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Effect of different oxygen species originating from the dissociation of O_2, N_2O and NO on the selectivity of the Pt-catalysed NH_3 oxidation

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Dedicated to Professor Dr. Fritz Fetting on the occasion of his 80th birthday.

Abstract

An effect of oxygen species formed from O_2, N_2O and NO on the selectivity of the catalytic oxidation of ammonia was studied over a polycrystalline Pt catalyst using the temporal analysis of products (TAP) reactor. The transient experiments were performed in the temperature range between 773 and 1073 K in a sequential pulse mode with a time interval of 0.2 s between the pulses of the oxidant (O_2, N_2O and NO) and NH_3. In contrast to adsorbed oxygen species formed from NO, those from O_2 and N_2O reacted with ammonia yielding NO. It is suggested that the difference between these oxidising agents may be related to the different active sites for dissociation of O_2, N_2O and NO, where oxygen species of various Pt-O strength are formed. Weaker bound oxygen species, which are active for NO formation, originate from O_2 and N_2O rather than from NO. These species may be of bi-atomic nature.

Keywords: TAP reactor; Ammonia oxidation; Product distribution; Reaction mechanism; Transient experiments in vacuum; Pt catalyst; Pt gauze; Adsorbed oxygen species

1. Introduction

The mechanism of ammonia oxidation over different Pt catalysts (single crystals, wires, gauzes and supported catalysts) has been thoroughly studied during the last three decades [1–9]. Research was especially focused on the factors controlling product distribution, i.e. the formation of NO, N_2O and N_2. Already in 1978, Gland and Korchak [1] suggested that different oxygen species are responsible for oxidation of ammonia to NO and to N_2. Since this time, the role of different oxygen species in the product formation in ammonia oxidation has not been systematically investigated.

The numerous studies of the interaction between molecular oxygen and platinum have shown that different oxygen species were formed on the catalyst surface depending on the temperature and oxygen partial pressure. Such species might be molecular oxygen, surface and subsurface oxygen atoms, oxygen species penetrated in the volume and Pt oxides. The catalytic relevance of these oxygen species has been highlighted earlier for various Pt-catalysed reactions. Mallens et al. [10] have shown that in partial oxidation of methane to syngas (CO and H_2) over polycrystalline Pt oxygen species of PtO_x nature contributed to CO formation and its further oxidation to CO_2. The role of adsorbed oxygen atoms was restricted to oxidation of CO to CO_2. Oxygen species dissolved in the bulk of Pt were assumed to be responsible for direct oxidation of methane to carbon dioxide. In general, the ideas about the participation of various oxygen species in different elementary steps of this Pt-catalysed reaction were later confirmed by Fathi et al. [11]. In contrast to Mallens et al. [10], the latter authors ascribed CO formation to chemisorbed oxygen species formed either via O_2 dissociation or to oxygen atoms diffusing from the bulk of Pt to the surface. Direct participation of adsorbed oxygen molecules in oxidation of methanol and methane over Pt(1 1 1) has been also reported in literature [12,13].

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In a recent transient mechanistic study of ammonia oxidation over Pt and Pt/Rh gauzes between 973 and 1173 K [8], it was suggested that weakly bound oxygen species were crucial for NO formation. This conclusion was based on the experimentally observed strong change of selectivity of NH_3 oxidation from preferential formation of NO to N_2 with an increase in time interval between O_2 and NH_3 pulses from 0 to 0.1 s [8]. Although the level of NH_3 conversion was the same, this increase in the time interval led to a decrease in NO yield by a factor of 30. This effect was ascribed to the decrease of the surface coverage by weakly bound oxygen species responsible for NO formation.

In order to further elucidate the effect of the nature of oxygen species in ammonia oxidation, the present study was focused on the analysis of product distribution in ammonia oxidation by oxygen species formed from O_2, NO and N_2O. These oxidants were chosen due to the fact that their interaction with Pt leads to the formation of oxygen species on the catalyst surface, which differ in their desorption behaviour [14–16] and reaction steps leading to their removal from the surface [15,17,18]. Based on the above background, the reactivity/selectivity of oxygen species originating form O_2, N_2O and NO towards NH_3 oxidation to NO was investigated under transient conditions between 773 and 1073 K in the temporal analysis of products (TAP) reactor operated in the sequential pulse mode.

2. Experimental

2.1. Catalyst and its characterisation

Knitted Pt gauze (Multinit® type 4, Degussa) made of polycrystalline Pt wire (0.12 g) was used in all the experiments. The content of near-to-surface impurities was controlled by XPS measurements, which showed that the main impurity were adsorbed carbon species. Also Zn and Pb were detected by XPS. The surface concentration of these impurities was 1 and 0.3%, respectively.

