Journal of Catalysis **194,** 130–139 (2000)
doi:10.1006/jcat.2000.2919, available online at http://www.idealibrary.com on IDEAL®

Oscillating Behavior in N_2O Decomposition over Rh Supported on Zirconia-Based Catalysts

2. Analysis of the Reaction Mechanism

G. Centi,[1] L. Dall'Olio, and S. Perathoner

Department of Industrial Chemistry and Materials Engineering, University of Messina, Messina, Italy

Received February 21, 2000; revised May 3, 2000; accepted May 4, 2000

The mechanism responsible for the oscillating behavior in N_2O decomposition of rhodium particles supported on zirconia-based oxides in the presence of oxygen and water is studied using transient reactivity and thermogravimetric tests. The behavior over different oxide supports is also reported. The results demonstrate that (i) the atomic oxygen produced in the decomposition of N_2O remains chemisorbed on the Rh surface, leading to its progressive accumulation, (ii) the activity of the catalyst increases progressively with increasing coverage of Rh with oxygen, and (iii) above a threshold concentration of oxygen on the Rh surface, a rapid reconstruction of Rh particles occurs with release of the chemisorbed oxygen and the start of a new oscillation cycle, but only in the presence of water in the feed. It is also shown that the presence of water in the feed, inducing the desorption of chemisorbed oxygen from the Rh surface, stabilizes a more reduced working state of the catalyst surface.

Key Words: **N_2O; Rh; oscillating behavior; zirconia; water; mechanism.**

INTRODUCTION

Steady-state multiplicity and a stable oscillating change between two active states have often been observed in heterogeneous catalysts and have been interpreted according to various reaction mechanisms, such as an adsorption-induced surface reconstruction (1), a subsurface reservoir of a reactant (2), and a periodic formation of an oxide or a carbon layer (3, 4). Such mechanisms responsible for the observed stable oscillations in the catalytic activity require, however, the presence of an oxidant and a reductant, such as in the oxidation of CO and hydrocarbons (1–8) or in the reduction of N_2O by CO over supported Pt catalysts (9, 10).

Much less frequently observed is the case of oscillations in the absence of a combination of a reductant and an oxidant and in the absence of possible thermally induced phenomena (8). The decomposition of N_2O on Cu/ZSM-5 catalysts (11–16) has recently been reported. The phenomenon was not fully understood and demonstrated. It was attributed to a periodic change in the copper oxidation state in the zeolite, with N_2O having the double role of reductant and oxidant (forming nitrate and N_2 species, respectively). The oscillations are determined by a different reaction rate of N_2O with the oxidized and reduced copper sites (15, 16) or by the presence of two different states of catalytic activity related to different coverages with adspecies (atomic oxygen produced from N_2O dissociation and nitrate) (13). In the first case, the mechanism can again be related to the case of oscillations due to redox reactions, but with the important difference that the reduction is associated with the spontaneous reduction of the copper sites, which is known occur at the reaction temperatures and oxygen partial pressures of the experiments of N_2O on Cu/ZSM-5 catalysts (17). In the second hypothesis for the reaction mechanism, the driving force for the oscillations may instead be related to the phenomena of adsorbate-induced changes in the surface reactivity.

In part 1 of this work (18) we reported that oscillations in N_2O decomposition can also be observed in a completely different catalytic system compared to Cu/zeolite catalysts: namely, on Rh supported on Zr-Nd mixed oxides (indicated hereafter as Rh-ZrNdOx). A characteristic feature of the Rh-ZrNdOx catalyst, in contrast to the case of Cu/ZSM-5, is that the oscillations in the decomposition of N_2O are observed only when water is fed together with N_2O and O_2. Other features of the oscillations, such as their characteristic shape and dependence on the reaction conditions, indicate that the mechanism responsible for the oscillations should be different from, although with reasonable points of analogy to, those proposed for Cu/ZSM-5 catalysts. A better understanding of the reaction mechanism responsible for

---

[1] To whom correspondence should be addressed at Dipartimento di Chimica Industriale ed Ingegneria dei Materiali, Università di Messina, Salita Sperone 31, 98166 Messina, Italy. Fax: +39-090-391518. E-mail: centi@unime.it.

0021-9517/00 $35.00

the oscillations in N_2O decomposition on Rh-ZrNdOx catalysts should not only provide better insight into the surface catalytic chemistry of N_2O decomposition on this catalyst, but also offer keys for a better understanding (i) in general of the surface phenomena responsible for steady-state multiplicity and *in situ* dynamic modification of the surface reactivity and (ii) specifically of the oscillations in N_2O decomposition on Cu/ZSM-5 catalysts.

On the other hand, the direct low-temperature decomposition of N_2O is a reaction of relevant industrial interest, as discussed in part 1 (18) and also recently reviewed (19, 20). In fact, N_2O is a powerful greenhouse gas and its emissions should be reduced to counteract atmosphere warming (20). N_2O is produced in relevant amounts, although in low concentrations, in several combustion or chemical processes. In particular, it is produced in the combustion of industrial waste containing nitrogen and in the chemical processes using nitric acid as oxidant (20), in addition to the case of adipic acid production in which, however, in contrast to the previous cases, N_2O is quite high (30% or above). While commercial catalysts exist for the latter case, Rh supported on zirconia-based catalysts are new interesting catalysts when N_2O concentration is low in the emissions, as for the former cited cases. In terms of total volume of N_2O emitted, the emissions where N_2O is present in low concentrations (below 1%) are more relevant than the case of adipic acid (20). It should also be mentioned that due to the rapidly growing number of applications of wet oxidation processes of N-containing waste (for example, wet oxidation of active sludges), which produce large amounts of N_2O, the market for low-temperature N_2O decomposition catalysts is estimated to grow considerably in the near future (20).

A further reason for interest in obtaining a better understanding of the oscillation behavior in the decomposition of N_2O on Rh-ZrNdOx is related to the possibility of obtaining information about the surface processes determining the surface reactivity of Rh supported on zirconia-type catalysts, which represent an important class of catalysts in, for example, automotive applications (21). Therefore, there are various reasons that stimulate interest in studying the mechanism of oscillations in the decomposition of N_2O on Rh-ZrNdOx.

