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Current Catalysis, 2014, *3*, 179-186

Cobalt Supported on Zirconia. Selective Catalytic Reduction of NO Using Propane as Reducing Agent

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Abstract: The catalytic behavior of a series of cobalt catalysts supported on zirconia in the selective catalytic reduction (SCR) of NO has been studied using propane as reducing agent. The catalysts were characterized by Raman Spectroscopy, Temperature Programmed Reduction (TPR), Diffuse Reflectance Spectroscopy UV-Vis (DRS) and X-ray Photoelectron Spectroscopy (XPS) to assess the physicochemical properties of cobalt species. Results for SCR of NO indicate that the activity is substantially related to the cobalt concentration and consequent nature of supported cobalt species. The formation of segregated oxidic phases on the catalytic surface produces an activity decrease. The most active catalyst contains Co(II) ions, interacting with the support, in tetrahedral coordination.

Keywords: Co/zirconia; surface characterization, SCR, NOx, C_3H_8.

1. INTRODUCTION

The removal of pollutants coming from combustion systems, of fixed or mobile sources, is a priority requirement to fulfill with increasingly strict regulations in order to protect the environment. Nitrogen oxides (NOx) are responsible for the photochemical smog generation, acid rain, decrease in the ozone layer and greenhouse effect. Although several wet and dry processes have been developed, most research has been focused on the selective catalytic reduction (SCR) to remove nitrogen oxides with ammonia and urea.

The NOx formed in combustion processes are composed by more than 90% NO. Recently, the process denominated "Fast SCR" has been developed whose reaction rate is almost 10 times superior than the one attained in the SCR process and higher NOx removal is achieved with respect to the traditional process. The high NOx conversion in the "Fast SCR" process can be reached using an oxidation catalyst that is placed before to the catalyst for the SCR, converting almost 50% of NO to NO_2 and this permit to reduce the catalyst volume in the SCR process [1].

The use of hydrocarbons instead of ammonia to reduce NOx to N_2 appears as a feasible technology in last decades. The use of cobalt catalysts exchanged in zeolitic systems or supported on oxidic environments has been extensively reported [2-15]. The utilization of cobalt catalysts supported on zirconia results of particular interest [3, 9, 11].

The physicochemical nature of supported cobalt phases depends strongly on the support and on the catalyst preparation method. In this respect, the metal concentration is an important operative variable since an increase in the oxidation state can lead to the formation of active phases for the secondary reaction of hydrocarbon oxidation and consequently to an activity decrease for the NO reduction. Likewise, the nature of cobalt sites depends on the metal-support interaction, including the metal oxidation state and its coordination.

In this work, results obtained with a series of catalysts with variable cobalt concentration supported on commercial monoclinic zirconia are presented. Specifically, characterization results of attained materials are presented, emphasizing on structural characteristics of the support and on physicochemical properties of active cobalt species as well as on results obtained in catalytic measurements.

The catalysts are applied to the SCR reaction by using propane as reducing agent in oxygen presence, while catalysts were characterized by Raman spectroscopy, diffuse reflectance spectroscopy (DRS), temperature programmed reduction (TPR) and X-ray Photoelectron Spectroscopy (XPS).

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2211-5455/14 $58.00+.00

2. EXPERIMENTAL

A series of catalysts was prepared by impregnation of commercial monoclinic zirconium oxide with aqueous solutions of $Co(NO_3)_2$, using a rotavapor equipment at room temperature for 6 hours. The impregnating solution was selected so as to get catalysts with nominal cobalt concentrations of 0.2, 0.5, 1.0, 1.5 and 2.0 g each 100 g catalyst. Materials were dried at 100 ºC after impregnation. These materials heated at 600ºC for 2 h were named $Co(x)/ZrO_2$ (where x=0.2, 0.5, 1.0, 1.5 and 2.0).

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

Raman spectra were performed with a Bruker 66 equipment with laser Nd:YAG emitting radiation of 1064 nm (9395 cm^{-1}).

Temperature programmed reduction (TPR) measurements were performed in a home-made equipment. The reactor was fed with a H_2/N_2 10:90 mixture and the heating rate was 10ºC/min from 50 up to 700ºC.

In order to supply more information about cobalt species present in the catalyst, diffuse reflectance spectroscopy analyses (DRS) were carried out in a Cintra equipment. Spectra of finely milled catalysts were recorded between 400 and 800 nm using $BaSO_4$ as reference.

