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Characterization of Co/ZrO$_2$ de-NO$_X$ thin film catalysts prepared by magnetron sputtering

P. Stefanov[a,]*, G. Atanasova[a], T. Marinova[a], J. Gómez-García[b], J.M. Sanz[b], A. Caballero[c], J.J. Morales[c], A.M. Cordón[c], and A.R. González-Elipe[c]

[a]*Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, G. Bonchev str. bl. 111113 Sofia, Bulgaria*
[b]*Departamento Física Aplicada C-XII, Universidad Autónoma de Madrid, Cantoblanco, E-28049 Madrid, Spain*
[c]*Departamento Química Inorgánica e Instituto de Ciencia de Materiales de Sevilla, Centro Mixto CSIC-Universidad de Sevilla, Centro de Investigaciones Científicas Isla de la Cartuja, Avda. Americo Vespucio, s/n, 41092 Sevilla, Spain*

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This paper reports the preparation and characterization of Co/ZrO$_2$ thin film catalysts. ZrO$_2$ thin films ($S_{BET} \sim 25\,m^2\,g^{-1}$) have been prepared at low temperature by magnetron sputtering. This procedure is typically used to get compact thin films and has been modified to prepare porous catalyst layers. The obtained results prove that this can be an interesting alternative for catalyst shaping of interest for different applications. Incorporation on the zirconia support of a well-dispersed cobalt phase is achieved by electrochemical and wetness impregnation methods. Catalyst thin films deposited on stainless-steel plates have been characterized by SEM and XPS. BET measurements, carried out according to a special procedure, have been used to determine the specific surface area of the thin film catalysts.

Catalytic tests for NO (1000 ppm) reduction with CH$_4$ or C$_3$H$_8$ (2500 ppm) in the presence or absence of O$_2$ (3%) in the reactant flow show that the thin film catalyst depicts a similar catalytic behavior than a Co/ZrO$_2$ powder catalyst prepared by conventional methods. The results can be summarized as follows: (i) with CH$_4$ in the absence of O$_2$, a maximum of 50% reduction of NO to N$_2$ was obtained at 823 K; (ii) a similar conversion was obtained at 623 K when O$_2$ was present in the reaction flow; (iii) with C$_3$H$_8$ a 90% conversion was obtained at 823 K without O$_2$, while no conversion at all was detected in the presence of O$_2$, although 90% of the hydrocarbon was oxidized to CO$_2$ and H$_2$O at this temperature. The advantages and possibilities of using non-conventional methods of synthesis of thin film catalysts are highlighted.

KEY WORDS: SCR of NO; magnetron sputtering; Co/ZrO$_2$; XPS.

1. Introduction

A very promising removal method of harmful NO$_x$ emissions is the selective catalytic reduction (SCR) [1–4]. This process has been applied in stationary sources of nitrogen oxides by employing ammonia as a reducing agent. During the last decade, a great effort has been dedicated to the development of catalysts that are able to reduce NO$_x$ by using hydrocarbons as reductive agents. Recently, Co-exchanged zeolites, which are active for the reduction of NO$_x$ with methane, have deserved a large interest as potential catalysts for that reaction [5–10]. Due to some technological difficulties associated with the stability of zeolites, recent investigations have focused on the study of oxide-based materials as active catalysts for the SCR reaction. Thus, Inaba *et al.* [11,12] have shown that SCR can proceed efficiently with Co/SiO$_2$ and Co/Al$_2$O$_3$ catalysts if cobalt is well dispersed on the surface of the support.

For many practical applications, and in particular for de-NO$_x$ processes, catalysts are prepared in the form of thin films or layers, which must be fixed on the surface of metal foils or other substrates. This form ensures a good heat conductance and an easy manufacturing in honeycomb-type structures that enable low-pressure drops under working conditions [13,14]. In this context, zirconia thin films may be an interesting catalyst support due to the good mechanical resistance and high thermal stability of this material. However, the preparation of zirconia thin film catalysts faces many problems in relation to (i) the preparation of porous ZrO$_2$ thin films with a good adherence on the metal substrate foils and (ii) the development of efficient procedures to disperse the active phases (e.g., metal particles) onto the porous ZrO$_2$. The present paper describes new experimental strategies addressing these problems for the preparation of Co/ZrO$_2$ thin film catalysts deposited on stainless-steel plates. The procedure used to prepare the zirconia thin films was magnetron sputtering (MS). This method is typically used for the preparation of compact thin films intended for optical or heat-resistant coatings [15,16]. Here, MS has been modified to get porous thin films with a high surface area. A good adhesion of the ZrO$_2$ thin films is a clear benefit of this method for the synthesis of thin film catalysts that will be used under conditions where continuous changes in temperature may lead to delamination or similar deleterious processes.