In part 1 (18) the analysis of the characteristic features of the oscillations and their dependence on reaction conditions suggested that water is not directly involved in the mechanism responsible for the oscillations, but is responsible mainly for favoring the accumulation of the oxygen produced by the dissociation of N_2O on the Rh surface and for weakening metal–support interactions, making surface *in situ* reconstruction of Rh particles possible when the concentration of chemisorbed oxygen on the Rh surface is above a certain limit. The accumulation of chemisorbed atomic oxygen over the Rh surface leads to an increase in the sticking coefficient of N_2O and thus to an increase in the rate constant of its decomposition, which contrasts with the parallel effect of a decrease in the number of free Rh sites for N_2O decomposition that leads to a decrease in the reaction rate. The combination of these two effects and the *in situ* reconstruction of Rh particles above a threshold of chemisorbed oxygen may explain the characteristic shape of the oscillations. Although this reaction mechanism is a reasonable interpretation of catalytic and kinetic data, further data in support of the hypothesis are necessary.

The objective of the work reported here was to analyze the reaction mechanism in N_2O decomposition on Rh-ZrNdOx catalysts using thermogravimetric tests, tests of transient reactivity as a function of catalyst pretreatment, and tests in which the evolution of oxygen from the catalyst is monitored during *in situ* oscillating N_2O decomposition, to further check the proposed mechanism.

EXPERIMENTAL

Preparation of Catalysts

The preparation of ZrNdOx catalyst is reported in detail in part 1 (18). The zirconia–neodymia mixed oxide support, with formal composition $Zr_{0.92}Nd_{0.08}\square_xO_{4-x}$ (where $x = 0.04$), was prepared using the sol-gel technique. Final calcination in air was carried out at 550°C for 4 h, giving a total surface area of 84 m^2/g using the BET method. The rhodium was added by incipient wet impregnation using an aqueous solution of $Rh(NO_3)_3 \cdot H_2O$ in order to have a final Rh loading of 1 wt%. After impregnation, the samples were dried, calcined at 500°C, and then activated by a reducing treatment. This procedure of reductive activation involved an initial treatment at 500°C in helium flow up to complete elimination of the adsorbed water and then a treatment in a flow of 50% H_2 in He at 500°C for 2 h followed by cooling to 200°C in the same type of flow, and finally mild reoxidation in a flow of 0.05% N_2O + 6% O_2 in helium for 3 h. The Rh-ZrNdO$_x$ catalyst was used for more than about 250 h in N_2O catalytic decomposition tests after which the oscillations in the catalytic decomposition of N_2O became regular. For shorter times on stream, oscillations were observed, but were less regular.

Rh supported on zirconia–lantania and on zirconia–alumina, samples that will hereafter be referred to as Rh-ZrLaO$_x$ and Rh-ZrAlO$_x$, respectively, were prepared with the same method used for the Rh-ZrNdO$_x$ catalyst. The loading of Rh, the content of lantania or alumina, and the procedure of calcination and activation were also the same as for Rh-ZrNdO$_x$. Rh supported on alumina, hereafter referred to as Rh-Al_2O_3, instead was prepared using a commercial γ-Al_2O_3 (Rhone-Poulenc, RP531; 106 m^2/g), while the loading of Rh, the procedure of addition, and the method of calcination and activation (including time of pretreatment) were the same as for the Rh-ZrNdO$_x$ catalyst.

Thermogravimetric Tests

Thermogravimetric tests were made using a Perkin–Elmer TG-2C apparatus modified to allow tests with a continuous stream passing through the head and a side stream, just above the furnace, to add the reactive components. A standard inert Pt pan was used to load approximately 13 mg of sample (Rh-ZrNdO$_x$) using the same pellet dimensions as those used for the catalytic tests (18).

Tests were made under isothermal conditions, after treatment at 480°C in a pure helium flow to remove adsorbed species. After cooling to a selected temperature in the He flow and stabilization of the weight, a feed containing N_2O in He (0.6 L/h) and passed through a saturator containing distilled water was added from the side entrance of the thermobalance to the main flow of pure He (3 L/h) passing through the head of the thermobalance, in order to have a feed concentration over the thermobalance pan of about 0.05% $N_2O + 1\%$ H_2O in helium. The saturator containing water could be bypassed to check the behavior in the absence of water in the feed.

Catalytic Tests

Catalytic tests were carried out with the same apparatus and using the same modalities as described in part 1 (18). A quartz fixed-bed reactor loaded with 0.5 g of catalyst (particles with diameters in the range of 0.1–0.3 mm) and equipped with an on-line mass-quadrupole system for the continuous analysis of the feed and of reaction products was used. The space velocity was 27,500 h^{-1}.

The same apparatus was used to check the transient behavior of the catalyst as a function of the catalyst pretreatment, made at 480°C for 20 min using different feeds as described above. After the pretreatment, the feed was switched to pure He flow and the reactor temperature was cooled to 320°C. After stabilization of the reactor temperature, the feed was switched to a mixture containing 0.05% N_2O, 6% O_2, and 2% H_2O in He (6 L/h) or 0.05% N_2O and 6% O_2 in He (6 L/h) and the catalytic behavior was monitored using the mass quadrupole apparatus. Blank tests with an empty reactor were made to determine the time of the system response, which was subtracted from the time of the system response when the catalyst (Rh-ZrNdO$_x$; 0.4 g) was present.

Surface Area

The surface area was determined with the BET method (N_2 adsorption at 77 K) using a Carlo Erba Sorpty 1750 instrument. The samples were pretreated by evacuation at 300°C. The surface areas of the sample before and after the catalytic tests were found to be nearly equivalent, taking into consideration the experimental error.

RESULTS

Influence of the Catalyst Composition on the Occurrence of Oscillations

The role of catalyst composition in determining the occurrence of the oscillations in N_2O decomposition was analyzed by studying the catalytic behavior of zirconia-based samples prepared and activated as Rh-ZrNdO$_x$ catalysts, but containing a different lanthanide ion instead of neodymium (Rh-ZrLaO$_x$) or a different trivalent ion such as aluminum (Rh-ZrAlO$_x$). The use of a zirconia-based mixed oxide instead of pure zirconia makes it possible to improve the surface area and to shift the activity to lower reaction temperatures, although due to the low content of the second element (10 wt%) the surface characteristics of the mixed oxide remain similar to those of zirconia (22). In addition, the behavior of Rh supported on commercial alumina, but prepared and activated as Rh-ZrNdO$_x$, was also analyzed. The results are reported in Fig. 1 (Fig. 1a, Rh-ZrLaO$_x$; Fig. 1b, Rh-ZrAlO$_x$; Fig. 1c, Rh-Al_2O_3) for typical reaction conditions in which Rh-ZrNdO$_x$ shows regular oscillations in N_2O decomposition (18).

