

The catalytic activity of Co/ZrO₂ for NO reduction with propane in O₂ presence

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Received 17 March 2003; accepted 6 June 2003

The selective catalytic reduction (SCR) of NO by propane in the presence of excess oxygen was studied on a Co/ZrO₂ catalyst. This system is present as active for the NO reduction to N₂. It was found that the addition of Co could improve the activity and selectivity of propane towards NO_x reduction. The activity depends strongly on the space velocity (GHSV) when the system works with low oxygen concentration and it is independent of the space velocity when the system operates with excess oxygen. The water vapor present in the feed produces deactivation in the catalyst as well as in the support.

KEY WORDS: NO selective reduction; Co/ZrO₂; propane.

1. Introduction

The NO_x decrease in gas emissions is a relevant environmental problem that may be accomplished by means of selective catalytic reduction (SCR) by hydrocarbons (SCR) [1–3]. The use of catalysts, including zeolites [4–9], basic metal oxide [10], SiO₂, TiO₂ [11,12] alumina [13–19] and ZrO₂ [20–25] reduces considerably the environmental problems caused by nitrogen oxides in exhaust gas purification.

According to the NO reduction mechanism, two factors seem to occur for the NO selective reduction, the hydrocarbon activation and the NO oxidation. The acidity and the presence of transition metals are considered to be related to these factors.

The activity strongly depends on Co loading and calcination temperature on Co/Al₂O₃ catalysts [16]. Some reports suggest that the Co⁺² dispersed surface was the active site for NO reduction, whereas Co₃O₄ catalyzed hydrocarbon combustion. A possible reason for the Co/Al₂O₃ higher selectivity calcined at high temperature is the high ratio of Co²⁺/Co₃O₄ ions. In a recent study, using propane as reducing agent in oxygen presence, we found that the activity of Co/Al₂O₃ catalysts for NO reduction is increased with the oxygen when the predominant cobalt phase is the cobalt aluminate.

Several authors have reported that the role of acid sites is to promote the NO oxidation step [26–28].

In this work, zirconium oxide is selected as support because it is well known that it exhibits a surface acidity

and cobalt with low loading to obtain highly dispersed Co⁺² ions and to avoid the Co₃O₄ formation that catalyzes the hydrocarbon combustion.

The aim of this work is to study how the doping of zirconium oxide with cobalt influences the activity and the selectivity of the catalyst for the NO reduction as well as to analyze the stability when wet feed is used in NO reduction with propane.

2. Experimental

2.1. Catalyst preparation

The zirconium hydroxide was obtained by hydrolysis of zirconium oxychloride, ZrOCl₂ · 6H₂O (Fluka). The necessary amount of ammonium hydroxide (Tetrahe-dron 28%) was added to zirconium oxychloride to reach a pH of 10. The product obtained by hydrolysis was filtered and washed up to the nonidentification of the ion chloride in the washing water, and finally the material was dried at 353 K for 24 h. The zirconium hydroxide was calcined at 873 K for 2 h, thus obtaining zirconium oxide.

A catalyst containing cobalt was prepared by impregnating 2 g of ZrO₂, in 500 cm³ of an aqueous solution of Co(NO₃)₂ in ammoniacal medium at room temperature and maintaining constant stirring for 6 h. The nominal concentration value for this catalyst was 0.2%. After impregnating the support, the material was washed and dried at 373 K. The calcination was carried out in a muffle from room temperature to 973 K and maintained at this temperature for 2 h. The material obtained will be named Co/ZrO₂.

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2.2. Catalyst characterization

The cobalt content was determined by the Atomic Absorption Spectroscopy (AAS) using an ILL equipment.

The superficial area of catalysts was determined in a Micromeritics Accusorb 2100E equipment using the BET method for its estimation.

X-ray diffraction (XRD) was performed on an X-ray diffractometer (Philips PW 1732/10) using Cu K α radiation and operated at 40 kV and 20 mA. The scan range was 20–65° and the scan speed was 1°/min.