XPS spectra were acquired on a Leybold-Heraeus LHS 10 spectrometer working in FAT mode (50 eV) using Al Kα radiation (1486.6 eV; 12 kV, 20 mA).The binding energy values (BE) were referenced to $Zr3d_{5/2}$ at 182.5 eV. Data analysis involved smoothing, non-linear Shirley-type background subtraction and curve fitting using mixed Gaussian–Lorentzian functions (Esca Tools 4.2 software, Surface Interface Inc., Mountain View, CA). Peak areas were obtained from the integration of the appropriate signal after data analysis and were used to determine the surface composition, using the sensitivity factors method [16]. Changes in Co 2p signal shape with Co content were analyzed by a curve fitting procedure with Co 2p doublet endowed with fixed spectroscopic parameters, but using variable position, full width at half maximum (FWHM) and intensities.

Catalytic performances were evaluated in a fixed bed quartz reactor (id = 0.8 cm) heated electrically using catalyst mass of 0.200 g. The temperature was measured with a K-type thermocouple in contact with the catalytic bed. The reaction mixture was obtained from four feed lines: O_2/He, C_3H_8/He, NO/He and He to close the balance. The feed flow composition was 1500 ppm of NO, 2000 ppm of C_3H_8 and 2.5% of O_2. The total flow rate was 50 ml/min and the space velocity was 30000 h^{-1}.

Reaction reagents and products were monitored with a gas chromatograph (Shimadzu GC-8A) provided with a thermal conductivity detector. The separation of products was performed with a concentric column CTRI of Altech. This system permits the identification and quantification of peaks of O_2, N_2, N_2O, CO_2, C_3H_8, CO and NO.

Conversions were calculated from the following reactions:

$$NO + 1/2\ O_2 \rightarrow NO_2 \quad (1)$$

$$10NO_2 + 2\ C_3H_8 \rightarrow 5\ N_2 + 6\ CO_2 + 8\ H_2O \quad (2)$$

$$C_3H_8 + 5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O \quad (3)$$

The conversion for the NO conversion into N_2 (Eq. 2) was calculated in terms of N_2 production as $X_{N2}= 2[N_2]/[NO]$. The propane conversion owing to the hydrocarbon combustion with oxygen (Eq. 3) was calculated as $X_{CO2comb} = 1/3\ [CO_2]/[C_3H_8]$ where $[N_2]$ and $[CO_2]$ are gas-phase concentrations after reaction and [NO], $[C_3H_8]$ are feed concentrations. The carbon balance was always better than 98%.

3. RESULTS AND DISCUSSION

3.1. Characterization

The bulk structure of $Co(n)ZrO_2$ catalysts was determined by powder X-ray diffraction. The XRD pattern of the ZrO_2 support (not shown) reveals lines of the monoclinic phase (2 θ = 28.2; 31.5; 34.5; 35.3; 49.3; 50.6; 54.1; 55.3). The crystalline phase of Co_3O_4 (2 θ = 31.2; 36.8; 59.35 and 65.35º) was observed in $Co(1.5)ZrO_2$ and $Co(2)/ZrO_2$ catalysts.

Raman spectroscopy was very useful to determine the catalysts structure since it allows identifying clearly bands due to the support as well as bands associated to oxidic cobalt species even as small entities. Owing to its high sensitivity to intermediate range order without long-range periodicity Raman spectroscopy can in fact disclose cobalt species which could not be detected by XRD.

The active modes for the monoclinic phase of ZrO_2 are at 180, 188, 223, 234, 305, 333, 345, 378, 475, 505, 534, 569, 618 and 634 cm^{-1}, while the active modes for Co_3O_4 spinel are 194, 482, 521, 618 and 691 cm^{-1} [17].

Fig. (**1**) presents the Raman spectrum of commercial zirconia as well as those of $Co(0.2)ZrO_2$ and $Co(0.5)ZrO_2$ catalysts.

Bands corresponding to the monoclinic polymorph are observed in the support spectrum. In the catalysts spectra with Co content > 0.2 wt% a band at about 690 cm^{-1}, attributed to the Co_3O_4 species, was observed already for the $Co(0.5)/ZrO_2$ catalyst (Fig. **1**, curve c). This fact evidences that cobalt oxidic species have been segregated in presence of very low cobalt content.

In order to know the interaction degree of cobalt species with the ZrO_2 support, studies of temperature programmed reduction were performed taking into account the reduction pattern of free cobalt oxides. CoO exhibits only one reduction signal in the range 355-450ºC with a maximum at 405ºC, attributed to the reduction of Co^{+2} to Coº. The TPR diagram of Co_3O_4 shows two reduction signals in the range 290-359ºC and 359-477ºC centered at about 350° and 400ºC, respectively. The first signal is attributed to the reduction of Co^{+3} to Co^{+2} and the second one to the reduction of Co^{+2} to Co^0.