Carbon species were almost completely removed by catalyst treatment in a flow of oxygen ($30\ ml\ min^{-1}$) at ambient pressure and 1073 K for 60 min. The state of the catalyst after oxygen treatment was characterised by XPS and XRD. The formation of detectable amounts of Pt oxides was excluded, since Pt_{4f} spectra reveal two peaks typical for metallic Pt at 71.2 and 74.5 eV as mentioned in [19]. In O1s region three peaks at 529.8, 530.9 and 531.8 eV were observed, indicating that at least three different types of oxygen species were formed during oxygen treatment.

The XRD analysis has shown that oxygen treatment leads to penetration of oxygen atoms into the volume of Pt. Oxygen species occupy probably interstitial sites in the Pt lattice. This conclusion is in agreement with the results of a recent combined XPS and XRD study of polycrystalline Pt having been treated by N_2O and O_2 at 10^5 Pa at temperatures above 873 K [20,21]. According to the results of these studies, peaks observed in O1s region at 529.8 and 530.9 eV were related to different oxygen atoms adsorbed on the catalyst surface. A peak at 531.8 eV was assigned to oxygen species dissolved in the Pt bulk.

Reactivity of oxygen species formed after Pt treatment in a flow of O_2 was previously studied using single pulse experiments with ammonia between 298 and 1073 K [7]. Since N_2 was the only nitrogen-containing product detected in the cited work, the contribution of these species to NO formation in the present experiments can be excluded. Oxygen species formed during oxygen-treatment were neglected by the calculation of oxygen balance. Single pulsing of NH_3 performed over oxygen-treated catalyst has shown that amount of water, which was the only oxygen-containing product, was low (3% even at 1073 K) [7]. Therefore, the formation of products in the present experiments was ascribed to ammonia oxidation by oxygen species formed during pulse of oxidizing agent (O_2, N_2O or NO). The amount of these species on the catalyst surface was estimated from oxygen balance calculated as a ratio of the amount of oxygen atoms supplied by the pulsed molecules of oxidant to the amount removed as non-reacted oxidant and oxygen-containing product in the oxidant pulse.

2.2. Transient experiments

Transient experiments were performed in the TAP-2 reactor system (for details see [22]). The present system was equipped with a home-made quartz-glass micro reactor ($d = 6$ mm, $L = 40$ mm). The Pt gauze catalyst was packed between two layers of quartz ($d_p = 250–355\ \mu m$) in the isothermal zone of the reactor. Before sequential pulsing of reactants the catalyst was treated in a flow of oxygen ($30\ ml\ min^{-1}$) at ambient pressure at 1073 K for 60 min. For single pulse experiments with NO and N_2O, additional treatment of the catalyst in a flow of hydrogen (10 ml/min, 4 h, 873 K) was performed. Hereafter, the pre-treated sample was exposed to vacuum (ca. 10^{-5} Pa). The reaction temperature was decreased stepwise by 100 K from 1073 to 773 K. After single pulsing of NO and N_2O at each temperature, oxygen species formed from NO and N_2O were removed by pulsing H_2 with a pulse size of ca. 10^{16} molecules until no water signal was observed.

In sequential pulse experiments the oxidizing agent (O_2, N_2O or NO) and ammonia were subsequently pulsed from two different pulse valves with a time interval of 0.2 s. Within this time period the main part of the oxidant has already left the reactor, only adsorbed oxygen species were still on the catalyst surface, when the second gas (NH_3) was introduced. Therefore, the reactivity/selectivity of these oxygen species towards NH_3 oxidation could be investigated. The set time interval was chosen in order to decrease the contribution of direct interaction of the oxidant molecules and ammonia and to assure detectable formation of NO, which drops strongly with an increase of this parameter. The former aspect is especially important for experiments with NO, since adsorbed NO molecules can directly react with NH_3.

Transient responses on pulsing $O_2/Xe = 1/1$, $N_2O/Xe = 1/1$, $N_2O/Ne = 1/1$, $NO/Xe = 1/1$, $NO/Ne = 1/1$ and NH_3 ($^{15}NH_3$)/$Ne = 1/1$ were recorded at the reactor outlet using a quadrupole mass spectrometer (QMS). The following atomic mass units (AMUs) were used for identification of different compounds:

44.0, 30.0, 28.0 (N_2O), 32.0 (O_2), 30.0 (NO), 28.0 (N_2), 18.0 (H_2O), 15.0 (NH_3), 2.0 (H_2), 20.0 (Ne) and 132.0 (Xe). For experiments with labelled ammonia, product formation was additionally monitored at AMUs 46, 31, 30 ($^{15}N_2O$), 32 (O_2), 31 (^{15}NO), 30 ($^{15}N_2$), 29 ($^{15}N^{14}N$) and 20 (Ne). In sequential pulse experiments, pulses were repeated 10 times for each AMU and averaged to improve the signal-to-noise ratio. In single NO and N_2O pulse experiments the number of pulses per each AMU was 20. Transient responses obtained in these experiments were treated separately, i.e. without averaging. Ne (99.998%), Xe (99.99%), O_2 (99.995%), NO (99.5%), N_2O (99 %), $^{14}NH_3$ (99.98%) and $^{15}NH_3$ (99.9%) were used without further purification. Isotopically labelled ammonia was purchased from ISOTEC.