The two catalysts based on Rh supported on zirconia-type oxides show the presence of defined oscillations in the temperature range 300–400°C, although they are less regular than those observed in the case of the Rh-ZrNdO$_x$ catalyst. No oscillations were noted using the Rh supported on alumina catalyst in a similar range of temperature and activity (Fig. 1c), nor were they observed on a range of other types of Rh-supported catalysts (23). This shows that the oscillations are a specific characteristic of Rh supported on zirconia-based oxides, while the role of the second element in the zirconia-based mixed oxide (neodymium, for example) is related mainly to a secondary change in the textural/surface properties that determines the presence of more or less regular oscillations in N_2O decomposition.

Oxygen Desorption from the Catalyst Surface during Oscillations

The mechanism proposed in part 1 (18) to interpret catalytic data in N_2O decomposition on Rh-ZrNdO$_x$ was based on a process of surface accumulation of atomic oxygen, produced by N_2O dissociation on the Rh surface and a rapid release in one step of the chemisorbed oxygen when its concentration was above a threshold limit. In order to check this hypothesis, an experiment was carried out in which the conversion of N_2O and the oxygen and nitrogen partial pressure in the feed (Fig. 2) were analyzed simultaneously.

To have enough sensitivity in the detection of the oxygen released from the catalyst, this experiment was possible only when oxygen was absent from the feed to the reactor. As shown in part 1 (18), although the oxygen partial pressure in the feed modifies the frequency and amplitude of the oscillations, it does not alter the basic features of the phenomenon and thus the experiment without oxygen in the feed is also representative of what happens in the presence of oxygen in the feed.

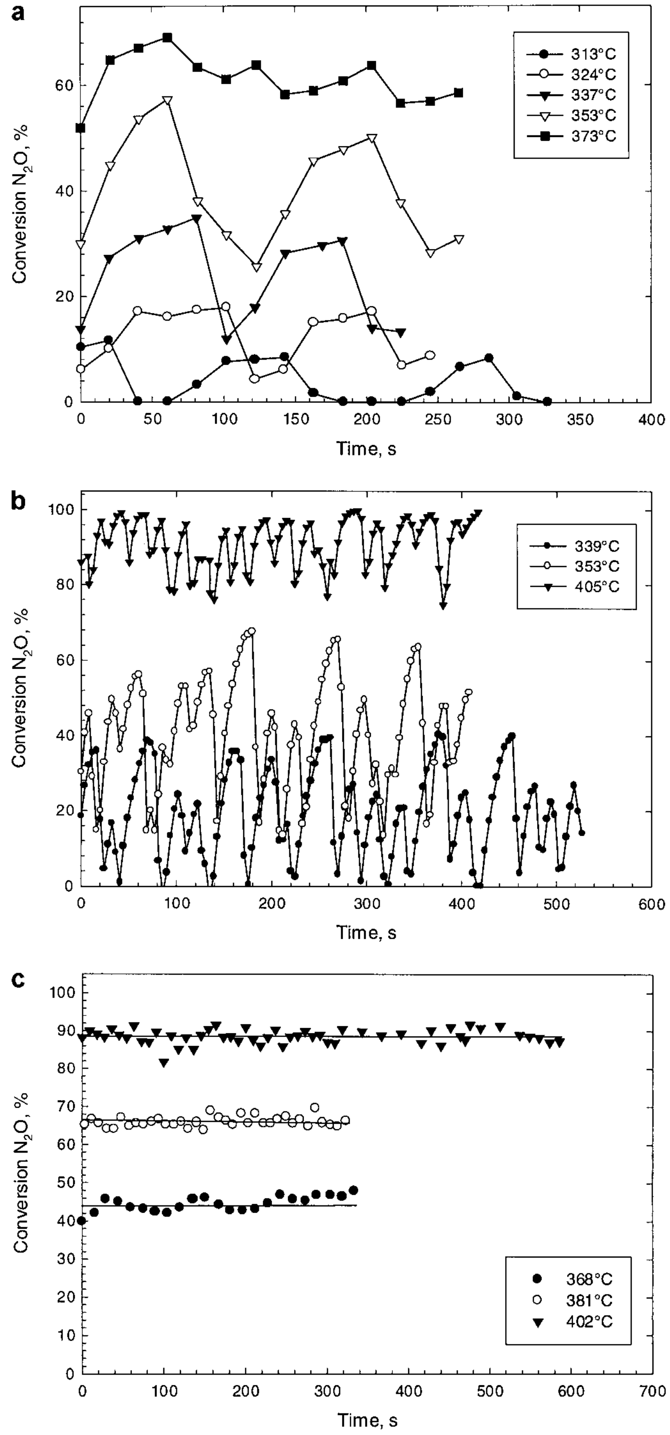

FIG. 1. Conversion of N_2O as a function of time for different reaction temperatures for Rh-ZrLaO_x (a), Rh-ZrAlO_x (b), and Rh-Al_2O_3 (c) catalysts. Feed: 0.05% N_2O, 2% H_2O, 6% O_2 in helium.

The formation of N_2 parallels the conversion of N_2O, while the formation of O_2 shows a different trend. During the first part of the cycle, when the conversion of N_2O and the formation of N_2 rapidly rise, the oxygen does not desorb. Oxygen starts to desorb only later, when the conversion of N_2O approaches a constant behavior. Furthermore, a clear peak in the desorption of oxygen is noted coincident with the rapid drop in N_2O conversion and N_2 formation. This can be better seen in the expansion of one cycle of the oscillations (Fig. 2b).

It may be noted also that during the sequence of cycles an increase in the background oxygen formation can be seen (Fig. 2a). This suggests that two different processes of oxygen desorption occur. The first, responsible for the peak in O_2 coincident with the drop in activity in N_2O decomposition, is due to the simultaneous release of oxygen and the dynamic reconstruction of the catalyst. The second desorption of oxygen, responsible for O_2 formation during the final part of the cycle and for the increase in the background O_2 formation, occurs via a different mechanism, tentatively via surface migration from the metal to the support interface, in agreement with previous observations (22).