TPR analysis of $Co(x)/ZrO_2$ system, Fig. (**2**), indicated that all samples contain reducible phases and the TPR pro-

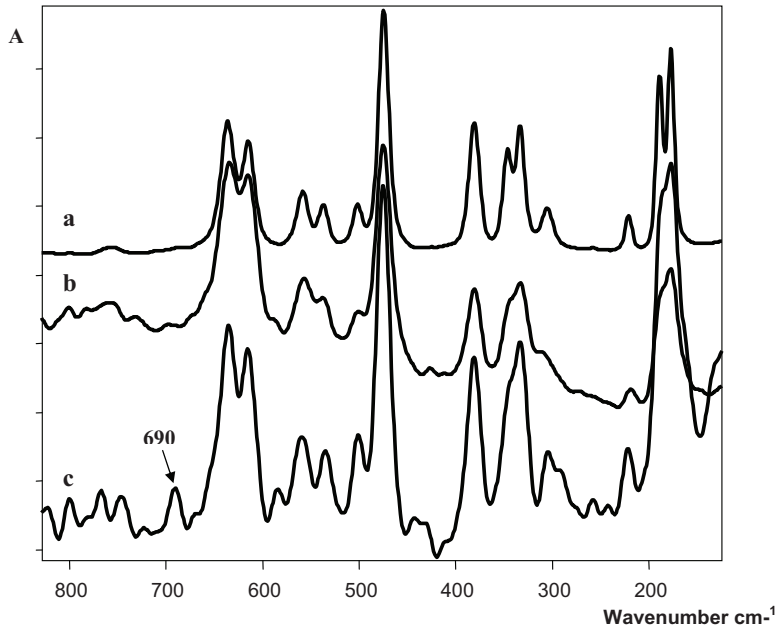

Fig. (1). Raman spectra: a) ZrO_2; b) $Co(0.2)/ZrO_2$ and c) $Co(0.5)/ZrO_2$.

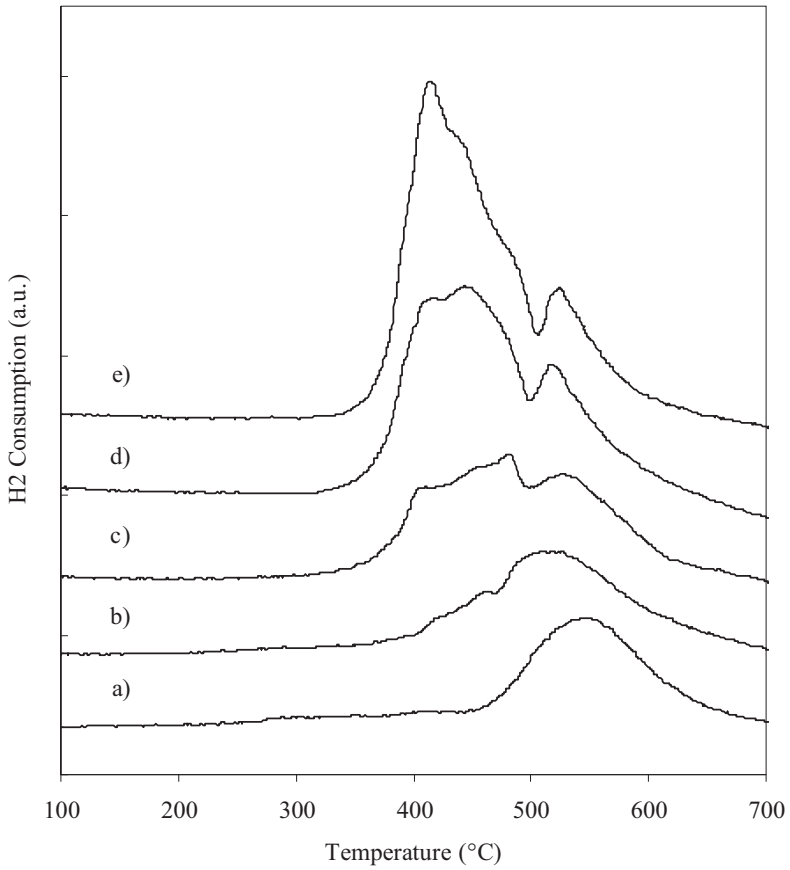

Fig. (2). Reduction diagram at programmed temperature of $Co(x)/ZrO_2$ catalysts: a) $Co(0.2)/ZrO_2$, b) $Co(0.5)/ZrO_2$, c) $Co(1)/ZrO_2$, d) $Co(1.5)/ZrO_2$ and e) $Co(2)/ZrO_2$.

files becoming more complex and shifted toward low Temperature at increasing Co loading.

The $Co(0.2)/ZrO_2$ catalyst (Fig. **2**, curve a) shows a reduction signal between 457 and 700ºC with maximum at 545ºC. This signal is associated with the reduction of ionic cobalt species (Co^{+2}) interacting with the zirconia support.

