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A New Dynamic Approach for N₂O Decomposition by Pre-reduced Rh/CeZrO_x Catalysts

Camille Moreau,^[a] Ángel Caravaca,^{*[a]} Philippe Vernoux,^[a] and Sonia Gil^{*[a]}

This study deals with the catalytic decomposition of N₂O into harmless N₂ and O₂, in view of its potential application to decrease the pollution from internal combustion engines. The key of this work was to pre-reduce a Rh/CeZrO_x catalyst under a H₂ based atmosphere, in order to enhance the amount of oxygen vacancies in the ceria-based support. The results demonstrated that both, Rh species and oxygen vacancies of the ceria-based support catalyze the N₂O decomposition reaction. However, the presence of high concentrations of H₂O

and O₂ strongly inhibited the catalytic activity. Nevertheless, small O₂ concentrations maintained the performance. Therefore, the pre-reduced Rh/CeZrO_x could be potentially used for the reduction of N₂O emitted by internal combustion engines working in stoichiometric conditions. In addition, a short injection of a reducing agent (e.g. H₂) allowed to partially recover the initial catalytic activity of the system. All in all, this study proposes a new potential approach to mitigate the overall N₂O greenhouse gas emissions.

Introduction

The harmful effects of N₂O related to the greenhouse effect and ozone layer depletion are nowadays well-known. N₂O emissions were recently included in the Greenhouse Gas (GHG) regulations^[1] due to its high-rise warning potential (N₂O constituted nearly 5% of total US greenhouse emissions in 2015^[2]). N₂O emissions are frequently observed in agricultural soil management^[3] as well as an undesirable byproduct of chemical processes such as adipic acid synthesis,^[4] together with industrial combustion devices^[5] and internal combustion engines^[6,7] (e.g. diesel). In this work we will focus on the latter, in view of the more and more stringent environmental regulations and, in particular, the foreseeable Euro 7 regulations concerning NO_x and N₂O emissions.

The current after-treatment catalytic systems for internal combustion engines are very efficient to reduce NO_x emissions (NO + NO₂). However, several studies have demonstrated that they potentially contribute to N₂O formation, where N₂O is mainly produced by the undesirable reaction between nitrogen containing compounds (NO, NO₂, HNO₃, NH₃ or R-NH_x) and oxygen.^[6–8]

In this sense, one of the most popular after-treatment technologies for the removal of NO_x is the so-called Selective Catalytic Reduction (SCR) with NH₃. Vanadium-based materials^[9] and Fe-exchanged zeolites^[10] are commonly used as catalysts. However, N₂O is produced on SCR catalysts at both, intermediate and high temperatures. At intermediate temperatures (200–250 °C), its formation is mainly attributed to the formation of surface ammonium nitrate species (non-selective products of the reaction between NO and NH₃), which are consequently

decomposed to produce N₂O (equation 1 and 2), while at high temperatures (400–450 °C) it is most likely due to ammonia oxidation (equation 3).

Therefore, additional post-treatment approaches should be developed to reduce N₂O emissions. In this sense, several catalytic materials have already been investigated for N₂O catalytic decomposition, leading to the production of harmless N₂ and O₂ (equation 4):

Non-noble metal-based catalysts, bare oxides (e.g., MnO₂, Co₃O₄, CuO), hexaaluminates (e.g., AM_xAl_{12–x}O₁₉ with A=La, Ba and M=Mn, Fe, Ni), hydrotalcites (e.g., Co₄MnAl, CoAl, Co₂Mg₂Mn₂), spinel oxides (AB₂O₄ with A=Mg, Ca, Mn, Co, Ni, Cu, etc., and B=Cr, Fe, Co) and perovskites (ABO₃, with A=La, Pr, etc., and B=Cr, Ba, Mn, Co, Fe, etc.) are some of the most studied catalysts for N₂O decomposition.^[11–14] In particular, several studies have proven that Rh supported on CeO₂ or CeO₂-based oxides are very effective catalysts for this process, due to the synergy between the metal and the active support.^[15–24] In other words, it seems that the enhanced activity could be attributed to the high oxygen storage capacity of the ceria support, together with the strong metal-support interactions between Rh and ceria. Most of these works agree that the reducibility of the support is a key parameter to enhance the performance of the catalyst for N₂O decomposition,^[19–22] and even some early studies suggest that pre-reduced Rh/CeO_x-based materials are very performing.^[15,16,18] In this case, the reduced CeO_x active sites would be re-oxidized with N₂O, allowing for its further

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decomposition. However, none of these studies investigated in detail the dynamic behavior of these pre-reduced materials.

