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Room temperature decomposition of N_2O in the presence of gaseous oxygen on prereduced Rh supported catalysts

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The room temperature decomposition of N_2O over prereduced Rh-based catalysts (Rh supported on ceria, zirconia and titania–alumina) is studied as a function of the oxygen content in the feed. Results indicate that Rh supported on titania–alumina shows lower degree of inhibition by gaseous oxygen on this reaction, attributed to the role of the metal particle–support interface region in the reaction. The effect of Rh loading and of the reaction temperature are consistent with the hypothesis.

Keywords: N_2O decomposition, Rh supported catalysts, CeO_2, ZrO_2, titania–alumina

1. Introduction

The United Nations Framework Convention on Climate Change (Kyoto conference in 1996) has put N_2O under attention, because nitrous oxide has 270 times the greenhouse potential of CO_2 (over a 100 year time horizon) [1]. As a result, some companies (mainly producers of adipic acid in which process N_2O forms in a large amount) already begun on a voluntary basis a programme for the reduction of N_2O emissions based mainly on a catalytic technology of N_2O decomposition [2]. However, due to a large variety of sources of N_2O for which this catalytic technology cannot be applied on a cost-effective basis, research activity has been focused on finding alternative methods, although still based on the use of heterogeneous catalysts, for the conversion or reuse of N_2O [3].

A specific problem is related to the fact that in several cases emissions are at near room temperature and often discontinuous, N_2O being produced in several discontinuous processes using nitric acid as an oxidant for the conversion of organic substrates. A suitable technology in this case would operate at the same temperature as the emissions and without problems when applied to discontinuous emissions. The decomposition of N_2O in a fixed-bed reactor using a prereduced catalyst possesses such characteristics. Several reduced catalysts, such as copper-based catalysts [4], are known to be active at room temperature in the decomposition of N_2O, but not in the presence of gaseous oxygen, while the O_2 concentration in the type of applications cited above is often a three orders of magnitude higher than the N_2O concentration. It is thus necessary to develop specific catalysts which, after reduction, are selectively oxidized by N_2O instead of O_2.

Such a type of catalyst may be useful also in indoor applications. In fact, although not toxic as other nitrogen oxides, N_2O acts as asphyxiant and sedative of the nervous system and by prolonged exposure gives rise to polyneuropathy and myelopathy. Its threshold limit value (TLV-TWA) is 50 ppm. N_2O is still largely used in anaesthetic operations, but a safety device which converts N_2O in the case of uncontrolled release could be necessary. Also in this case, the device may be based on a fixed bed of prereduced catalyst, if the problem of its selective reoxidation by N_2O instead of O_2 can be solved.

No data are available in literature on such a type of problem, but Imamura and Okamoto [5] reported that a catalyst based on Rh(3%)–CeO_2 prereduced with H_2 at 500 °C (1 h) showed a complete activity in N_2O decomposition at room temperature for relatively long times (higher than using other types of oxide support). The effect of oxygen was not reported, but the possibility of applying similar kinds of catalyst to the room temperature selective conversion of N_2O in the presence of gaseous O_2 may be hypothesized. The aim of this work is to explore this possibility. It should be clarified that the reaction is not the stoichiometric reoxidation by N_2O of the exposed metal sites reduced by hydrogen pretreatment, because even considering 100% metal dispersion the amount of N_2O decomposed is two orders of magnitude higher than the stoichiometric amount, and, on the other hand, without the noble metal the supports are nearly inactive in the same conditions.

2. Experimental

2.1. Preparation of the catalysts

CeO_2, ZnO, ZrO_2 and a titania–alumina mixed oxide have been used as supports for Rh added in all cases by an

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incipient wet impregnation method using an aqueous solution of rhodium nitrate in order to have a final loading of Rh of 0.5–3%, as reported in table 1. After impregnation, the samples were dried, calcined at 500 °C and then activated by reductive treatment as described elsewhere [6,7]. The samples will be called hereinafter with the following code: Rhx–S, where x is a number which denotes the amount of Rh by weight and S the type of support (Ce for CeO_2, Zn for ZnO, Zr for ZrO_2, and TA for TiO_2–Al_2O_3). The surface area of the samples is reported in table 1.

