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Performance of the $CeZrO_2$ mixed oxide in the NO_x decomposition

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Abstract

The present work aims to evaluate the performance of the $CeZrO_2$ mixed oxide for the NO_x decomposition in the absence of a noble metal. The $Ce_{75}Zr_{25}O_2$ mixed oxide was prepared by co-precipitation of hydroxides and was characterized by X-ray diffraction (XRD) before and after pre-treatments, thermogravimetric analysis (TG) and temperature programmed desorption of NO (TPD). XRD results allowed confirming the formation of a solid solution. TG results showed slight loss of mass during the reduction of the mixed oxide. TPD results showed NO decomposition even at room temperature either for reduced or calcined samples, however a significant decrease of the temperature of the NO decomposition besides an increasing amount of N_2 for the reduced sample, which is attributed to superficial structure changes of the mixed oxide.
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Keywords: NO decomposition; NO TPD; Cerium oxide; Zirconium oxide; Solid solution

1. Introduction

The control of atmospheric emission became very important due to the great development that humanity has been trying in the last decades. Air pollution generated from mobile sources became a problem of general interest. In the last 60 years, for instance, the world vehicles fleet increased from about 40 million vehicles to more than 700 million, and the perspective is that this number reaches 920 million automobiles up to 2010 [1].

Among the atmospheric emissions, NO_x are the most important pollutants and about 95% is in the form of NO, reaching 10 million tons per year, originated from natural sources while 40 million tons per year from anthropogenic sources [2]. The NO_x is released after oxidation of nitrogen compounds in fuels. It can also be generated by reaction between nitrogen and oxygen in air and fuel burning for steam generation and industrial process.

Noble metals are used in the three-way catalysts for exhaust gases in cars, which contain additives that improve the catalytic performance and durability. Ceria showed multiple functions, such as, high oxygen storage capability, that during NO_x decomposition at lean conditions increases the conversion of NO_x to N_2, and at rich conditions the oxidation of CO and HC. Ceria also promotes the NO_x decomposition improving stability, avoiding metal deactivation, which occurs by superficial oxygen accumulation on the metal [3]. In the case of Rh/CeO_2 the deactivation is slower than on Rh/Al_2O_3 during NO_x decomposition, which may be attributed to oxygen spillover from the metal to reduced ceria.

The promoter increases the performance of the catalyst and is less sensitive to concentration variations of exhaust gases during normal conditions. The efficiency under transient conditions decreases, as the catalyst ages, partly because ceria loses its ability to store and release (as CO_2 and H_2O) oxygen. As reported in the literature, the deactivation occurs because sintering of ceria particles, which renders bulk ceria inactive to redox mechanism of Ce^{4+} to Ce^{3+}. Therefore, it is necessary to search thermal stable oxygen storage materials, which can resist high temperatures and long periods of time [4].

Literature reported that for stabilizing ceria against sintering it was necessary to dope with rare earth elements, such as La_2O_3 and Ga_2O_3, however these materials were not effective [5,6]. More recently, it has been shown that the addition of ZrO_2 to ceria improves the oxygen storage capacity. XRD analysis showed that Zr was incorporated into the ceria lattice thereby forming a ceria–zirconia solid solution [7–9].

Hori et al. [10] studied the effect of zirconia on the oxygen storage capacity of the Pt/CeO_2 catalyst. These catalysts were

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prepared at two different low temperature methods, and these materials were less sensitive to sintering and presented high surface area. The authors concluded that the optimal Zr concentration was found to be 25 mol% Zr in ceria.

There are few other papers using $CeZrO_2$ mixed oxide in the environmental catalysis [11–15]. Noteworthy is that in these cases the mixed oxide were tested in the absence of noble metals for NO_x reduction, aiming to explain the nature of such oxide without the influence of noble metals, like Rh, Pd or Pt, and already largely explored for the NO_x reduction.

These mixed oxides are interesting for NO_x reduction, however it is not clear how the oxygen storage affects the reaction mechanism when compared to simple oxides. There are several parameters affecting this reaction, however, one major difficulty is linked to the variability of the properties of these mixed oxides [16].