Based on those previous studies, this work describes a potentially new approach for the removal of N_2O produced by automotive sources, including internal combustion engines operating under lean conditions (i.e. under O_2 excess in the combustion chamber) and under stoichiometric conditions. The idea is to use a pre-reduced Rh/CeZrO_x catalyst as active material for N_2O decomposition. The choice of $\text{CeO}_2\text{--ZrO}_2$ as active support was based on the premises that the addition of zirconia enhances both, the oxygen storage capacity, the reducibility and more importantly, the thermal stability of the ceria support.^[16,17,24] The partially reduced catalytic support will be re-oxidized by N_2O , allowing for its decomposition into harmless N_2 and oxygen species. Once the support is completely oxidized, short injections of reducing gas (e.g. H_2) would allow to bring the catalyst back to the pre-reduced active state. In addition, the influence of the presence of O_2 and H_2O in the feed stream was studied, together with the possibility to work in a cyclic operation mode, in view of its further practical implementation.

Results and Discussion

Support and catalyst characterization

The chemical composition, together with the physico-chemical and textural properties of the CeZrO_x support and the Rh/CeZrO_x catalyst (as-prepared after calcination) were obtained by ICP-OES, N_2 -adsorption/desorption and XRD, respectively (Table 1). Rh (0.87% wt.) was introduced by impregnation on the support, followed by its calcination under air flow at 500°C (see experimental section). As expected, both specific surface area (SSA) and total pore volume slightly decreased after Rh incorporation. Both support and catalyst presented a type IV isotherm based upon the IUPAC classification (not shown here), which is characteristic of mesoporous materials with H3-type of hysteresis.^[25] Even after Rh addition, the mesopores diameter distribution, which are calculated using the Barrett-Joyner-Halenda (BJH) method, was similar to the corresponding support and centered at around 8 nm.

X-ray diffraction patterns of the Rh/CeZrO_x catalyst and the support are shown on Figure 1. Both spectra follow exactly the same pattern, with characteristic peaks associated to ceria-based oxides (at $2\theta = 29.3^\circ, 33.9^\circ, 48.7^\circ, 57.8^\circ, 60^\circ, 70^\circ$ and 78°) with a fluorite structure based on a face-centered cubic cell.^[16,17,24] No diffraction peaks related to zirconia phases (ZrO_2)

Figure 1. X-ray powder diffraction patterns of Rh/CeZrO_x catalyst and the corresponding CeZrO_x support.

were observed, suggesting that zirconium was integrated in the ceria (CeO_2) matrix, leading to the formation of a solid solution. Nevertheless, no peaks of Rh or Rh_2O_3 were observed, which could be attributed to its uniform distribution on the surface (high metal dispersion) and the low metal-loading.

The reducibility of Rh/CeZrO_x catalyst and the CeZrO_x support, a key parameter in this study, was evaluated by Temperature Programmed Reduction (H_2 -TPR) with hydrogen. Figure 2 shows the TPR profiles. Regarding the support, its reduction starts at 400°C , leading to the formation of one non-symmetrical peak centered at $\sim 600^\circ\text{C}$. This peak could be attributed to the partial reduction of Ce^{4+} ^[19] since Zr^{4+} cations are not expected to be reduced in this temperature range.

However, together with a much smaller peak at a similar temperature, two new reduction peaks ($T_{\text{max}} \approx 80$ and 170°C , respectively) were observed for the Rh/CeZrO_x catalyst. These new peaks could be attributed to the simultaneous reduction of Rh_2O_3 (equation 5), together with the reduction of Ce^{4+} cations since the ratio H_2/Rh is much greater than the stoichiometry of reaction 5.^[19,20,22]

It is worth noting that, in both cases, the H_2 uptake corresponds to partial reducibility of CeO_2 to $\text{CeO}_{1.6}$ (see Table 1), which clearly indicates that both, the surface and an important part of the bulk ceria are reduced in this temperature range. These results suggest, on the one hand, that the presence of Rh strongly catalyzed the partial reduction of the CeZrO_x support due to the spillover of hydrogen, in good agreement with previous studies on Rh/CeO_2 -based catalysts.^[19,20,22] On the other hand, considering that most of the

Table 1. Physico-chemical, textural and redox properties.

