

Structural aspects of the Co/ZrO₂ catalytic system: Effect of the chemical synthesis

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Received 16 July 2004; received in revised form 9 September 2004; accepted 21 September 2004

Abstract

In this work, the application of the Co/ZrO₂ catalytic system was studied as catalyst for the reaction of selective reduction of nitrogen oxides with propane in oxygen presence. Particularly, the influence of the preparation method on the catalytic activity of these materials was studied. It was possible to observe that the activity depends, markedly, on the physicochemical properties of the material and these ones on the preparation method. The catalyst that shows higher activity is the one that presents a crystalline structure, preferably, monoclinic, where the cobalt is present as Co²⁺ species occupying tetrahedral sites and these cobalt species do not present reduction up to 1000 °C.

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Keywords: Co/ZrO₂ oxide; Chemical synthesis; Crystal structure

1. Introduction

During the last decade, chemical research has been driven towards the development of new routes to improve our quality of life through the protection of the natural environment. In this context, the use of hydrocarbons as reducing agents for the abatement of nitrogen oxides seems to be an available clean technology to solve a part of the urgent environmental problem. The reaction, known as selective catalytic reduction (SCR) of NO_x by hydrocarbons is based on the use of a wide variety of oxidic catalysts with different composition and structure [1–3]. Hence, promoted alumina and alumino-silicates (zeolites and clays) as well as binary systems (ZrO₂–TiO₂, SiO₂–TiO₂, etc.) and mixed oxides containing transition metals are widely used as SCR catalysts [4–10]. Transition metals as Cu, Ni and Co improve the catalytic performance [11]. The exchanged Co-zeolite is one of

the most known and widespread system, for which the SCR-activity is correlated, in detail, with the structural feature [5,12,13]. However, oxide systems based on the Co presence are not so particularly studied from the point of view of the matrix structural behaviour. In this sense, it is observed that the effect of active Co in the oxide lattices depends strongly on the composition of the support and on the preparation method of the catalyst. An increase of the metal loading does not always lead to the formation of a more active phase for the SCR reaction which can lead to the competitive hydrocarbon combustion reaction [14]. So, it is necessary to know well the nature of the metal–support interaction (including metal–diffusion processes) to analyze the effectiveness of the catalysts. In this aspect, the TPR technique seems to be a very useful tool to know the reducibility and so the magnitude of the interaction.

In this broad context, the activity of the Co/ZrO₂ system for the SCR reaction has been recently studied [7,10,15]. However, the polymorphism of the ZrO₂ host matrix and the effect of structural changes according to the synthesis conditions (starting materials, temperature, pH, reaction time,

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heating steps, etc.), can affect the availability and activity of cobalt. For this reason, it seems to be interesting to analyze this catalytic system from the point of view of the support structural behaviour including the study of some Co physico-chemical properties in the different ZrO₂ structural types. The catalysts are applied to the SCR reaction by using propane as reducing agent in oxygen presence, while their characterization of catalysts has been done with the aid of X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS), as well as thermal techniques (differential scanning calorimetry (DSC), thermogravimetry (TGA) and temperature programmed reduction (TPR)).

2. Experimental

2.1. Catalyst preparation

The ZrO₂·*n*H₂O (named the precursor) was obtained by hydrolysis of ZrOCl₂·6H₂O (p.a. Fluka) with NH₄OH to reach pH = ~10. The product was filtered and washed until the complete elimination of chloride ions. Then, the solid was dried at 100 °C for 24 h.

A first way to obtain the catalyst was the treatment of the ZrO₂·*n*H₂O precursor with the adequate Co(NO₃)₂ solutions by means of a rotavapor equipment, for 6 h at room temperature. Nominal concentrations of 0.2 and 2 g Co/100 g catalyst were selected. These catalysts heated at 600 °C for 2 h were named Co(*x*)/ZrO₂ (rotavap) (where *x* = 0.2 and 2, respectively).