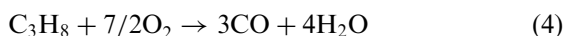
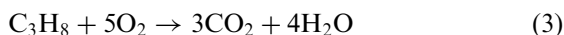
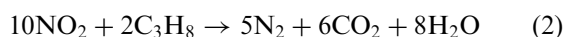
In order to supply more information about cobalt species present in the catalyst, diffuse reflectance spectroscopy (DRS) analyses were carried out in a Varian Super Scan 3 equipment. The spectra of catalysts finely milled were recorded between 200 and 800 nm.

2.3. Reaction experiments

Catalytic reactions were evaluated in a fixed bed reactor constructed in quartz (i.d. = 0.8 cm), heated electrically and the temperature measured by means of a thermocouple of the K type in contact with the catalytic bed. The reaction mixture was obtained from four feed lines individually controlled: NO/He, C₃H₈/He, O₂/He, and He to close the balance at 1 bar. The reaction contained 1500 ppm of NO, 2000 ppm of C₃H₈ and variable concentration (0.8–2.5%) of O₂. The total flow rate was 50 mL/min, the catalyst mass range used was 0.200 to 0.400 g and gas hourly space velocities (GHSVs) were in the range 15 000–30 000 h^{−1} (based on the ZrO₂ apparent bulk density of 2 g cm^{−3}).

Reaction products were monitored with a gas chromatograph Shimadzu model GC-8A provided with a thermal conductivity detector (TCD). The separation of products was performed with a concentric column CTRI of Altech. This system permits the identification and quantification of peaks of O₂, N₂, N₂O, CO₂, C₃H₈, CO, and NO.

Conversions were calculated from the following reactions:



The conversion for the NO reduction (equation (2)) was calculated in terms of N₂ production as $X_{\text{N}_2} = 2[\text{N}_2]/[\text{NO}]$. The propane conversion originated by the hydrocarbon combustion with oxygen (equations (3) and (4)) was calculated as $X_{\text{CO}_2\text{comb}} = (1/3 [\text{CO}_2] - 1/2, 5 [\text{N}_2])/[\text{C}_3\text{H}_8]$ and $X_{\text{CO}} = 1/3 [\text{CO}]/[\text{C}_3\text{H}_8]$ where [N₂], [CO₂], and [CO] are gas-phase concentra-

tions after reaction and [NO] and [C₃H₈] are feed concentrations. The carbon balance was always better than 98%. The propane selectivity is defined as the ratio of the amount of propane that reacted with nitric oxide to the total amount of propane consumed.

3. Analysis and discussion of results

3.1. Catalyst characterization

The Co/ZrO₂ catalyst is a pale pink-colored material with a cobalt content of 0.17 g for each 100 g of material (AAS). A low cobalt charge was selected to obtain a material with a high metal dispersion.

Table 1 summarizes results of the specific surface area of the fresh support and catalyst (ZrO₂, Co/ZrO₂) and postreaction support and catalyst (ZrO_{2 post}, Co/ZrO_{2 post}). All treatments of the fresh support (NO reduction with wet feed or calcination during catalyst preparation) lead to its sintering, and the specific surface area changes from 49.5 to 33–35 m²/g. The support sinters during catalyst preparation (Co/ZrO₂) and in the course of the reaction (ZrO_{2 post}). On the other hand, the specific surface area of Co/ZrO₂ catalyst does not suffer changes between the fresh material and the one used with dry feed or wet feed. In all these cases, the specific surface area is 34–35 m²/g.

XRD profiles of ZrO₂, Co/ZrO₂ catalyst and of the support extracted from the reactor after performing the NO reduction with wet feed, ZrO_{2 post}, are shown in figure 1. The ZrO₂ has both crystalline structures monoclinic ($2\theta = 28.3$ and 31.5) PDF = 37–1484 and tetragonal ($2\theta = 30.3$) PDF = 27–997, this last one with lower crystallinity degree. The support impregnation with cobalt salt and subsequent calcination to give the Co/ZrO₂ catalyst did not produce significant changes in the crystalline structure of the ZrO₂ support. A slight increase in height is observed only in the principal peaks of the monoclinic phase ($2\theta = 28.3$ and 31.5). This slight difference with the original support is also observed in the ZrO_{2 post} sample extracted from the reactor after the NO reduction with wet feed.

