Journal of Catalysis **192,** 224–235 (2000)
doi:10.1006/jcat.2000.2847, available online at http://www.idealibrary.com on IDEAL®

Oscillating Behavior in N_2O Decomposition over Rh Supported on Zirconia-Based Catalysts: The Role of the Reaction Conditions[1]

G. Centi,[2] L. Dall'Olio, and S. Perathoner

Department of Industrial Chemistry and Materials Engineering, University of Messina, Messina 98166, Italy

Received November 26, 1999; revised February 10, 2000; accepted February 15, 2000

Rhodium particles supported on zirconia doped with neodymium oxide show an oscillating behavior in N_2O decomposition in the presence of oxygen and water, but the oscillating behavior occurs only when the zirconia surface is hydrated. The phenomenon is ascribed to a dynamic process of surface accumulation of atomic oxygen (produced by N_2O dissociation) on the Rh surface and reconstruction of these supported Rh particles above a level of oxygen coverage, with a rapid drop in the activity and release of gaseous dioxygen. This *in situ* reconstruction of Rh particles, however, may occur only on a hydrated surface. © 2000 Academic Press

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

INTRODUCTION

N_2O is a powerful greenhouse gas, with an effect around 300 times greater than that of CO_2 (over a 100-year time span), due to its long lifetime. Furthermore, it participates in the chemical cycles leading to the destruction of the ozone layer. Therefore, the Kyoto Protocol on greenhouse gas emissions established that N_2O emissions should be monitored and it is also expected that new emission limits will be introduced soon (1).

N_2O is produced by various sources, both natural and related to human activities, but the only type of emissions which can be brought under effective control within a limited number of years are those associated with the production of chemicals (principally, synthesis and use of nitric acid) and combustion processes (in particular, the combustion of municipal and industrial waste in fluidized bed reactors) (2). The first type of emissions can be further broken down, depending on their concentrations of N_2O into (i) those containing a concentration above 1% (principally, adipic acid production) and (ii) those with an N_2O concentration below 1% (all the others). Catalysts and technical solutions are available commercially for the first class of emissions (catalytic decomposition of N_2O or reuse for phenol synthesis from benzene (3, 4)). However, no suitable techno-economical solution has yet been fully developed for the second class of emissions, although some suggestions have been put forward (1). It is worth noting that in terms of the total amount of N_2O emitted, the second class of emissions exceeds the first. Therefore, there is a need to develop new catalysts and economically viable technologies to treat emissions containing diluted (<1% v/v) concentrations of N_2O. In particular, a key problem is to develop catalysts that are active in N_2O decomposition at low reaction temperatures (<400°C) in the presence of the other typical components of industrial emissions, such as O_2, H_2O, NO, etc. (5).

In the investigation of catalysts active in the reaction conditions outlined above, Rh supported on a zirconia-based oxide containing lanthanide ions as promoters was found to show better properties in comparison to unpromoted or commercial catalysts (5). Rh supported on zirconia has attracted considerable interest recently, because unlike the case with alumina as the support, Rh_2O_3 interacts weakly with the support and can thus be more easily reduced (6, 7), sometimes leading to enhanced reactivity. It is also known that lanthanide-modified zirconia shows not only better thermal stability (8) than zirconia alone, but also different surface characteristics (strength of the hydroxyl groups (9), for example) and reactivity (10, 11), although the latter effects are very dependent on the type and concentration of lanthanide. For example, Loong *et al.* (8) observed that due to their different oxidation states, ionic radii, and other characteristics, Nd^{3+} and Ce^{4+} solid solutions with zirconia possess different structural and surface characteristics.

Similarly, lanthanide-promoted catalysts were found to have an improved activity and resistance to deactivation by oxygen and water in N_2O decomposition, both of which depend on the nature of the lanthanide ion dopant (5). In particular, Zr–Nd mixed oxides were found to show interesting activity properties in this reaction, but under some specific reaction conditions, after long-term *in situ* activation during catalytic tests, the rhodium supported on a Zr–Nd mixed

---

[1] Part 1 of two parts. Part 2, Analysis of the Reaction Mechanism, submitted for publication February 2000.

[2] To whom correspondence should be addressed. Fax: +39-90-391518. E-mail: centi@unime.it.

0021-9517/00 $35.00

oxide showed an oscillating behavior in N_2O decomposition when water was present in the feed.

An oscillating catalytic reactivity has been observed in various cases (12–19), especially in the case of the oxidation of CO and hydrocarbons. Numerous mechanisms have been proposed, such as adsorption-induced surface reconstruction (12), development of a subsurface reservoir of a reactant (16), and periodic formation of an oxide or a carbon layer (17, 18). The reduction of N_2O by CO over supported Pt catalysts also shows steady-state multiplicity due to a combination of adsorbate-induced Pt surface-phase transformation and self-exclusion of CO during adsorption on the Pt surface (20, 21).

Oscillations are less frequently observed in the absence of a combination of a reductant and an oxidant, and in the absence of possible thermally induced phenomena (19). The decomposition of N_2O on Cu/ZSM-5 catalysts (22–26) has recently been observed. The phenomenon was attributed to a periodic change in the copper oxidation state in the zeolite, with N_2O acting both as a reductant and as an oxidant and a different reaction rate of N_2O with the oxidized and reduced copper sites (26), or to the presence of two different states of catalytic activity related to different coverages with adspecies (atomic oxygen and nitrate) (24).

Although contrasting observations were made about the role of oxygen in the decomposition of N_2O on Cu/ZSM-5 (24, 26), both research groups agreed that (i) a reduced copper species (Cu^+) was the more active and (ii) its oxidation to an oxidized (Cu^{2+}) species, less active in N_2O decomposition, was responsible for the change in catalyst activity between two active states. It is thus reasonable to assume that the redox process may be inhibited by the presence of gaseous oxygen and water. In the case of Rh on Zr–Nd mixed oxide, however, the oscillating behavior was observed in the presence of an oxygen concentration 2 orders of magnitude higher than that of N_2O and was inhibited by the absence of water in the feed, thus indicating the different nature of the process. It is therefore worth studying the oscillation behavior in the decomposition of N_2O on Rh supported on Zr–Nd mixed oxides in greater depth, to gain 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 (7).

The aim of this work is to analyze the features of the oscillating behavior, the factors on which it depends, the possible reaction mechanism, and why the oscillations are triggered by the presence of water in the feed. The dependence of oscillating behavior on experimental parameters (temperature and feed composition) is described in this work. Part 2 will deal with analysis of the possible reaction mechanism, using thermogravimetric parallel tests, tests of transient reactivity as a function of catalyst pretreatment, and tests where the evolution of oxygen from the catalyst is monitored during *in situ* oscillating N_2O decomposition.

EXPERIMENTAL

Preparation of Catalysts

The zirconia and zirconia–neodymia mixed oxide supports, the latter with formal composition $Zr_{0.92}Nd_{0.08}\square_{0.04}O_4$, were prepared using the sol–gel technique. Zirconium isopropoxide is solubilized at a 1 : 5 ratio in anhydrous ethyl alcohol. Then an $H_2O–C_2H_5OH–CH_3COOH$ solution with or without the nitrate salt of the lanthanide ion is added in drops to the first solution until a final molar ratio $Zr(OR)_4 : H_2O : C_2H_5OH : CH_3COOH = 1 : 5 : 3.2 : 0.05$ is reached. The gel is aged for 40 min, then filtered, washed several times with doubly distilled water up to a constant pH of washing solution, dried overnight at 260°C, and finally calcined in air at 550°C for 4 h. The final surface areas are 78 and 84 m^2/g for the samples without and with Nd dopant, respectively. The rhodium on these supports 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%. The two samples, with and without Nd dopant, will hereinafter be referred to as $Rh–ZrO_2$ and $Rh–ZrNdO_x$, respectively.