In this work, we also report about the preparation and characterization of final Co/ZrO$_2$ de-NO$_x$ thin film

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* To whom correspondence should be addressed.

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Table 1
BET surface and some XPS data of samples

No.	Samples	Specific surface area (m^2/g)	XPS[a] I_{Co2p}/I_{Zr3d}	BE Zr3d$_{5/2}$ (eV)	BE S2p (eV)	BE Co2p$_{1/2}$ (eV)
1	ZrO$_2$/stainless-steel	25	–	182.5	169.2	–
2	Co/ZrO$_2$/stainless-steel	25	0.06	182.2	–	797.0
3	Co/S–ZrO$_2$/stainless-steel	18	0.09	182.3	169.2	797.5

[a] The I_{Co2p}/I_{Zr3d} ratio was estimated from Co2p$_{1/2}$ and Zr3d peak areas.

catalysts. Cobalt is loaded by different methods on the zirconia thin films previously deposited on stainless-steel by MS. Electrochemical deposition and wetness impregnation have been selected as procedures for the incorporation of cobalt into the ZrO$_2$ thin films. The obtained results indicate that the electrochemical deposition, a typical method for planar electrodes, is the most efficient way for cobalt deposition on ZrO$_2$ thin film catalysts. Moreover, it is shown that this procedure is simple and very reproducible since the whole process is controlled by the mere selection of electrochemical variables such as voltage and current. We had previously shown that this method may ensure a high dispersion and an appropriate bonding of metal phases on the surface of the oxide supports in the form of thin films [17,18]. Recently, it has been reported that the modification of a zirconia surface by sulfates considerably increases the dispersion degree of metals such as Mn, Fe, Ni and Cu [19,22]. A similar increase of dispersion has also been observed for cobalt impregnated on sulfated zirconia [23]. Therefore, wetness impregnation of a zirconia thin film that had been previously sulfated has also been intended for the preparation of Co/ZrO$_2$ thin film catalysts.

Finally, to prove the suitability of Co/ZrO$_2$ thin film catalysts for the removal of NO with hydrocarbons, reaction experiments with these systems have been carried out and the results compared with those obtained with Co/ZrO$_2$ powder catalysts prepared by conventional methods.

2. Experimental

2.1. Sample preparation

The zirconia films were deposited by rf magnetron sputtering from a zirconium target. The substrates were stainless-steel plates of dimensions ($2 \times 2 \times 0.05\,cm^3$) suitable to be fitted within a plate reactor for catalytic tests. These plates had an approximate weight of 0.8–1.0 g. An rf power of 220 W and a mixture (50%) of Ar and O$_2$ gases up to a total pressure of 10^{-2} torr were used for the preparations. The temperature of the substrate was kept at around 20 °C by cooling the porthole samples with a liquid nitrogen flow. The growth rate was ~6 nm/min. The films had a thickness of around 1 μm and the amount of ZrO$_2$ per plate was 10 mg as determined by weight.

The electrochemical deposition of Co on the zirconia films (i.e. Co/ZrO$_2$ sample) proceeded with some extra zirconia deposition. This procedure ensured that no cobalt clustering occurred during deposition. The electrochemical codeposition of both zirconia and Co was done by using an electrolyte containing 65 g/L of ZrCl$_4$ diluted in absolute ethyl alcohol, to which 0.02 g/L of a suitable surface-active substance (PEG) and 50 g/L of CoCl$_2$ were added. A current density of 110 A/dm^2 was maintained for 40 s. These samples had a surface area of approximately 25 m^2/g (table 1). The amount of deposited Co was estimated by X-ray photoelectron spectroscopy (XPS) in terms of I_{Co2p}/I_{Zr3d} intensity ratio as shown in table 1.

