Catalysis Letters Vol. 91, Nos. 3–4, December 2003 (© 2003)

Transient studies of direct N_2O decomposition over Pt–Rh gauze catalyst. Mechanistic and kinetic aspects of oxygen formation

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Received 22 May 2003; accepted 24 September 2003

For elucidating the mechanistic aspects of oxygen formation during N_2O decomposition over commercial woven Pt–Rh gauze, transient experiments were carried out in the temporal analysis of products (TAP) reactor by pulsing $N_2{}^{16}O$ over ^{18}O-pretreated gauze catalyst at temperatures typical of industrial ammonia burners (1073–1273 K). The transient responses of N_2O and the products of its decomposition (O_2 and N_2) were fitted to two different mechanistic models. From the isotopic studies and the fitting of transient experiments, two separate routes of oxygen formation during catalytic N_2O decomposition have been identified. Oxygen is produced via both (i) interaction of N_2O with adsorbed oxygen species formed from N_2O and (ii) recombination of adsorbed oxygen species on the catalyst surface. The relative contribution of these reaction pathways depends on the reaction temperature.

KEY WORDS: N_2O decomposition; platinum; rhodium; gauze; mechanism; kinetics; transient experiments; TAP; isotope.

1. Introduction

Nitrous oxide (N_2O) has been identified as a strong greenhouse gas and a significant contributor to the destruction of ozone in the stratosphere. During the manufacture of weak nitric acid, N_2O is produced as an unwanted by-product of the oxidation of ammonia over the Pt–Rh gauze catalysts. The high impact of N_2O on the environment as well as the ongoing agreements and prospective regulations call for the development of efficient and economical systems for N_2O mitigation in this source [1,2]. From a fundamental perspective, the mechanism of catalytic ammonia oxidation, and more specifically the steps involved in N_2O formation, have not been unambiguously unraveled [2]. An even more fundamental question is the ability of noble metal gauze catalysts to decompose N_2O at typical reaction temperatures in the burner (1073–1273 K), and if so, to what extent.

Many studies have been devoted to investigate the N_2O decomposition reaction over platinum catalysts in different forms: wires [3–5], sponges [6], gauzes [7], and foils [8] in a wide range of temperatures (760–1500 K) and partial pressures of N_2O (0.5–53 kPa) and O_2 (0–66 kPa). The reaction rate was described as proportional to the partial N_2O pressure, with O_2 having a negative effect due to reversible adsorption [3–9]. Also, rhodium catalysts have been studied in the reaction, including rhodium foils [8], rhodium black [10], and supported rhodium catalysts [11]. To the author's knowledge, there is no available experimental data on N_2O decomposition over Pt–Rh alloys at high temperatures.

Two different mechanisms of N_2O decomposition over oxide and metal catalysts have been suggested [12]. The reaction is described by the nonreversible formation of active atomic oxygen species (O-s) deposited by N_2O (equation (1)), followed by subsequent formation of gas-phase oxygen via reversible recombination of two adsorbed oxygen species (equation (2), Langmuir–Hinshelwood mechanism). Originally, this mechanism was suggested by Hinshelwood *et al.* [3] to explain the inhibiting effect of oxygen on the decomposition of N_2O over platinum wires. Alternatively, Riekert *et al.* [9] have postulated that chemisorbed oxygen species formed from N_2O can be removed from platinum surface via a direct interaction with N_2O (equation (3), Eley–Rideal mechanism). Inhibition by oxygen was explained by the fact that gas-phase oxygen adsorbs over the platinum surface initially as a molecular oxygen blocking active sites for N_2O decomposition (equation (4)).

$$N_2O + s \longrightarrow N_2 + O - s \tag{1}$$

$$2O - s \rightleftarrows O_2 + 2s \tag{2}$$

$$N_2O + O - s \longrightarrow N_2 + O_2 + s \tag{3}$$

$$O_2 + s \rightleftarrows O_2 - s \tag{4}$$

It has to be noted that the above reaction schemes have been suggested taking into account the inhibiting effect of gas-phase oxygen on N_2O decomposition. However, no experimental evidences for O_2 formation have been provided. Besides, previous studies have been mainly