After impregnation, the samples were dried, calcined at 500°C, and then activated by reductive treatment. This procedure of reductive activation involved an initial treatment at 500°C in helium flow up to complete elimination of the adsorbed water, then a treatment in a flow of 50% H_2 in He at 500°C for 2 h followed by a cooling to 200°C in the same type of flow, and finally a mild reoxidation in a flow of 0.05% $N_2O + 6\%$ O_2 in helium for 3 h. The reductive treatment makes it possible to enhance the dispersion of rhodium and improve catalytic activity in N_2O decomposition. Finally, 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 evident.

After this procedure, samples were characterized by X-ray diffraction analysis which indicated the presence of a tetragonal phase of zirconia in both cases.

Catalytic Tests

Catalytic tests were carried out in a quartz fixed-bed reactor equipped with an online mass quadrupole system for the continuous analysis of the feed and of reaction products. Results were corrected to consider overlap in the fragmentation in the mass intensities. The feed was prepared by mixing calibrated amounts of already diluted mixtures of the single components in helium. Water was added to the feed using an infusion pump. The line to and from the reactor was heated to 150°C to avoid condensation of products.

Tests were carried out using 0.5 g of catalyst in the form of particles with diameters of the order of 0.1–0.3 mm in range and a space velocity of 27,500 h^{-1}. The uniform axial temperature profile of the catalytic bed was monitored using a thermocouple. Preliminary checks were made to ensure the absence of diffusion limitations on the reaction rate.

RESULTS

Figure 1 shows a comparison of catalytic behaviors in the decomposition of N_2O of Rh–ZrO_2 and Rh–$ZrNdO_x$ samples using different feed compositions. In the absence of oxygen in the feed, Rh supported on the zirconia catalyst is active in the 250–350°C temperature range, but the presence of oxygen and water in the feed significantly depresses activity, shifting it to reaction temperatures 100–150°C higher or more, depending on feed composition. The addition of the lanthanide ion to zirconia, however, reduces inhibition by oxygen and water. The Rh–$ZrNdO_x$ catalyst is thus active in the 300–400°C temperature range even in the presence of oxygen and water in the feed.

In particular, the Rh–$ZrNdO_x$ catalyst shows, a conversion of N_2O of between approximately 30 and 80% in the 320–380°C temperature range. In this temperature range oscillations in the decomposition of N_2O were observed in the Rh–$ZrNdO_x$ catalyst (data shown in Fig. 1 refer to average conversion determined by integration of the mass quadrupole response over a 30-min time period). As will be discussed in more detail in part 2, the presence of a Zr–Nd mixed oxide is not what determines the observed oscillations in the decomposition of N_2O, but is probably necessary to shift the activity to the right temperature range to make the oscillations more evident.

Figure 2 shows the effect of reaction temperature on oscillations in catalyst activity in the decomposition of N_2O in the presence of oxygen and water in the feed. The temperature range in which oscillations were observed went from an upper temperature of around 370°C (Fig. 2) to a lower temperature of around 310–320°C, the latter mainly conditioned by too low catalyst activity (Fig. 1).

The characteristic features of oscillations in the decomposition of N_2O are the following:

- a duration of around 1–2 min;
- a slow period of increase in conversion, with a faster initial rate which steadily decreases (phase 1);
- a very fast collapse of activity (phase 2) after the maximum reached in the first phase; and
- the absence of an induction time between consecutive cycles.

The increase in reaction temperature does not significantly affect the duration of the cycle, but mainly influences the initial rate of increase in conversion during phase 1.

The effect of oxygen concentration for a reaction temperature of 341°C (average temperature in the range where oscillations were observed) is shown in Fig. 3. Although oxygen influences the frequency of oscillations, it is worth noting that oscillations are observed even for an oxygen concentration in the feed of 10%, which corresponds to an $O_2/N_2O = 200$ concentration ratio.

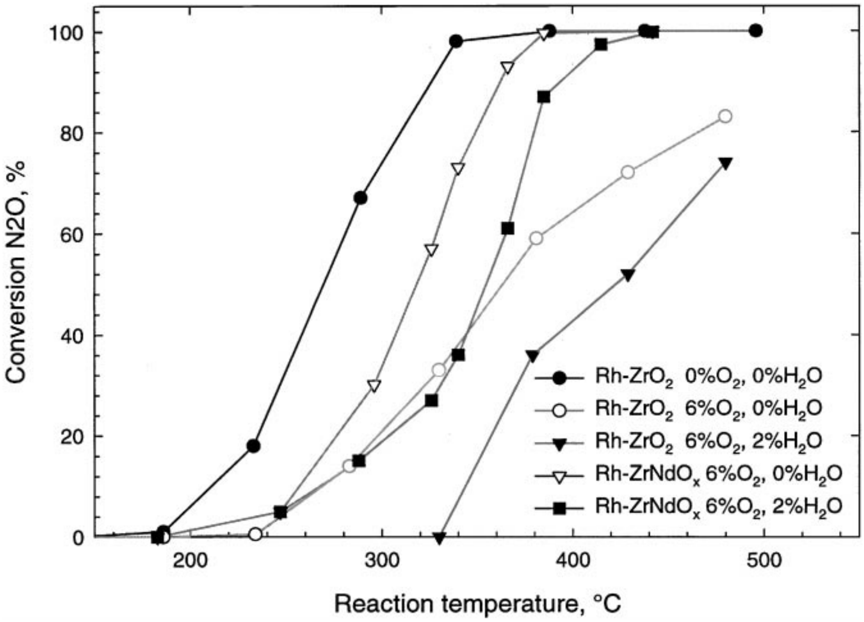

FIG. 1. Conversion of N_2O as a function of the reaction temperature for Rh–ZrO_2 and Rh–$ZrNdO_x$ catalysts using different feed compositions. Feed: 0.05% N_2O, water, and oxygen as indicated in the legend, helium as balance.