3. Results and discussion

3.1. Catalytic decomposition of NO and N_2O

Single pulsing of NO over Pt gauze treated in hydrogen has shown that NO decomposed to N_2 in the temperature range between 773 and 1073 K. N_2O was observed only at 773 K. Gas-phase oxygen was not detected in the whole temperature range. The formation of N_2 indicates that NO dissociates as suggested for different Pt catalysts [23–25]. Transient responses of NO, N_2O and N_2 corresponding to the first, fourth and ninth pulses recorded at respective AMU as well as molar fractions (in brackets) of these gas-phase components are exemplified in Fig. 1. The amount of decomposed NO as well as the amount of formed products decreases with the number of pulses. Since gas-phase O_2 was not detected and the amount of N_2O was considerably lower than that of decomposed NO, the inhibition of NO decomposition with the number of pulses is explained by blocking the active sites by oxygen atoms originating from NO dissociation. A similar observation was previously reported for NO decomposition over Pt(1 1 1) [15] and Pt(2 1 1) [26].

N_2 was also observed upon N_2O pulsing over hydrogen-treated Pt gauze. Molecular oxygen was detected in the gas phase only at 855 and 950 K. Similar to the experiments with NO, Pt activity towards N_2O decomposition decreases with number of NO pulses. Changes in the intensity of transient responses of N_2O, N_2 and O_2 at 855 K are shown in Fig. 2. The decrease in the amount of converted N_2O is accompanied by a decrease in the amount of formed N_2 and by a slight increase in the amount of O_2. Since the molar fraction of oxygen (ca. 4% at the end of experiments) was much lower than expected from oxygen balance (ca. 12%), it was assumed that those oxygen species, which remain on the surface, block active sites for N_2O decomposition. An increase in coverage by oxygen species favours, however, the formation of O_2, since gas-phase O_2 is formed via interaction of N_2O with adsorbed oxygen species according to the mechanistic scheme of N_2O decomposition under transient conditions [18]. Based on absence of O_2 in the gas-phase at 1050 K, it is suggested that oxygen species penetrates into the volume of Pt as reported for interaction of O_2 with hydrogen-treated Pt sponge at 1073 K [27]. This effect, however, considerably complicates the estimation of the amount of oxygen species on the surface, which could be available for reaction with NH_3. Therefore, Pt gauze treated in hydrogen is not suitable for the studies of ammonia oxidation by adsorbed oxygen species formed from different oxidants.

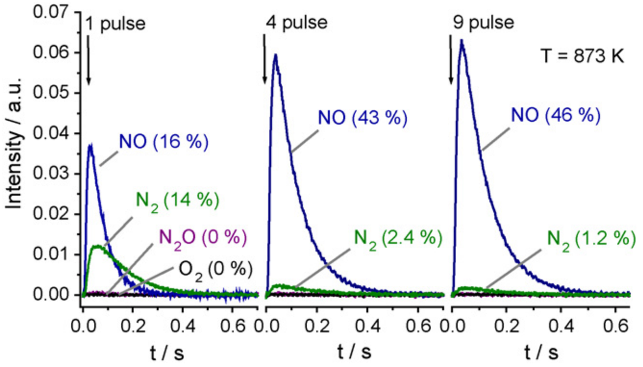

Fig. 1. Changes of transient responses and molar fractions of NO, N_2O, O_2 and N_2 with the number of NO pulses during NO decomposition at 873 K.

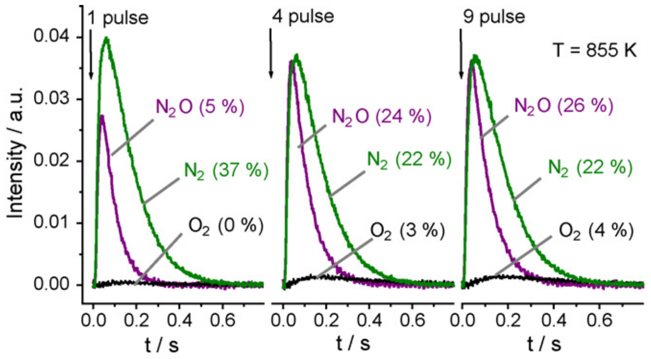

Fig. 2. Changes of transient responses and molar fractions of N_2O, O_2 and N_2 with the number of N_2O pulses during N_2O decomposition at 855 K.