DRS spectra of Co/ZrO₂ show a maximum absorption at 600 nm corresponding to the transition $^4\text{A}_2(\text{F}) \rightarrow ^4\text{T}_1(\text{P})$ of the Co(II)_t (tetrahedral) and besides, it is possible to observe bands of charge transfer

Table 1
BET surface area of catalysts samples

Materials	Treatment	S _{BET} (m ² /g)
ZrO ₂	Fresh	49.5
ZrO _{2 post}	Post reaction wet feed	33
Co/ZrO ₂	Fresh	35
Co/ZrO _{2 post}	Post reaction dry feed	33
Co/ZrO _{2 post}	Post reaction wet feed	34

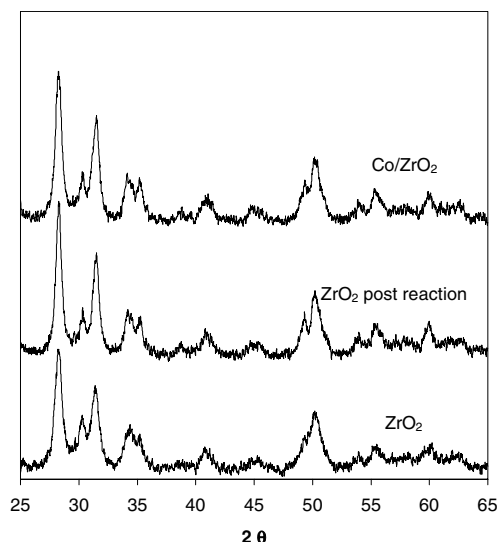


Figure 1. Powder X-ray patterns of catalysts.

Co–O placed in the UV region of the spectrum (400–200 nm) [29–31].

3.2. Catalytic results

3.2.1. Catalytic activity of ZrO₂ and Co/ZrO₂

Figure 2(a) shows the NO conversion for ZrO₂ and Co/ZrO₂ catalysts using a mixture containing 1500 ppm of NO, 2000 ppm of C₃H₈, 2.5% of O₂, He as balance and GHSV = 30 000 h⁻¹. On ZrO₂ and Co/ZrO₂ samples, the NO conversion reached a maximum as a function of temperature. The conversion of the Co/ZrO₂ catalyst is 50% higher than the conversion using the ZrO₂ support and the NO conversion reached the maximum at the same temperature for both samples. This makes us suppose that the function of transition metals (Zr and Co) is the same and that the cobalt addition does not modify the reaction mechanism. The C₃H₈ conversion always increases with the temperature for Co/ZrO₂ and ZrO₂ catalysts (figure 2(b)). The activity for the C₃H₈ combustion is similar for both materials. However, the selectivity (figure 2(a)) that shows for the catalyst Co/ZrO₂ is higher than the selectivity of the support.

3.2.2. Influence of the space velocity and the oxygen concentration

The dependence of NO conversion on oxygen content (O₂: 0.8 and 2.5%) was studied for two gas space velocities (GHSV: 15 000 and 30 000 h⁻¹).

Figure 3(a) shows the temperature dependence of NO conversion of the Co/ZrO₂ catalyst. At GHSV = 15 000 h⁻¹, it is observed that the NO conversion to N₂ is not modified with the oxygen concentration in the feed up to 700 K. Above this temperature, when the O₂ concentration decreases, the N₂ conversion increases. The NO conversion into N₂ obtained for