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1011-372X/03/1200–0211/0 © 2003 Plenum Publishing Corporation

carried out over single metallic (platinum or rhodium) systems (foils, wires) in closed vessels, which might be limited by diffusion limitations particularly at high temperatures. Therefore, a more specific experimental approach is required to assess the mechanism of N_2O decomposition; in particular, the route(s) leading to oxygen production over noble metal alloy catalysts in the form of gauze, as typically applied in NH_3 oxidation during nitric acid production, where N_2O is produced. In this study, we have applied the temporal analysis of products (TAP) technique in combination with an isotopic technique in order to derive mechanistic and kinetic insights into formation of oxygen during N_2O decomposition over a commercial woven Pt–Rh gauze catalyst at high temperatures (1073–1273 K). This technique as compared to the previously used one, enables the study of the primary reaction steps of interaction between gas-phase molecules and the catalytic active surfaces in the absence of mass transport limitations.

2. Methods

2.1. Catalyst and procedures

Commercial woven Pt(95%)–Rh(5%) gauze catalyst (K.A. Rasmussen, $1024\,\mathrm{mesh/cm^2}$ and wire diameter of $76\,\mu\mathrm{m}$, figure 1) was used for studying transient decomposition of N_2O in the temporal analysis of products (TAP) reactor. The TAP-2 reactor system has been described in detail elsewhere [13]. One piece of the as-received gauze of ca. $28\,\mathrm{mm}^2$ and weighing 20 mg was placed between two layers of quartz in the isothermal zone of a quartz reactor (6 mm i.d.). Prior to the experiments, the as-received Pt–Rh gauze was pretreated in an oxygen flow for 2 h at 1273 K and ambient pressure. Then the oxidized gauze was exposed to vacuum (ca. 10^{-4} Pa), and pulse experiments were carried out in the temperature range of 1073–1273 K. Pulses containing a small amount of reactants diluted by an inert gas ($10^{14} - 5 \times 10^{14}$ molecules per pulse) were injected in the reactor via two high-speed valves. For such pulse sizes, the transient responses are a function of gas–solid interactions and not influenced by collisions between gas-phase molecules. Thus, primary heterogeneous reaction steps are under investigation. Two types of pulse experiments were carried out:

1. Single-pulse experiments. Gas mixtures of a certain composition ($^{16}O_2 : Ne = 1:1$ or $N_2O : Ne = 1:1$) were pulsed into the reactor, and transient responses were monitored at the reactor outlet using a quadrupole mass spectrometer (Hiden Analytical) at AMUs related to feed molecules, reaction products, and inert gas. For each AMU, pulses were repeated 10 times and averaged to improve the signal-to-noise ratio.

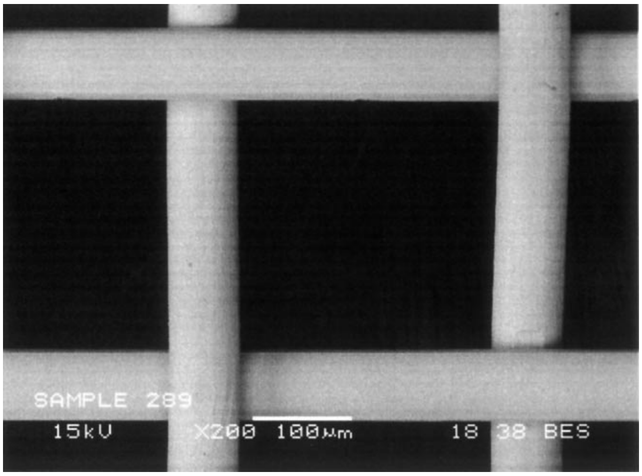

Figure 1. SEM micrograph of the Pt–Rh gauze used in this study.