The experiment reported in Fig. 2 shows two important aspects related to the mechanism of N_2O decomposition on the Rh-ZrNdO_x catalyst:

- During the first step of increase in the conversion of N_2O, no desorption of the oxygen produced during the dissociation occurs (Fig. 2b); at the final part of the cycle, oxygen starts to desorb via a different mechanism involving probably the migration from the metal to the support.
- Simultaneously with the rapid drop in the activity in N_2O conversion, there is a peak in the desorption of oxygen (Fig. 2b).

This experiment confirms that (i) the oxygen produced during N_2O dissociation remains stuck to the catalyst surface, and reasonably on the Rh surface, although indications are that it also tend to migrate from the metal to the support, (ii) the progressive accumulation of oxygen on the catalyst leads to an increase in the reaction rate, and (iii) the rapid decrease in activity is related to reconstruction of the catalyst, which leads to release of the chemisorbed oxygen.

Weight Changes during in Situ Experiments

The process of surface accumulation of the oxygen produced by N_2O dissociation and one-step desorption with a parallel change in the surface reactivity can also be monitored in parallel thermobalance experiments. The results for two reaction temperatures are summarized in Fig. 3. Tests were made in the absence of oxygen in the feed, in order to better analyze the weight change due to accumulation on the catalyst of the oxygen produced by N_2O dissociation, but in the presence of water in the feed necessary for the occurrence of the oscillations (18).

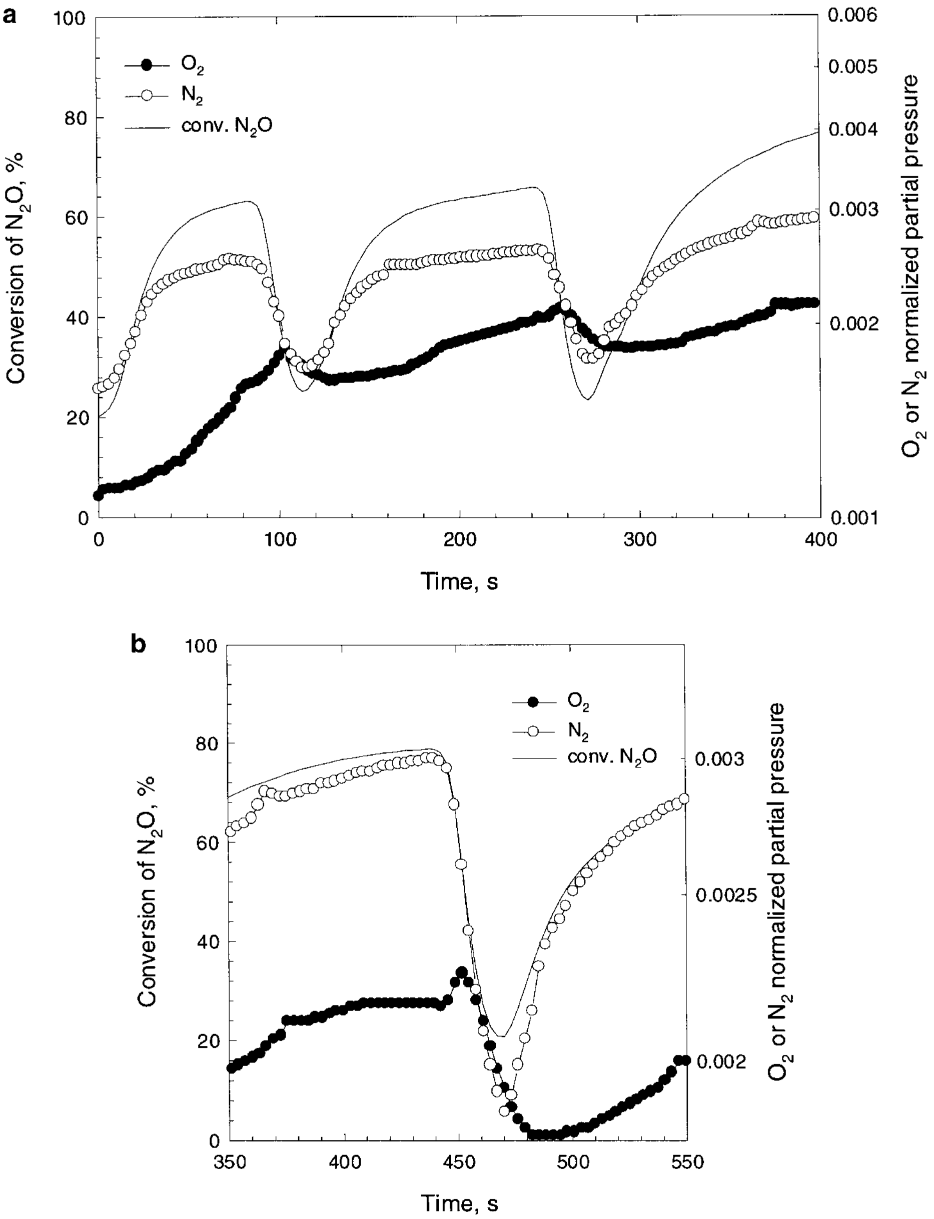

FIG. 2. Conversion of N_2O and oxygen or nitrogen normalized partial pressure (O_2 or N_2 partial pressure in quadrupole detector divided by the total pressure in the quadrupole chamber; the value is proportional to the effective O_2 or N_2 partial pressure in the feed) as a function of time for Rh-ZrNdOx. Feed: 0.05% N_2O, 0% O_2, 2% H_2O, remainder He; reaction temperature was 341°C. In Fig. 2b an expansion of a single cycle is reported.

Although the oscillations appear to be more symmetrical with respect to the shape of oscillations in N_2O decomposition activity, reasonably due to an attenuation of the time response in thermobalance experiments (the weight response was mediated to eliminate the effect of vibrations, due to the small weight change being monitored—on the order of 1×10^{-5} g), there is good agreement between change in weight and change in activity in terms of frequency of the oscillations and the effect of the reaction temperature on the amplitude of the oscillations. At 340°C the mean maximum weight change is approximately 0.1 wt%, while at 360°C it is about 0.03 wt%, corresponding to a mean maximum change in the conversion of approximately 60 and 10–15%, respectively (18). The frequency of cycles in the thermobalance experiments is about 5×10^{-3} Hz, which also agrees with that observed in the catalytic tests (18).