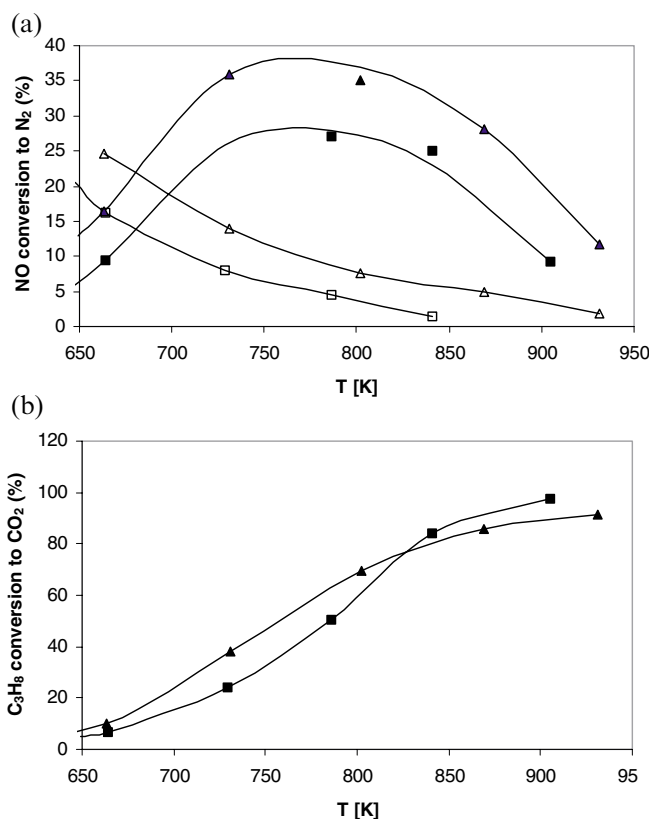


Figure 2. (a) NO conversion and selectivity as a function of temperature. Co/ZrO₂: NO conversion to N₂ (▲), selectivity (△) ZrO₂: NO conversion to N₂ (■), selectivity (□). GHSV = 30 000 h⁻¹. Feed composition: 1500 ppm NO, 2000 ppm C₃H₈, 2.5% O₂ and He as balance. (b) C₃H₈ conversion to CO₂ as a function of temperature. Co/ZrO₂ (▲), ZrO₂ (■). Reaction conditions were the same as those in figure 2(a).

2.5% O₂ presents a maximum conversion near 44% at 760 K. When the O₂ concentration in the stream was 0.8%, a complete conversion to N₂ was obtained, and the NO into N₂ conversion increased sharply from 820 K. The CO presence in reaction products (figure 3(b)) could reduce the cobalt oxide to Co⁰ and the NO adsorbed on the metal in a dissociative chemisorption with recombination on N adsorbed atoms to form N₂. Besides, the CO can also act as reagent in the NO reduction reaction [32].

At GHSV = 30 000 h⁻¹ (figure 3(a)), it is possible to observe that the NO conversion to N₂ is higher for the feed with higher oxygen concentration up to 800 K. For the mechanism of the NO reduction with hydrocarbon in the presence of excess oxygen, it is accepted that the key step of the reaction is the transformation of NO into NO₂ [33]. The increment of oxygen concentration increases the NO₂ concentration and the N₂ formation rate [16,18,19,34–36]. When the temperature is high, two factors can diminish the NO reduction rate. The NO₂ equilibrium concentration decreases with the temperature; besides, the hydrocarbon combustion with the