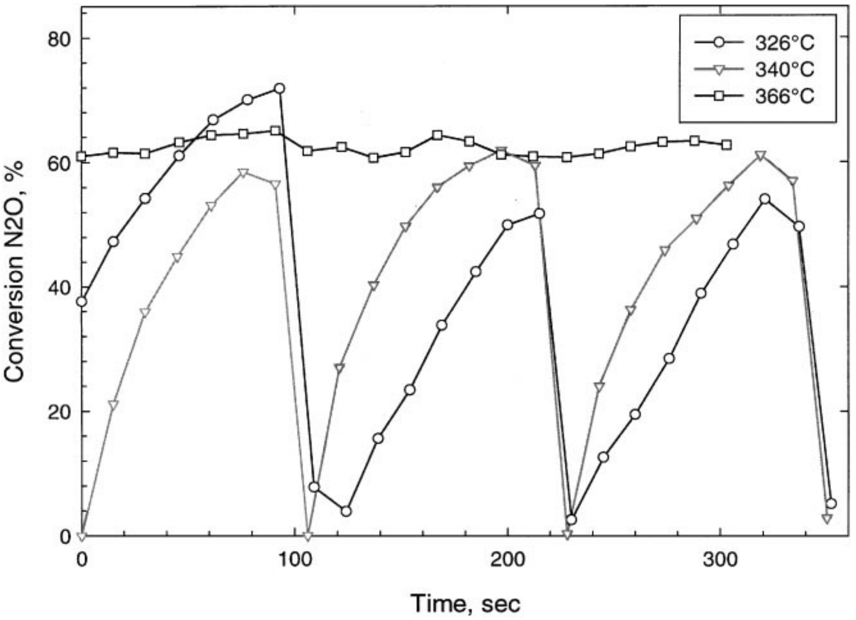

FIG. 2. Effect of the reaction temperature on the oscillations in the Rh–ZrNdO_x catalyst activity in N_2O decomposition. Feed: 0.05% N_2O, 2% H_2O, 6% O_2, remainder He.

The concentration of oxygen in the feed mainly influences the frequency of the oscillations. The period of the oscillations (e.g., the time after which minimum conversion of N_2O is obtained again) goes from around 190 s (absence of O_2) to around 80 s, whereas the initial rate of increase during phase 1 or decrease during phase 2 does not significantly change.

The effect of water concentration in the feed for the same reaction temperature as the tests in Fig. 3 is shown in Fig. 4. As with oxygen, the concentration of water also influences the frequency of the oscillations, but not the initial rate of increase during phase 1. The effect of water, however, is more drastic than that of oxygen, because an increase in water concentration from 1% to 2%, for example, roughly halves the period (Fig. 4), whereas in the case of oxygen an increase in concentration by around 1 order of magnitude was necessary for a similar halving of the period of the oscillations (Fig. 3).

Furthermore, unlike in the case of oxygen, the absence of water in the feed prevents detection of the presence of oscillations in the decomposition of N_2O. This result also differentiates the oscillations observed in Rh–ZrNdO_x systems from those observed previously in other catalytic systems (22–26) detected in the absence of water in the feed.

It is worth noting that notwithstanding the influence of feed composition on catalyst activity (Fig. 1), the temperature for the tests in Figs. 3 and 4 was chosen to keep conversion of N_2O within a good detectable range, in order to avoid possible artifacts when conversion is too low or too high to clearly detect the presence of oscillations.

The effect of the concentration of N_2O in the feed is shown in Fig. 5. N_2O also influences the duration of the oscillations (although its effect is not very significant), but not the initial rate of increase during phase 1 (with the exception of the data obtained at the lower N_2O concentration (0.02%) which are influenced by reduced analytical sensitivity). It is worth noting that in this case, unlike the increase in the concentrations of O_2 and H_2O, the magnitude of the oscillations (i.e., the difference in conversion of N_2O from the minimum to the maximum values observed) increases.

Figure 6a shows a comparison of the effect of the concentration of the reactants on the frequency and amplitude of the oscillations at 341°C. The frequency (10^{-3} Hz) indicates the mean number of cycles per second, determined from the mean time necessary in the oscillations to reach the conversion minimum. The amplitude of the oscillations (conversion %) indicates the mean change in conversion of N_2O during the cycles from minimum to maximum values. The two parameters characterizing the oscillations have opposite trends for O_2 and H_2O, i.e., the frequency increases with an increase in the concentration, whereas the amplitude decreases. On the other hand, both parameters increase with an increase in the concentration of N_2O in the feed, thus indicating a different influence of N_2O on the oscillation dynamics. The concentration of oxygen has a more limited effect on oscillations when compared to water and N_2O (especially the latter), which considerably influence the characteristics of the oscillations.

The amount of N_2O decomposed per cycle (10^{-6} mol) as a function of the concentration of the reactants is summarized

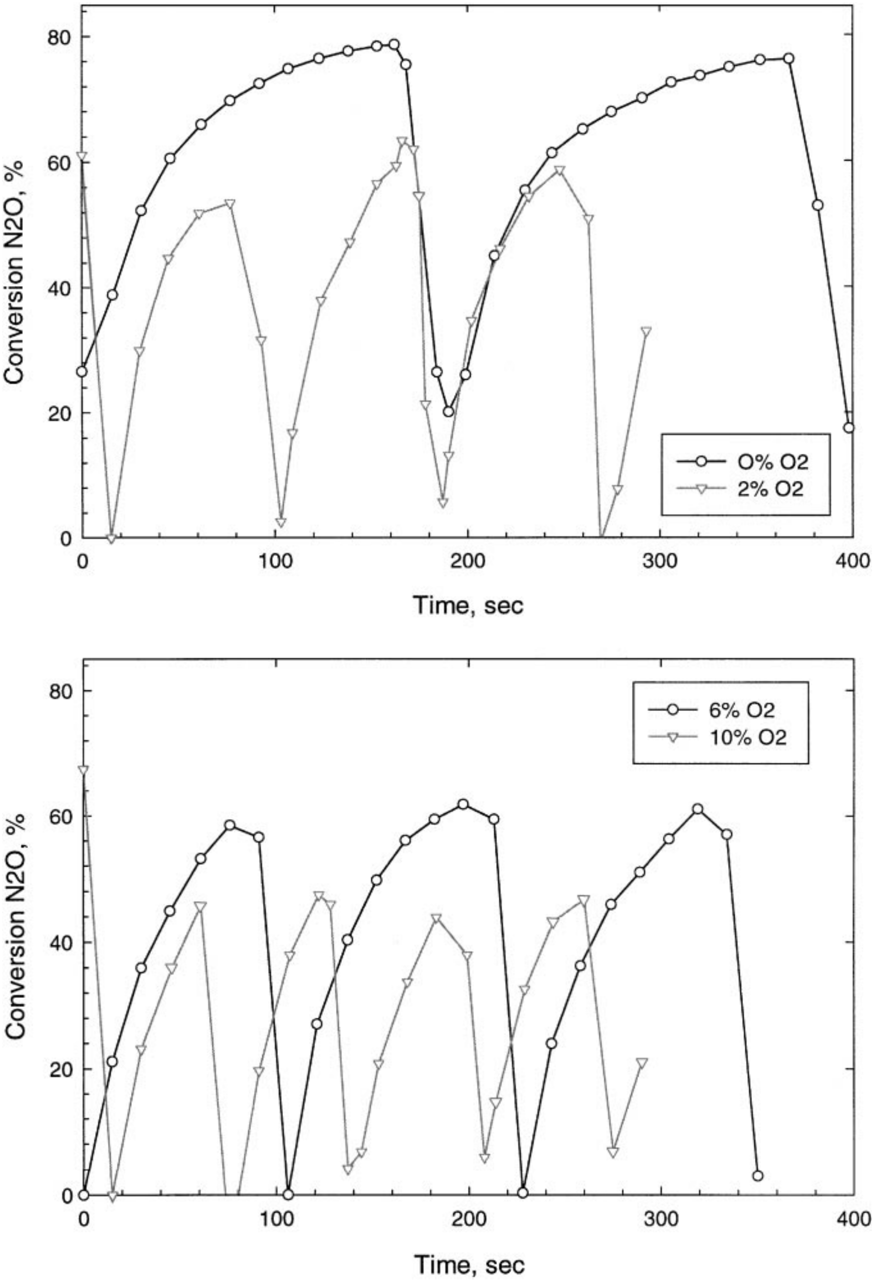

FIG. 3. Effect of the oxygen concentration on the oscillations in the Rh–ZrNdO$_x$ catalyst activity in N_2O decomposition. Feed: 0.05% N_2O, 0–10% O_2, 2% H_2O, remainder He; reaction temperature = 341°C.

in Fig. 6b. Again, the different dependence of this parameter on the concentration of N_2O with respect to that of O_2 and H_2O should be noted, as well as the lesser dependence of this parameter on the concentration of oxygen in the feed.