Some zirconia films were sulfated by stirring the samples for 30 min in a 0.5 M H$_2$SO$_4$, solution (i.e. S–ZrO$_2$ samples). The samples were then washed up in a 0.05 M H$_2$SO$_4$ solution, so that most of the residual sulfate ions were removed. Then, the plates were dried, first at 45 °C and then at 110 °C. They were finally calcined at 500 °C for 1 h. After this treatment, the BET-specific surface area of the plate samples was measured and an average value of 25 m^2/g was obtained (table 1).

The 8% Co/S–ZrO$_2$ catalyst was prepared by incipient wetness impregnation of the S–ZrO$_2$ sample with an aqueous solution of $CoCl_2 \cdot 6H_2O$. According to previous investigations with powdered zirconia, this salt leads to a high Co dispersion [24]. After impregnation, the sample was calcined in air for 1 h at 500 °C. A surface area of 18 m^2/g was measured for this sample (table 1). To ensure that the ZrO$_2$ thin films have a good adhesion on the stainless-steel plates, the samples were subjected to several heating cycles with mixtures of O$_2$/H$_2$O up to 500 °C. After 10 cycles, no delamination was observed.

A conventional 3% Co/ZrO$_2$ powder catalyst was used as a reference sample to compare the reactivity of the thin film catalyst. This sample was prepared by wetting impregnation of a ZrO$_2$ powder prepared by forced hydrolysis according to a procedure previously described [25]. This powder had a specific surface area of 45 m^2/g, as determined by the conventional BET method.

2.2. Catalytic tests

Catalytic tests with the thin film catalysts have been carried out in a reactor setup where up to 20 stainless-steel plates can be incorporated. A full description of this reactor setup used for catalytic testing of plates has been published recently [25]. An important parameter to ascertain the catalytic efficiency is the mass of active phase put into the reactor. In our case, each plate contained ~10 mg of Co/ZrO$_2$ catalyst. Therefore, the 20 plates usually placed in the reactor contain about 200 mg of the catalytic phase. This amount is equivalent to that typically used for catalytic tests with powder catalyst samples in conventional tubular reactors.

The reaction setup consisted of a gas chromatograph (Varian 3800) supplied with a TCD, a Porapack N column and a molecular sieve column (5 A pore size). Data are collected and analyzed in a chromatographic station GC. For the reaction tests carried out here, NO and CH_4 or C_3H_8 were diluted in He (1000 and 2500 ppm, respectively), while O_2 was supplied directly to the gas mixture (3%). Mass-flow controllers were used for dosing the gases to the reactor, with a total flow of 100 mL/min. NO was totally reduced to N_2, while CO_2 and H_2O were the sole oxidation products of the hydrocarbons. The results are expressed as percentage of conversion of NO and the hydrocarbons.

Prior to the reaction tests, the catalysts were heated either in the plate or in the tubular reactor at 673 K in a mixture of He/O_2 (3%) for 3 h after applying an ascendant heating ramp of 10 K/min. The reaction was followed while heating the sample from room temperature up to 723 K with a ramp of 1 K/min, followed by a temperature constant period (3 h) and then a descendent cooling ramp (1 K/min). Sample injections were done into the GC every 20 min. The results presented in the next section were taken from the cooling side of the reaction protocol. Possible delamination of the ZrO$_2$ layer after several reaction cycles was checked by weighting the plates before and after the reaction and by scanning electron microscopy (SEM) observation of the samples.

2.3. Characterization

X-ray photoelectron spectroscopy (XPS) characterization was performed in an ESCALAB Mk II system with a residual pressure of 10^{-7} Pa using Mg Kα radiation ($h\nu = 1253.6$ eV). Binding energies (BE) were referenced to the C1s line at 285.0 eV.

The surface morphology of the samples was examined by SEM (Philips XL30 or JEM-200CX) after every step of the deposition process. Some magnetron sputtered zirconia films were also deposited by MS on silicon substrates and observed in cross section.

Glancing angle (0.7°) X-ray diffraction showed that all the zirconia films crystallized in the monoclinic phase.