The amount of Rh on the catalyst during these experiments is approximately 1.3×10^{-6} mol. A weight change of 0.1 wt% corresponds to an accumulation of about 8.4×10^{-7} mol of atomic oxygen. This shows that the process of surface reconstruction with release of the stored atomic

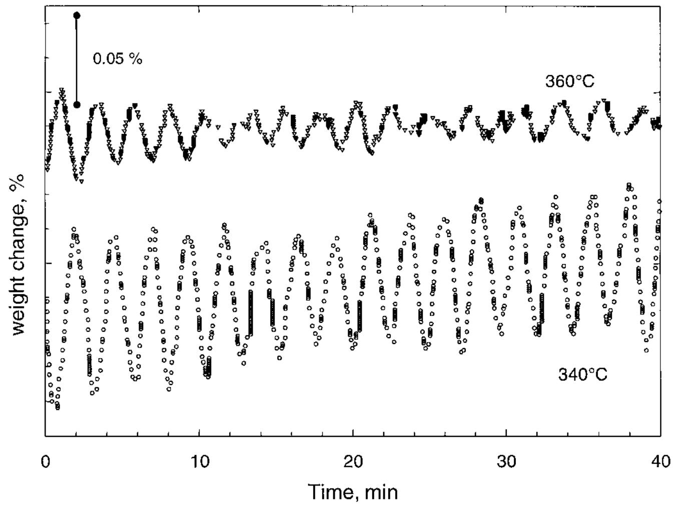

FIG. 3. Thermogravimetric tests of the weight change of Rh-ZrNdOx at different reaction temperatures. Feed: 0.05% N_2O, 0% O_2, 1% H_2O, remainder He.

oxygen produced by N_2O dissociation occurs when the amount of accumulated monoatomic oxygen corresponds to approximately 60% of all Rh atoms.

The determination of dispersion and specific surface area of Rh particles using conventional methods does not give directly usable data, because prereduction of the catalyst is necessary and thus the method gives information on a different situation than that present during the process of N_2O decomposition occurring in the presence of gaseous O_2 (18). Values of approximately 40 m^2/g Rh, depending on the temperature of prereduction, that indicate good dispersion of Rh on the zirconia–neodymia support were obtained. Assuming thus that nearly 60% of the Rh atoms are available on the surface or subsurface for storing the monoatomic oxygen produced by N_2O dissociation, thermobalance experiments suggest that the process of surface reconstruction with release of the stored oxygen occurs when the surface of the Rh particles is nearly completely covered by the oxygen produced in the dissociation process.

The role of the presence of water in the feed was also analyzed in thermogravimetric experiments. The results at 340°C for the Rh-ZrNdO_x catalyst are shown in Fig. 4. After about 10 min of feed composed of only 0.05% N_2O in He, water vapor is added to the feed. A rapid decrease in the weight is observed, after which oscillations in the weight start to become visible. It is worthwhile to note that after addition of water to the feed, a weight increase may be expected due to adsorption of water. The evident decrease in weight thus indicates that desorption of chemisorbed or lattice oxygen of the catalyst may instead occur. Although surprising, this is consistent with previous spectroscopic studies on Cu-ZrO_2 catalysts (24) that clearly showed that faster reduction and reoxidation of the copper ion were possible only on a hydroxylated surface.

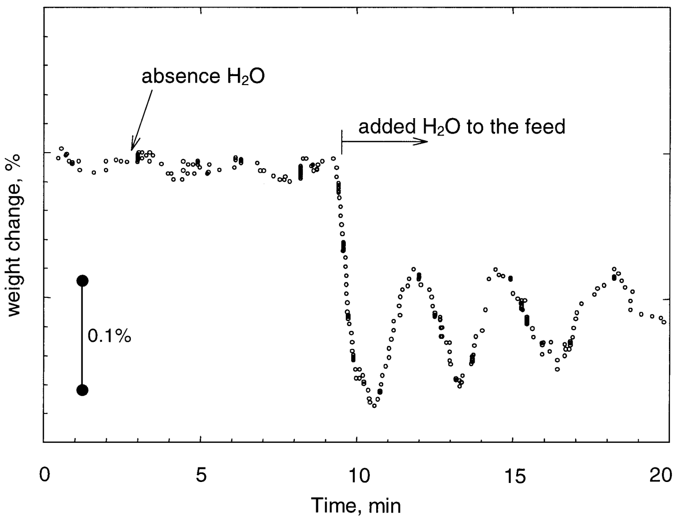

FIG. 4. Thermogravimetric tests of the weight change at 340°C of Rh-ZrNdOx after water vapor was added to the feed. Other conditions were as described in the legend to Fig. 3.

Role of Catalyst Pretreatment

To obtain information on the influence of catalyst pretreatment on the occurrence and induction time of oscillations in N_2O decomposition, tests were made in which the catalyst was preheated at higher temperature (480°C) using different feed compositions, cooling the reactor in an inert flow to a reaction temperature of 320°C, and sending, after stabilization of the temperature, a feed containing 0.05% N_2O, 6% O_2, and 2% H_2O in helium. The results of the transient activity in N_2O decomposition after the introduction of the latter feed are shown in Fig. 5 for three different

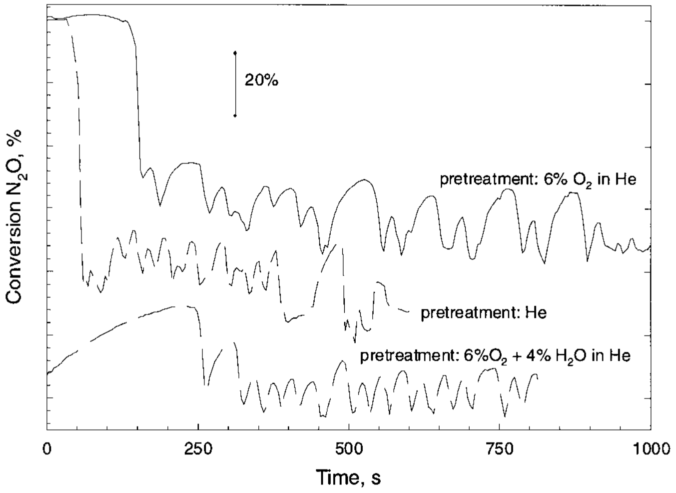

FIG. 5. Effect of the pretreatment on transient reactivity of Rh-ZrNdOx at 320°C in a feed of 0.05% N_2O, 6% O_2, and 2% H_2O in He. Pretreatment (480°C, 20 min): flow of (1) 6% O_2 in He, (2) 6% $O_2 + 4\%$ H_2O in He, and (3) pure helium. After the pretreatment, the reactor was cooled to 320°C in a pure He flow.

types of pretreatment at high temperature: (i) 20 min in a feed of 6% O_2 in helium, (ii) 20 min in a feed of 6% $O_2 + 4\%$ H_2O in helium, and (iii) 20 min in a feed of pure helium.