TPR diagrams of $Co(0.5)/ZrO_2$, $Co(1)/ZrO_2$, $Co(1.5)/ZrO_2$ and $Co(2)/ZrO_2$ catalysts show reduction sig-

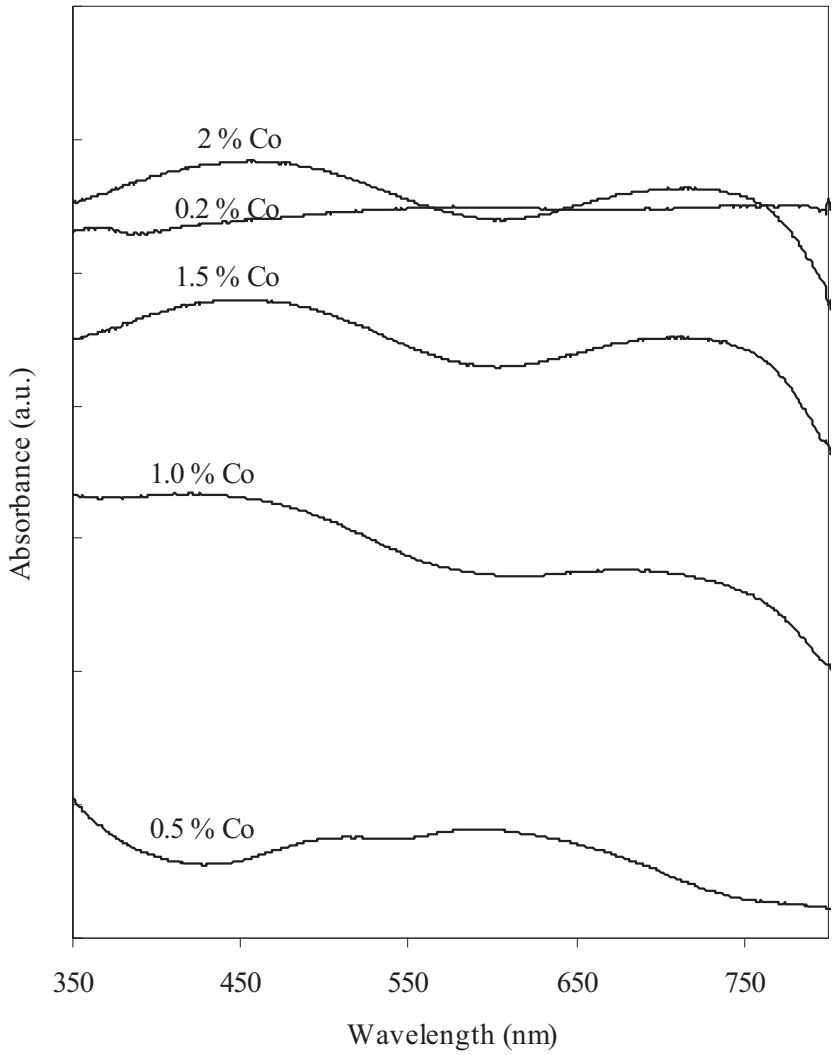

Fig. (3). Diffuse reflectance spectra of $Co(x)/ZrO_2$ catalysts.

nals at low temperature (lower than 460°C). These signals can be associated with the reducibility of cobalt species segregated in form of Co_3O_4. The areas of these signals are associated with the cobalt concentration and increases with Co content. In all TPR diagrams, the signal of high temperature, associated with the reduction of cobalt-zirconia interacting species, is present. The presence of reducible species at lower temperature generates an increase of reducibility of the most interacted species. The decrease of the reduction temperature of cobalt(II) species interacted with the support is attributed to the generated Co° contribution.

The cobalt concentration increase originates an increase in the system reducibility evidenced with the appearance of two or more reduction signals. In agreement with XRD and Raman finding, when increasing the metallic content part of cobalt forms structures interacting with the support and part segregates in form of Co(II) and Co(III) oxides.

Diffuse reflectance spectra of catalysts are shown in Fig. (**3**), in the range between 400 and 800 nm. The Co(II) in an oxidic environment with octahedral coordination shows an absorption maximum around 500 nm, while in tetrahedral coordination such maximum is at about 600 nm, with an higher extinction coefficient [11].

The spectrum of the bulk oxide Co_3O_4 is dominated by the presence of two bands in the range 400 - 500 nm and 700 - 800 nm.

The diffuse reflectance spectrum of $Co(0.2)ZrO_2$ catalyst (Fig. (**3**), curve a) presents an absorption band of very low intensity that it extends in a wide range of wavelengths (400 – 800 nm). However, an absorption maximum is noticed at about 600 nm, characteristic of Co(II) in tetrahedral coordination [11].