A second way of catalyst preparation was from the ZrO₂·*n*H₂O precursor, previously treated at 600 °C for 2 h. This thermal treatment allows the formation of a crystalline ZrO₂. The catalyst was obtained by impregnating the crystalline phase with Co(NO₃)₂ solution in an ammonium medium. The nominal Co concentration was 0.2 (% Co). This Co-precursor was again thermally treated at 600 °C for 2 h. This catalyst was identified as Co(0.2)/ZrO₂ (monoclinic).

2.2. Catalyst characterization

The cobalt content was determined by the atomic absorption spectroscopy (AAS) using an ILL equipment. All samples were thermally treated at 600 °C.

The surface 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 Kα radiation and operated at 40 kV and 20 mA. The scan range was 20–65° and the scan speed was 1° min⁻¹.

Transformations occurring during calcination of hydrous zirconia, ZrO₂·*n*H₂O and of precursors of catalysts were studied using differential scanning calorimetry (DSC) and thermogravimetry (TGA).

Temperature programmed reduction (TPR) measurements were performed in homemade equipment. The reactor was fed with a H₂/N₂10:90 mixture and the heating rate was 10 °C min⁻¹ from 50 up to 1000 °C.

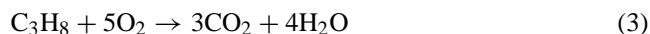
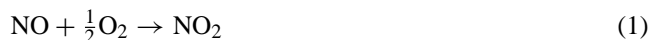
In order to supply more information about cobalt species present in the catalyst, diffuse reflectance spectroscopy analyses (DRS) were carried out in a Cintra equipment. Spectra of finely milled catalysts were recorded between 200 and 800 nm.

2.3. Catalytic measurements

Catalytic reactions were evaluated in a reactor of fixed bed constructed in quartz (i.d. = 0.8 cm), heated electrically. The temperature was 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 flow contained 1500 ppm of NO, 2000 ppm of C₃H₈ and 2.5% of O₂. The total flow rate was 50 ml min⁻¹. The used catalyst mass was 0.200 g whereas the space velocity was 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. 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 (Eq. (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 (Eq. (3)) was calculated as $X_{\text{CO}_2\text{comb}} = 1/3[\text{CO}_2]/[\text{C}_3\text{H}_8]$ where [N₂] and [CO₂] are gas-phase concentrations after reaction and [NO], [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 reacted with nitric oxide to the total amount of propane consumed.

3. Results and discussion

3.1. Catalysts characterization

It is well known that zirconia can exist in the monoclinic, tetragonal, orthorhombic and cubic (fluorite) structure. The monoclinic polymorph, commonly named baddeleyite, is stable up to ~1200 °C, and transforms to the tetragonal phase as

the temperature increases. On cooling, this high-temperature tetragonal form transforms to the monoclinic phase with a large hysteresis so that the tetragonal \rightarrow monoclinic transformation occurs between 1100 and 900 °C. On the other hand, high-temperature tetragonal phase gives the cubic fluorite-type form by heating at \sim 1900 °C. However, the polymorphism of ZrO_2 is very interesting because the stabilization of a low-temperature tetragonal phase (or metastable tetragonal phase) is observed when zirconia has been doped with cations and eventually with anion, depending also on the experimental conditions of crystallization. This tetragonal phase, resembling a distorted fluorite structure, results in high surface areas and good thermal stability. The formation of metastable tetragonal phase can be attributed to the presence of anionic vacancies [9,16].

Likewise, the literature shows abundant information related to the structural stabilization of the tetragonal phase by the effect of guest cations such as K(I), Na(I), Ca(II), Mg(II), Y(III), La(III), etc. generating a “disordered anion-deficient fluorite-type structure”. The defect clusters in the MO_{2-x} compounds correspond to tightly bound vacancies along a body diagonal (1 1 1). So, the central cations are coordinated by six oxygen atoms. The geometry of these clusters depends on the guest cations and account for the wide range of stability. The strong ordered effects in the $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and CaO-ZrO_2 systems are not only attributed to a vacancy model, the possible formation of microdomains of ordered superstructures has also been suggested [17]. The key mechanism is the monolayer of the active component put on the gel surface. Thus, during calcination, the growth of grains, the sintering between the grains and the possibility to transform to the monoclinic form are all repressed. Once the metal loading exceeds the dispersion threshold, the surplus salt or oxide will remain as a segregated crystalline phase. Higher values of divalent cations lead to the mixed oxide formation of different structural types.