A highly sensitive Brunauer–Emmet–Teller (BET) method [26] was used to determine the specific surface area of the ZrO$_2$ films, both before and after the incorporation of the Co species. The method uses a system of differential manometers to measure the pressure drop due to N_2 adsorption in a system with a defined volume. The procedure ensures an accuracy of 0.1 m^2/g. A requirement is that the pressure equilibrates in the linear part of the adsorption isotherm. The value of specific surfaces determined by this method for the thin film catalysts were confirmed by the results obtained by Ar adsorption isotherms.

3. Results and discussion

3.1. BET measurements

Table 1 reports the specific surface area of the zirconia films as deposited on stainless-steel by MS and after the different treatments mentioned in the experimental section. It is worth mentioning that such values of specific surface area are rather unusual for thin film materials prepared by MS. This procedure is typically intended for the fabrication of compact thin films. The modifications incorporated in our case have enabled the preparation of porous ZrO$_2$ thin films with a surface area of 25 m^2/g. In this respect, it is also interesting that the high specific surface area of the original thin film catalysts (i.e., 25 m^2/g) remains practically unchanged after the electrochemical codeposition of Co and zirconia. This result evidences an efficient dispersion of Co and that clustering does not occur to a large extent. By contrast, after the deposition of Co by wetness impregnation on the sulfated sample, a certain reduction of the specific surface area is found (cf. table 1).

3.2. SEM characterization

Figure 1 shows the surface morphology as observed by SEM of the original zirconia films deposited by magnetron sputtering. In addition, we include a cross-section SEM micrograph of a film deposited on Si(100) under the same conditions. This micrograph clearly shows that the film has an open and columnar structure of tapered crystallites with a triangular form (shark teeth). This type of morphology is congruent with the high value of the specific surface area measured by BET. The average diameter of the columns is 40–50 nm.

Figure 2 shows SEM micrographs of the Co/ZrO$_2$ catalyst thin films after the electrochemical codeposition of zirconia and Co directly on the ZrO$_2$ surface. Interestingly, no big particles of Co are observed in this sample. In fact, the micrograph in figure 2(b), taken at a higher magnification, shows only small changes in the microstructure and morphology of this sample in comparison with the original ZrO$_2$ thin films. Therefore, the formation of big agglomerates of Co can be