In summary, the main difference between NO and N_2O is the fact that no gas-phase O_2 was observed upon NO decomposition, while N_2O decomposes yielding O_2. This experimental result indicates that dissociation/decomposition of NO and N_2O results in the formation of different oxygen species, which probably differ in their binding strength with Pt sites. In the next section selectivity of oxygen species formed from NO and N_2O for NH_3 activation is compared with that of oxygen species originating from O_2. The presented experiments were performed in a sequential pulse mode, i.e. ammonia was pulsed after the oxidant with a time interval of 0.2 s.

3.2. Product formation in sequential pulsing of O_2, N_2O or NO and NH_3

N_2 was the main nitrogen-containing product of ammonia oxidation (Fig. 3) with all the used oxidising agents (O_2, N_2O or NO). This result coincides with earlier studies performed over Pt and Pt/Rh gauze above 973 K [8]. Beside N_2, H_2 and H_2O were also formed in the NH_3 pulse. In contrast to single NH_3 pulsing over oxygen-treated Pt gauze [7], water was the main hydrogen-containing product at all temperatures in the present

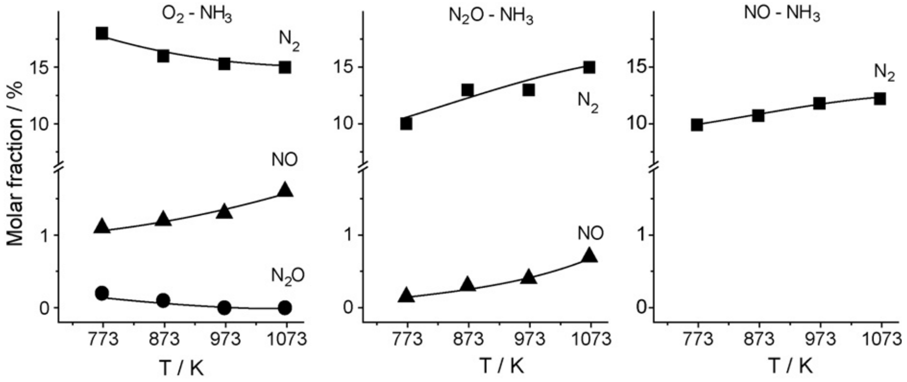

Fig. 3. Molar fractions of nitrogen-containing products formed in the NH_3 pulse vs. temperature during sequential pulsing of O_2 and NH_3, of N_2O and NH_3 as well as of NO and NH_3 with a time interval of 0.2 s.

experiments. Mieher and Ho have postulated [4] that NO formation takes place only if oxygen is left over after the reactions responsible for water formation are completed. Therefore, the prevailing formation of H_2O is a definite sign of at least local excess of oxygen, which assure NO formation in the sequential pulse experiments. Reaction pathways of N_2, H_2O and H_2 formation as well as the factors determining their contribution to the product formation in ammonia oxidation over Pt and Pt/Rh gauzes under transient conditions have been previously discussed in [7–9]; therefore, these aspects are mentioned below only if required for better understanding.

3.2.1. Sequential pulsing of O_2 and NH_3

When O_2 and NH_3 were sequentially pulsed over Pt gauze, reaction products, i.e. NO, N_2O and N_2, were observed in the NH_3 pulse only (Fig. 3). Transient responses of O_2, NO, N_2O and N_2 recorded at 773 K are shown in Fig. 4. The transient responses were normalised for better comparing their shapes and the order of appearance, from which important mechanistic information can be derived. A strong decrease in the intensity of oxygen transient response upon entering NH_3 (after ca. 0.2 s) indicates that oxygen species adsorbed on the Pt surface during the preceding O_2 pulse react with NH_3 before they can desorb. A very sharp transient response of NO appeared directly, after NH_3 entered the reactor. N_2O was detected with a short delay after NO. The transient response of N_2 was shifted to longer times as compared to those of the previous gas-phase products and had the broadest shape. Taking into account these observations, it is concluded that NO is the only primary product of ammonia oxidation by adsorbed oxygen species formed from O_2. The primary NO formation was reported earlier for ammonia oxidation over Pt and Pt/Rh gauzes with adsorbed oxygen species above 973 K [8]. The sharp shape of the NO signal clearly indicates that NO reacts further to N_2O and N_2. These secondary transformations of formed NO as well as the lower amount of oxygen species available on the surface due to oxygen desorption during first 0.2 s of the O_2 pulse explain the lower amount of NO (Fig. 3) as compared to the pulsing of NH_3/O_2 mixtures [7]. The shape and the order of appearance of the transient response of N_2O (Fig. 4) indicate that N_2O is also an intermediate in N_2 formation at ca. 10 Pa. The intermediate role of N_2O in N_2 formation in ammonia oxidation was earlier established for Pt and Pt/Rh catalysts at temperatures above 1023 K and pressures of 160 Pa [8,9]. The decrease of N_2O formation with temperature (Fig. 3) is explained by its catalytic decomposition at high temperatures in agreement with previous studies [18,28–30].