Therefore, main goal of this work is to study the NO_x decomposition on a mixed oxide ($CeZrO_2$) without the presence of a noble metal and to compare with supported metal oxides. It is important to stress that these mixed oxides are not inactive in the NO_x decomposition and proving this is the main reason of this study.

2. Experimental

2.1. Mixed oxide preparation

The preparation method was presented previously [10]. A $Ce_{75}Zr_{25}O_2$ mixed oxide was prepared by co-precipitation, using solutions of $(NH_4)_2Ce(NO_3)_6$ and $ZrO(NO_3)_2$ (Aldrich), in the presence of an excess NH_4OH (Merck). Then, the precipitate was washed until eluting water showed a neutral pH. The material was calcined at 500 °C for 2 h.

2.2. Mixed oxide characterization

The XRF analysis was performed on a Rigaku RIX 3100 equipment. BET specific surface area was measured by N_2 adsorption (ASAP 2000 – Micromeritics). Crystalline phases were characterized by X-ray diffraction (XRD), using the Rigaku D-MAX 2200 equipment. Structure modifications of the mixed oxide were observed by XRD in situ after pre-treatment with He at 500 °C and reduction at the same temperature. Thermal analysis was performed in a thermo balance Rigaku TG 8110 apparatus under pure N_2 flow at 500 °C and than H_2 flow at 500 °C.

NO decomposition was measured on a temperature programmed desorption (TPD) equipment, coupled to a quadrupole mass spectrometer (Balzers), equipped with an acquisition data system. The catalyst was reduced with pure H_2, raising the temperature at 10 °C/min from room temperature up to 500 °C and held constant for 1 h. Then, NO was adsorbed at room temperature flowing 1%NO/He for approximately 15 min. During TPD, the temperature was raised at 20 °C/min, from room temperature up to 500 °C and then kept constant for 15 min.

3. Results and discussion

3.1. Textural characterization

The XRF analysis presented composition of 75 mol% CeO_2 and 25 mol% ZrO_2, as expected. The BET surface area was 94 m^2/g and volume pore was 0.11 cm^3/g. Results are comparable to those presented by González-Velasco et al. [13,14] using mixed oxides with different contents of CeO_2 and ZrO_2, (Rhodia) and Yao et al. [15] using mixed oxide coated over alumina. According to González-Velasco, the surface area of $Ce_{68}Zr_{32}O_2$ mixed oxide was 110 m^2/g and pore volume was 0.25 cm^3/g, while the later one coated on alumina was 84 m^2/g. Recently, Letichevsky et al. [17] suggested a co-precipitation method attempting to identify the most important parameters affecting structural changes and redox properties of $CeZrO_2$. They concluded that the key point for the mixed oxide formation is using the $(NH_4)_2Ce(NO_3)_6$ precursor instead of the $Ce(NO_3)_3$. As pointed out, the solution chemistry of cerium is complex, because cerium ions may undergo complexation and hydrolysis, depending on the ion concentration, pH and the eventual addition of a strong oxidizing agent in the solution. Such solution parameters are rarely strictly the same when preparing $CeZrO_2$ samples, which can explain the different results, reported so far in the literature [17].

3.2. X-ray diffraction (XRD)

The XRD analysis is essential for the identification of mixed oxides parameters for a solid solution and the investigation of segregated phases. Fig. 1 shows the X-ray diffractogram of the $Ce_{75}Zr_{25}O_2$ mixed oxide. It shows that the presence of zirconium shifted the CeO_2 lines at 2θ from 28.6° and 33.1° to 29.0° and 33.4°, respectively. According to the literature [10,18], it characterizes the structure of a solid solution cerium–zirconium with a cubic structure.