Sample	Rh [%wt] ^[a]	SSA [m^2g^{-1}] ^[b]	Total pore volume [cm^3g^{-1}] ^[b]	Pore size [nm] ^[b]	Crystal size [nm] ^[c]	H_2 uptake [mmol] ^[d]	Ce oxidation degree [CeO_x] ^[d]
Rh/CeZrO_x	0.87	89	0.20	8.1	7.4	0.21	$x = 1.61$
CeZrO_x	–	98	0.21	8.3	7.3	0.19	$x = 1.58$

[a] According to ICP results, [b] Calculated by BET, t-plot and BJH methods, respectively, [c] and [d] According to XRD and H_2 -TPR results, respectively.

Figure 2. H_2 -TPR profiles associated with the Rh/CeZrO_x catalyst and the corresponding support. Experimental conditions: 0.1 g sample, heated ($10^\circ\text{C min}^{-1}$) to 600°C , in a reducing atmosphere (1 % v/v H_2/Ar , 30 mL min^{-1}).

catalyst is reduced at temperatures before 200°C , it seems that there exists a significant interaction of Rh with the support. According to these results, 500°C was chosen as a suitable reduction temperature to maximize the amount of oxygen vacancies in the ceria-based support to enhance the reduction of N_2O .

Catalytic performance on N_2O decomposition

Intrinsic activity for catalytic N_2O decomposition

The first experiments of N_2O decomposition were performed at 450°C on the Rh/CeZrO_x catalyst under a N_2O (200 ppm, He balance) reaction atmosphere. Prior to the catalytic tests, the catalyst was reduced at 500°C under a pure H_2 atmosphere (1 hour). Figure 3a shows the evolution of N_2O , N_2 and O_2 concentrations with time. A total decomposition of N_2O into N_2 was observed for the whole duration of the experiment. However, the release of O_2 to the gas stream was only observed after 20 min. This indicates that, during this period of time, oxygen atoms produced by the N_2O decomposition are used to re-oxidize the support.

Nevertheless, a different dynamic trend was observed with the pre-reduced support alone under the same reaction conditions (Figure 3b). In this case, a full conversion of N_2O into N_2 was only observed for 15 minutes (where no O_2 was produced). After that, the N_2 production started to decrease on account of the lower N_2O decomposition activity. However, O_2 production was only observed at the end of the experiment, where the activity was stable and almost negligible.

The most interesting results were obtained at low reaction temperatures (250°C). Under these conditions, the pre-reduced Rh/CeZrO_x catalyst (Figure 3c) exhibited a dynamic trend similar to that observed for the support alone at high temperatures (Figure 3b). However, no N_2O conversion was found with the reduced CeZrO_x support alone at this reaction temperature (Figure 3d).

These results suggest, first of all, that Rh/CeZrO_x is an exceptional catalyst for N_2O decomposition, in good agreement with previous studies over Rh/ceria-based catalysts.^[15–24] In addition, they also clearly point out the important synergy

Figure 3. Catalytic performances of A) Rh/CeZrO_x catalyst and B) CeZr support for N_2O decomposition at 450°C ; C) Rh/CeZr catalyst and D) CeZr support at 250°C . Operating condition: 0.2 g (catalyst + SiC); Gas flow: 10 L/h. Reactive mixture: 200 ppm N_2O , He as a balance.

between Rh and the reduced support, even at low reaction temperatures. Even though the reaction mechanism for N₂O decomposition on Rh/ceria-based materials is still under debate, we could rationalize the observed results according to the following reaction steps, as previously suggested in the studies performed by the team of A. Bueno-Lopez.^[19–22]

First of all, it is generally accepted that the decomposition of N₂O on noble metal-based catalysts occurs with the successive reduction and oxidation of the noble metal (Rh in the present study) active sites by N₂O molecules following an Eley-Rideal mechanism. Considering the catalyst is initially in a reduced state, we could propose that N₂O decomposition takes place according to steps 1 and 2:

In addition, the formation of O₂ could occur by the recombination of two oxygen atoms located in two Rh oxidized sites, following a Langmuir-Hinshelwood mechanism:

It is worth noting that the recombination of oxygen atoms and the desorption of O₂ by Eley-Rideal or Langmuir-Hinshelwood mechanisms (steps 1–3) has been considered the rate-limiting step for N₂O decomposition on other transition metal-based catalysts.^[26,27] However, steps 1–3 do not explain the high performance of the support alone (Figure 3b) for N₂O decomposition at 450 °C and the time shift observed between the N₂ and O₂ production. It is therefore reasonable to assume that the reaction mechanism on ceria-zirconia is more complex. The active participation of CeO_x in this process has been previously reported.^[19–22] First of all, according to the TPR tests (Figure 2) it can be considered that the surface of ceria-zirconia is mostly reduced at the beginning of the experiment after the pre-reduction at 500 °C, leading to the production of surface oxygen vacancies. Under the N₂O reaction atmosphere, the reduced support will restore the oxygen balance by re-oxidation of the vacant sites with the oxygen of the N₂O molecules. In other words, N₂O will react, most probably on surface oxygen vacancies, with the reduced support, leading to its oxidation (Ce^{δ+} into Ce⁴⁺) and the further production of N₂ (step 4). This explains why during the first stage of the catalytic experiments (Figures 3a, b and c) N₂O was decomposed and only N₂ was observed as a reaction product. The oxidized support is believed to be able to transfer oxygen to the noble metal (step 5) due to the strong metal support interactions. This oxygen transfer step would lead to the production of two new different N₂O decomposition active sites: reduced ceria (denoted as Ce*) and oxidized Rh (most likely Rh₂O₃, denoted as Rh*–O), further leading to steps 2 and 4, respectively. This mechanism indicated that the N₂O decomposition over Rh/CeZrO_x catalyst occurs with the successive reduction and oxidation of the catalyst active sites.

Once the support (surface and bulk) is completely oxidized with N₂O (i.e. after 60 min at 450 °C, and after 40 min at 250 °C), the activity is stabilized, and a dynamic sequence of steps 1–5 would explain the residual steady-state activity observed (where outlet oxygen concentration corresponds to stoichiometric value for N₂O decomposition reaction).

In any case, this experiment clearly demonstrates that a pre-reduced Rh/CeZrO_x catalyst exhibits a unique and extraordinary performance for the decomposition of N₂O. Previous studies have already pointed out the importance of the reducibility of the catalyst. For instance, Parres-Esclapez et al. suggested that the rate-limiting step for N₂O decomposition is the active sites reduction,^[20] while the early works of S. Imamura proved that similar pre-reduced catalysts are very performing for this catalytic process.^[15,16,18] Therefore, the enhanced activity could be attributed to the intrinsic activity of the metallic active phase (Rh, steps 1–3) in strong interaction with a reduced ceria-based support (steps 4–5), where the rate-limiting steps for N₂O decomposition on Rh/CeZrO_x based-catalysts seem to be the both, the reduction of the support, together with the oxygen desorption from the metal/metal-oxide (Rh*/Rh*–O) active sites.

Influence of water and oxygen on N₂O decomposition.

In order to use the catalyst in real gas streams, having good catalytic activity in N₂O/He reaction atmosphere is not sufficient. Its activity must be studied in the presence of potential inhibitors. Therefore, in this section we will discuss the results obtained in the presence of steam and oxygen, as is typically the case in exhausts of lean-burn and stoichiometric combustion engines.

Figures 4a–b show the dynamic response for N₂O decomposition in the presence of 5% H₂O on the pre-reduced Rh/CeZrO_x catalyst (500 °C 1 h in H₂) at high (450 °C) and low (250 °C) reaction temperatures, respectively. Compared to the results under N₂O/He reaction atmosphere previously described, a clear inhibiting effect by steam can be observed. At high reaction temperatures, even though almost complete N₂O conversion into N₂ was reached during the whole duration of the experiment, the moment at which the O₂ evolution in the gas phase was observed happened much earlier. This phenomenon is also observed at lower temperature, together with a negligible activity at the steady state. These results seem to indicate an important inhibition of the catalytic active sites for N₂O decomposition, i.e. Rh*/Rh*–O (steps 1–3) and Ce*/Ce*–O (steps 4–5) by H₂O.

A similar H₂O poisoning effect has been previously reported for Rh/ceria-based catalysts in the N₂O decomposition reaction.^[22,24,28] It is generally assumed that H₂O and N₂O are in competitive adsorption on the oxygen-vacancies of the reduced ceria-zirconia support, inhibiting the N₂O reduction activity of

Figure 4. Catalytic activity of Rh/CeZrO_x catalyst for N₂O decomposition at A) 450 °C and B) at 250 °C. Operating condition: 0.2 g (catalyst + SiC); Gas flow: 10 L/h. Reactive mixture: 200 ppm N₂O, 5% H₂O, and He as a balance.

the oxide. In other words, as suggested by Parres-Escapaz et al.,^[22] the previously proposed step 4 strongly competes with step 6 (re-oxidation of the reduced ceria by H₂O), where:

The competition between N₂O and H₂O would explain the shorter “activated-state” (where the activity is maximized) at both high and low temperatures, and the lower activity at the steady-state observed in Figure 4b.