Table 1 gives the Co content, the specific area and the majority crystalline phase (from the XRD analysis) for the studied catalysts. Pure ZrO_2 datum in similar experimental conditions is included with comparative purposes.

The impregnation of precursor leads to materials with similar surface areas, comparable to that obtained from undoped precursor (in similar experimental conditions). The lower surface area observed in the $\text{Co}(0.2)/\text{ZrO}_2$ (monoclinic) can be attributed to the thermal treatments (the first one associated to the support crystallization and the second one to the catalyst preparation).

Table 1
Physicochemical properties of catalysts

Catalyst	Cobalt (%) (AAS)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	% monoclinic phase
ZrO_2 (pure)	–	49.5	84
$\text{Co}(0.2)/\text{ZrO}_2$ (rotavap)	0.2	50.1	68
$\text{Co}(2)/\text{ZrO}_2$ (rotavap)	2	48.0	25
$\text{Co}(0.2)/\text{ZrO}_2$ (monoclinic)	0.17	35.1	89

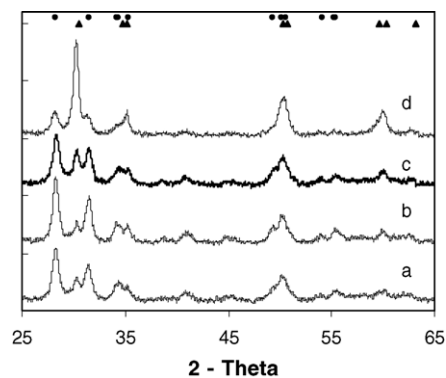


Fig. 1. XRD patterns of support and catalysts: (a) ZrO_2 , (b) $\text{Co}(0.2)/\text{ZrO}_2$ (monoclinic), (c) $\text{Co}(0.2)/\text{ZrO}_2$ (rotavap) and (d) $\text{Co}(2)/\text{ZrO}_2$ (rotavap). (▲) Tetragonal phase and (●) monoclinic phase.

The estimation of the ZrO_2 structural types has been made by means of the semiquantitative XRD analysis given by Garvie and Nicholson [18] and more recently modified by Su et al. [19]. So, the proportion of tetragonal (PDF 881007) and monoclinic (PDF 881451) forms depend on the preparative method.

XRD patterns of catalysts are shown in Fig. 1. The pure ZrO_2 is obtained by heating the $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ precursor at 600 °C. Regarding catalysts, $\text{Co}(0.2)/\text{ZrO}_2$ (monoclinic) prepared by impregnation of the crystalline ZrO_2 , and $\text{Co}(0.2)/\text{ZrO}_2$ (rotavap), obtained from impregnation of the precursor gel, show the XRD typical lines of the monoclinic ZrO_2 phase (PDF 86-1451). The crystallinity of the former is slightly increased by effect of the heating time.

As it is known a dopant presence influences the ZrO_2 phase composition favouring the formation of tetragonal polymorph. The $\text{Co}(0.2)/\text{ZrO}_2$ (rotavap) and $\text{Co}(2)/\text{ZrO}_2$ (rotavap) catalysts, both prepared from the impregnation of precursor, clearly show the tetragonal metastable stabilization, which is surely originated by the Co(II) incorporation into the precursor during the first step of the thermal treatment. The process, strongly dependent on the Co(II) content, reveals that the $\text{Co}(2)/\text{ZrO}_2$ (rotavap) catalyst adopts predominantly the tetragonal crystalline structure. The fact that no additional lines of segregated cobalt-oxides are observed because of the low cobalt content.