Figure 7a shows the dependence of the frequency and amplitude of the oscillations, and of the amount of N_2O decomposed per cycle, on reaction temperature. All these parameters increase with an increase in reaction temperature, rather like the dependence observed on the N_2O concentration. However, in the case of reaction temperature, unlike the case of N_2O, the rate of initial increase of conversion after the minimum depends on this parameter. This is shown in Fig. 7b which indicates the rate of conversion change during the initial period of phase 1 in the oscillations, i.e., at the start of the increase in N_2O conversion. In order to quantify the parameter characterizing the oscillations, the rate constant of N_2O depletion (k_{N_2O}) was estimated using a first-order rate model with respect to N_2O concentration and a plug flow type reactor model, which both proved to give a good approximation of the kinetic behavior of the

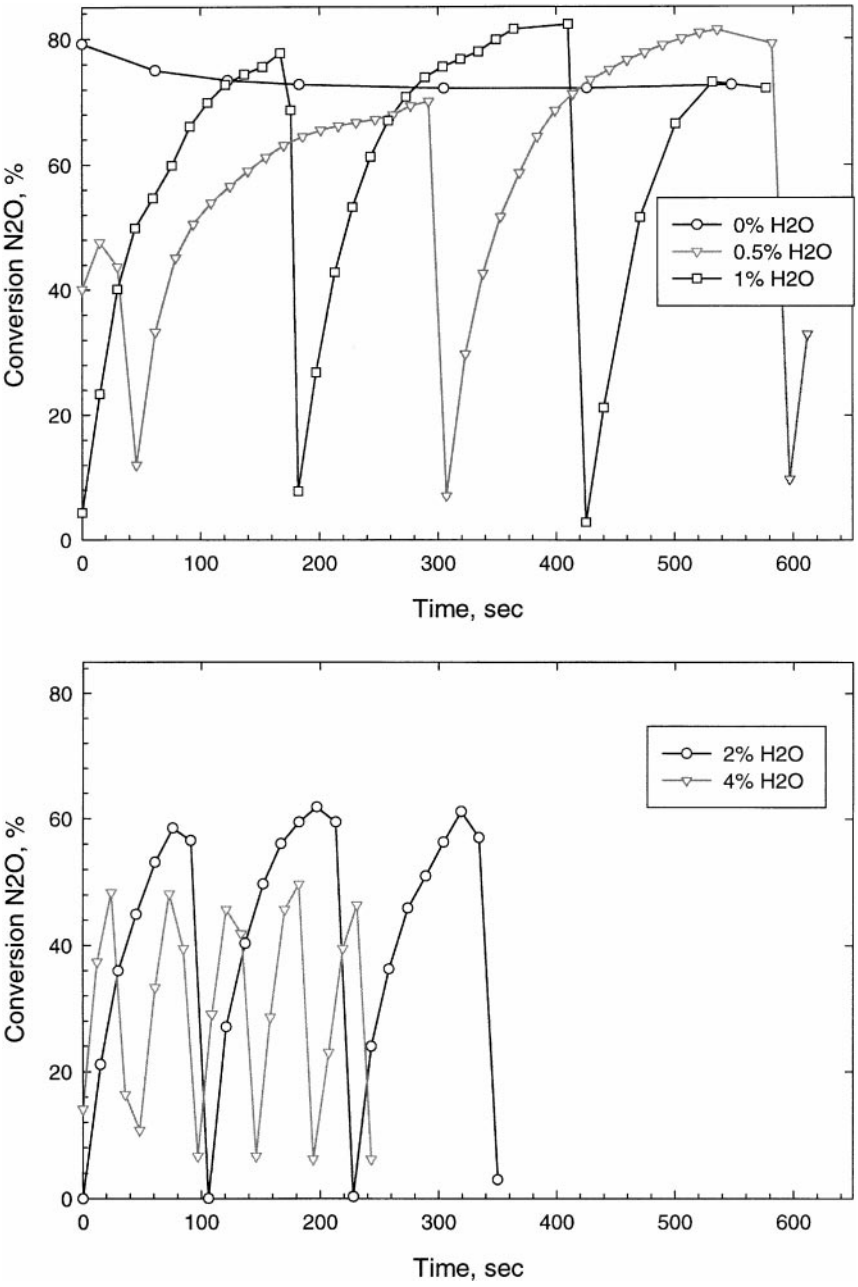

FIG. 4. Effect of the water concentration on the oscillations in the Rh–ZrNdO$_x$ catalyst activity in N_2O decomposition. Feed: 0.05% N_2O, 0–4% H_2O, 6% O_2, remainder He; reaction temperature = 341°C.

Rh/Zr–Nd oxide catalyst within the range of experimental conditions of the present tests (27). The rate of change of k_{N_2O} during approximately the first 15 s in phase 1 of each oscillation was estimated and averaged over a series of cycles. The values for a 0% concentration of water in the feed were not considered, since no oscillations were observed in this case (Fig. 4), nor were data for a 0.02% N_2O concentration (Fig. 5), because oscillations were not well developed.

In agreement with the qualitative observation made previously, the rate of the initial change of k_{N_2O} in phase 1 (Fig. 7b) is independent (within experimental error) of the concentration of the reactants. This indicated that the phenomenon responsible for the increase in the conversion of N_2O during the initial part of phase 1 is independent of the feed composition, i.e., is probably influenced neither by the rate of chemisorption of N_2O, nor by the adsorption of O_2 or H_2O, although the feed composition determines the occurrence of the phenomenon (for example, oscillation does not occur in the absence of water in the feed).