When 5% O₂ was added to the N₂O/H₂O reaction atmosphere, the inhibiting effect for N₂O decomposition was, as expected, much more pronounced at both high and low temperatures (Figure 5). In this case, the activity was constant since the beginning of the experiment, as opposed to the

Figure 5. Catalytic activity of Rh/CeZrO_x catalyst for N₂O decomposition at A) 450 °C and B) at 250 °C. Operating condition: 0.2 g (catalyst + SiC); Gas flow: 10 L/h. Reactive mixture: 200 ppm N₂O, 5% H₂O, 5% O₂, He as a balance.

dynamic trends previously observed in Figures 3 and 4. The O₂ poisoning effect has also been previously reported for this catalytic process,^[20,22–24] and could be attributed to its chemisorption on the reduced catalytic active sites (Rh* and Ce*). It would lead to the reversed step 3 and the re-oxidation of Ce* to Ce*–O, limiting therefore the amount of active sites for the reduction/decomposition of N₂O. This additional O₂ inhibition could also be attributed to the formation of nitro-surface species, which are not really considered as reaction intermediates of N₂O decomposition. These species would cover part of the ceria surface, preventing the N₂O chemisorption and decomposition.

In any case, the results described in this section clearly suggest a strong competition for the catalytic active sites in presence of both H₂O and O₂, leading to a drastically decreased catalytic activity for N₂O decomposition, notably at low temperature. Thus, Ce^{δ+} cations are rapidly oxidized by water and oxygen. In other words, the oxygen vacancies of the ceria support are quickly filled by oxygen atoms, limiting the chemisorption and further decomposition of N₂O.

These results also confirm, however, that this catalyst would be only efficient at high temperatures (450 °C) for internal combustion engines working under lean-burn conditions (O₂ excess). Its activity seems to be negligible at low temperature. Nevertheless, engines working under stoichiometric conditions (e.g. gasoline engines) release a much lower amount of O₂ in the exhaust gas (<1%). In the next experiments we investigated the performance of the pre-reduced Rh/CeZrO_x catalyst in the presence of water (5%) and lower O₂ concentration (900 ppm) at high (450 °C) and low (250 °C) temperatures (Figure 6).

At high temperature (Figure 6a), as expected, even in the presence of both inhibitors, both Rh- and Ce- based active sites are able to catalyze the N₂O decomposition. As in the previous experiments, the activity was enhanced during the first minutes

Figure 6. Catalytic activity of Rh/CeZrO_x catalyst using 900 ppm of O₂ for N₂O decomposition at 450 °C (A) and 250 °C (B). Operating condition: 0.2 g (catalyst + SiC); Gas flow: 10 L/h. Reactive mixture: 200 ppm N₂O, 5% H₂O, 900 ppm O₂ and He as a balance.

of the catalytic test, since the pre-reduction of the catalyst increased the production of available active sites for N_2O reduction. On the other hand, very interestingly, a high catalytic performance could be observed at low temperature (Figure 6b) during the first minutes of the experiment, as opposed to the previous experiment (Figure 5b) under high oxygen excess in the reaction atmosphere. The activity seems to gradually decrease as the catalyst is oxidized.

From this experiment we can conclude that the presence of small amounts of oxygen in the feed stream did not inhibit the N_2O decomposition reaction in a drastic manner. Indeed, the catalyst exhibited a significant activity during the first minutes under the reaction environment even at low temperatures. Therefore, the results obtained clearly suggest that the catalytic system proposed in this study could be suitable for N_2O decomposition (even at low temperatures) as long as: i) the catalyst is pre-reduced, and ii) the amount of O_2 in the reaction atmosphere is sufficiently low, as encountered in combustion engines exhausts working under stoichiometric conditions. However, since the activity is optimized during the first minutes under the reaction stream, the remaining question is: “could the catalyst be regenerated by a subsequent re-reduction treatment?”. If that is the case, working in a cyclic operation mode would allow to enhance the performance for N_2O reduction towards the production of harmless gases.