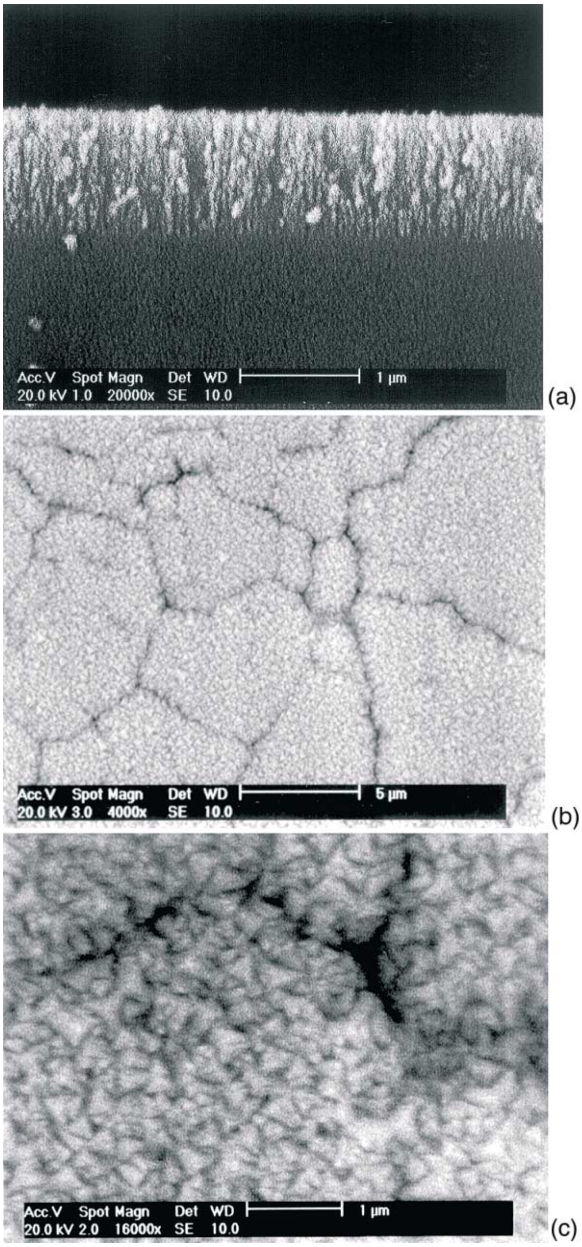

Figure 1. (a) Cross-section SEM micrograph of a ZrO$_2$ thin film deposited on Silicon, (b) and (c) SEM micrographs at different magnifications of the top surface of a ZrO$_2$ thin film deposited on 304 stainless-steel plates at different magnifications. The cracks correspond to the grain boundaries of the 304 stainless-steel plate.

discarded. Figure 3 shows SEM micrographs of a sulfated zirconia thin film after deposition of Co by wetness impregnation. In figure 3(a), two zones can be distinguished. The differences between the lighter (zone 1) and the darker (zone 2) zones are probably generated during the sulfatation of the zirconia surface. Figure 3(b) is a SEM micrograph of zone 1 taken at a higher magnification. In this zone, the surface morphology remains unmodified as compared with that of the original zirconia film. Figure 3(c) shows an enlarged SEM micrograph of zone 2. This second zone presents a slightly different surface morphology, which is associated with the sulfatation of the zirconia surface. The observed modifications, consisting of a kind of stratification of compact layers, support the observed decrease in specific surface from 25–18 m^2/g. In none of the cases big particles of Co can be detected in either zones 1 or 2. Therefore, as a general assessment, it appears that SEM and XPS (see next section) results indicate that the Co^{2+} ions are probably incorporated as isolated species and that big cobalt oxide particles are not formed on the surface of zirconia.

3.3. XPS characterization

XPS was used for chemical characterization of the surface of the differently prepared samples. It was found that both the lineshape and the measured BE values of the Zr3d$_{5/2}$ line in the different samples agree with those expected for ZrO$_2$ [27]. These results confirm that the zirconia films remain chemically unchanged after the different treatments.

Table 1 summarizes the measured binding energies (BE) of the Zr3d$_{5/2}$, S2p and Co2p$_{1/2}$ lines for the different samples. The S2p peak position (169.2 eV) in both S–ZrO$_2$ and Co/S–ZrO$_2$ samples is characteristic of the S(VI) state of sulfur in sulfate groups [27]. In addition, the Co2p$_{1/2}$ and O1s XPS spectra of the Co/ZrO$_2$ and Co/S–ZrO$_2$ samples are shown in figure 4. The formation of isolated Co^{2+} species instead of oxide clusters or particles can be deduced from the shape of the Co2p peak. In fact, it is known that a spinel Co$_3$O$_4$ phase of cobalt oxide forms at the surface of CoO particles exposed to air. This phase is easily recognized by XPS because its Co2p peak has a very small satellite and a BE slightly lower than that of the Co^{2+} species in bulk CoO [28]. The shape of the Co2p$_{1/2}$ peak in figure 4 (the Co2p$_{3/2}$ peak is not available because of superposition with an Auger peak of oxygen), particularly the high intensity of its satellite, is a clear indication that no Co$_3$O$_4$ has been formed. This discards the formation of well-defined particles of Co oxide and supports the incorporation of Co^{2+} species on the surface of the ZrO$_2$. Moreover, the Co2p$_{1/2}$ peak position for both Co/ZrO$_2$ and Co/S–ZrO$_2$ samples appears slightly shifted toward higher binding energy with respect to the value expected for Co^{2+} ions in bulk CoO (i.e., 796.3) [28]. The measured values are close to the BE of isolated Co^{2+} ions occupying tetrahedral sites in cobalt aluminate CoAl$_2$O$_4$ (i.e., 797.0–797.4 eV) [29,30]. All this evidence suggest that Co is in the form of Co^{2+} ions directly bonded to lattice oxygen atoms of the zirconia surface. It is likely that an energetically favored Co–zirconia interaction leads to both a good dispersion of the metal phase and the stabilization of the Co as isolated ion species. For the sulfated zirconia, the measured BE value of the Co2p$_{1/2}$ line was slightly higher than for the electrochemically deposited Co.