The oxide supports have been prepared in the case of ceria and zinc oxide by precipitation with $(NH_4)_2C_2O_4$ and NH_4OH of a Ce or Zn nitrate aqueous solution maintained at pH in the 4–5 pH range, ageing, washing, drying and calcination at 600 °C for 3 h. For zirconia and titania–alumina a sol–gel preparation starting from metal isopropoxides and acid catalysis (CH_3COOH) plus a small amount of acetylacetonate to moderate the rate of gelification has been used, as described eslewhere [6,7].

Table 1
Characteristics of catalysts used and their activity on weight and surface area bases in the room temperature decomposition of N_2O in the absence of oxygen in the feed.

Code	Surface area (m^2/g)	Activity[a]	Specific activity[b]
Rh1–Ce	34	10.1	2.9
Rh1–Zn	26	0.2	0.1
Rh1–Zr	63	5.3	0.8
Rh1–TA	113	4.3	0.4

[a] Activity (values $\times 10^5$): total moles of N_2O decomposed at room temperature per gram catalyst after reduction at 500 °C (1 h) with a flow of 70% H_2 in helium. The amount of N_2O decomposed is determined from breakthrough curves up to a conversion level of $N_2O \geqslant 90\%$.

[b] Specific activity (values $\times 10^6$): activity as above, but referred to square meter of surface area of the catalyst.

2.2. Catalytic tests

Catalytic tests were carried out in a quartz fixed-bed reactor equipped with an on-line mass-quadrupole system for the continuous analysis of the feed and of reaction products as described elsewhere [6–9]. Tests were made using 0.5 g of catalyst in the form of particles with diameters of the order of 0.1–0.2 mm and a space velocity of 30 000 h^{-1}.

The catalysts were prereduced *in situ* at 500 °C before the catalytic tests with a flow of 70% H_2 in He for 0.5 h. After switching the feed to pure helium, the reactor was cooled down to room temperature and after stabilization of the temperature, the reaction feed was sent to the reactor starting at the same time to monitor the conversion of N_2O. The delay in the system response, determined in blank tests without the catalyst, was subtracted. The moles of N_2O converted were determined from the corrected breakthrough curves, estimating the amount of N_2O converted up to a conversion $\geqslant$90%.

3. Results

3.1. Role of the support in relation to the effect of oxygen

The breakthrough curve for the room temperature N_2O decomposition in the absence of oxygen on the prereduced Rh1–Ce catalyst is reported in figure 1. The amount of N_2O decomposed per gram of catalyst and per square meter of surface area, up to a conversion level of N_2O $\geqslant$90% is reported in table 1.

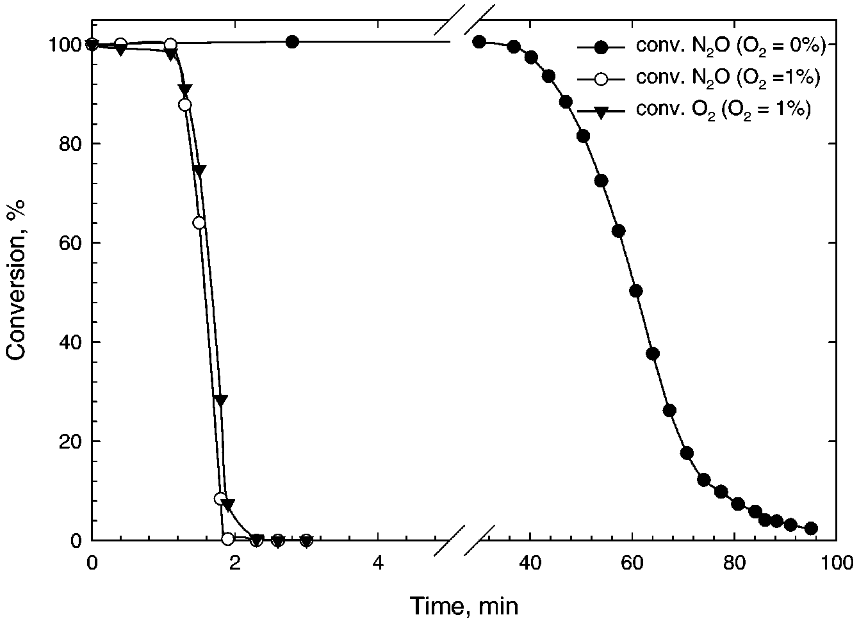

Figure 1. Breakthrough curves for N_2O decomposition at room temperature on prereduced Rh1–Ce. Feed: (a) 0.05% N_2O in helium and (b) 0.05% N_2O + 1% O_2 in helium.