The transformation of the $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ (gel) into the crystal is a complex and cooperative process entailing dehydration, dehydroxylation, olation, oxolation and nucleation steps by the growth of the nuclei to form observable crystallites [20,21]

Fig. 2 shows the DSC thermal behaviour of the precursor, without and after treatment with solution of cobalt-salt, including that of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as comparison. This last one shows a series of successive endothermic signals up to 300 °C. Patterns of the precursors of catalysts are characterized by a series of low temperature endothermic signals (water loss), whereas the exothermal effects, associated to crystallization processes, prevail above 300 °C. The

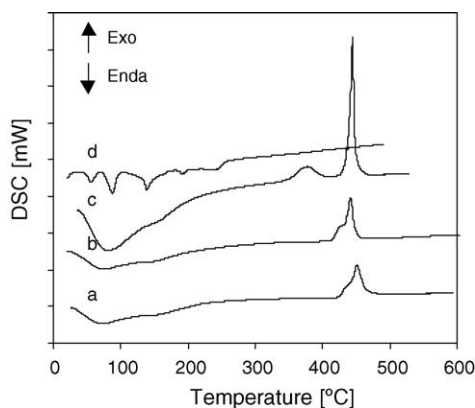


Fig. 2. DSC curves of catalyst precursors: (a) Co(2)/ZrO₂ (rotavap), (b) Co(0.2)/ZrO₂ (rotavap), (c) ZrO₂·*n*H₂O and (d) Co(NO₃)₂·6H₂O.

corresponding TGA analysis (do not show here) presents, in all cases, a gradual mass loss up to 500 °C. The patterns a, b and c are quite similar in shape, showing exothermic signals between 350 and 500 °C. However, the introduction of cobalt reduces the amplitude of these signals and shift them to a higher temperature. It is interesting to remark that the thermal behaviour of pure ZrO₂·*n*H₂O clearly show splitting of these signals that is not observed in the doped samples. The first exothermic signal at 378 °C can be associated to the oxolation of hydroxyl groups to form embryonic oxide nuclei and the second one can be attributed to the crystal growth process [21]. Although the dopant presence retards significantly the nucleation process (from 378 to 443 °C for pure ZrO₂·*n*H₂O and Co(2)/ZrO₂ (rotavap) precursors, respectively) the growth of embryonic oxide is only slightly affected (444 and 451 °C, respectively).

The stabilization of tetragonal zirconia as increasing Co loading can be related with a complex arrangement process, which is different from the kinetic point of view than that observed in undoped zirconia.

Regarding the reducibility, Fig. 3 shows TPR profiles of all catalysts including that of the ZrO₂ sup-

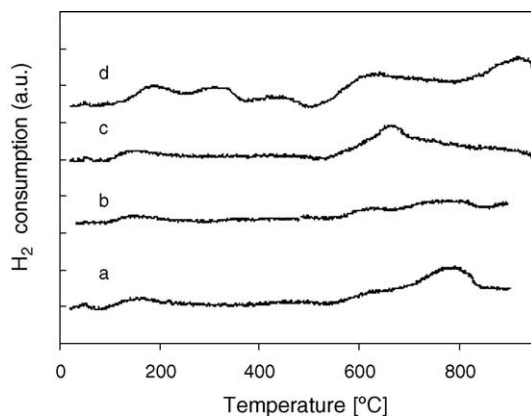


Fig. 3. Hydrogen TPR profiles of Co catalysts ZrO₂ supported: (a) ZrO₂, (b) Co(0.2)/ZrO₂ (monoclinic), (c) Co(0.2)/ZrO₂ (rotavap) and (d) Co(2)/ZrO₂ (rotavap).

port. In general, all samples show low H₂ consumption. ZrO₂ sample (mainly monoclinic) shows very weak signals ranged between 530 and 830 °C that can be attributed to the formation of oxygen vacancies. TPR pattern of Co(0.2)/ZrO₂ shows no appreciable TPR signal. The weak reduction peaks observed in the support are neither observed. This effect could be assigned to a strong cobalt–support interaction.