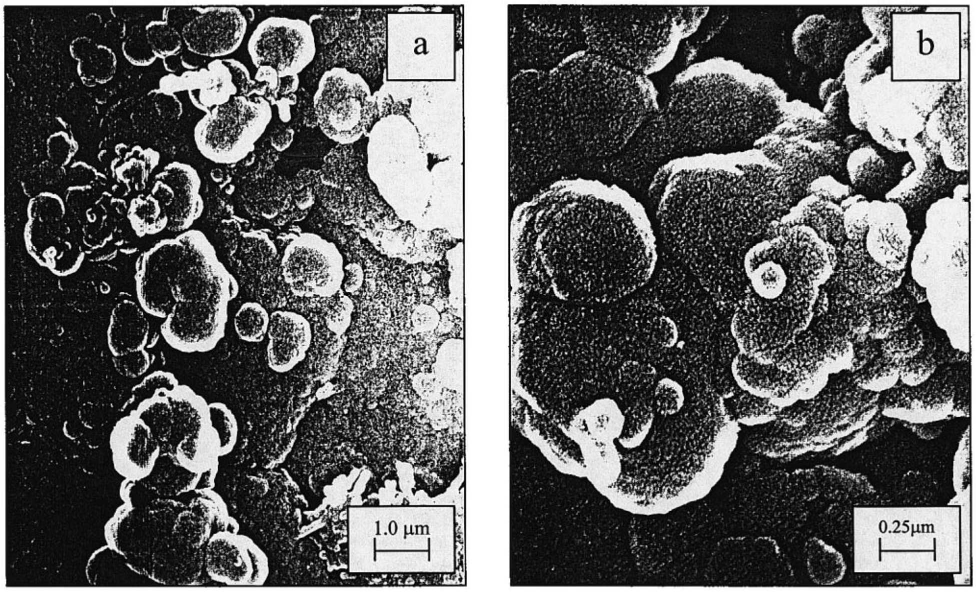

Figure 2. SEM micrographs of different magnifications of Co deposited electrochemically on the zirconia thin films.

According to the previous argument, this shift would suggest an increase of the dispersion degree of the Co phase. However, the slight differences in this parameter might also reflect a difference in the type of oxygen atom species directly bonded to the Co^{2+} ions (e.g., a possible direct interaction between Co^{2+} and SO$_4^=$ species).

Figure 4 also shows the O1s spectra for Co/ZrO$_2$, S–ZrO$_2$ and Co/S–ZrO$_2$ samples. In all cases, it is found that an O1s peak is centered at 530.0 eV, which is characteristic of the oxide ions in ZrO$_2$ [27]. In the case of S–ZrO$_2$ and Co/S–ZrO$_2$ samples, a well-resolved shoulder appears at higher BE. This shoulder can be attributed to surface sulfate and/or hydroxyl species that become stabilized on the zirconia surface by the sulfatation treatment. We have suggested that in the case of S/ZrO$_2$ samples the Co^{2+} ions could be coordinated by SO$_4^=$ or OH$^-$ species, thus leading to Co^{2+} complexes with a more ionic character than those formed on unsulfated zirconia. On the basis of IR data, this possibility has been previously discussed in reference [23].

3.4. Catalytic tests and stability of Co/ZrO$_2$ thin film catalysts

Catalytic tests with the thin film catalysts were carried out as described in the experimental section by using either CH$_4$ or C$_3$H$_8$ as reductants. Reaction tests with and without O$_2$ (3%) in the reaction mixture were carried out. For comparison, similar catalytic tests were done with a Co/ZrO$_2$ powder catalyst prepared by a classical method and for a ZrO$_2$ thin film catalyst. The main objective of these catalytic studies is to investigate