The type of oxide support and the test conditions are comparable with those reported by Imamura and Okamoto [5] as the preferable to obtain the highest transient activity. The results in terms of features of the breakthrough curve (figure 1) and amount of N_2O decomposed (table 1) are in good agreement with those reported by Imamura and Okamoto [5], indicating the reproducibility of the data. However, when the activity is analysed in the presence of 1% oxygen in the feed (figure 1) the activity reduces by a factor 35, around two times higher than the ratio of concentrations between oxygen and N_2O in the feed (factor 20). This points out that this catalyst does not show a selective reoxidation by N_2O against O_2. A higher concentration of oxygen in the feed leads to a nearly complete absence of conversion of N_2O.

The use of zinc oxide as the support for rhodium, cited from Imamura and Okamoto [5] also as a highly active sample in room temperature N_2O decomposition, instead was not found to allow a high level of removal of N_2O in the absence of oxygen (table 1) and activity was negligible in the presence of O_2. Therefore, a different kind of support for the rhodium was used.

In previous studies using Rh-based catalysts for N_2O decomposition [6,7], we observed that zirconia and titania play an active role in the catalytic reaction, because the presence of oxygen vacancies at the support–Rh particle interface considerably influences the steady-state activity in N_2O decomposition in the presence of oxygen. In fact, the monoatomic oxygen produced from N_2O dissociation remains on the Rh surface and tends to cover it, while oxygen vacancies at the interface increase the rate of migration of this chemisorbed oxygen to the support and its desorption leading thus to an increase in the rate of reaction [8]. Although cited data refer to higher reaction temperatures, in the 300–400 °C range, a similar reaction mechanism was supposed to be possible also at room temperature on prereduced catalysts. Zirconia- and titania-based catalysts were thus analysed. A titania support containing 10% alumina as a textural promoter was used instead of pure titania, because using the latter a relevant loss of surface area was noted after the prereduction treatment. Titania–alumina samples prepared by a sol–gel method, when the amount of alumina was not exceeding about 20%, were instead found to be more thermally resistant to sintering than pure titania prepared with the same method, although surface properties remained similar to those of pure titania [10].

The behavior of the prereduced Rh1–Zr sample in the room temperature decomposition of N_2O using a feed containing variable oxygen concentrations up to a value of 6% (corresponding to a $O_2 : N_2O$ ratio of 120) is reported in figure 2. The behavior in the absence of oxygen in the feed shows that the activity is about half of that of the Rh1–Ce sample on a weight basis and less than one third on a surface area basis (table 1), as reasonably expected being more difficult the reduction of zirconia during the pretreatment. When oxygen is present in the feed, there is still the very large reduction in the activity in N_2O r.t. decomposition, but less marked than in the case of Rh1–Ce and some activity, although low, is shown from the catalyst even using an $O_2 : N_2O$ ratio of 120 in the feed (figure 2). Furthermore, while increasing oxygen concentration in the feed from 0 to 1% leads to a decrease of a factor 35 in the amount of N_2O decomposed up to 90% of level of conversion (thus a factor similar to that of Rh1–Ce), the further increase of the oxygen concentration from 1 to 6% leads to a decrease of a factor 1.8 only.