Cyclic operation mode: Catalyst sites regeneration

In all catalytic experiments previously discussed, regardless the operation temperatures, the Rh/CeZrO_x catalyst was previously reduced in a H_2 -based atmosphere at 500°C for 1 h. We have clearly demonstrated that this pre-reduction treatment allows to increase the amount of active sites for N_2O decomposition. In this section we propose to work in a cyclic operation mode under the presence of H_2O (5%) and a low O_2 concentration (900 ppm). The catalytic tests were performed at high (450°C) and low (250°C) reaction temperatures. Prior to the first tests at each temperature, the catalyst was reduced at 500°C , as previously explained. However, in an attempt to regenerate its activity, the catalyst was re-reduced after the first tests. This second reduction treatment was performed at the operation temperature, i.e., at 450°C (for the high temperature tests) and 250°C (for the low temperature ones) with a shorter H_2 exposure (10 minutes). Afterwards, a second catalytic test was performed at each temperature under the same reaction atmosphere than the first one.

Figure 7 shows the catalytic performances at high temperature for the first and second cycle (after re-reduction) respectively, and Figure 8 show the results obtained at low temperature. While at 450°C , the performances observed for the 2 catalytic tests are completely identical, at 250°C , a decreased activity was observed after the H_2 -regeneration treatment. It seems therefore that the catalyst was not completely re-reduced at 250°C , in good agreement with the H_2 -TPR results, where we could observe that a residual high temperature small peak remained after the two low temper-

Figure 7. Catalytic activity of Rh/CeZrO_x catalyst at 450°C during A) a first catalytic cycle (with previous catalyst reduction at 500°C) and B) a second catalytic cycle (with previous catalyst reduction at 450°C). Operating condition: 0.2 g (catalyst + SiC); Gas flow: 10 L/h. Reactive mixture: 200 ppm N_2O , 5% H_2O , 900 ppm O_2 and He.

Figure 8. Catalytic activity of Rh/CeZrO_x catalyst at 250°C during A) a first catalytic cycle (with previous catalyst reduction at 500°C) and B) a second catalytic cycle (with previous catalyst reduction at 250°C). Operating condition: 0.2 g (catalyst + SiC); Gas flow: 10 L/h. Reactive mixture: 200 ppm N_2O , 5% H_2O , 900 ppm O_2 and He.

ature reduction peaks. Nevertheless, a significant part of the catalytic activity was recovered in the second test even after a “short” period of H_2 at 250°C , reaching a maximum N_2O conversion of 60% during the first minutes of the N_2O decomposition catalytic test.

The reaction conditions are not optimized and further studies should be performed to completely understand the reaction mechanism for N_2O decomposition on a pre-reduced Rh/CeZrO_x catalyst, together with the required temperature and duration of the H_2 reduction periods. However, the main implications of these last experiments are that this catalytic system exhibits enhanced performance provided that the catalyst is efficiently pre-reduced (even at low temperatures), and that the dynamic behavior could be cycled by short pulses

of a reducing agent, which allow to regenerate the active sites for N_2O decomposition. Even though H_2 was used in this study as a reductant, other reducing agents could be suggested to efficiently reduce the catalyst, such as CO and un-burned hydrocarbons (usually present in the exhaust stream of internal combustion engines). Working in a cyclic operation mode with short injections of reducing agents has been already proposed as an efficient technology for the reduction of nitrogen oxides (NO_x : $\text{NO} + \text{NO}_2$) by means of the so-called "lean NO_x trap technology".^[29] That means that eventually this technology could be implemented for the additional decomposition of N_2O . To the best of the authors' knowledge, such catalyst regeneration under a short time H_2 -injection has never been reported for N_2O decomposition in presence of water and oxygen inhibitors. Therefore, the approach proposed in this study exhibits high potential for practical applications for the efficient removal of N_2O , in view of the upcoming increasingly stringent European regulations. Further experiments will be performed to verify the catalyst efficiency under real gas streams, including the presence of NO_x in the feed stream.

Conclusions

The following conclusions could be obtained from this study:

- Pre-reduced Rh/CeZrO_x catalysts exhibit a dynamic performance for N_2O decomposition. The reduced ceria support plays a drastically important role, being oxidized as it takes the oxygen from the N_2O molecule via surface oxygen vacancies.
- The presence of high concentrations of H_2O and O_2 , as is typically the case for internal combustion engines working under lean-burn conditions, strongly inhibits the activity for N_2O decomposition. This poisoning effect could be attributed to the strong competition between N_2O and these molecules on the pre-reduced catalyst active sites.
- Under high concentration of water, but in the presence of a small O_2 amount, as it could be the case for stoichiometric internal combustion engines, the inhibiting effect was drastically lowered, and the catalyst exhibits a sufficient performance for N_2O decomposition.
- The initial catalytic activity could be partially recovered by short periods of a reducing agent (e.g. H_2) even at low reaction temperatures. Therefore, we could suggest to work in a cyclic operation mode, in order to maximize the performance of the Rh/CeZrO_x catalysts for N_2O decomposition.