In all cases, after an induction time ranging from 1 to 4 min, oscillations in the decomposition of N_2O start to become evident, although the frequency and regularity of the oscillations depend on the type of pretreatment. Furthermore, not only the induction time, but also the modality of approaching the oscillating regime, depends on the type of pretreatment. In both pretreatments in the absence of water in the feed, both in the presence and in the absence of oxygen, the initial activity is 100% and after an induction time abruptly decreases to a lower value after which oscillations become evident. The induction time is approximately three times higher for the pretreatment in the presence of oxygen than in pure helium, contrary to that expected if the higher initial activity is related only to catalyst reduction during the higher temperature catalyst pretreatment.

In the case of the pretreatment in the presence of water and oxygen in the feed, the initial activity is instead low and progressively increases to a maximum value after approximately 4 min, after which there is a rapid decrease in the N_2O conversion and then oscillations become evident. This result is further indication that the presence of water in the feed during pretreatment considerably influences the catalytic reactivity and the working state of the catalyst surface.

To obtain further information on the role of water during pretreatment in changing catalyst reactivity, a different type of experiment was carried out (Fig. 6). In these tests, the same pretreatment at high temperature (480°C) in pure helium flow (20 min) was made, but after the reactor was cooled to the reaction temperature (320°C), the catalyst was further pretreated (10 min) using a feed containing a different concentration of water in helium. After the water vapor was removed from the line, a feed containing 0.05% N_2O and 6% O_2 in helium (i.e., without water vapor) was introduced and the transient catalytic activity in N_2O decomposition was monitored. Due to the absence of water in the feed, oscillations in N_2O decomposition were not observed in this case, but the data obtained give information on the effect of water in changing the initial state of the catalyst toward N_2O decomposition.

In the case of pretreatment in helium only, the initial activity is 100% and only slowly declines to a conversion of N_2O of about 70%. In contrast to the case of Fig. 5, when water was present in the reaction feed, the conversion is initially 100% for about 8 min (against 1 min in the case of Fig. 5) and then takes around 25 min to reach a stationary value (against a few seconds in the case of Fig. 5 and furthermore for a more drastic decrease in the conversion). These data clearly show that the presence of water in the feed, together with N_2O and O_2, determines a complete change in the dynamic reactivity characteristics of the catalyst.

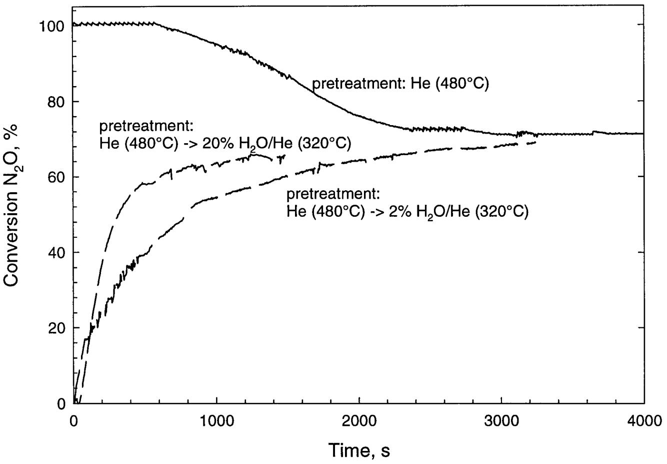

FIG. 6. Effect of the pretreatment on transient reactivity of Rh-ZrNdOx at 320°C in a feed of 0.05% N_2O and 6% O_2 in He. Pretreatment at 480°C (20 min) in a flow of pure He for all samples; the reactor was then cooled to 320°C in a pure He flow and the catalyst was further treated for 10 min in a flow of (1) pure He, (2) 2% H_2O in He, and (3) 20% H_2O in He. Before admission of the reaction feed (0.05% N_2O and 6% O_2 in He), water vapor was removed from the lines by sending a pure He feed for 1 min.

In the case of the pretreatment at 320°C in the flow of water and helium, the initial catalyst activity is nearly zero and only slowly increases to a constant conversion value that coincides with that observed in the case of the pretreatment with a helium-only flow. The transient change in catalyst activity is in agreement with that observed in Fig. 5 for the higher temperature pretreatment in the presence of water in the feed, although in this case the time to reach stationary activity is longer and the abrupt decrease in conversion after which the oscillating activity starts is absent.

The initial low-level activity and slow increase in activity in the case of pretreatment in the presence of water in the feed cannot be attributed simply to a competitive effect of chemisorbed water, because (i) as the concentration of water in the feed in the pretreatment at 320°C (Fig. 6) increases from 2 to 20%, the induction time to reach the stationary activity becomes shorter, and (ii) the same type of trend is also observed in the experiments of Fig. 5 (for the higher temperature pretreatment in the presence of water in the feed), for which water is present in the reaction feed during N_2O decomposition. The role of water must therefore be related to a change in the working state of the catalyst during the catalytic reaction.

DISCUSSION

In part 1 (18) the following working model to explain the oscillations in N_2O decomposition on the Rh-ZrNdOx catalyst was suggested:

(i) N_2O decomposes over the free sites of the Rh surface, but the atomic oxygen produced in decomposition remains chemisorbed on the Rh surface, leading to its progressive accumulation.

(ii) The sticking coefficient for N_2O increases progressively with the increase in the coverage of Rh with oxygen (thus leading to an increase in the rate constant), but at the same time the number of available free sites on the Rh surface decreases, leading to a decrease in the reaction rate; the cumulative effect of these two contrasting phenomena explains the characteristic shape of the oscillations during phase 1 (increase in conversion).