2. Sequential pulse experiments. Gas mixtures of a certain composition ($^{18}O_2 : Ne = 1:1$, $N_2O : Xe = 1:1$, and $^{16}O_2 : Xe = 1:1$) were sequentially pulsed from two pulse valves with different time delays. The following interactions were studied:

- $^{16}O_2$ and N_2O or $^{18}O_2$ and N_2O

As in the case of single-pulse experiments, pulses were repeated 10 times for each AMU and averaged to improve the signal-to-noise ratio.

N_2O (2.0), Ne (4.5), Xe (4.0), $^{16}O_2$ (4.5), and $^{18}O_2$ (96–98% ^{18}O) were used without additional purification. Isotopically labeled oxygen was purchased from Cambridge Isotope Laboratory. For mass spectroscopic identification of the different compounds, the following AMUs were used: 130 (Xe), 44 (N_2O), 36 ($^{18}O_2$), 34 ($^{18}O^{16}O$), 32 (O_2, $N^{18}O$), 30 (N_2O, NO), 28 (N_2O, N_2), and 20 (Ne).

2.2. Modeling

For deriving kinetic parameters of N_2O decomposition over the Pt–Rh gauze, transient responses of N_2O, N_2, and O_2 were fitted to two different kinetic models, with the same number of parameters. The models were selected taking into account the different reaction routes of oxygen formation. The parameter estimation procedure was based on a numerical solution of partial differential equations [14], which described the processes of diffusional transport, adsorption/desorption, and reaction in the TAP-reactor.

Model 1. N_2O decomposition and reversible dissociative adsorption of oxygen occur on the same active site

This model assumes that there is only one type of active surface site, "s", responsible for N_2O decomposition. The formation of gas-phase oxygen takes place via the reversible recombination of surface oxygen species previously deposited by N_2O. This means that gas-phase oxygen and N_2O compete for the same active sites

$$N_2O + s \xrightarrow{k_1} N_2 + O - s$$

$$2O - s \underset{k_3}{\overset{k_2}{\rightleftarrows}} O_2 + 2s.$$

Model 2. N_2O decomposition with two independent routes of oxygen formation

This model is similar to Model 1, but the recombination of two oxygen species formed from N_2O is irreversible. Besides, molecular oxygen can also be formed via the reaction of gas-phase N_2O with surface oxygen species deposited by N_2O in the first step

$$N_2O + s \xrightarrow{k_1} N_2 + O - s$$

$$N_2O + O - s \xrightarrow{k_2} N_2 + O_2 + s$$

$$2O - s \xrightarrow{k_3} O_2 + 2s.$$

3. Results and discussion

3.1. *TAP studies with nonlabeled molecules*

Nitrogen and oxygen were the only gas-phase products of N_2O decomposition over the Pt–Rh gauze in the temperature range from 1073 to 1273 K. During single pulsing of N_2O, the degree of N_2O conversion was ca. 60% at 1073 K and increased up to ca. 80% at 1273 K. Thermal decomposition of nitrous oxide over quartz filling of the TAP-reactor did not exceed 6% at 1073 K, but increased strongly at higher temperatures. Therefore, all the transient experiments were performed at 1073 K. In order to prove if the presence of O_2 influences the decomposition of N_2O in transient experiments, O_2 and N_2O were sequentially pulsed with different time delays between O_2 and N_2O pulses. The results are presented in figure 2. When O_2 and N_2O are simultaneously pulsed ($\Delta t = 0$s), the degree of N_2O conversion is ca. 40%. The N_2O conversion increases up to 60% with an increase in the time delay up to 1 s. This indicates that oxygen inhibits the decomposition of N_2O over the Pt–Rh gauze. This agrees with previous studies on N_2O decomposition over Pt- and Rh-based catalysts [3,4,6,8].