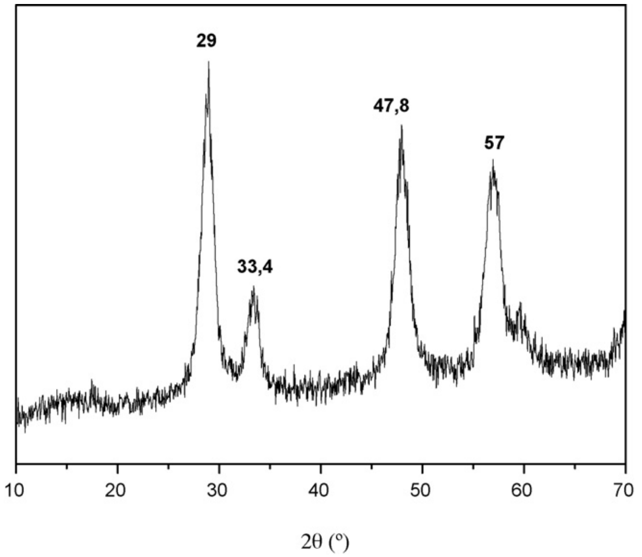

Fig. 1. X-ray diffraction patterns.

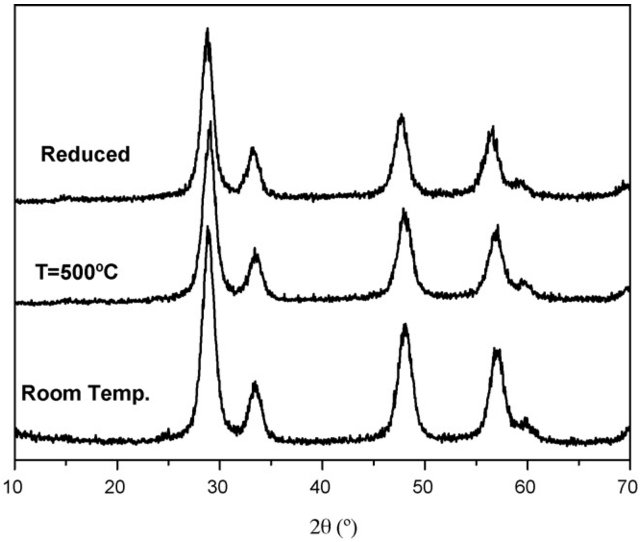

Fig. 2. X-ray diffraction patterns at room temperature, after treatment with He at 500 °C and after reduction with H_2 at the same temperature.

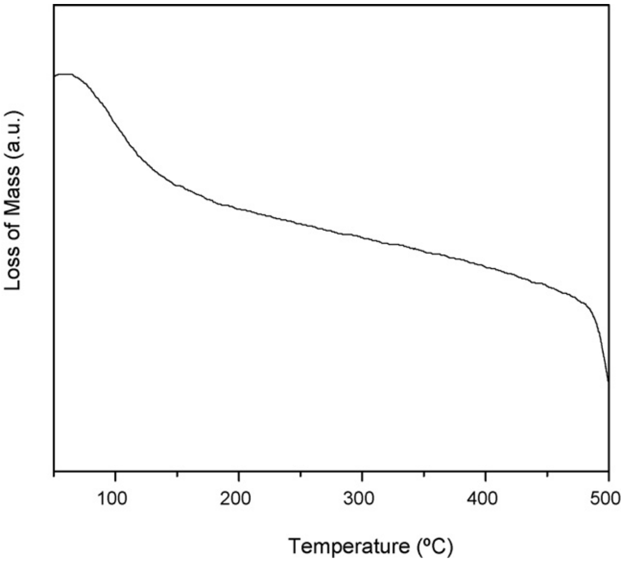

Fig. 3. Thermogravimetric analysis of $CeZrO_2$.

Yao et al. [15] observed through XRD and TEM for $CeZrO_2$ mixed oxide supported on alumina with different oxide contents that particle sizes decreased with increasing zirconia loading, indicating that the addition of Zr improved the dispersion of particles and retarded sintering. Moreover, zirconia enhanced the stability of the support and supported phases.

In order to verify the efficiency of the Zr loading in preventing ceria sintering, X-ray diffraction patterns of the sample were obtained after pre-treatment and after reduction at 500 °C. The X-ray diffraction patterns are displayed in Fig. 2.

Noteworthy the results did not show phase changes after thermal treatments in the X-ray diffraction results.

Table 1 presents the crystallite sizes from the first two peaks of the $CeZrO_2$ mixed oxide at room temperature, after the pre-treatment with He at 500 °C and after reduction at the same temperature.