The Co(0.2)/ZrO₂ (rotavap) catalyst shows a TPR signal at a ~650 °C, attributed to the reduction of Co species in the zirconia matrix. It is also known that the Zr(IV) density in the 1 1 1 and 1 0 1 preferential planes of the tetragonal ZrO₂ is lower than that of the monoclinic form, leaving available species for the H₂ reduction [22].

Unlike the TPR behaviour observed in the above catalysts, the Co(2)/ZrO₂ (rotavap) presents two TPR signals (up to 350 °C) which can be related to the Co (II, III)–Co⁰ reduction of the segregated and dispersed Co₃O₄ oxide [23,24]. For this reason, a cobalt concentration higher than 2% would not improve the stabilization process by increasing the segregation of cobalt oxide. A similar behaviour is observed in the CuO–ZrO₂ system for higher contents of impregnating copper solution [25,26]. Other TPR signals are observed above 400 °C assigned to the reduction of Co species interacted with the support. Two types of factors are responsible for the enhancement of the cobalt reducibility: the structural arrangement of the majority tetragonal phase and the synergism from the low temperature reduction products of the Co₃O₄ segregated phase.

DRS spectra are shown in Fig. 4. As it is largely reported, Co(II) octahedral and Co(II) tetrahedral species in oxide environment can be distinguished by the presence of strong absorption bands centred in the 500 and 600 nm, respectively [27].

Whereas the Co(0.2)/ZrO₂ (monoclinic) presents a very broad band (ranged between 400 and 800 nm) centred at ~605 nm, typical of tetrahedral coordination, the Co(0.2)/ZrO₂ (rotavap) shows a lower absorption with a maxi-

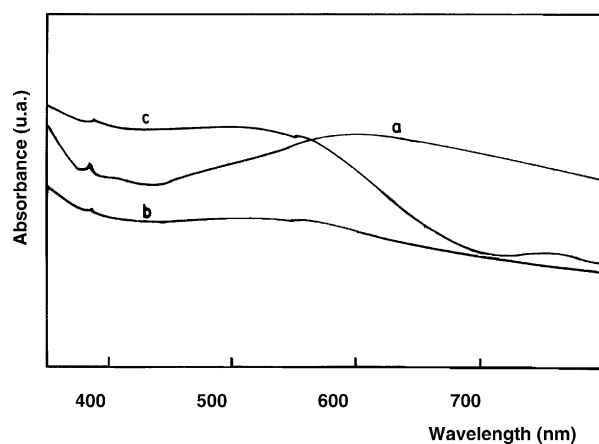


Fig. 4. DRS spectra: (a) Co(0.2)/ZrO₂ (monoclinic), (b) Co(0.2)/ZrO₂ (rotavap) and (c) Co(2)/ZrO₂ (rotavap).

Table 2
Catalytic performances of catalysts

T (°C)	Conversions of NO to N ₂ % (C ₃ H ₈ to CO ₂ (x) %)		
	Co(0.2)/ZrO ₂ (rotavap)	Co(2)/ZrO ₂ (rotavap)	Co(0.2)/ZrO ₂ (monoclinic)
325	1 (1)	2 (12)	4 (2)
375	2 (2)	6 (42)	13 (4)
425	8(4)	7 (76)	27 (20)
475	15(10)	6 (98)	37 (42)
525	21 (30)	8 (100)	35 (65)
575	24 (57)	10 (100)	31 (76)
625	17 (86)	2 (100)	20 (86)

mum at 520 nm, revealing the predominance of Co(II) octahedral species over the tetrahedral ones [27].

In the DRS spectrum of Co(2)/ZrO₂ (rotavap) catalyst, two signals centered at 750 and 500 nm, respectively, can be suggested. The first one can be attributed to the Co(III) species from segregated Co₃O₄ oxide [27], whereas the second one is typical of Co(II) in octahedral coordination. This last one has also been observed in Co(0.2)/ZrO₂ (rotavap) catalyst.