The models described in Section 2.2 were used for fitting the experimental transient responses of nitrous oxide, nitrogen, and oxygen during N_2O single pulsing at 1073 K. This temperature was chosen since noncatalytic N_2O decomposition over the reactor material (SiO_2) can be neglected in comparison to the catalytic N_2O decomposition over the Pt–Rh gauze. The parameter estimation in the fitting of the pulse responses was performed with a wide range of possible values for the rate constant (k_i) and total number of adsorption sites (C_t), using genetic and simplex algorithms implemented in the software applied [14]. Discrimination between these two models is given in figure 3, where the simulated and experimental responses of N_2O and products of its decomposition are shown. Model 1 cannot correctly describe oxygen formation, and thus no set of parameters was found to fit the measured responses in this case. The best fitting of the transient responses of N_2O, N_2, and O_2 was obtained assuming Model 2. Kinetic parameters of N_2O decomposition assuming this model are given in table 1. The main objective of this work was to derive mechanistic insights into the routes of oxygen formation during N_2O decomposition over Pt–Rh gauze using a transient technique, rather than the development of a detailed kinetic model. Nevertheless, the above model discrimination already suggests that oxygen formation over this system occurs via both Langmuir–Hinshelwood (equation (2)) and Eley–Rideal (equation (3)) mechanisms. It is surprising that Model 2, giving the best fit, does not include any reaction step accounting for the inhibiting effect of oxygen on N_2O decomposition. This can be explained by the fact that under TAP-reactor conditions, readsorption of oxygen formed from N_2O does not strongly influence the shape of oxygen-transient response, as long as this step is slower than the formation of oxygen from N_2O. The data on inhibition of N_2O decomposition by gas-phase oxygen (figure 2) are in agreement with this assumption. Under TAP-reactor conditions, the inhibiting effect of oxygen is considerably lower than under steady state conditions, where the rate of N_2O decomposition decreases ca. 10 times when oxygen is added at similar partial pressures as N_2O [15]. For steady state studies, oxygen adsorption and desorption are assumed to be in quasi-equilibrium under N_2O decomposition conditions. In dynamic operation (transient kinetics), this limitation is absent, since gas-phase oxygen is continuously removed from the reactor. This may be the cause for the discrepancies found in the influence of oxygen on N_2O decomposition under transient and steady state conditions. In order to

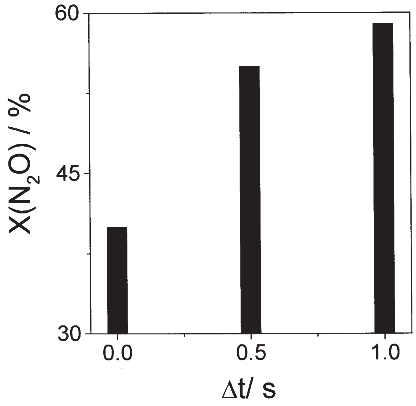

Figure 2. Conversion of N_2O versus time delay during sequential pulsing of O_2 and N_2O over the Pt–Rh gauze at 1073 K.