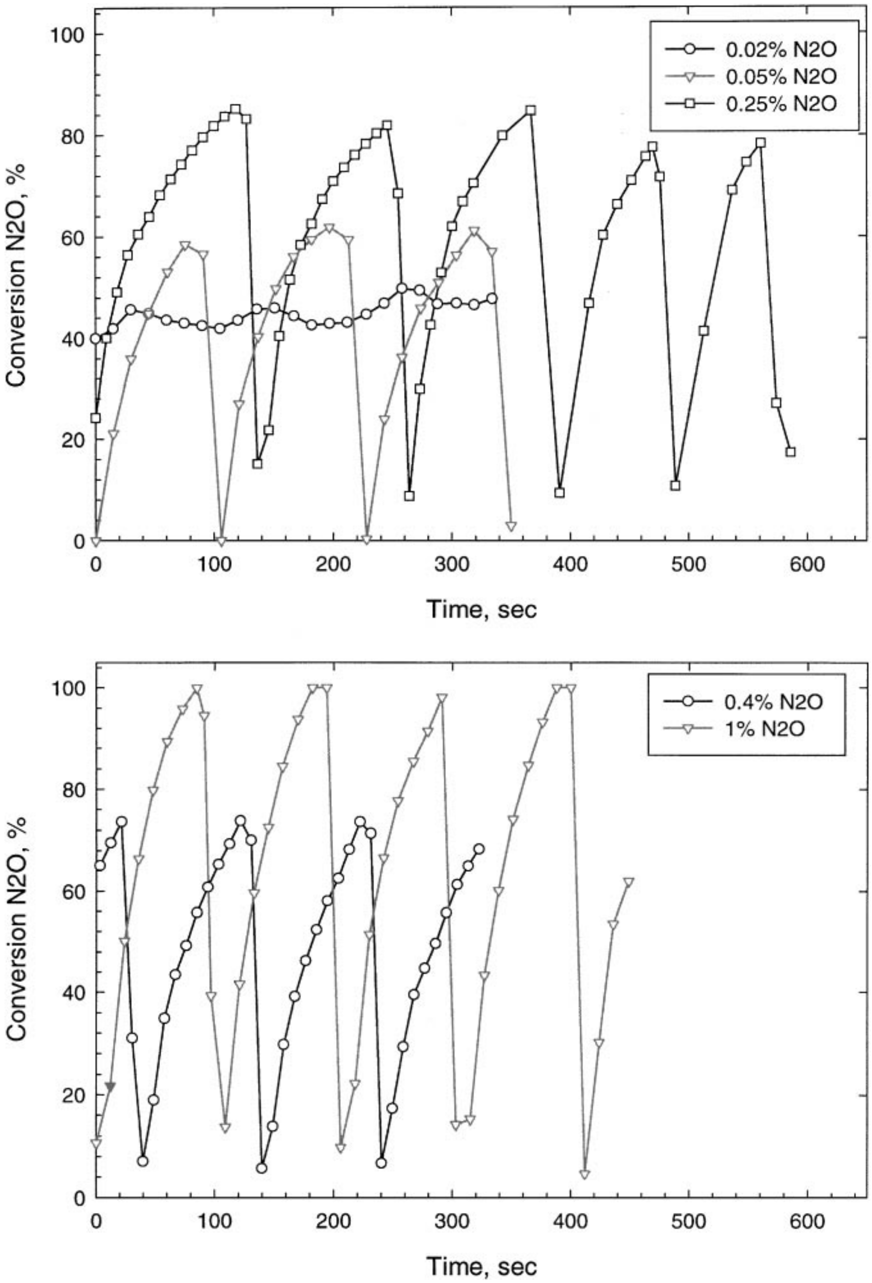

FIG. 5. Effect of the N_2O concentration on the oscillations in the Rh–ZrNdO$_x$ catalyst activity in N_2O decomposition. Feed: 0.02–1% N_2O, 2% H_2O, 6% O_2, remainder He; reaction temperature = 341°C.

The initial change of the rate constant in step 1, however, is nearly linearly dependent on the increase in the reaction temperature, suggesting that it is determined by a kinetic reaction influenced by the reaction temperature.

DISCUSSION

Oscillations in the decomposition of N_2O have been observed for Cu/ZSM-5 catalysts (22–26), in particular for overexchanged zeolites which contain dimeric or polymeric type copper species. In fact, notwithstanding different ideas on the reaction mechanism, as indicated in the Introduction, there is agreement that the key step in the mechanism responsible for the oscillating behavior is the redox change from a reduced (Cu^+) state to an oxidized state (Cu^{2+} dimeric species containing a bridging and labile oxygen (26)).

The question is therefore whether this reaction mechanism may be applied in its general features to the present case of oscillations in the Rh–ZrNdO$_x$ catalyst,

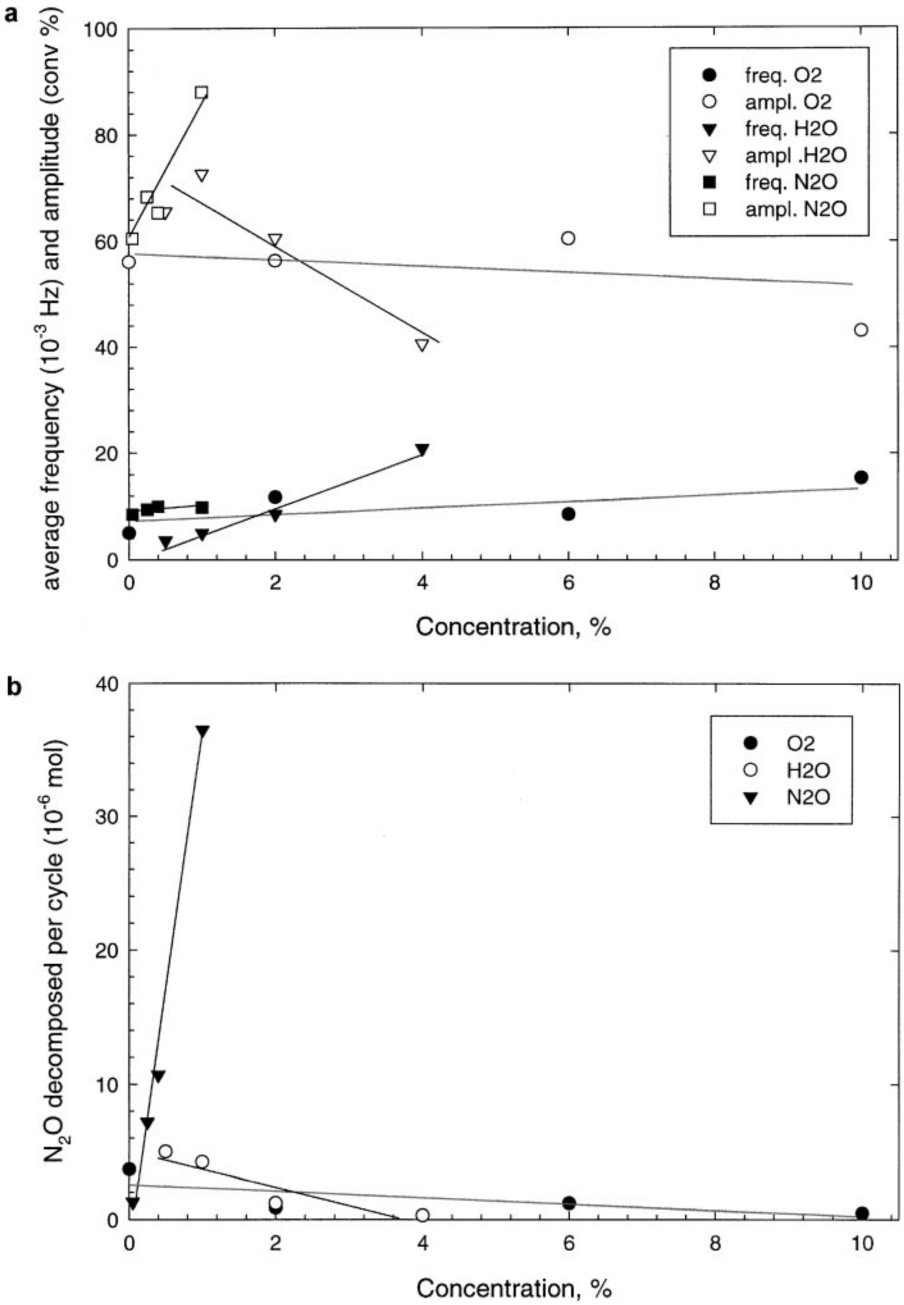

FIG. 6. (a) Average frequency (10^{-3} Hz) and amplitude (conversion, %) of the oscillations and (b) number of moles of N_2O decomposed per cycle (10^{-6} mol) at 341°C as a function of the concentration of the reactants in the feed. Other reaction conditions as in Figs. 3–5.

notwithstanding the clear differences in the catalyst system with respect to Cu/ZSM-5 catalysts.