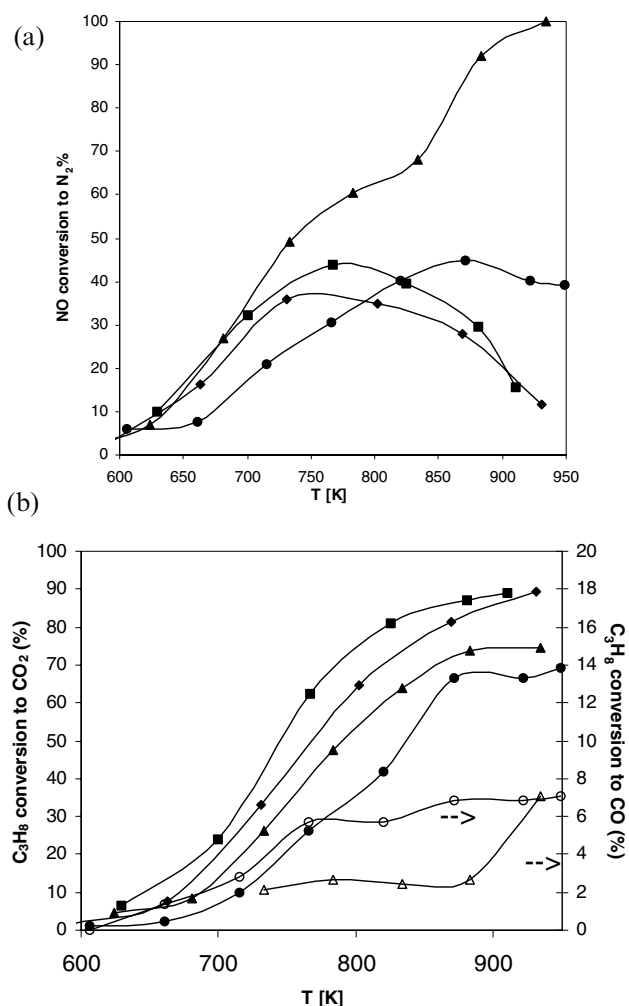


Figure 3. (a) NO conversion to N₂ over Co/ZrO₂ catalyst. 15000 h⁻¹ (GHSV): (▲) 0.8% O₂, (■) 2.5% O₂. 30000 h⁻¹ (GHSV): (●) 0.8% O₂, (◆) 2.5% O₂. Feed composition: 1500 ppm NO, 2000 ppm C₃H₈, 0.8 or 2.5% O₂ and He as balance. (b) C₃H₈ conversion to CO₂ over Co/ZrO₂ catalyst. 15000 h⁻¹ (GHSV): (▲) 0.8% O₂, (■) 2.5% O₂. 30000 h⁻¹ (GHSV): (●) 0.8% O₂, (◆) 2.5% O₂. C₃H₈ conversion to CO, empty symbol. Reaction conditions were the same as those in figure 3(a).

oxygen competes with the principal reaction (equation (2)) thus decreasing the hydrocarbon concentration available for the reaction. Figure 3(b) shows that the hydrocarbon conversion in the combustion reaction (equation (3)) for 910 K is 87%; this means that only 260 ppm of C₃H₈ are available to react in the reaction (equation (2)) when the O₂ concentration is 2.5%. With this hydrocarbon amount it would be possible to reduce 1300 ppm of NO, this representing an 86% conversion. As the conversion value obtained at 910 K is lower than this value, it is supposed that this fact is caused by the NO₂ decrease by the equilibrium shifting toward the NO.

Figure 4 shows the propane selectivity for the Co/ZrO₂ catalyst. When the oxygen concentration is

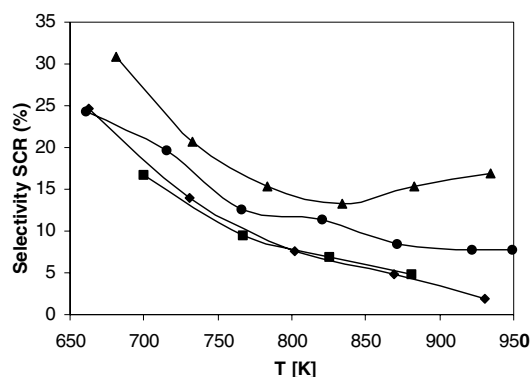


Figure 4. Influence of the GHSV and oxygen concentration in the selectivity for the SCR over Co/ZrO₂. 15000 h⁻¹ (GHSV): (▲) 0.8% O₂, (■) 2.5% O₂. 30000 h⁻¹ (GHSV): (●) 0.8% O₂, (◆) 2.5% O₂.

high, the selectivity is maintained without changes as the GHSV is doubled from 15000 to 30000 h⁻¹. This catalyst can be used in a wide range of space velocities with an oxygen excess in the feed giving mean conversions at low temperatures (700–800 K).

3.2.3. Influence of the water vapor presence in the catalytic performance of the Co/ZrO₂ system

As most exhaust streams containing NO_x also contains 2–18% water vapor [5,37,38], it is interesting to take into account the response of catalysts in wet feed. The support (ZrO₂) and the catalyst (Co/ZrO₂) have been tested in a wet feed with 8% water vapor. The performance after reaction in wet feed was also measured in dry feed in order to discriminate between reversible and irreversible effects. Figures 5 and 6 show the temperature dependence of NO conversion to N₂ and C₃H₈ conversion to carbon oxides for support (ZrO₂) and catalyst (Co/ZrO₂), respectively. Data show that both catalysts studied here exhibit a much lower performance in a wet feed for NO reduction to N₂.