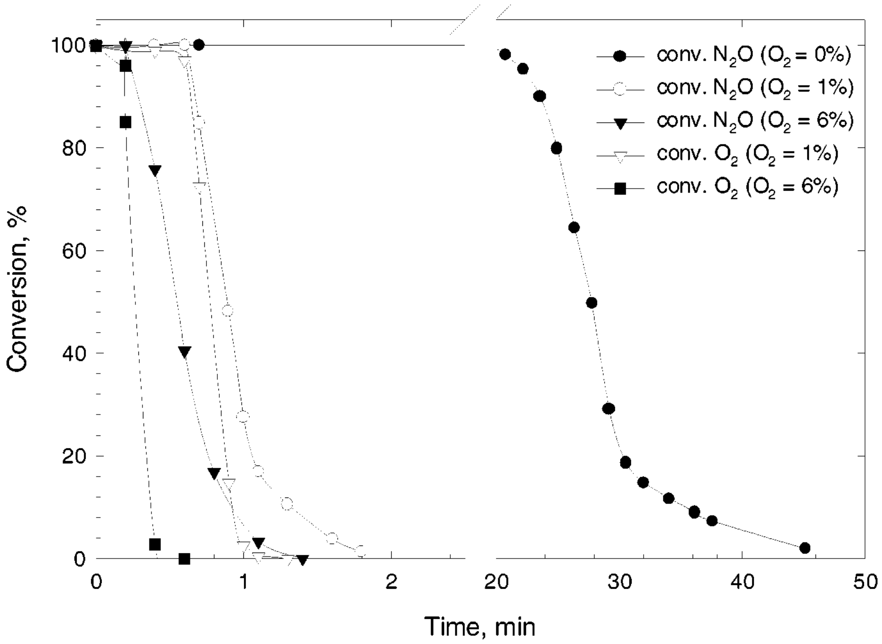

Figure 2. Breakthrough curves for N_2O decomposition and oxygen consumption at room temperature on prereduced Rh1–Zr. Feed: 0.05% N_2O, oxygen concentration as indicated in the legend and helium.

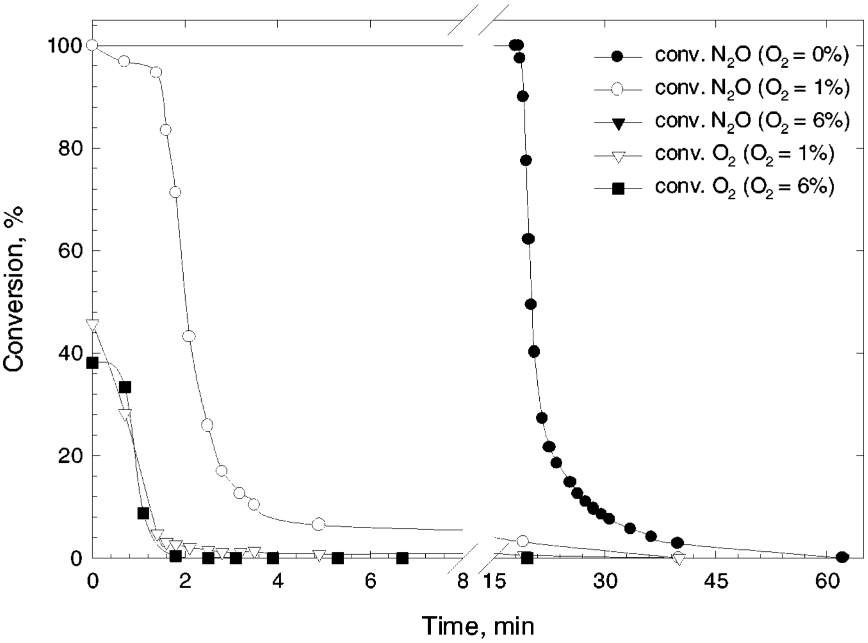

Figure 3. Breakthrough curves for N_2O decomposition and oxygen consumption at room temperature on prereduced Rh1–TA. Feed: 0.05% N_2O, oxygen concentration as indicated in the legend and helium.

The breakthrough curves for N_2O decomposition at room temperature and of oxygen conversion on the Rh1–TA sample for different oxygen concentrations in the feed are reported in figure 3. The activity on a weight basis in the absence of oxygen in the feed of this catalyst is much lower than that of Rh1–Ce and lower also than that of Rh1–Zr, a difference that becomes much larger when the activity on a surface area basis is considered (table 1).

However, when the activity is analyzed in the presence of oxygen in the feed a different behavior is noted. For an O_2 concentration of 1%, two aspects should be remarked with respect to the Rh1–Zr and Rh1–Ce samples: (i) the initial conversion of oxygen is not 100%, but lower, and (ii) the drop in activity with respect to the case of absence of oxygen in the feed is much lower. The activity in N_2O r.t. decomposition (up to 90% of conversion level in the breakthrough curves) drops by a factor 12 with respect to a factor 35 in the previous cases. Furthermore, the further increase of the concentration of oxygen to 6% does not lead to a further decrease in the activity; the decrease factor was 1.8 for Rh1–Zr and around 10 for Rh1–Ce.

The effect of oxygen to N_2O ratio in the feed on the inhibition of the room temperature activity in N_2O decomposition is summarized in table 2 as a function of the type of support.

Table 2
Effect of oxygen on the decrease of N_2O removal at room temperature (in the breakthrough curves up to a level of conversion $\geqslant$90%) as a function of the nature of the support in samples containing 1% Rh.