Oscillations in the decomposition of N_2O over Cu/ZSM-5 catalysts are characterized by the following features (22–26):

- they occur when the feed is N_2O diluted in helium or nitrogen, i.e., in the absence of water in the feed;
- they have a symmetrical shape; in addition, Turek (24) reported an expansion of the oscillations, which indicates a switchover between two active states; in fact, he observed that after a period of nearly constant activity there is an abrupt change in the conversion to a different value which remains constant for a different length of time than in the first case; and
- they are inhibited (26) or not affected (24) by oxygen.

Conversely, oscillations on the Rh–ZrNdO$_x$ catalyst (i) occur only when water is present in the feed (Fig. 4), (ii) are clearly asymmetric in shape and do not show

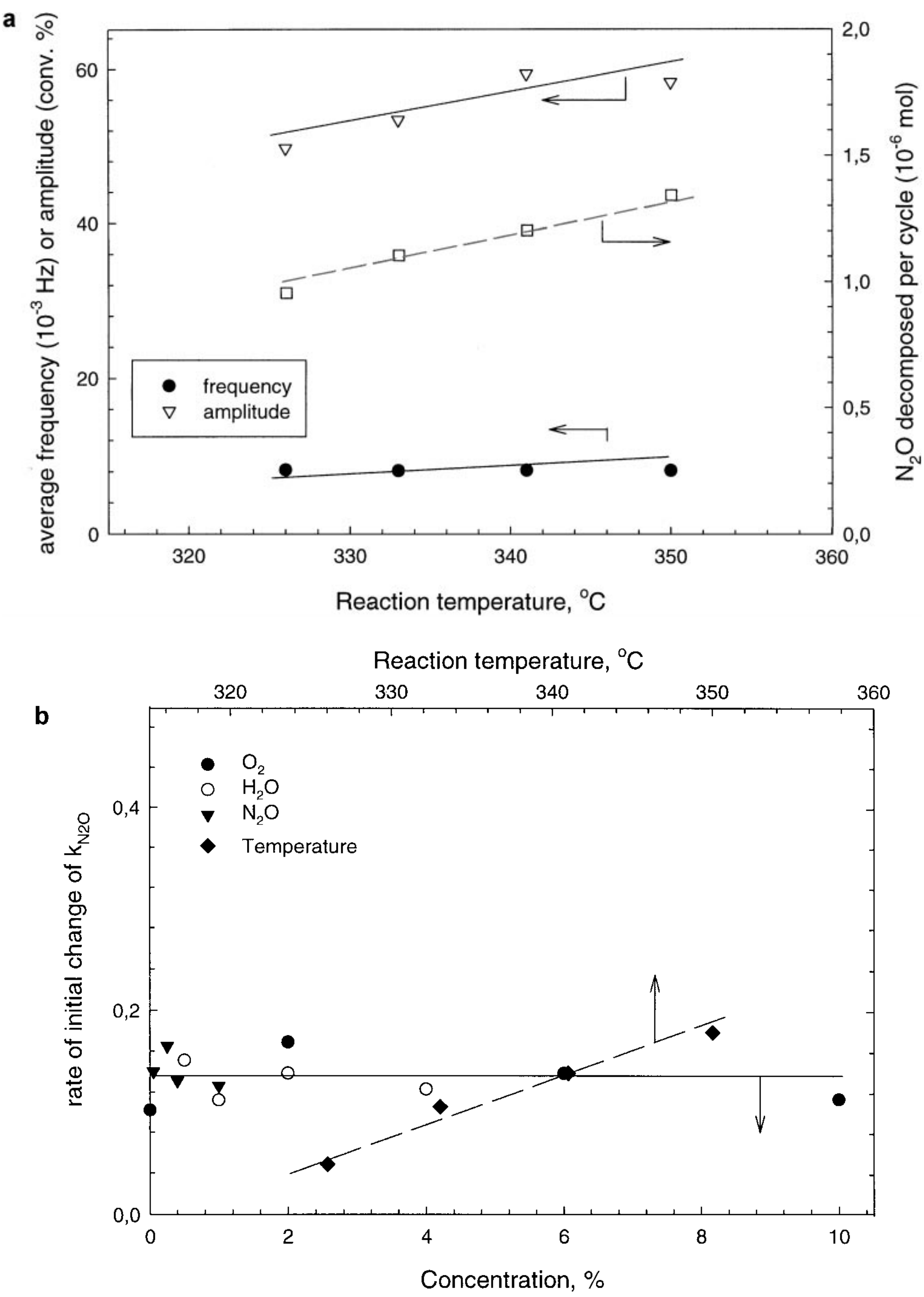

FIG. 7. (a) Average frequency (10^{-3} Hz) and amplitude (conversion, %) of the oscillations and number of moles of N_2O decomposed per cycle (10^{-6} mol) at 341°C as a function of the reaction temperature. Feed composition as in Fig. 2. (b) Rate of initial change in the kinetic constant of N_2O depletion during phase 1 of oscillations (k_{N_2O}, see text) as a function of the concentration of oxygen, water, and N_2O in the feed (concentration of the other components in the feed as reported in Figs. 3, 4, and 5, respectively) and of the reaction temperature (feed composition as in Fig. 1).

induction time, and (iii) were observed to change oxygen over a wide range (0–10%), although oxygen influences the characteristics of the oscillations.

These observations indicated the different natures of the two phenomena responsible for the oscillations in the decomposition of N_2O over Cu/ZSM-5 and Rh–ZrNdO$_x$. The mechanism responsible for the effect is probably also different.

The most striking feature of the phenomenon observed on the Rh–ZrNdO$_x$ catalyst is the fact that oscillations are triggered by the presence of steam in the feed, a characteristic aspect of this phenomenon not previously observed.

There are two possible effects of water in determining the oscillating phenomenon: (i) it can change the surface state of a zirconia-based support, i.e., the hydration of zirconia determines a change in the interaction between the support and the Rh particles and this change determines the occurrence of the oscillations, although it is not the driving force for the oscillations itself, and (ii) water is directly involved in the oscillation mechanism.

In characterizing the chemistry and surface properties of copper ions supported on zirconia (28) it was noted that copper ions show a different reducibility and reoxidizability, depending on the hydroxylation state of the zirconia, because on the hydroxylated zirconia surface copper ions show reduced interaction with the substrate. Rh particles supported on doped zirconia showed reduced interaction with the support with respect to other oxide supports such as alumina (7). The doping of zirconia with small amounts of trivalent ions was observed to create oxygen vacancies on the surface which promote the dispersion of Rh particles and their stability against thermal sintering (29). This effect is absent in the presence of water which inhibits the formation of the oxygen vacancies. Rh particles supported on zirconia were found to show an *in situ* activation phenomenon in N_2O decomposition when treated in helium at a high temperature, due to the creation of these oxygen vacancies which promote desorption of oxygen from the Rh surface and the dispersion of Rh particles (30). Here again, the effect is absent in the presence of steam in the feed.