From the obtained results it is evident that the preparation method determines the structural characteristics of the catalysts. In fact, both, the ZrO₂ structural type and the Co environment in the host lattice can be modified by the synthesis. The Co incorporation into the Zr-precursor leads to crystalline materials with a higher proportion of ZrO₂ tetragonal structure.

At higher Co loading, the presence of Co(III) is observed, associated to segregated Co₃O₄ [27] This means that there is a limit for the incorporation of guest species. The formation of spinel phase (Co₃O₄) is favored by two factors: the formation of Co superficial clusters as the cobalt content increases and the ability of cobalt ions to be oxidized to Co(III) upon exposure in an oxidant atmosphere. On the other hand, Co(III) incorporation in the zirconia lattice is less probable due to the very low ionic radius (0.545 Å).

For the Co(0.2)/ZrO₂ (monoclinic) catalyst, the cobalt effect on the support surface is surely governed by topological effects. This can be related to the shifting of O²⁻ ions of the ZrO₇ polyhedra to give a superficial close packing. The Co(II) cations can be arranged in the holes left by the anions in a tetrahedral coordination. So, this environment, suggested by DRS, can be theoretically supported by the crystal field theory (d⁷ Co(II) configuration). The close packed arrangement could explain the no reducibility of Co(II) surface species.

From the physicochemical characterization, the principal difference between the catalysts (prepared from ZrO₂·nH₂O precursor and from the crystalline monoclinic ZrO₂) is associated to structural features of the matrix. Whereas the former is stabilized as tetragonal phase due to the Co-doping (in octahedral coordination), the second one has not the possibility of structural re-arrangement from the pre-established monoclinic form. Slight changes only at superficial level could be suggested, because the bulk structure is not affected according to XRD data. Similar behaviour has been reported on the Cu/ZrO₂ system [25].

3.2. Catalytic results

Table 2 shows the NO conversion to N₂ by using propane as reductor agent. The propane conversion to CO₂ is shown between brackets. The studied catalysts are active for the NO reduction and the activity depends on their physicochemical properties. The Co(0.2)/ZrO₂ (monoclinic) catalyst presents the highest activity: a NO conversion of 37% is reached at 480 °C with a good space velocity (GHSV = 30,000 h⁻¹). It is interesting to remark that this value can be increased if results were expressed in function of the surface area (in particular, because this material presents the lowest area). This catalyst is the one that presents a crystalline structure, preferably, monoclinic, where the cobalt is present as Co(II) species occupying tetrahedral sites and these cobalt species do not present reduction up to 1000 °C. In this sense, the another catalysts reach lower conversion at higher temperatures: The Co(0.2)/ZrO₂ (rotavap) and Co(2)/ZrO₂ (rotavap) catalyst show a NO/N₂ conversion of 24 and 10% at 575 °C respectively. These lower conversions can be associated to the lower availability of Co ions for the Co(0.2)/ZrO₂ (rotavap) or to the presence of Co₃O₄ segregated phase for the Co(2)/ZrO₂ (rotavap) which increases the propane combustion.

4. Conclusions

The activity of the Co/ZrO₂ catalysts for the NO reduction by means of propane in the presence of oxygen depends on their physicochemical properties which are markedly associated to the preparation method.

Catalyst based on the Co impregnation on the monoclinic ZrO₂, where the cobalt is present as Co(II) species occupying tetrahedral sites, results to be more active than that obtained from the amorphous ZrO₂·nH₂O. The Co role in the zirconia monoclinic matrix is related to the presence of strongly interacted “CoO₄” isolated units, which show an unreducible behaviour in the whole range of temperature (up to 1000 °C).

Acknowledgements

Financial support for this project has been obtained from CONICET, UNSL and UNLP. Nestor Bernava is acknowledged for thermal analysis.

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