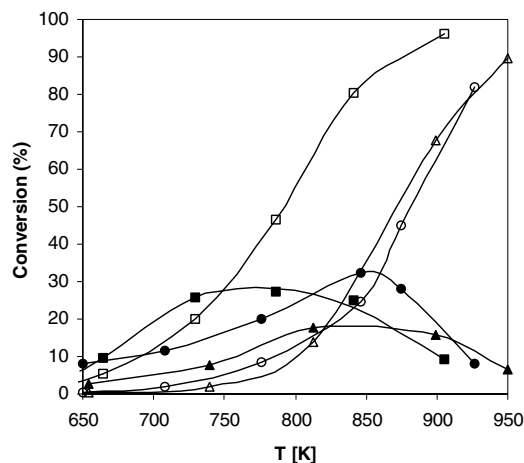


Figure 5. Influence of presence of water vapor on the catalytic performance of ZrO₂: (■) dry feed, (▲), feed with 8% of water vapor and (●) dry feed after reaction in the presence of water vapor. Empty symbol: C₃H₈ conversions to CO₂. GHSV = 30000 h⁻¹. Feed composition: 1500 ppm NO, 2000 ppm C₃H₈, 2.5% O₂ and He as balance.

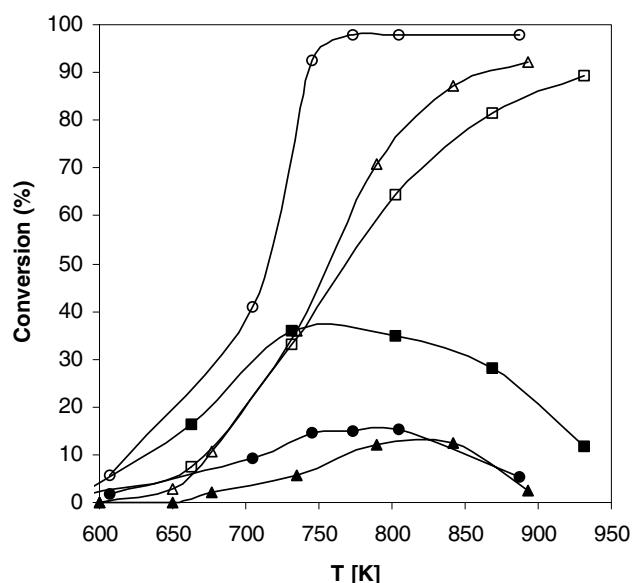


Figure 6. Influence of presence of water vapor on the catalytic performance of Co/ZrO₂: (■) dry feed, (▲), feed with 8% of water vapor and (●) dry feed after reaction in the presence of water vapor. Empty symbol: C₃H₈ conversions to CO₂. Reaction conditions were the same as those in figure 5.

The activity decrease is more important in the Co/ZrO₂ catalyst than in the support. For the catalyst, the NO conversion to N₂ decreases from 36 to 12% and the temperature at which the maximum NO conversion occurs is shifted towards higher temperatures, approximately 60 K. Meanwhile, over the support the activity drops from 28 to 17% with similar shifting of the temperature where the maximum activity appears.

The support activity decrease could be attributed to its sintering, the superficial area of the support decreases from 49.5 to 33 m²/g (table 1). A drastic activity reduction in the support (figure 5) is also observed for the secondary reaction of propane combustion for wet feed, as for example, at 850 K with dry feed the propane conversion is near 90%, while with wet feed the support presents 40% of propane conversion. Special attention must be focused on the fact that the water presence has modified in a higher extent, the hydrocarbon combustion rate with respect to the NO reduction. These results would indicate that the water effect was produced on the material and that it was not only a competitive adsorption process.

No significant changes in the superficial area appear in the Co/ZrO₂ catalyst before and after the reaction with wet feed.