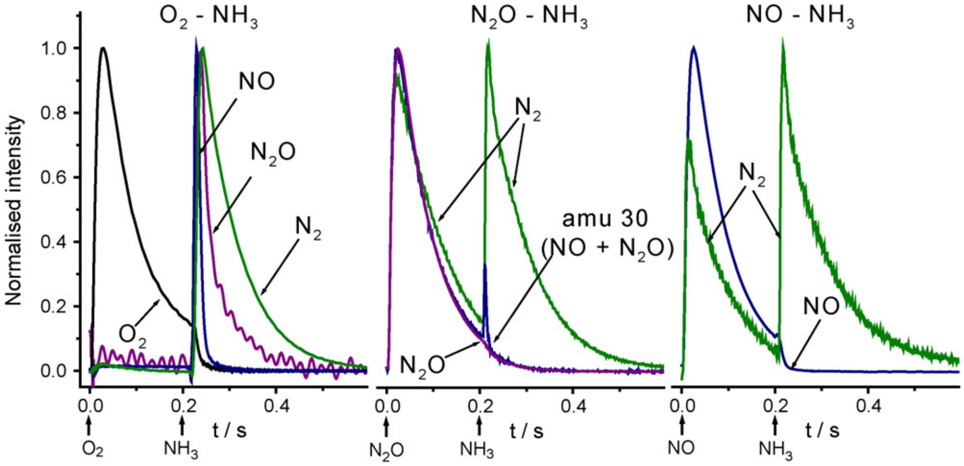

Fig. 4. Normalised responses of nitrogen-containing products recorded during sequential pulsing of O_2 and NH_3, of N_2O and NH_3 as well as of NO and NH_3 with a time interval of 0.2 s at 773 K.

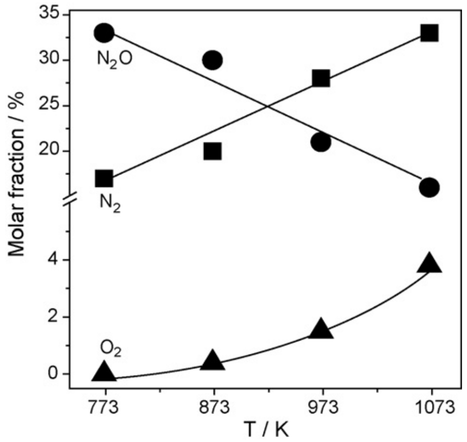

Fig. 5. Molar fractions of N_2O, N_2 and O_2 formed in the N_2O pulse vs. temperature when N_2O and NH_3 were pulsed sequentially with time interval of 0.2 s.

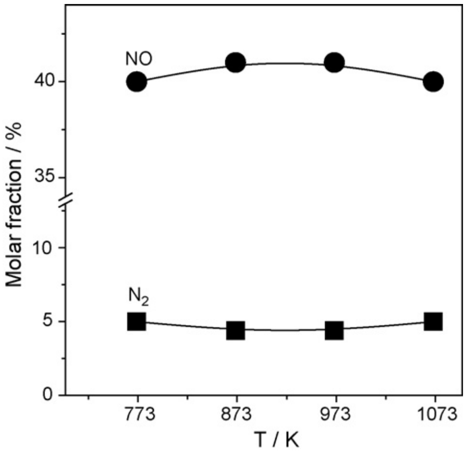

Fig. 6. Molar fractions of NO and N_2 formed in NO pulse vs. temperature when NO and NH_3 were sequentially pulsed with time interval of 0.2 s.

3.2.2. Sequential pulsing of N_2O and NH_3

In these experiments, reaction products were observed in both N_2O and NH_3 pulses (Fig. 3). The subsequent discussion starts with the description of product formation in the oxidant pulse followed by that in the NH_3 pulse.

N_2 and O_2 were detected in the N_2O pulse. The temperature dependence of the molar fractions of N_2O, N_2 and O_2 is shown in Fig. 5. In agreement with earlier observations [18,28–30] the amount of decomposed N_2O as well as the amount of N_2 and O_2 formed increased with temperature. However, similar to the N_2O decomposition over hydrogen-treated Pt gauze, the amount of formed O_2 was significantly lower (ca. 4%) than expected from O_2 balance for stoichiometric N_2O decomposition (ca. 17%). The low amount of gas-phase O_2 indicates that oxygen species originating from N_2O stay on the surface until they react with subsequently pulsed ammonia.