All these indications suggest, therefore, that hydration of the zirconia surface reduces the metal–support interaction and that this effect may influence the appearance of the oscillating behavior in the decomposition of N_2O. On the other hand, if water plays a direct role in the N_2O decomposition mechanism, for example by reacting with the monoatomic oxygen species generated by N_2O decomposition, oscillations may be expected to be independent of the type of support used for Rh particles, whereas oscillations were observed only for zirconia-based catalysts and not for Rh supported on alumina or silica.

Therefore, the most likely role of water in triggering the oscillations on the Rh–$ZrNdO_x$ catalyst is to bring about a change in the nature of the interaction between the noble metal and the substrate, although further studies are necessary to better clarify this point. The effect of Nd-doped zirconia in changing the surface acid strength of Brønsted sites (8, 9), however, is in agreement with the above hypothesis and may explain why more regular oscillations were observed in the doped sample in comparison to the undoped sample (27).

On hydroxylated zirconia Rh particles show reduced interaction with the substrate, whereas in the absence of water the presence of oxygen vacancies at the Rh–zirconia interface enhances the rates of desorption from the Rh surface (30) of the oxygen atoms (produced during N_2O decomposition) which otherwise tend to remain chemisorbed over the Rh surface, leading to its progressive covering. It is thus reasonable to suppose that on a hydroxylated zirconia surface the Rh particles tend progressively to be covered by the oxygen produced during the decomposition of N_2O and that due to the reduced metal–support interaction (and thus weaker stabilization of Rh particles) above a certain level of surface coverage with oxygen, a reconstruction of the Rh surface occurs which leads to the release of the chemisorbed oxygen and resumption of the cycle responsible for the oscillations. In the absence of water in the feed, due to both the stronger metal–support interaction (29) and the role of interfacial oxygen vacancies in desorbing oxygen from the Rh surface (30), the oscillation phenomenon does not occur.

It is known, on the other hand, that the sticking coefficient of molecules on a metal surface may to a large extent depend on the coverage by oxygen of the surface and coverage-dependent reaction rates were often used in the kinetic reaction models to simulate oscillating phenomena (19).

It is thus possible to suggest the following working model to explain the oscillations in N_2O decomposition on the Rh–$ZrNdO_x$ catalyst:

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

It may be noted that due to the very low concentration of N_2O for which oscillations are observed (below 0.05%; Fig. 5) and thus the very low heat released during the decomposition of N_2O, the oscillations cannot be explained by non-isothermal phenomena.

Although present data do not allow us to be more specific on the nature of the mechanism of the *in situ* reconstruction of Rh particles, a tentative hypothesis may be advanced. In fact, it has been reported that (i) adsorbed N and O atoms can restructure the Rh surface (31–33), (ii) Rh(111) crystalline plane is predominant for smaller Rh particles, whereas Rh(100) and Rh(110) crystalline planes dominate in larger Rh particles (34), (iii) the different Rh faces show different reactivity and adsorption behavior toward nitrogen oxides (34), and (iv) NO induces the breakdown of Rh particles, due to the formation of mobile nitrosyl complexes (35).

It may be thus supposed that the mechanism of N_2O dissociation on the Rh surface may occur either by direct decomposition to O adatom and gaseous N_2 or through dissociation to NO and N adatom with further dissociation of NO to N and O adatoms, a well-known reaction which occurs on Rh surfaces. N_2 forms then by recombination of N adatoms. It was demonstrated that increasing oxygen coverage over the Rh surface forces N adatoms into high coverage islands and thus increases the order of magnitude of the rate of desorption of N_2 (36). Possibly, this is an additional explanation for the increase in the reaction rate of N_2O dissociation increasing coverage by O adatoms (rising part of the oscillations). However, at the highest coverages of chemisorbed atomic oxygen on the Rh surface, the dissociation of NO becomes no longer possible and NO may instead form chemisorbed nitrosyl species which induce the reconstruction of the Rh surface and the breakdown of Rh particles to form smaller Rh particles with contemporaneous release of chemisorbed atomic oxygen. In small rhodium particles different crystalline planes predominate (probably Rh(111)) and thus it may be reasonable that the transformation is accomplished by a drastic decrease of catalyst activity in N_2O decomposition. However, smaller crystallites are not very stable and the progressive accumulation of oxygen atoms, produced by N_2O dissociation, leads to the sintering of Rh particles and the reconstruction of surface to Rh(100) or Rh(110) crystalline planes. This is consistent with the general observation that on fcc {111} surfaces atomic adsorbates may induce reconstruction resulting in 4-fold or even 5-fold sites (33). This mechanism of reconstruction can explain the observations, although it does not clarify the specific role of the oxygen and water interaction. Probably thus the mechanism can be more complex, involving surface rhodium hydroxide species. Specific spectroscopic studies are need to clarify this question.

The mechanism outlined above to explain the oscillations will be further supported by data in part 2, but remains speculative and thus must be considered as a working model to analyze the phenomenon. It is however, worth analyzing whether the features of the oscillations can be described when modeled on a kinetic basis. Using a simple approach, it is possible to write the following sequence of steps according to the mechanism suggested above:

$$N_2O + {}^* - k_1 \rightarrow N_2 + O^* \qquad [1]$$

$$N_2O + O^* + {}^* - k_2 \rightarrow N_2 + 2O^* \qquad [2]$$

$$(O^*)_n - k_3 \rightarrow \frac{n}{2} O_2. \qquad [3]$$

There are two competitive reactions in N_2O decomposition (Eqs. [1] and [2]), characterized by two rate constants (k_1 and k_2), which describe the reaction on a free Rh site (*) or the reaction on a free Rh site with the participation of a chemisorbed oxygen (O^*). Above a certain concentration of chemisorbed oxygen (indicated as $(O^*)_n$), a rapid release of chemisorbed oxygen occurs (Eq. [3]), due to surface reconstruction.

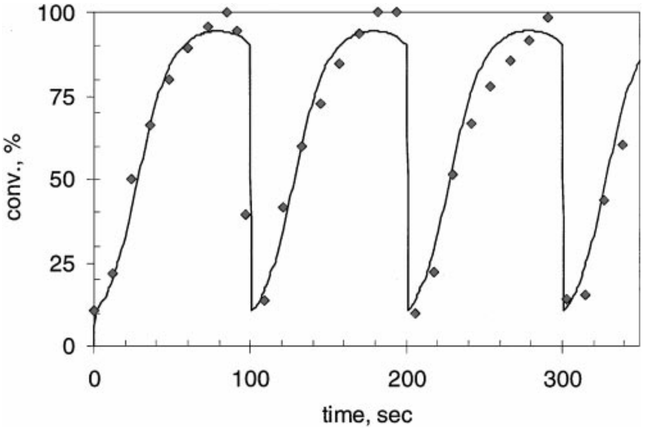

FIG. 8. Experimental data (symbols) and calculated conversion (solid line, see text) at 341°C for a feed composition of 1% N_2O, 2% H_2O, and 6% O_2 in helium. Rate constants in the kinetic model: $k_1 = 1.35 \times 10^4$, $k_2 = 9.12 \times 10^{10}$, $k_3 = \infty$, contact time = 0.13 s.