(iii) Above a threshold concentration of oxygen on the Rh surface, rapid reconstruction of Rh particles occurs with release of the chemisorbed oxygen and the start of a new oscillation cycle.

The data obtained in the present study give further evidence in support of this hypothesized reaction mechanism responsible for the oscillations in N_2O decomposition on the Rh-ZrNdOx catalyst.

The first question in the proposed mechanism regards the hypothesis that the atomic oxygen produced by N_2O decomposition remains chemisorbed on the rhodium surface and progressively accumulates. The data in Fig. 2 show that there is no desorption of O_2 in the first part of the oscillations, when the conversion of N_2O increases, although they show that in part oxygen may desorb via a different mechanism, probably involving surface migration from the metal to the support and then its desorption. The tests reported in Fig. 2 correspond to tests with a feed mixture containing N_2O and H_2O in helium, but no gaseous oxygen, except for traces due to impurities. However, the observation of the absence of desorption of O_2 from the catalyst during the rising part of the oscillations may be extended to the case of the presence of O_2 in the feed, because as noted in part 1 (18), oxygen affects the frequency and amplitude of the oscillations, but not their characteristic shape.

The second aspect of the first question regards the concept that oxygen remains lodged on the Rh surface. As shown elsewhere (23), Rh largely promotes the activity of zirconia-based oxides in N_2O conversion and thus it is reasonable to indicate that the reaction of N_2O decomposition occurs on the Rh surface and that the oxygen produced in this reaction remains lodged on the Rh surface. Thermogravimetric data (Fig. 3) are consistent with this hypothesis, indicating that the weight change during oscillations is consistent with the creation of an oxygen layer on the Rh particles. Data in Fig. 2, although demonstrating that oxygen does not desorb during the first part of the cycle (when there is a rapid rise in N_2O conversion; see in Fig. 2b the expansion of the first part of the cycle starting from time 480 s), show that for longer times during the cycle itself oxygen starts to desorb. The shape of the oxygen curve does not parallel that of N_2 (Fig. 2), indicating that although both are formed via N_2O dissociation, the mechanisms of desorption of nitrogen and oxygen are different. An increase in the background oxygen is also noted in the series of cycles (Fig. 2), also indicating a process of oxygen desorption that occurs on a time scale different from the process of dissociation of N_2O. As shown elsewhere (18, 22), the metal–support interface and especially the presence of oxygen vacancies at the interface play a relevant role in determining the reaction rate in Rh on zirconia-based catalysts. The phenomenon was interpreted on the basis of the hypothesis that the atomic oxygen produced from N_2O dissociation migrates from the Rh surface and accumulates at the perimeter area between Rh particles and the support, from which they then desorb. The same mechanism is reasonably responsible for the desorption of oxygen in the final part of the cycle and for the increase in the background oxygen formation. Data in Figs. 2 and 3 thus provide good support for the first step in the proposed reaction mechanism (dissociation of N_2O at the Rh surface and progressive accumulation on it of the atomic oxygen produced from this reaction), although the results in Fig. 2 indicate that part of the chemisorbed oxygen may desorb via a mechanism that probably involves the surface migration to the support as the first step.

The second question in the proposed reaction mechanism regards the hypothesis that the sticking coefficient for N_2O increases progressively with an increase in coverage of the Rh with oxygen, leading to a progressive increase in the conversion of N_2O. The data in Fig. 2 regarding the rising part of the oscillations demonstrate this hypothesis well. Data on the transient catalyst activity after higher temperature pretreatment (Fig. 5) further support this hypothesis. After treatment at higher temperature with a flow containing oxygen, and thus probably after oxidation of the surface of the Rh particles occurs, the catalyst activity is 100% and remains complete for a time on stream approximately three times higher (after cooling to 320°C and starting of the feed containing N_2O, O_2, and H_2O) than when the same type of pretreatment is made in a flow of pure helium (thus more reducing than a flow of oxygen in helium).

The data in Fig. 5 further show that when the pretreatment is made in the presence of water in the feed, the initial activity is very low. This is further demonstrated by the data reported in Fig. 6 that show that the effect cannot be attributed to an inhibition effect on N_2O chemisorption due to chemisorbed water. Comparison of the transient change in catalyst activity in the case of the data of Figs. 5 and 6, where the difference in feed composition is related to the presence (Fig. 5) and the absence (Fig. 6) of water in the reaction feed, also shows that after an induction time there is a considerable decrease in the conversion of N_2O after which the oscillations start to become evident, when water is present in the feed.

It may be concluded that both the absence of oxygen desorption during the rising part of the oscillations (Fig. 2) and the effect of the high-temperature pretreatment (Fig. 5) demonstrate that the catalyst activity is higher over an "oxidized" Rh surface than over a "reduced" Rh surface (i.e., after desorption of the chemisorbed oxygen). The data do not provide information on whether there is an effective change in the sticking coefficient for N_2O or instead a progressive change in the intrinsic reactivity of the Rh surface in passing from a reduced to an oxidized state. Reasonably, both concepts are valid, because both N_2O adsorption and dissociation can be faster on a Rh surface near a chemisorbed oxygen atom.

The third question in the proposed mechanism is related to the concept that above a certain concentration of oxygen on the Rh surface, rapid reconstruction of Rh particles occurs with release of the chemisorbed oxygen and the start of a new oscillation cycle. The data reported in Fig. 2 show that parallel to the abrupt decrease in conversion, there is a desorption of oxygen from the catalyst surface. It may thus be concluded that in the presence of water in the feed catalyst reconstruction that leads to the desorption of chemisorbed oxygen may occur. The reduced catalyst (i.e., after desorption of oxygen) shows a much lower activity in N_2O decomposition that the oxidized catalyst. This explains why pretreatment of the catalyst in the presence of water in the feed leads to a nearly zero initial activity in contrast to the case of pretreatment in the presence of oxygen or even a helium-only flow (traces of oxygen as contaminant and due to leakage were present in the helium). The thermogravimetric data in Fig. 4 further support the evidence that in the presence of water in the feed a "reduction" of the catalyst occurs with a decrease in its weight, instead of an increase as more reasonably expected due to chemisorption of water.