NO, N_2, H_2 and H_2O were detected in the NH_3 pulse. NO was identified taking into consideration the difference of the shapes of the transient responses at AMU 44 and 30 after 0.2 s (Fig. 4). In the time interval of 0–0.2 s the signals at both AMUs belong to N_2O and, respectively, their shapes are the same. After 0.2 s the intensity of the signal recorded at AMU 44 decreased continually, whereas the signal at AMU 30.0 shows an additional maximum between 0.2 and 0.23 s. Based on this experimental observation, it is concluded that NO is formed via NH_3 oxidation by oxygen species formed in the N_2O pulse. The narrow shape of the NO transient response (Fig. 4) indicates that similar to sequential pulsing of O_2 and NH_3, NO reacts subsequently with NH_3. The amount of nitrogen-containing products (NO and N_2) increases with temperature (Fig. 3). The observed increase is ascribed to the temperature-induced increase in the coverage by oxygen species provided by N_2O.

3.2.3. Sequential pulsing of NO and NH_3

Similar to the N_2O-NH_3 experiments, sequential pulsing of NO and NH_3 resulted in product formation in both NO and NH_3 pulses (Fig. 4). N_2 was the only gas-phase product of NO decomposition (Fig. 6). As in single NO pulse experiments, no O_2 was detected in the gas phase. The absence of O_2 but the presence of N_2 evidences that oxygen species formed from NO stay on the catalyst surface, until NH_3 is pulsed.

Fig. 4 illustrates transient responses of sequential pulsing of NO and NH_3. The transient response of NO decreases strongly, when NH_3 enters the reactor. This decrease indicates that adsorbed NO species interact with NH_3. Mechanistic aspects of these interactions were discussed previously [9,31]. The contribution of the interactions between adsorbed NO molecules and NH_3 fragments towards overall N_2 formation was determined from experiments with isotopically labelled ammonia ($^{15}NH_3$). An application of $^{15}NH_3$ allows distinguishing the source of nitrogen atoms in the product molecules and estimating the upper contribution of the reaction of NO molecules with ammonia fragments. In these experiments NO and $^{15}NH_3$ were pulsed sequentially in the same manner as in the experiments with non-labelled NH_3. The highest molar fraction of $^{15}N^{14}N$ detected in the $^{15}NH_3$ pulse at 1073 K did not exceed 17% of total N_2 formation in the NH_3 pulse. Therefore, the oxidation of NH_3 by oxygen species originating from NO was the main process of nitrogen formation in sequential pulsing of NO and NH_3.

No relevant signs for NO formation were detected in the NH_3 pulse. The absence of NO in the NH_3 pulse was proven by experiments with isotopically labelled NH_3 ($^{15}NH_3$). In this case, ^{15}NO formed in the NH_3 pulse can be distinguished from previously pulsed NO, since these NO isotopes have different characteristic AMUs (31 and 30, respectively). The absence of NO in these experiments cannot be related to the extremely low coverage by oxygen, since. In order to compare the amount of oxygen species formed from NO and N_2O, respective oxygen coverage was calculated as a difference between the amount of pulsed molecules of oxidant and the amount of oxidant detected at the reactor outlet. For experiments with N_2O, the amount of oxygen atoms removed as gas-phase O_2 was respectively subtracted. The coverage by oxygen species originating from N_2O was estimated to be 0.06 assuming 2×10^{15} surface Pt atoms. During sequential pulsing of NO and NH_3, the coverage by oxygen species amounted to 0.1. Based on the above results, it was concluded that oxygen species formed from O_2 or N_2O

differ from those from NO in their reactivity/selectivity towards ammonia oxidation to NO. This conclusion supports the concept of different (weakly and strongly bound) oxygen species involved in the product formation, intuitively suggested for ammonia oxidation [8].

The difference between O_2 (N_2O) and NO in providing various oxygen species of different selectivity may be related to the process of oxidant activation. This assumption is supported by our experimental data in Section 3.1 on direct NO and N_2O decomposition over hydrogen-treated Pt gauze. In contrast to N_2O, no gas-phase O_2 was observed upon NO decomposition, although N_2 (decomposition product) was detected in the both experiments. A difference in desorption behaviour of oxygen species formed from O_2 and NO, repeatedly reported in literature [14–16], indicates that oxygen species formed from these two oxidants differ in the strength of binding to Pt. Desorption of oxygen species formed via NO dissociation over polycrystalline Pt achieves its maximum at temperatures being ca. 200 K higher than that of oxygen species formed from O_2 [14]. This is also valid for a Pt(1 1 1) surface; however, the difference between desorption maxima of oxygen species originating from O_2 and NO is less marked than for polycrystalline Pt and amounts to ca. 100 K [15,16]. Assuming that polycrystalline Pt consist mainly of domains with (1 1 1) orientations, the difference in the oxygen desorption pattern can be ascribed to the extremely marked structure sensitivity of NO dissociation as compared to that of O_2. The following activity order of different Pt surfaces towards NO decomposition was established: Pt(1 0 0) > Pt(1 1 0) > Pt(1 1 1) [32]. Pt(1 0 0) is able to decompose 50% of adsorbed NO [32], whereas over Pt(1 1 1) NO decomposition occurs mainly on defect sites [33]. According to this aspect, it is suggested that oxygen atoms originating from NO are located on defects or special sites with certain geometry and are mainly strongly bound, whereas oxygen atoms formed from O_2 or N_2O do not adsorb selectively. Respectively, a significant part of the latter species is bound less strongly than species adsorbed on defects. XPS characterisation of the catalyst treated in a flow of oxygen at 10^5 Pa have shown that oxygen atoms of surface PtO_x can be neglected in the present scheme, since no signs of surface Pt oxides were found. Moreover, in the studied temperature range their existence is unlikely, since a PtO_x phase is stable on the surface of single crystals under UHV conditions only at temperatures up to 873 K [34].