The spectrum corresponding to $Co(0.5)/ZrO_2$ catalyst (Fig. (**3**) ,curve b) shows a better resolution with two absorption maximums at about 500 and 600 nm assigned to cobalt(II) species in octahedral and tetrahedral coordination, respectively [11]. These results are in agreement with the ones achieved by Raman spectroscopy and TPR.

Spectra obtained with catalysts of higher Co load show clearly absorption bands associated to the presence of Co_3O_4 (400 - 500nm and 700 - 800nm).

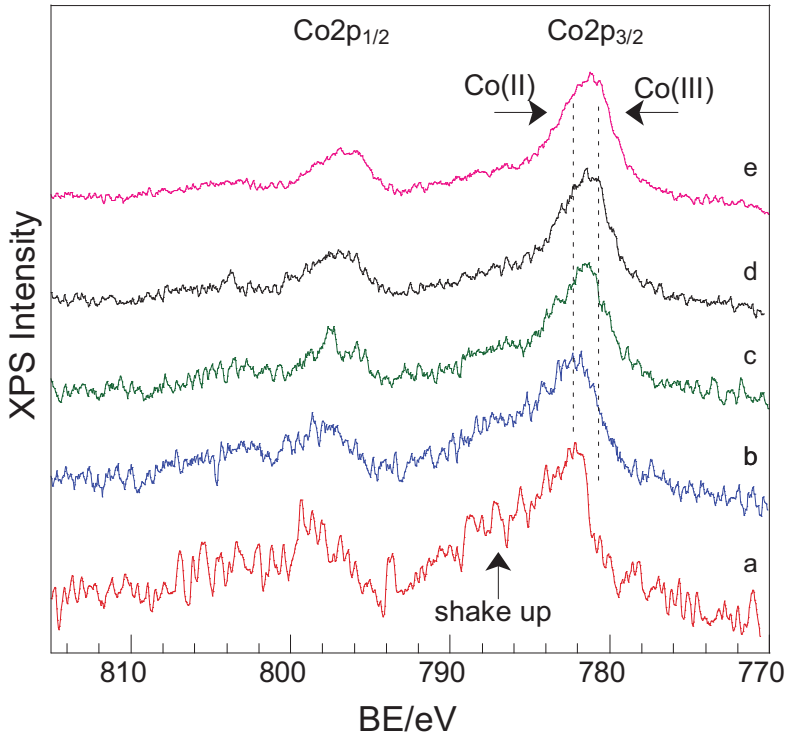

Fig. (4). Co2p XPS spectra as a function of cobalt content: a) Co(0.2)/ZrO_2, b) Co(0.5)/ZrO_2, c) Co(1)/ZrO_2, d) Co(1.5)/ZrO_2 and e) Co(2)/ZrO_2.

Table 1. XPS parameters of Co(x)/ZrO_2 samples.

Sample	Co2p3/2 /eV	Δp-s (Is/Ip)	$(nCo/nZr)_{bulk}$	$(nCo/nZr)_{surface}$
Co(0.2)/ZrO_2	782.2	5.1 0.60	0.0041	0.083
Co(0.5)/ZrO_2	782.3	5.3 0.52	0.0105	0.15
Co(1)/ZrO_2	782.0(4.4) 781.3 (50%) 782.9 (50%)	6.0 0.20	0.021	0.24
Co(1.5)/ZrO_2	781.6(3.8) 781.4 (80%) 782.4 (20%)	5.2 0.35	0.032	0.35
Co(2)/ZrO_2	781.4(3.7) 780.8 (90%) 782.6 (10%)	5.1 0.20	0.043	0.44

XPS analysis, performed to determine the state and the surface composition of the active phase, confirmed the coexistence of various cobalt species with different dispersion degree, depending on cobalt content.

Changes of the Co2p region with Co content are illustrated in Fig. (**4**). Table **1** summarizes the results obtained from curve fitting procedures and signals integration. The slight shift to lower BE and the decrease in the satellite-main peak intensity of the Co2p peaks at increasing Co content clearly indicate the formation of Co(III) species.

Co(II) has the $Co2p_{3/2}$ at 780.5 eV with a spin-orbit splitting of 15.8 eV and a shake up satellites at 5.4 eV from the main peaks (Δp-s) with a satellite-main peak ratio 0.60-0.70 [13]. Co(III) has a BE about 0.9 eV lower than that of Co(II) because of final state effects and a very small satellite [18, 19]. Therefore the presence of Co(III) yields peak broadening, an increase in the spin orbit separation and a decrease of the satellite-main peak ratio.

As shown in Table **1**, at increasing cobalt concentration, the binding energy decreases gradually; the intensity of the satellite peak also decreases indicating a progressive increase of the concentration of Co(III) species. The BE of $Co2p_{3/2}$ at 782.2 eV for Co(0.2)/ZrO_2 and Co(0.5)/ZrO_2 samples is consistent with Co(II).