Experimental Section

Rh/CeZr catalyst preparation method

Ceria/zirconia mixed oxide powder, denoted as a CeZrO_x support ($\text{Ce}_{0.66}\text{Zr}_{0.34}\text{O}_{2.7}$, 57.6% wt. of cerium oxide) was provided by Marion Tech company. Rhodium/Ceria-Zirconia powder was obtained by impregnation of rhodium nitrate $\text{Rh}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ to the Ceria-zirconia support ($\text{Rh}/\text{Ce}_{0.66}\text{Zr}_{0.34}\text{O}_2$ catalyst) for 2 hours under

vacuum at 90 °C. The resulting powder was dried at 80 °C overnight and calcined at 500 °C (6 hours) under air flow.

Support and catalysts characterization

The chemical composition of the catalyst was quantitatively determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) on a flame Perkin Elmer M1100 spectrometer. Before the measurement, the metal oxides were dissolved using a mixture of inorganic acids (H_2SO_4 , HNO_3 and HF). Powder X-ray diffraction (XRD) patterns were obtained using a Bruker D8 diffractometer ($\text{CuK}\alpha$ radiation at 0.154184 nm) equipped with a Ni filter and 1-D fast multistrip detector (LynxEye, 192 channels on 2.95°). The diffractograms were collected at 2 θ with steps of 0.02° from 4° to 80° for the total acquisition time of 32 min. Phase identification was carried out using the Diffrac.Eva software (Bruker) and the ICDD-PDF4+ database. Nitrogen adsorption and desorption isotherms were measured at –196 °C on a Micromeritics ASAP 2020 surface area and porosity analyzer. The sample was firstly degassed at 350 °C for a night under primary vacuum. The specific surface area was calculated from the linear part using the Brunauer-Emmett-Teller (BET) method. The porous volume and the pore size distribution were calculated using the Barrett-Joyner-Halenda (BJH) method. The reducibility of the support and catalyst was examined by hydrogen temperature programmed reduction (H_2 -TPR) using mass spectrometer detection (Hiden, HPR 20). Prior to the test, the catalyst (about 100 mg) was firstly pre-treated at 500 °C for 1 hour in a O_2 5% flow (30 ml min^{–1}) and then cooled down to room temperature in helium flow. 1% H_2/He (30 ml min^{–1}) as the reducing gas was introduced and the reactor was heated from 25 to 600 °C with a rate of 10 °C min^{–1}. H_2 consumption was quantitatively calculated by time integration of H_2 -TPR profiles.

Catalytic test for N_2O catalytic decomposition

The catalytic performances were evaluated for N_2O decomposition at 250 and 450 °C in the absence and presence of water and oxygen (0.2 g of catalyst + SiC, including 0.04 g of catalyst, gas flow of 10 L h^{–1}, reactive mixture: 200 ppm N_2O , 0–5% H_2O , 0–5% O_2 and He balance). A U tubular quartz reactor (16 mm in internal diameter) was used for this purpose. Prior to the catalytic experiments, the catalyst was reduced in pure H_2 at 500 °C for 1 hour. All reactants were introduced by BROOKS's mass flow controllers and water vapor fraction was supplied by means of a temperature-controlled saturator. All lines placed downstream from the saturator were heated above 100 °C to prevent condensation. Gas effluents (N_2 , O_2 and N_2O) were analyzed with a micro gas chromatograph (SRA% GC–R3000) and an infrared-ultraviolet spectroscopy (EMERSON IR/UV X-STREAM Enhanced XEGP).