Alternatively, the weakly and strongly bound oxygen species can be ascribed to molecularly and atomically adsorbed oxygen species, respectively. The adsorbed molecular oxygen is very active species, which reacts with hydrazine [32] and hydrogen atoms [35] on Pt (1 1 1) at 130 and 105 K, respectively. Direct participation of oxygen molecules has been previously suggested for oxidation of methane and methanol reactions at higher temperatures. Molecular beam studies of methane oxidation on Pt(1 1 0) at 650 K [13] indicated a parallel surface reaction of adsorbed carbon species formed from CH_4 with short-lived adsorbed oxygen molecules and oxygen atoms formed by dissociation of these oxygen molecules. During oxidation of methanol over Pt(1 1 1), studied in vacuum at 100 K by means of IRAS [12], oxygen molecules participated directly in formation of formate intermediates. The existence of the latter species was also proven for steady-state methanol oxidation under atmospheric pressure and temperatures from 330 to 400 K.

According to the mechanistic concept of N_2O decomposition over Pt gauze under transient conditions [18], oxygen molecules are formed from N_2O. In contrast to NO dissociation, molecularly adsorbed oxygen also originates upon activation of gas-phase O_2 [36,37] and is a precursor in the formation of atomically adsorbed oxygen species. The presence of O_2 in the gas-phase in O_2-NH_3 and N_2O-NH_3 sequential pulse experiments represents the decisive difference to experiments with NO. This fact is consistent with our assumption that molecular forms of oxygen might be responsible for NO formation. The lower amount of NO formed in N_2O-NH_3 sequential pulsing as compared to experiments with O_2 is explained by limited O_2 formation via N_2O decomposition.

The main argument against the direct participation of adsorbed oxygen molecules in ammonia oxidation is their fast dissociation on platinum and respectively the absence of experimental evidence for the presence of these species at reaction temperatures. This argument is based on the UHV studies of oxygen interaction with well-defined and clean Pt surfaces of single crystals. However, this situation may be different for industry-relevant reaction conditions, when oxygen partial pressure is considerably higher than in surface science studies. For example, other adsorbats can change the surface residence time of adsorbed oxygen molecules due to a decrease in the amount of free Pt sites required for dissociation of O_2 molecules or even their stabilization, as observed by Mieher and Ho in UHV [4] for molecular oxygen co-adsorbed with ammonia on a Pt(1 1 1) surface in the temperature range from 144 to 160 K. According to these aspects, neglecting of oxygen molecules as active species only from the ‘‘common sense’’ is not justified. We hope that the present work will motivate further detailed studies, which will eventually provide decisive evidences in support or rejection of alternatives suggested in this publication.

4. Conclusions

Ammonia oxidation over Pt gauze by O_2, N_2O and NO was studied by means of transient experiments in vacuum, where the oxidant and ammonia were sequentially pulsed with a time delay of 0.2 s. The obtained results revealed that the nature of oxygen species plays a crucial role in NO formation. Oxygen species originating from N_2O and O_2 were able to form NO from NH_3 in contrast to oxygen species formed from NO. It is suggested that the difference in the selectivity of these oxygen species towards subsequent ammonia oxidation is determined by the strength of their binding, i.e. weakly bound oxygen species are required for NO formation. The formation of weakly and strongly bound oxygen species can be related to the different surface sites required for the dissociation of the oxidants. Alternatively weakly bound species may be assigned to adsorbed oxygen species of bi-atomic nature. In that case, the selectivity of oxygen species towards NO formation can be related to the ability of the oxidant for generation of adsorbed oxygen atoms and molecules.

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References

[1] J.L. Gland, V.N. Korchak, J. Catal. 53 (1978) 9.

[2] M. Asscher, W.l. Guthrie, T.-H. Lin, G.A. Somorjai, J. Phys. Chem. 88 (1984) 3233.