Catalyst	Inhibition factor[a]		
	0[b]	20[b]	120[b]
Rh1–Ce	0	35	270
Rh1–Zr	0	35	65
Rh1–TA	0	12	13

[a] Presence of oxygen in the feed with respect to the case of absence of oxygen in the feed on prereduced samples. Values calculated from breakthrough curves up to a conversion level of N_2O $\geqslant$90%.

[b] $O_2:N_2O$ ratio in the feed.

3.2. Effect of rhodium loading

The effect of the loading of rhodium on zirconia and titania–alumina supports, using as indexes of the behavior the activity at room temperature in the anaerobic decomposition of N_2O (moles of N_2O decomposed up to a conversion level $\geqslant$90%) and the “inhibition factor” (decrease of activity with respect to the case in the absence of oxygen in the feed) for a concentration of oxygen of 6% in the feed, is shown in figure 4.

Increasing the loading of rhodium, the activity increases for both types of support nearly linearly, evidencing the specific role of the noble metal in the reaction. However, the “inhibition factor” decreases increasing the Rh loading, pointing out the specific role of the Rh–support interface in determining the behavior in the decomposition of N_2O in the presence of oxygen.

3.3. Effect of reaction temperature

The effect of the reaction temperature during N_2O decomposition on the behavior of the Rh1–TA sample is shown in figure 5, using as indexes of the behavior the same as used to discuss the effect of Rh loading.

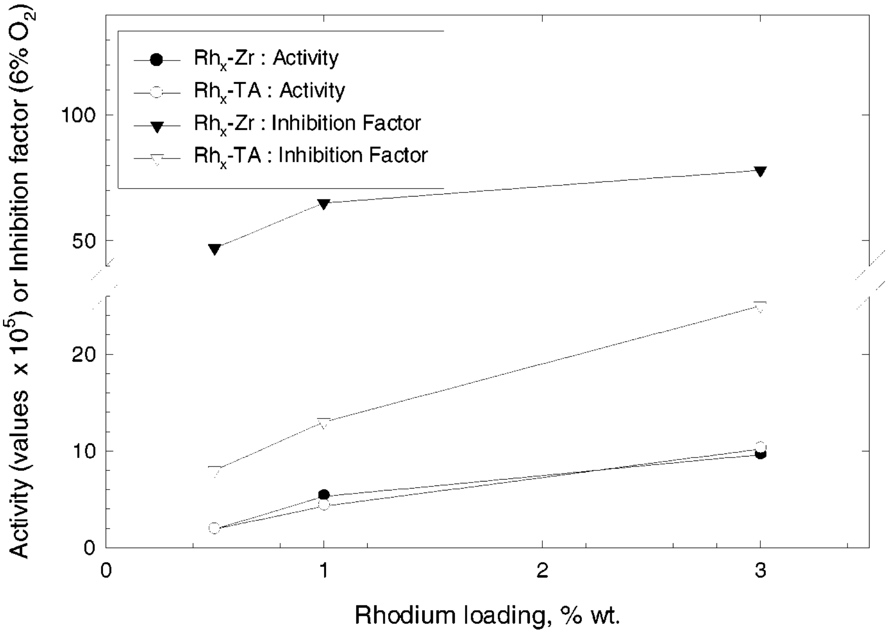

Figure 4. Effect of rhodium loading on zirconia and titania–alumina supports on the behavior in N_2O decomposition at room temperature on prereduced catalysts. Indexes of catalytic behavior: (1) *activity* (values $\times 10^5$): moles of N_2O decomposed per gram of catalyst in the anaerobic decomposition at room temperature up to a conversion level $\geqslant 90\%$; (2) *inhibition factor*: decrease of activity, with respect to the case in the absence of oxygen in the feed, for a concentration of oxygen of 6% in the feed.

