechanisms [3,9,10,14] consider the dissociation of ammonia to NH_2 and hydrogen atoms, which in turn react with adsorbed NO yielding HNO species. HNO and NH_2 species participate in the reaction pathways leading to N_2 and N_2O (Eqs. (1)–(5)). Although some indications for HNO species were obtained by EELS studies [15], their existence is still controversial:

$$\text{s-NH}_2 + \text{s-NO} \rightarrow N_2 + \text{s-H}_2O + \text{s} \quad (1)$$

$$\text{s-NH}_2 + \text{s-NO} \rightarrow N_2O + 2\text{s-H} \quad (2)$$

$$2\text{s-HNO} \rightarrow N_2O + \text{s-H}_2O + \text{s} \quad (3)$$

$$\text{s-HNO} + \text{s-H} \rightarrow \text{s-N} + H_2O + \text{s} \quad (4)$$

$$2\text{s-N} \rightarrow N_2 + 2\text{s} \quad (5)$$

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Later concepts [6,7] are based on a more general approach excluding the participation of HNO or NH_2 species. Nitrogen atoms are considered as a key intermediate in N_2 [6,7] and N_2O [7] formation (Eqs. (6)–(8)):

$$2\text{s-N} \rightarrow N_2 + 2\text{s} \tag{6}$$

$$\text{s-NO} + \text{s-N} \rightarrow N_2O + 2\text{s} \tag{7}$$

$$\text{s-NO} + \text{s-N} \rightarrow N_2 + \text{s-O} + \text{s} \tag{8}$$

However, these concepts ignore the experimental observations that adsorbed ammonia fragments dominate on the Pt surface at low temperatures under oxidative conditions [16–18]. Therefore, further mechanistic examinations of the interactions between NO and NH_3 are needed. The present study was aimed at detailed understanding of reaction pathways leading to N_2 and N_2O in the NH_3–NO interaction over an industrially relevant knitted Pt gauze by means of transient experiments with isotopic tracers. NO decomposition, which also yields N_2 and N_2O over Pt catalysts [19–21], was taken into consideration in order to estimate its contribution to the overall product formation in NO reduction by NH_3. The transient experiments were performed in the temperature range from 323 to 973 K using the TAP-2 reactor. This technique enables the study of primary heterogeneous reaction steps due to the suppression of any possible gas-phase interactions. Due to the small amount of pulsed molecules, highly exothermic NH_3–NO reaction can be studied under isothermal conditions as it was earlier shown for ammonia oxidation [22].

2. Experimental

Knitted Pt gauze (Multinit® type 4, Degussa) made of polycrystalline Pt wire was used as a catalyst. The geometric surface area (0.002(4) $m^2\,g^{-1}$) of the catalyst coincides well with the BET surface area (0.002(3) $m^2\,g^{-1}$), determined by low-temperature adsorption of Kr, which was used because of the low surface area of the catalyst.

The TAP reactor system has been described in detail elsewhere [23,24]. A single piece of the catalytic gauze (ca. 120 mg) was placed between two layers of inert quartz particles (sieve fraction 250–350 μm) in the isothermal zone of a quartz-made micro reactor (i.d. = 0.006 m, *L* = 0.04 m). Before pulse experiments the gauze was pre-treated in a flow of O_2 (30 ml/min) at 1073 K for 1 h at atmospheric pressure to remove carbon deposits from the catalyst surface. For studying direct NO decomposition, the Pt gauze was treated in a flow of hydrogen (10 ml/min) at 873 K for 4 h at atmospheric pressure. After pre-treatment, the reactor was evacuated and the catalyst was exposed to vacuum conditions (10^{-5} Pa). During a single pulse the pressure in the catalyst zone increased to ca. 10 Pa.

Additionally, after NO pulsing at a specified reaction temperature the catalyst was treated by hydrogen pulsing (ca. 10^{16} molecules/pulse) in order to remove oxygen species formed from NO (Section 3.1). H_2 was pulsed over the gauze until no water signal was anymore observed at the reactor outlet. For experiments below 873 K this pulse treatment was performed at 873 K, while for experiments above this temperature, the H_2-pulse treatment was carried out at the same temperature.

Transient experiments were performed using $^{14}NO/Ne = 1{:}1$, $^{15}NO/Ne = 1{:}1$ and $^{14}NH_3/Ne = 1{:}1$ mixtures in the temperature range between 323 and 973 with 100 K intervals. The time interval between the NH_3 and ^{15}NO pulses was 0.2 s. The pulse size was kept for all experiments in the range of 5×10^{14} to 9×10^{14} molecules enabling operation in the Knudsen diffusion regime.

Ne (99.998%), Xe (99.99%), ^{15}NO (99.5%), $^{14}NH_3$ (99.98 wt.%) were used as delivered. Isotopically labelled nitric oxide was purchased from ISOTEC. The following atomic mass units (AMUs) were used for mass-spectroscopic identification of different compounds: 44, 30, 28 (N_2O), 32 (O_2), 30 (NO), 28 (N_2), 18 (H_2O), 15 (NH_3), 2 (H_2), 20 (Ne) and 132 (Xe). In experiments with ^{15}NO, transient responses were additionally recorded at the AMUs: 46, 31, 30 ($^{15}N_2O$), 45, 31, 30, 29 ($^{15}N^{14}NO$), 31 (^{15}NO), 30 ($^{15}N_2$), 29 ($^{15}N^{14}N$).

3. Results

3.1. Decomposition of NO over platinum gauze

During NO pulsing over hydrogen-treated Pt gauze N_2 and N_2O were the only reaction products in the temperature range from 323 to 973 K. No O_2 was observed in the gas phase over the whole temperature range. However, the activity of hydrogen-treated Pt was not stable; the amount of decomposed NO as well as the amount of products decreased with the number of NO pulses as exemplified in Fig. 1 for 573 K. This decrease is more pronounced for N_2O than for N_2. The self inhibition of NO decomposition is discussed in Section 4.1.

The distribution of N_2O and N_2 formed from NO changes with temperature. The temperature dependence of the molar fractions of NO, N_2O and N_2, which correspond to the initial activity of Pt, is shown in Fig. 2. N_2O formation prevails at low

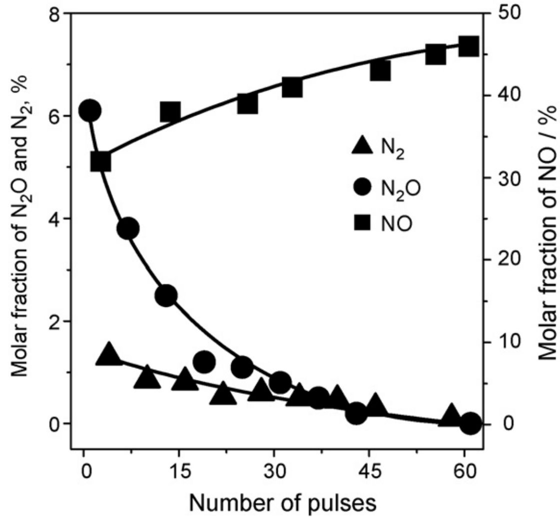

Fig. 1. Molar fractions of NO (■), N_2 (▲) and N_2O (●) as a function of number of NO pulses over hydrogen-treated Pt gauze at 573 K.