[3] J.M. Bradley, A. Hopkinson, D.A. King, J. Phys. Chem. 99 (1995) 17032.

[4] W.D. Mieher, W. Ho, Surf. Sci. 322 (1995) 151.

[5] A.C.M. van den Broek, J. van Grondelle, R.A. van Santen, J. Catal. 185 (1999) 297.

[6] E.V. Rebrov, M.H.J.M. de Croon, J.C. Schouten, Chem. Eng. J. 90 (2002) 61.

[7] M. Baerns, R. Imbihl, V.A. Kondratenko, R. Kraehnert, W.K. Offermans, R.A. van Santen, A. Scheibe, J. Catal. 232 (2005) 226.

[8] J. Pérez-Ramírez, E.V. Kondratenko, V.A. Kondratenko, M. Baerns, J. Catal. 227 (2004) 90.

[9] J. Pérez-Ramírez, E.V. Kondratenko, V.A. Kondratenko, M. Baerns, J. Catal. 229 (2005) 303.

[10] E.P.J. Mallens, J.H.B.J. Hoebnik, G.B. Marin, Catal. Lett. 33 (1995) 291.

[11] M. Fathi, F. Monnet, Y. Schuurman, A. Holmen, C. Mirodatos, J. Catal. 190 (2000) 439.

[12] M. Endo, T. Matsumoto, J. Kubota, K. Domen, C. Hirose, Surf. Sci. 441 (1999) L931.

[13] D.T.P. Watson, J.J.W. Harris, D.A. King, J. Phys. Chem. B 106 (2002) 3416.

[14] M.J. Mummey, L.D. Schmidt, Surf. Sci. 109 (1981) 43.

[15] J.L. Gland, B.A. Sexton, Surf. Sci. 94 (1980) 355.

[16] J.L. Gland, B.A. Sexton, G.B. Fischer, Surf. Sci. 95 (1980) 587.

[17] A.-P. Egl, F. Eisert, A. Rosen, Surf. Sci. 382 (1997) 57.

[18] V.A. Kondratenko, M. Baerns, J. Catal. 225 (2004) 37.

[19] M. Peuckert, H.P. Bonzel, Surf. Sci. 145 (1984) 239.

[20] R. Kraehnert, E. Kondratenko, J. Radnik, M. Schneider, L. Wilde, M. Baerns, D. Herein, in: Proceedings of the 13th International Congress on Catalysis, Paris, France, 2004.

[21] R. Kraehnert, E. Kondratenko, J. Radnik, M. Schneider, L. Wilde, D. Herein, XXXVII, Jahrestreffen Deutscher Katalytiker, Weimar, Germany, 2004, p. 95.

[22] J.T. Gleaves, G.S. Yablonsky, P. Phanawadee, Y. Schuurman, Appl. Catal. A 160 (1997) 55.

[23] S. Sugai, K. Takeuchi, T. Ban, H. Miki, K. Kawasaki, Surf. Sci. 282 (1993) 67.

[24] C. Rottländer, R. Andorf, C. Plog, B. Krutzsch, M. Baerns, J. Catal. 169 (1997) 400.

[25] C.J. Weststrate, J.W. Bakker, E.D.L. Rienks, C.P. Vinod, S. Lizzit, L. Petaccia, A. Baraldi, B.E. Nieuwenhuys, Surf. Sci. 600 (2006) 1991.

[26] R.J. Mukerji, A.S. Bolina, W.A. Brown, Surf. Sci. 547 (2003) 27.

[27] E.P.J. Mallens, A reaction path analysis of the catalytic partial oxidation of methane by transient experiments, Ph.D. thesis, Eindhoven, 1996, p. 146.

[28] G.A. Papapolymerou, L.D. Schmidt, Langmuir 1 (1985) 488.

[29] C.G. Takoudis, L.D. Schmidt, J. Catal. 80 (1983) 274.

[30] L. Riekert, M. Staib, Ben. Bunsenges. Physik. Chem. 67 (9) (1963) 976.

[31] V.A. Kondratenko, M. Baerns, Appl. Catal. B, in press.

[32] R.J. Gorte, L.D. Schmidt, J.L. Gland, Surf. Sci. 109 (1981) 367.

[33] C.T. Campbell, G. Ertl, J. Segner, Surf. Sci. 115 (1982) 309.

[34] M. Salmeron, L. Brewer, G.A. Somorjai, Surf. Sci. 112 (1981) 207.

[35] M.Y. Smirnov, V.V. Gorodetskii, J.H. Block, J. Mol. Catal. A: Chem. 107 (1996) 359.

[36] C.T. Campbell, G. Ertl, H. Kuipers, J. Segner, Surf. Sci. 107 (1981) 220.

[37] C. Puglia, A. Nilsson, B. Hernnäs, O. Karis, P. Bennich, N. Martensson, Surf. Sci. 342 (1995) 119.