Table 2. Maximum NO conversion to N_2 reached over catalysts.

Catalyst	Maximum NO Conversion to N_2	Temperature of the Maximum
Co (0.2)/ZrO_2	67	450-600ºC
Co (0.5)/ZrO_2	12	456ºC
Co (1.0)/ZrO_2	9	523ºC
Co (1.5)/ZrO_2	5	550ºC

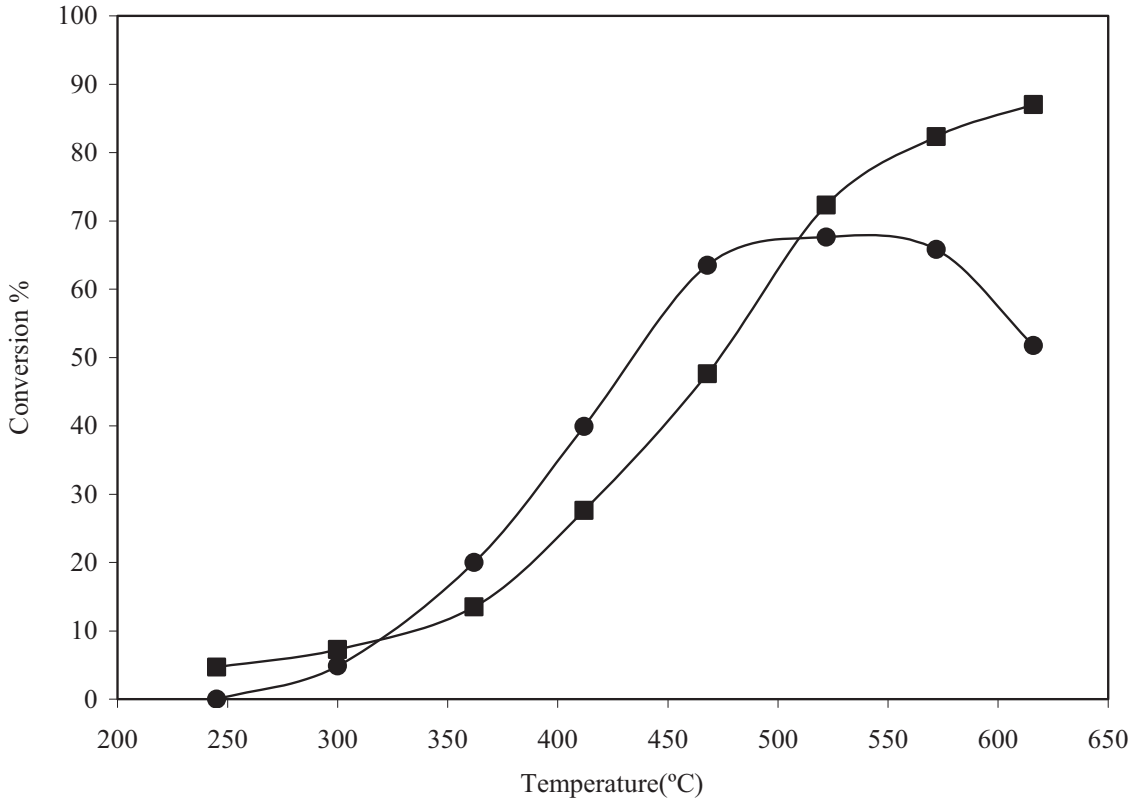

Fig. (5). NO conversion to N_2 (■) and propane conversion to CO_2 (●) as function of temperature for the Co(0.2)/ZrO_2 catalyst.

For catalysts with cobalt concentration equal or higher than 1.0 wt% the main $Co2p_{3/2}$ peak present two components at 781.4 eV and at 782.4 eV with a satellite. In the most concentrated sample, the intensity of Co(III) species represents 90% of the total intensity.

Atomic ratios were applied to relate bulk to the surface composition, using the nominal Co concentration. Comparing the atomic compositions, the $(nCo/nZr)_{surface}$ were higher than the $(nCo/nZr)_{bulk}$ values, indicative of surface enrichment of cobalt species. Nevertheless, surface composition increases with cobalt loading supporting the spreading of the interacting cobalt species.

3.2. Catalytic Results

Table **2** indicates the maximum NO conversion to N_2 reached over catalysts used in the reduction reaction of nitric oxide using propane as reducing agent in presence of oxygen excess.

Results suggest a strong dependence of the activity on cobalt load and that the Co(0.2)/ZrO_2 catalyst is the most active catalyst of the whole series. Fig. (**5**) represents results with this catalyst for the evolution toward NO conversion and of propane combustion to CO_2 as function of temperature.