Figure 6 shows that wet feed increases the hydrocarbon combustion for Co/ZrO₂ catalyst slightly and the activity decreases considerably for the NO reduction. The decrease for the NO reduction could be originated by two factors: the increase of hydrocarbon combustion and in the decrease of vacant sites for the

reaction because of the competitive water adsorption. The former could be associated with an incipient change of cobalt oxidation, from Co⁺² to Co₃O₄, which is favored by increasing temperature.

The hydrocarbon combustion with dry feed, measured on the catalyst used with wet feed up to 900 K, is noticeably incremented while the activity for the NO reduction is not decreased. The complete combustion is achieved at a temperature 200 K lower than with the fresh catalyst. This indicates that, during the reaction with wet feed at high temperature, a significant change in the material could have occurred. This increase in the combustion rate can also produce an important decrease of the hydrocarbon concentration available for the NO reduction and in this way the N₂ generation is decreased. The catalyst with cobalt suffers an irreversible deactivation for the NO reduction reaction, while the reaction with wet feed up to 950 K generated a very active catalyst for the combustion reaction. Probably, an oxidation of isolated Co⁺² ions was produced, generating segregated oxidic phases, Co₃O₄. These oxidic phases may have been formed during the high temperature yet run out of Co⁺² ions swept together by the wet feed. The Co₃O₄ presence increases the combustion [39,40].

Instead, the support after reaction with water up to 950 K gives the same conversion than the fresh support for the NO reduction reaction but this occurs at higher temperature (figure 5) and the hydrocarbon combustion appears decreased. The high combustion presented by the fresh material was not recovered.

3.2.4. The dependence of catalytic activity on cobalt content and support

The activity of Co/ZrO₂ was compared with that obtained over a Co(0.4)/Al₂O₃ catalyst Co(0.4)/Al₂O₃ (table 2). The Co/ZrO₂ catalyst is more active than the Co(0.4)/Al₂O₃ one for the NO reduction by propane. Besides, while the Co/ZrO₂ catalyst does not present propane to CO conversion in the presence of oxygen

Table 2
Catalytic performances of Co-based catalysts

T (K)	Conversions of NO to N ₂ % (C ₃ H ₈ to CO _x %) ^a		
	Co/ZrO ₂	Co(2)/ZrO ₂ ^b	Co(0.4)/Al ₂ O ₃ ^c
600	4 (2)	2 (12)	–
650	13 (4)	6 (42)	–
700	27 (20)	7 (76)	3 (5)
750	37 (42)	6 (98)	6 (10)
800	35 (65)	8 (100)	17 (65)
850	31 (76)	10 (100)	27 (90)
900	20 (86)	2 (100)	20 (100)

^aReaction conditions: NO = 1500 ppm, C₃H₈ = 2000 ppm, O₂ = 2.5%. Catalysts mass = 200 mg.

^bCo loading = 2%.

^cCo loading = 0.4%.

(2.5%), the Co(0.4)/Al₂O₃ catalyst shows propane to CO conversion of approximately 25% at 850 K.

The dependence of catalytic activity on cobalt content is shown in table 2. The catalyst Co(2)/ZrO₂ (2% of cobalt) shows lower activity than the Co/ZrO₂ (0.2% of cobalt) for the NO reduction and higher activity for the propane conversion.

4. Conclusions

- The Co/ZrO₂ catalytic system is present as active for the NO reduction with propane. The activity depends strongly on the space velocity (GHSV) when the system works with low oxygen concentration and is independent of the space velocity when the system operates with excess oxygen.
- The support presents activity although the cobalt presence makes the system more active; this could be attributed to the presence of Co⁺² ions that, in agreement with the bibliography previously presented, are sites responsible for the NO oxidation to NO₂, which is subsequently reduced to N₂ by the hydrocarbon.
- The water vapor presence in the feed produces an irreversible deactivation in the catalyst as well as in the support. This deactivation is more important in the material containing cobalt. This water deactivation effect is probably due to changes in the cobalt oxidation state from Co⁺² to Co₃O₄.

Acknowledgments

Financial support for this work has been obtained from CONICET, UNSL, and UNLP.

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