Figure 8 shows a comparison of the estimated behavior based on the above kinetic model (reaction rates based on Eqs. [1]–[3] as elementary steps integrated over time and reactor bed, assuming a plug flow reactor model) with the experimental data. Notwithstanding the simple model adopted, a good description of the key features of the oscillating phenomenon is possible. Even if this does not prove the validity of the model, the good agreement indicates that the suggested mechanism may be a reasonable means of interpreting the data.

It should be remarked that there is some discrepancy regarding especially the final part of phase 1 of the oscillations, which indicates that the kinetic model should be improved. As discussed before, the mechanism of change in the population of adspecies and surface reconstruction is more complex. It being not possible at the present stage to describe in detail the mechanism, an improved kinetic model to fully describe the oscillations in N_2O decomposition may be possible only after further investigations.

However, it is worth noting that the model can also explain the dependence of oscillations on experimental parameters. In fact, it is reasonable to expect that the initial reaction rate on the free Rh surface depends not on the concentration of reactants in the feed, since a large number of free Rh sites are available, but mainly on the reaction temperature which influences k_1 (Fig. 7b). It is also possible to explain why oxygen has a much more limited influence on the characteristics of the oscillations than other reactants (Fig. 6a), because it dissociates over the Rh surface at a much lower rate than N_2O. Therefore, the frequency of the oscillations increases (Fig. 6a), but the amount of N_2O decomposed per cycle decreases (Fig. 6b), whereas an increase in the concentration of N_2O causes both parameters to increase much more dramatically.

CONCLUSIONS

The Rh–ZrNdO$_x$ catalyst shows the presence of oscillations in the decomposition of N_2O only when water is fed together with N_2O and O_2. Analysis of the characteristic features of the oscillations and their dependence on reaction conditions suggests that water is not directly involved in the mechanism responsible for the oscillations, but is mainly responsible for favoring the accumulation of the oxygen produced by the dissociation of N_2O on the Rh surface and for weakening the metal–support interaction, making a 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 which 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 explains the characteristic shape of the oscillations. A simple kinetic model based on the suggested mechanism correctly describes the characteristic features of the oscillations.

REFERENCES

1. Centi, G., Perathoner, S., and Vazzana, F., *CHEMTECH* **29**(12), 48 (1999).
2. Kapteijn, F., Rodriguez-Morasol, J., and Moulijn, J. A., *Appl. Catal. B: Environ.* **9**, 25 (1996).
3. Uriarte, A. K., Rodkin, M. A., Gross, M. J., Kharitonov, A. S., and Panov, G. I., *Stud. Surf. Sci. Catal.* **110**, 857 (1997).
4. Panov, G. I., Uriarte, A. K., Rodkin, M. I., and Sobolev, V. I., *Catal. Today* **41**, 365 (1998).
5. Centi, G., Dall'Olio, L., Perathoner, S., Vazzana, F., Marella, M., Tomaselli, M., and Mantegazza, M. (1999). Submitted for publication.
6. Yao, H. Y., Stepien, H. K., and Gandhi, H. S., *J. Catal.* **61**, 547 (1980).
7. Burch, R., and Loader, P. K., *Appl. Catal. A: Gen.* **143**, 317 (1996).
8. Loong, C. K., Thiyagarajan, P., Richardson, J. W., Ozawa, M., and Suzuki, S., *J. Catal.* **171**, 498 (1997).
9. Loong, C. K., Richardson, J. W., and Ozawa, M., *J. Catal.* **157**, 636 (1995).
10. Fornasiero, P., Di Monte, R., Rao, G., Kaspar, J., Meriani, S., Trovarelli, A., and Graziani, M., *J. Catal.* **151**, 168 (1989).
11. Ozawa, M., and Kimura, M., *J. Less Common Metals* **171**, 195 (1991).
12. Ertl, G., *Adv. Catal.* **37**, 213 (1990).
13. Kobayashi, M., Kanno, T., Takeda, H., and Fujisaki, S., *Appl. Catal. A: Gen.* **151**, 207 (1997).
14. Tenchev, K. K., Petrov, L. A., Savelieva, G. A., and Sass, A. S., *Appl. Catal. A: Gen.* **83**, 31 (1992).
15. Schröder, U., *J. Catal.* **146**, 586 (1994).
16. Basset, M. R., and Imbihl, R., *J. Chem. Phys.* **93**, 811 (1990).
17. Yeates, R. C., Turner, J. E., Gellman, A. J., and Somorjai, G. A., *Surf. Sci.* **149**, 175 (1985).
18. Collins, N. A., Sundaresan, S., and Chabal, Y., *Surf. Sci.* **180**, 136 (1987).
19. Schüth, F., Henry, B. E., and Scmidt, L. D., *Adv. Catal.* **39**, 51 (1995).
20. Sadhankar, R. R., and Lynch, D. T., *J. Catal.* **149**, 278 (1994).
21. Sadhankar, R. R., Ye, J., and Lynch, D. T., *J. Catal.* **146**, 511 (1994).
22. Lintz, H. G., and Turek, T., *Catal. Lett.* **30**, 313 (1995).
23. Turek, T., *Appl. Catal. B: Environ.* **9**, 201 (1996).
24. Turek, T., *J. Catal.* **174**, 98 (1998).
25. Ciambelli, P., Garufi, E., Pirone, R., Russo, G., and Santagata, F., *Appl. Catal. B: Environ.* **8**, 333 (1996).
26. Ciambelli, P., Di Benedetto, A., Garufi, E., Pirone, R., and Russo, G., *J. Catal.* **175**, 161 (1998).
27. Vasumini, I., Thesis, University of Bologna, Italy, 1998.
28. Morterra, C., Giamello, E., Cerrato, G., Centi, G., and Perathoner, S., *J. Catal.* **179**, 111 (1998).
29. Centi, G., Panzacchi, B., Perathoner, S., and Pinna, F., "Proceedings, 12th International Congress on Catalysis, Granada, Spain," June 2000, paper 042, to be published.
30. Centi, G., Dall'Olio, L., and Perathoner, S., *Appl. Catal. A: Gen.* **194–195**, 79 (2000).
31. Baraldi, A., Dhank, V. R., Comelli, G., Kishkinova, M., and Rosei, R., *Appl. Surf. Sci.* **68**, 395 (1993).
32. Kalakkad, D., Anderson, S. L., Logan, A. D., Pena, J., Braunschweig, E. J., Peden, C. H. F., and Datye, A. K., *J. Phys. Chem.* **97**, 1437 (1993).
33. Titmuss, S., Wander, A., and King, D. A., *Chem. Rev.* **96**, 1291 (1996).
34. Peden, C. H. F., Belton, D. N., and Schmieg, S. J., *J. Catal.* **155**, 204 (1995).
35. Krause, K., and Schmidt, L. D., *J. Catal.* **140**, 424 (1993).
36. Belton, D. N., DiMaggio, C. L., and Ng, K. Y. S., *J. Catal.* **144**, 273 (1993).