The curve representing NO conversion to N_2 passes through a maximum reaching conversions near 70% between 450 and 600ºC. The NO reduction to N_2 decreases at high temperature but the activity continues to be acceptable (~50%), even when the propane conversion to CO_2 is high (~85%). The activity obtained can be associated to the presence of Co(II) species interacting with the support and in tetrahedral coordination. According to literature data the Co(II) sites can be responsible for the oxidation of NO to NO_2 [9].

Catalysts with cobalt content higher than 0.2 wt% show very little activity. In these catalysts, cobalt species were

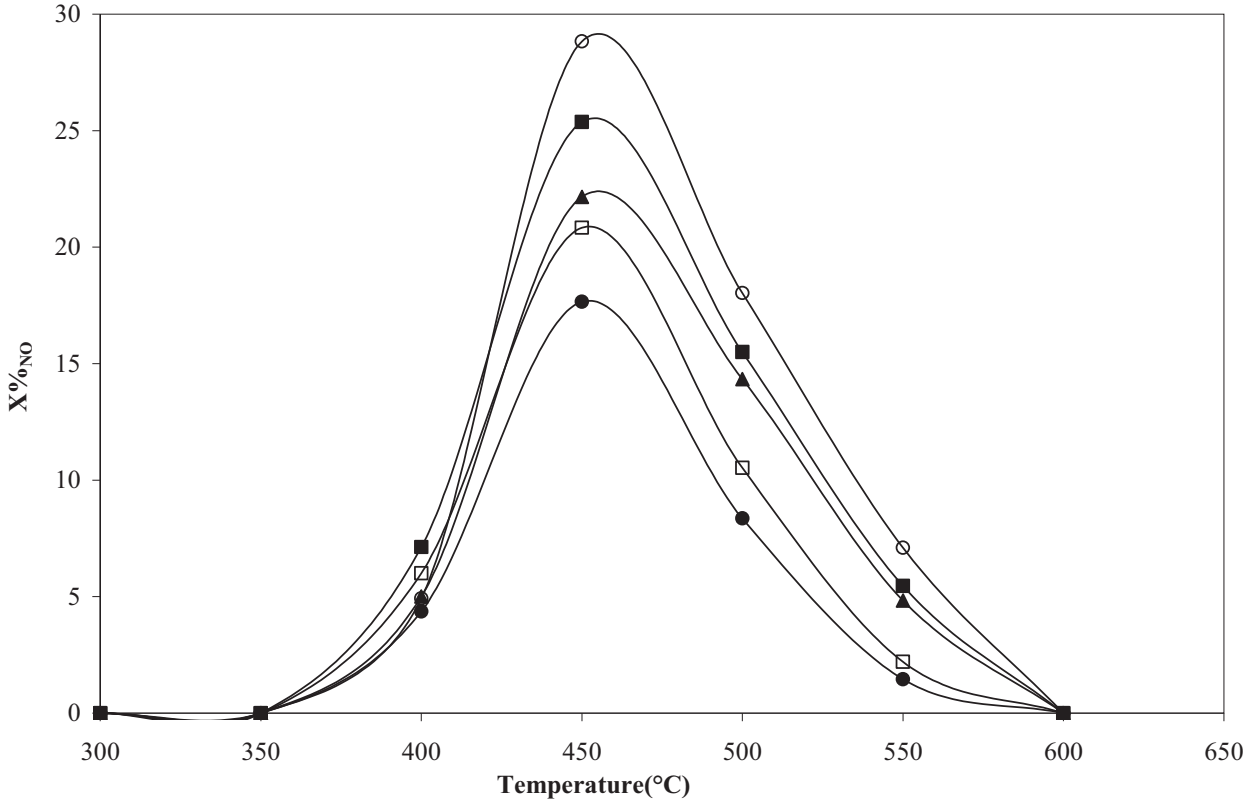

Fig. (6). NO conversion to NO_2: (○) 0.2% Co, (■) 0.5%Co, (▲) 1.0%Co, (□) 1.5%Co, (●) 2.0%Co.

identified both as structures interacting with the zirconia surface and oxides separate phases. The latter species can cover cobalt sites interacting with the support and/or they could accelerate the secondary combustion reaction. The poor catalytic results achieved with $Co(0.5)/ZrO_2$, $Co(1)/ZrO_2$ and $Co(1.5)/ZrO_2$ catalysts prevented to perform catalytic tests with the $Co(2)/ZrO_2$ catalyst since this one has the higher amount of segregated cobalt oxide species.