The presence of water in the feed, therefore, not only gives rise to competitive chemisorption with N_2O, as usually indicated for other catalysts active in N_2O decomposition (20), but remarkably changes the redox characteristics of the catalysts, as well as the dynamic processes during the catalytic reaction, as exemplified by comparison of the different transient behavior shown in Figs. 5 and 6.

The present data, however, cannot clarify the details of the mechanism responsible for the effect of water on the dynamic behavior of Rh particles and why their reconstruction with desorption of chemisorbed oxygen occurs. The data in Fig. 1 clarify that these phenomena are a general feature of Rh supported on the zirconia-based catalyst, although not of other types of oxide supports. The role of the second component in the zirconia-type mixed oxide, besides that of a structural promoter to stabilize thermal resistance against sintering (22), is that of modifying the surface properties, thus making the oscillations more regular and detectable.

It should be mentioned that although oscillations were also observed after short times on stream, relatively long times (more than about 200 h) were necessary to detect regular oscillations, when the neodymia component was present. The characterization of the samples before and after this *in situ* activation procedure, however, did not allow elucidation of the reasons for this induction period, which thus remain an open question.

Loong *et al.* (25, 26) reported that the surface acidity characteristics in lanthanide-modified zirconia mixed oxides, and in particular the strength of the hydroxyl groups, depend on the lanthanide ion. We also observed (22) that the surface acidity characteristics in zirconia–alumina can be progressively changed by increasing the relative content of alumina in the mixed oxide. It is thus reasonable to hypothesize that the main effect of the second element in the zirconia-based oxide support is that of modifying the surface acidity characteristics and in particular the strength of the hydroxyl groups. In the presence of a hydroxylated environment of the zirconia surface the Rh particles show a much weaker interaction with the oxide support and thus can give rise to *in situ* reconstruction phenomena not possible when a stronger interaction with the support is present, such as on a dehydroxylated zirconia surface or on other types of oxide supports. This explains the effect of water on the dynamic features of the Rh-$ZrNdO_x$ catalyst and the role of the second element in the zirconia-based mixed oxide support in determining the presence of regular oscillations in N_2O decomposition. However, more detailed studies using advanced characterization techniques, such as scanning tunneling microscopy, would be necessary to better understand the reasons for this phenomenon.

The effect of water on the working state of Rh particles on zirconia-based catalysts is not necessarily related to the reaction of N_2O decomposition, but is a general feature of these catalysts. Rh on zirconia catalysts are interesting catalysts in various catalytic reactions (21) and are a key component in commercial three-way catalysts for the treatment of exhaust gas emissions from vehicles (27). The present data on the role of water and N_2O in determining the working state of Rh particles offer a key with which to analyze the data of this type of catalyst also in other kinds of reactions, as well as an opportunity to change or tune their reactivity.

REFERENCES

1. Ertl, G., *Adv. Catal.* **37**, 213 (1990).
2. Basset, M. R., and Imbihl, R., *J. Chem. Phys.* **93**, 811 (1990).
3. Yeates, R. C., Turner, J. E., Gellman, A. J., and Somorjai, G. A., *Surf. Sci.* **149**, 175 (1985).
4. Collins, N. A., Sundaresan, S., and Chabal, Y., *Surf. Sci.* **180**, 136 (1987).
5. Kobayashi, M., Kanno, T., Takeda, H., and Fujisaki, S., *Appl. Catal. A Gen.* **151**, 207 (1997).
6. Tenchev, K. K., Petrov, L. A., Savelieva, G. A., and Sass, A. S., *Appl. Catal. A Gen.* **83**, 31 (1992).
7. Schröder, U., *J. Catal.* **146**, 586 (1994).

8. Schüth, F., Henry, B. E., and Schmidt, L. D., *Adv. Catal.* **39**, 51 (1995).
9. Sadhankar, R. R., and Lynch, D. T., *J. Catal.* **149**, 278 (1994).
10. Sadhankar, R. R., Ye, J., and Lynch, D. T., *J. Catal.* **146**, 511 (1994).
11. Lintz, H. G., and Turek, T., *Catal. Lett.* **30**, 313 (1995).
12. Turek, T., *Appl. Catal. B Env.* **9**, 201 (1996).
13. Turek, T., *J. Catal.* **174**, 98 (1998).
14. Ciambelli, P., Garufi, E., Pirone, R., Russo, G., and Santagata, F., *Appl. Catal. B Env.* **8**, 333 (1996).
15. Ciambelli, P., Di Benedetto, A., Garufi, E., Pirone, R., and Russo, G., *J. Catal.* **175**, 161 (1998).
16. Ciambelli, P., Di Benedetto, A., Pirone, R., and Russo, G., *Chem. Eng. Sci.* **54**, 2555 (1999).
17. Centi, G., and Perathoner, S., *Appl. Catal. A* **132**, 179 (1995).
18. Centi, G., dall'Olio, L., and Perathoner, S., *J. Catal.* **192**, 224 (2000).
19. Kapteijn, F., Rodriguez-Morasol, J., and Moulijn, J. A., *Appl. Catal. B Env.* **9**, 25 (1996).
20. Centi, G., Perathoner, S., and Vazzana, F., *CHEMTECH* **29**(12), 48 (1999).
21. Burch, R., and Loader, P. K., *Appl. Catal. A Gen.* **143**, 317 (1996).
22. Centi, G., Marella, M., Meregalli, L., Perathoner, S., Tomaselli, M., and La Torretta, T., *in* "Advanced Catalysts and Nanostructured Materials" (W. R. Moser Ed.), Chap. 4, p. 63. Academic Press, San Diego, 1996.
23. Centi, G., Dall'Olio, L., and Perathoner, S., *Appl. Catal. A Gen.* **194–195**, 79 (2000).
24. Morterra, C., Giamello, E., Cerrato, G., Centi, G., and Perathoner, S., *J. Catal.* **179**, 111 (1998).
25. Loong, C. K., Thiyagarajan, P., Richardson, J. W., Ozawa, M., and Suzuki, S., *J. Catal.* **171**, 498 (1997).
26. Loong, C. K., Richardson, J. W., and Ozawa, M., *J. Catal.* **157**, 636 (1995).
27. Fornasiero, P., Di Monte, R., Rao, G., Kaspar, J., Meriani, S., Trovarelli, A., and Graziani, M., *J. Catal.* **151**, 168 (1989).