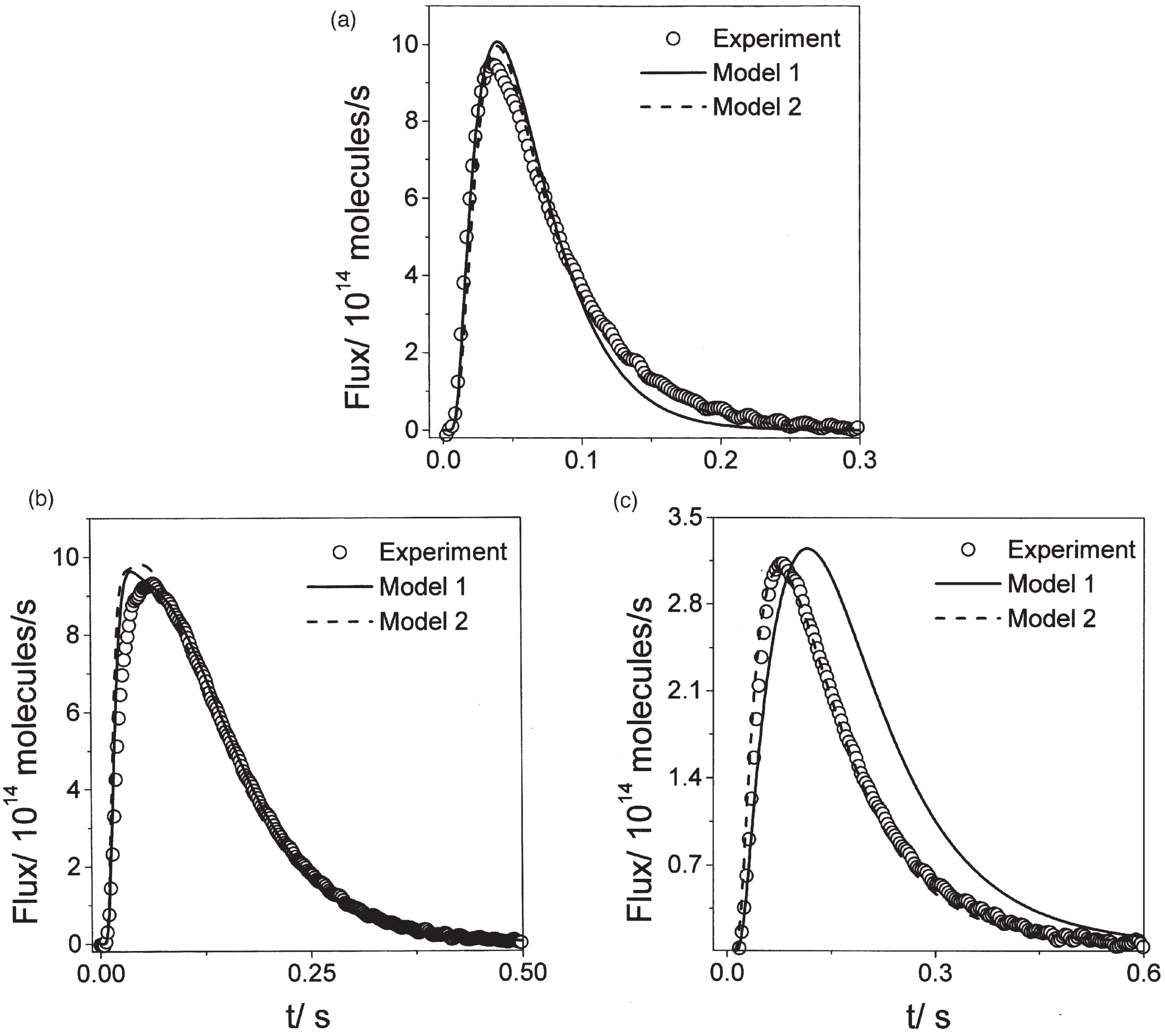

Figure 3. Comparison between experimental and simulated responses of (a) N_2O, (b) N_2, and (c) O_2 during single pulsing of N_2O over the Pt–Rh gauze at 1073 K.

support this idea, we repeated the fitting procedure over Model 2, assuming that the reaction step of oxygen formation via recombination of two surface oxygen species is reversible. In this case, sensitivity analysis shows that the objective function is nonsensitive to the parameter of oxygen adsorption over two catalyst sites.

Table 1
Kinetic parameters of N_2O decomposition over Pt–Rh gauze at 1073 K assuming Model 2

Kinetic parameter	Value
$C_t \cdot k_1$ (s^{-1})	5.9×10^3
$C_t \cdot k_3$ (s^{-1})	5.1×10^1
k_2 (m^3_{cat} mol^{-1} s^{-1})	3.1×10^2

Note: $C_t = C_o + C_s$, where C_o and C_s are concentrations of adsorbed oxygen species and free active catalyst sites respectively.