These results show that until 500 °C the addition of Zr to CeO_2 contributes to a thermal stability, since no sintering was observed.

3.3. Thermogravimetric analysis (TG)

Fig. 3 displays the TG profile with increasing temperature. Results show loss of mass, indicating at low temperature water loss and, above 150 °C decreasing loss of mass until 480 °C, corresponding to 1% of weight loss. Abruptly mass loss around 500 °C suggests structure changes. However, the continuous decay of mass between 150 °C and 480 °C suggests little changes that may be attributed to superficial structure changes.

Table 1
Crystallite size of the peaks (1 1 1) and (2 0 0)

Peak	Room temperature	$T = 500$ °C	After reduction
(1 1 1)	58 Å	57 Å	59 Å
(2 0 0)	60 Å	57 Å	62 Å

3.4. Temperature programmed desorption (TPD)

Recently [19], the NO dissociation was observed during the adsorption at room temperature on Pd supported on $Ce_{75}Zr_{25}O_2$. This result was unexpected and was attributed to the contribution of the support. Therefore, the adsorption–desorption process was now studied over the mixed oxide alone, aiming to explain the role of the mixed oxide under different pre-treatment conditions.

Figs. 4 and 5 display the NO adsorption and desorption profiles on calcined sample, respectively, while Figs. 6 and 7 the NO adsorption and desorption profiles on reduced sample, and Table 2 presents the selectivity to N_2 and N_2O from the TPD of $CeZrO_2$ mixed oxide.

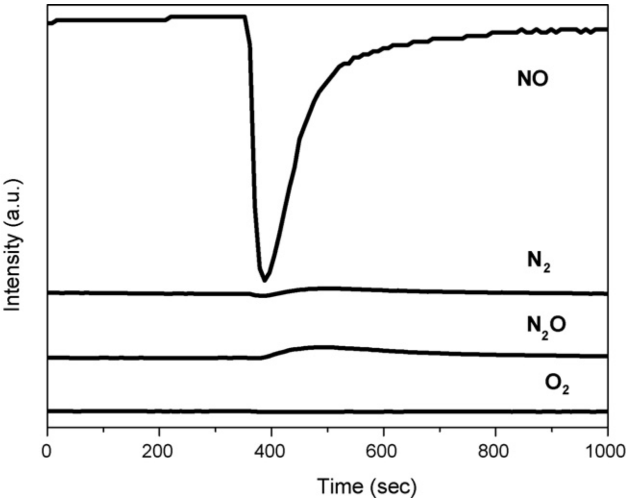

Fig. 4. NO adsorption at room temperature on calcined $CeZrO_2$.

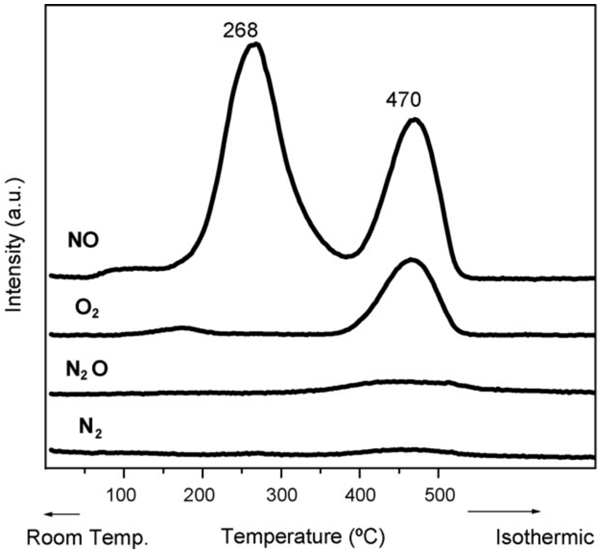

Fig. 5. TPD of adsorbed NO on calcined $CeZrO_2$.