The activity for the SCR reaction can be associated to the catalyst capacity to oxidize the NO to NO_2. The activity of $Co(x)/ZrO_2$ catalysts in the NO oxidation reaction was studied for $Co(x)/ZrO_2$ samples at temperature programmed reaction. The experiments were performed from 200 to 600ºC at a heating rate of 5ºC/min. The reactor was fed with a mixture containing 3000 ppm of NO, in presence of O_2 (10%v/v) and balance nitrogen. Results are shown in Fig. (**6**). NO oxidation started at about 400°C reaching the maximum conversion at about 450ºC. At temperature higher than 450ºC, the conversion drastically increased, reaching about 19% at 500ºC for the Co(0.2) catalyst, the most active for NO oxidation to NO_2. When the cobalt concentration increased, the activity of catalysts decreased both in the oxidation and in the SCR reaction.

$$2\ NO + O_2 \dashrightarrow 2\ NO_2 \qquad (4)$$

A decrease in the activity for the SCR reaction is the presence of the secondary and competitive reaction of hydrocarbon oxidation. Fig. (**7**) shows the results for the propane conversion to CO_2 as function of temperature.

Results show that the secondary combustion reaction increases with the presence of Co_3O_4 as separate phase in the catalysts. These materials reach the total conversion of hydrocarbon and leave lower availability of reducing agent for the principal reaction. Nevertheless, between 400 and 500ºC all systems have the sufficient amount of reducer so as to achieve the main reaction. Therefore, the lower activity of catalysts with cobalt loadings higher or equal to 0.5% could not be produced only by a competence of the secondary reaction but also by the change in the nature of cobalt species. Probably, particles of oxides segregated diminish the access to Co(II) sites, which are responsible for NO oxidation to NO_2.

4. CONCLUSION

Catalysts presented in this work were studied in the NO selective reduction reaction using propane as reducing agent in oxygen excess presence. Results suggest that the activity of cobalt species supported on zirconia is substantially related with the cobalt concentration. The formation of oxidic phases segregated on the catalyst surface causes an activity decrease. These oxidic species are generated from a very low threshold concentration (0.5wt%) and it was possible to observe them by spectroscopic techniques (Raman, DRS and XPS). The catalyst with the lowest cobalt concentration (0.2wt%) has Co(II) ions interacting with the support, in tetrahedral coordination and shows high NO conversion to N_2 (66%) using a good space velocity (30000 h^{-1}).

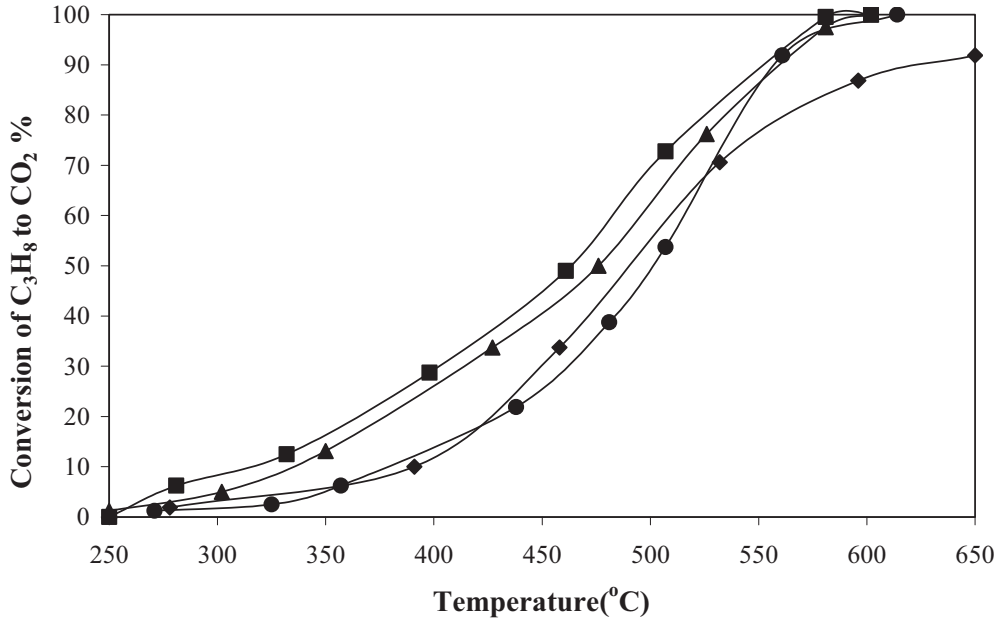

Fig. (7). Propane conversion to CO_2 accompanying the NO reduction to N_2: (♦) 0.2% Co, (●) 0.5%Co, (▲) 1.0%Co, (■) 1.5%Co.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

ACKNOWLEDGEMENTS

The financial support for this project has been obtained from ANPCyT, CONICET and UNLP.

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Received: June 06, 2013 Revised: December 12, 2013 Accepted: December 17, 2013