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Greenhouse emissions • After-treatment emission • Nitrous oxide decomposition • Rh/Ce–Zr catalyst • oxygen vacancies • hydrogen regeneration

- [1] D. R. Kanter, J. A. Wentz, J. N. Galloway, W. R. Moomaw, W. Winiwarter, *Environ. Sci. Policy* **2017**, *67*, 44–51.
- [2] K. Larsen, J. Larsen, W. Herndon, S. Mohan, T. Houser, *Energy Nat. Resour.* **2017**.
- [3] D. L. Mummey, J. L. Smith, G. Bluhm, *Agric. Ecosyst. Environ.* **1998**, *70*, 79–87.
- [4] R. A. Reimer, C. S. Slaten, M. Seapan, T. A. Koch, V. G. Triner, in (Eds.: J. van Ham, A. P. M. Baede, L. A. Meyer, R. Ybema), Springer Netherlands, Dordrecht, **2000**, pp. 347–358.
- [5] B. Feng, H. Liu, J. Yuan, Z. Lin, D. Liu, B. Leckner, *Energy Fuels* **1996**, *10*, 203–208.
- [6] C. P. Cho, Y. D. Pyo, J. Y. Jang, G. C. Kim, Y. J. Shin, *Appl. Therm. Eng.* **2017**, *110*, 18–24.
- [7] V. A. Kondratenko, U. Bentrup, M. Richter, T. W. Hansen, E. V. Kondratenko, *Appl. Catal. B* **2008**, *84*, 497–504.
- [8] R. Burch, J. P. Breen, F. C. Meunier, *Appl. Catal. B* **2002**, *39*, 283–303.
- [9] L. Casagrande, L. Lietti, I. Nova, P. Forzatti, A. Baiker, *Appl. Catal. B* **1999**, *22*, 63–77.
- [10] S. Brandenberger, O. Kröcher, A. Tissler, R. Althoff, *Catal. Rev.* **2008**, *50*, 492–531.
- [11] F. Kapteijn, J. Rodriguez-Mirasol, J. A. Moulijn, *Appl. Catal. B* **1996**, *9*, 25–64.
- [12] M. Konsolakis, *ACS Catal.* **2015**, *5*, 6397–6421.
- [13] M. Tian, A. Wang, X. Wang, Y. Zhu, T. Zhang, *Appl. Catal. B* **2009**, *92*, 437–444.
- [14] M. Tian, X. D. Wang, T. Zhang, *Catal. Sci. Technol.* **2016**, *6*, 1984–2004.
- [15] S. Imamura, N. Okamoto, Y. Saito, T. Ito, H. Jindai, *J. Jpn. Pet. Inst.* **1996**, *39*, 350–356.
- [16] K. Hashimoto, N. Toukai, R. Hamada, S. Imamura, *Catal. Lett.* **1998**, *50*, 193–198.
- [17] S. Imamura, R. Hamada, Y. Saito, K. Hashimoto, H. Jindai, *J. Mol. Catal. A* **1999**, *139*, 55–62.
- [18] S. Imamura, J. Tadani, Y. Saito, Y. Okamoto, H. Jindai, C. Kaito, *Appl. Catal. A* **2000**, *201*, 121–127.
- [19] A. Bueno-López, I. Such-Basáñez, C. Salinas-Martínez de Lecea, *J. Catal.* **2006**, *244*, 102–112.
- [20] S. Parres-Esclapez, M. J. Illán-Gómez, C. S.-M. de Lecea, A. Bueno-López, *Appl. Catal. B* **2010**, *96*, 370–378.
- [21] S. Parres-Esclapez, I. Such-Basáñez, M. J. Illán-Gómez, C. Salinas-Martínez de Lecea, A. Bueno-López, *J. Catal.* **2010**, *276*, 390–401.
- [22] S. Parres-Esclapez, M. J. Illán-Gómez, C. S.-M. de Lecea, A. Bueno-López, *Int. J. Greenhouse Gas Control* **2012**, *11*, 251–261.
- [23] S. S. Kim, S. J. Lee, S. C. Hong, *Chem. Eng. J.* **2011**, *169*, 173–179.
- [24] M.-J. Kim, H. J. Kim, S.-J. Lee, I.-S. Ryu, H. C. Yoon, K. B. Lee, S. G. Jeon, *Catal. Commun.* **2019**, *130*, 105764.
- [25] G. Leofanti, M. Padovan, G. Tozzola, B. Venturelli, *Catal. Today* **1998**, *41*, 207–219.
- [26] Y. Zhu, X. Wang, A. Wang, G. Wu, J. Wang, T. Zhang, *J. Catal.* **2011**, *283*, 149–160.
- [27] Y. Zhang, X. Wang, Y. Zhu, T. Zhang, *Appl. Catal. B* **2013**, *129*, 382–393.
- [28] H. Zhu, Y. Li, X. Zheng, *Appl. Catal. A* **2019**, *571*, 89–95.
- [29] G. Liu, P.-X. Gao, *Catal. Sci. Technol.* **2011**, *1*, 552–568.

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