3.2. *TAP studies with isotopes*

To further investigate the mechanism of N_2O decomposition, an isotopic exchange technique was used. The idea was to follow the distribution of isotopic labeled oxygen in gas-phase oxygen. In these experiments, the Pt–Rh gauze was pretreated at a certain reaction temperature by $^{18}O_2$ pulsing in vacuum. After ca. 1 min, N_2O was pulsed over the pretreated gauze at the pretreatment temperature. The transient responses of N_2O decomposition over the ^{18}O-pretreated Pt–Rh gauze at 1073 and 1173 K are presented in figure 4. Nitrogen, labeled ($^{16}O^{18}O$) and nonlabeled ($^{16}O_2$) oxygen were detected at the reactor outlet, $^{16}O_2$ being the main oxygen isotope. $^{18}O_2$ signal was at the detection limit and is not shown in figure 4. From the data presented in figure 4, it can be observed that the transient response of labeled oxygen ($^{16}O^{18}O$) is significantly shifted to shorter times than the nonlabeled

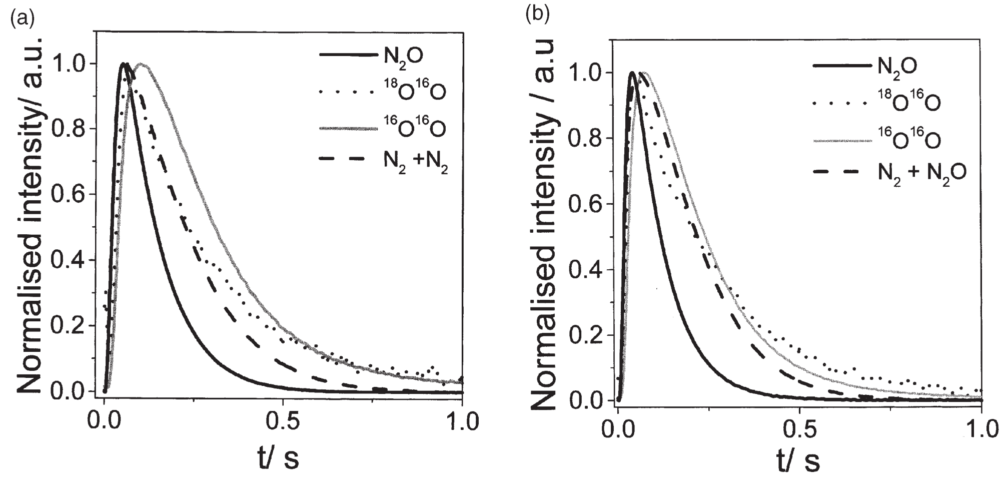

Figure 4. Normalized transient responses of N_2O pulsing at (a) 1073 K and (b) 1173 K over Pt–Rh gauze, which was pretreated at the reaction temperature by $^{18}O_2$ pulsing.

oxygen ($^{16}O_2$). This means that the formation of labeled oxygen is faster than the formation of nonlabeled oxygen. On the basis of the above experimental and fitting results as well as on literature data [3,4,6], the following mechanistic scheme for N_2O decomposition can be assumed considering the presence of preadsorbed labeled oxygen species and their participation in N_2O decomposition and oxygen formation (equations (5–9)). Equation (5) describes N_2O decomposition over a reduced active metal site. Formation of gas-phase oxygen occurs via interaction of N_2O with active oxygen species (equations (6) and (8)). Oxygen is additionally formed via equations (7) and (9).