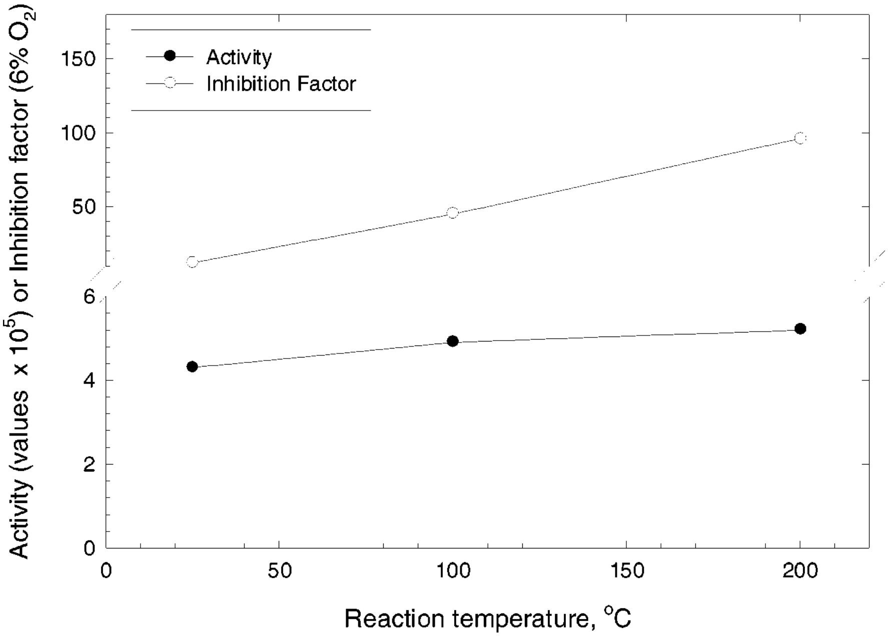

Figure 5. Effect of the reaction temperature on the behavior in N_2O decomposition of prereduced Rh1–TA catalyst. Indexes of catalytic behavior as reported in figure 4.

Increasing the reaction temperature leads to an increase of the activity, although not very relevant, indicating that the reaction is not kinetically controlled. Reasonably, the small increase in the activity can be attributed to an increase in the bulk diffusion rate of chemisorbed oxygen, produced from N_2O decomposition, from the metal to the support. In contrast, the "inhibition factor" considerably drops, the reoxidation of catalyst by gaseous oxygen being favored instead of that by N_2O.

4. Discussion and conclusions

The investigation of the selective decomposition of N_2O at room temperature in the presence of gaseous oxygen on supported Rh-based catalysts shows that both the nature of the support and the reaction conditions considerably influence the possibility of a selective conversion of N_2O in the presence of oxygen. Prereduced Rh supported on titania–alumina and with a loading of around 1% shows the better combination of activity in r.t. N_2O decomposition and reduced inhibition from oxygen. Although the present types of catalysts still do not show enough performance to be applied on a practical scale, the data evidence the relevant role of the nature of the support in determining the selective conversion of N_2O in the presence of oxygen and therefore indicate the possibility of further improvements, when the mechanism determining this behavior can be better understood.

Present data do not allow the clarification of the mechanism controlling the selective transformation of N_2O at r.t. in the presence of oxygen and the role of the support. However, it can be evidenced that the dispersion of Rh is not the determining factor, because on the examined catalysts the amount of N_2O decomposed in anaerobic conditions follows an inverse trend with respect to the sensitivity of the catalyst to the inhibition by gaseous oxygen (tables 1 and 2). If the N_2O decomposition activity is only related to the available metallic surface area, the same trend with and without oxygen in the feed should be expected.

On the other hand, the activity is dependent on the level of Rh loading (figure 4) and this suggests that probably the active sites for the decomposition are located at the Rh particle–support interface and thus considerably influenced by the nature of the support. Reasonably, during prereduction oxygen vacancies are created near the Rh surface which activates hydrogen that diffuses then over the support reducing it. When N_2O and O_2 are fed to the prereduced catalyst, they compete for reoxidation. The considerable drop of activity when O_2 is present with respect to the case when it is absent, but the less relevant effect by further increase of oxygen (table 2), suggests that oxygen reoxidizes faster than N_2O lattice oxygen vacancies of the support, but near to Rh particles, where N_2O decomposition is catalyzed, the inverse occurs. This explains why (i) small amounts of oxygen lead to a considerable inhibition in r.t. N_2O decomposition, but the effect is much less relevant and furthermore very dependent on the nature of the support when the oxygen concentration in the feed is further increased (table 2), and (ii) the role of Rh loading on the behavior. Increasing the loading of Rh, the metal surface area and thus the activity increases, but decreases the role of metal particle–support interfacial region. The effect of the reaction temperature, favoring oxygen activation, is consistent with this indication.

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