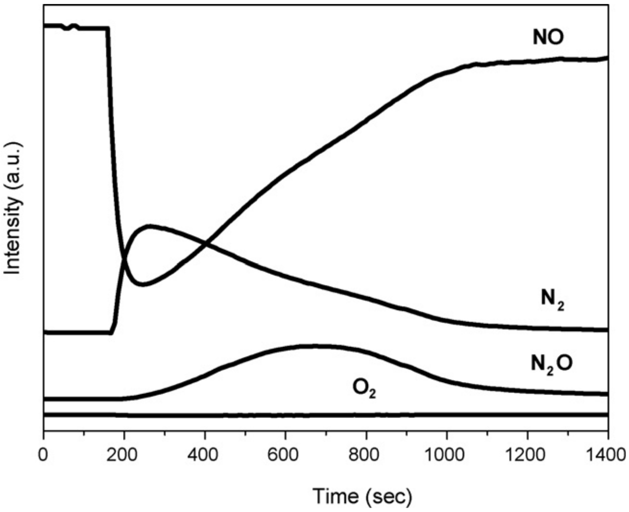

Fig. 6. NO adsorption at room temperature on reduced $CeZrO_2$.

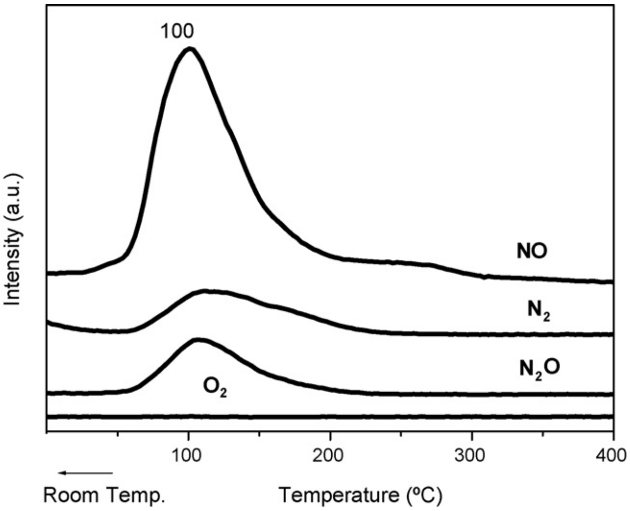

Fig. 7. TPD of adsorbed NO on reduced $CeZrO_2$.

Table 2
Selectivity from NO TPD

Sample	Selectivity (%)	
	N_2	N_2O
Calcined	18.4	8.1
Reduced	97.9	0

Results show significant dissociation of NO to N_2 and N_2O during the adsorption at room temperature. Moreover, comparing the TPD profiles on calcined and reduced samples, higher dissociation of NO was observed on reduced sample, suggesting higher activity for the NO decomposition and higher formation of N_2 at lower temperature on reduced sample.

Although no changes were observed on the mixed oxide structure (XRD) after the thermal treatment and no reduction was observed during TPR (not shown), few loss of mass up to 500 °C (TG) evidence that the reduction treatment promotes superficial vacancies in the mixed oxide structure, facilitating the NO adsorption and decomposition at lower temperature. Noteworthy is that the TPD profile of the reduced sample does not evidence oxygen desorption. One possible explanation is that the oxygen released during the decomposition of NO is consumed to re-oxidize the mixed oxide. It allows suggesting that during the reduction only superficial changes occurred, as reported in the literature [12,20–22].

Mello et al. [19] have reported similar results, observing NO dissociation at room temperature, and NO dissociation occurring at lower temperature on the Pd/$CeZrO_2$ catalyst when compared to Pd-8Mo/Al_2O_3. They observed N_2 and N_2O formation around 150 °C, which is very similar to these results, however here in the absence of a noble metal. Therefore, it is important evidence that the $CeZrO_2$ mixed oxide is active to the NO dissociation at low temperatures.

4. Conclusions

The performance of a $CeZrO_2$ mixed oxide for the NO decomposition in the absence of a noble metal was studied. The XRD results confirmed the formation of a $Ce_{75}Zr_{25}O_2$ solid solution. Although no changes were observed during the pre-treatment and reduction up to 500 °C, NO was easily dissociated at room temperature during adsorption and during desorption at very low temperature on calcined and reduced samples. However, the reduced mixed oxide has a higher ability to dissociate NO to N_2 at lower temperature, evidencing that $CeZrO_2$ mixed oxide is very active to NO decomposition in absence of a noble metal, which may be attributed to superficial structure changes.

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