$$N_2{}^{16}O + s \longrightarrow N_2 + {}^{16}O - s \tag{5}$$

$$N_2{}^{16}O + {}^{16}O - s \longrightarrow N_2 + {}^{16}O_2 + s \tag{6}$$

$${}^{16}O - s + {}^{16}O - s \rightleftarrows {}^{16}O_2 + 2s \tag{7}$$

$$N_2{}^{16}O + {}^{18}O - s \longrightarrow N_2 + {}^{16}O{}^{18}O + s \tag{8}$$

$${}^{16}O - s + {}^{18}O - s \rightleftarrows {}^{16}O{}^{18}O + 2s \tag{9}$$

From the above reaction scheme, the transient responses of $^{16}O^{18}O$ and $^{16}O_2$ should have the same shape, if equation (9) would be the only route of formation of labeled oxygen. If $^{16}O^{18}O$ is formed as a product of secondary interaction between $^{16}O_2$ originated from N_2O and surface ^{18}O species, its transient response must be delayed in comparison to the response of $^{16}O_2$, since $^{16}O_2$ has to be formed previous to its participation in the oxygen isotopic exchange. According to equations (6) and (8) and taking into account the presence of surface ^{18}O species in the experiments with N_2O, transient responses of $^{16}O_2$ and $^{16}O^{18}O$ formed during N_2O decomposition should be shifted in the same order as presented in figure 4. This conclusion is based on the fact that the formation of gas-phase $^{16}O_2$ can only occur if atomic ^{16}O species are previously formed from N_2O (equation (6)), and, subsequently, they can react with N_2O producing gas-phase oxygen, while $^{18}O^{16}O$ is formed via interaction of preadsorbed ^{18}O species with N_2O. However, from the results presented in figure 4, it is obvious that the shape of transient responses of labeled ($^{18}O^{16}O$) and nonlabeled oxygen ($^{16}O_2$) changes differently with an increase in temperature. The time difference between the maxima of the $^{18}O^{16}O$ and $^{16}O_2$ transient responses becomes lower and the intersection of $^{18}O^{16}O$ and $^{16}O_2$ transient responses is shifted to higher intensities. On the basis of these results, two separate routes of oxygen production during N_2O decomposition over woven Pt–Rh gauze are plausible:

1. Recombination of adsorbed oxygen species (equations (7) and (9)).
2. Reaction of N_2O (gas-phase or adsorbed) with adsorbed oxygen species via equations (6) and (8).

At this stage, it is not possible to draw a definitive conclusion on which mechanism prevails at a certain temperature. Still, a certain dependence has been found. From a kinetic point of view, it would be expected that the recombination of two surface oxygen species (equations (7) and (9)) will be accelerated by temperature stronger than the oxygen formation (equations (6) and (8)). Apparent activation energies reported in literature for N_2O decomposition over platinum wires are in the range of 136–151 kJ/mol [3,5,16], while the energy of recombination of oxygen species with the formation of gas-phase oxygen over Pt(111) was reported to be higher [17,18]. This energy is a function of the oxygen coverage and varies from 180 to 214 kJ/mol with a decrease in coverage by oxygen species. It can also be expected that Langmuir–Hinshelwood mechanism of oxygen formation will prevail under steady state ambient pressure conditions, because coverage by oxygen species is higher, and, therefore, recombination of oxygen species, which is reaction of second order with respect to the coverage, is increased stronger than equation (6). Our future studies aim at elucidating the mechanism of N_2O decomposition over pure platinum and Pt–Rh gauzes under steady state ambient pressure conditions and establish a comparison with the transient studies reported here.

4. Conclusions

A mechanistic scheme has been suggested for describing the catalytic N_2O decomposition over a commercial woven Pt–Rh gauze under transient conditions at temperatures that are relevant for the high-temperature ammonia oxidation. In this model, the decomposition of N_2O takes place over both reduced metal sites and oxygen species formed from N_2O. With regard to oxygen formation during N_2O decomposition at 1073–1173 K, two different and simultaneous reaction pathways are proposed: (i) recombination of adsorbed oxygen species and (ii) interaction of N_2O (gas-phase or adsorbed) with adsorbed oxygen species results in oxygen formation. The first reaction pathway is tentatively proposed to prevail with an increase in temperature.

Acknowledgment

Norsk Hydro Agri ASA is gratefully acknowledged for financial support and for permission to publish this work.

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