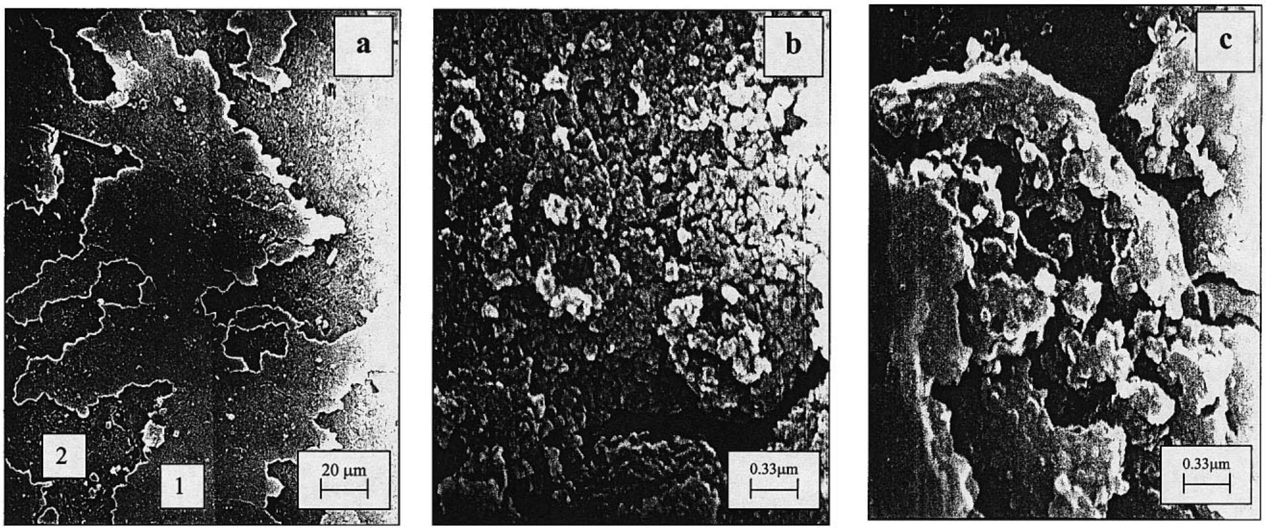

Figure 3. SEM micrographs of Co deposited by impregnation on sulfated zirconia thin films.

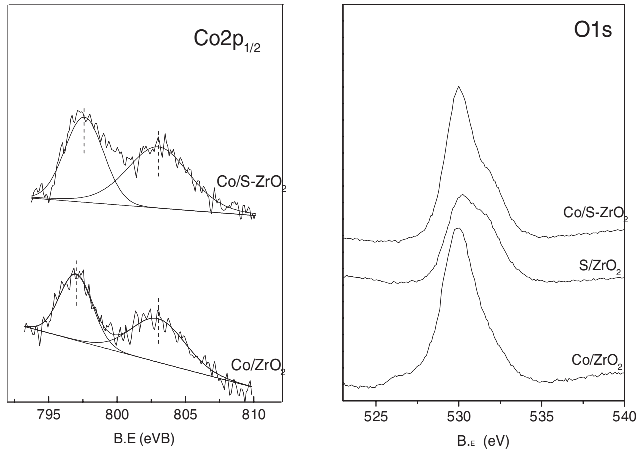

Figure 4. Co2p$_{1/2}$ and O1s photoelectron spectra of zirconia films after different treatments to load Co, as labeled.

thin films as catalysts for de-NO$_x$ processes. In the course of these studies, we have also shown that they can withstand catalytic cycles without delamination or other degradation processes.

Figure 5 shows the conversion efficiencies of NO into N_2 and CH_4 into H_2O and CO_2 for the Co/ZrO$_2$ samples. With CH_4, the conversion of NO into N_2 reaches about 40–50% at 823 K. In the presence of oxygen, a similar conversion degree is attained at a much lower temperature (623 K). With C_3H_8, the conversion of NO into N_2 is much higher, reaching 80% at 723 K. In the presence of 3% O_2 no conversion is observed, while at 673 K direct oxidation of propane begins. Note that, owing to the reaction stoichiometry and the concentrations of both the NO and the hydrocarbon in the reactant flow, no clearly measurable decrease in the amount of hydrocarbon is to be expected because of its direct oxidation with NO (i.e., the reaction adjusts to the following stoichiometry:

$$(2n + m/2)\mathrm{NO} + \mathrm{C}_n\mathrm{H}_m \rightarrow 1/2(2n + m/2)\mathrm{N}_2 + n\mathrm{CO}_2 + m/2\mathrm{H}_2\mathrm{O}).$$

On the other hand, the ZrO$_2$ thin films presented some activity for the conversion of NO with CH_4 in the presence of O_2 at a temperature that was ~200 °C higher

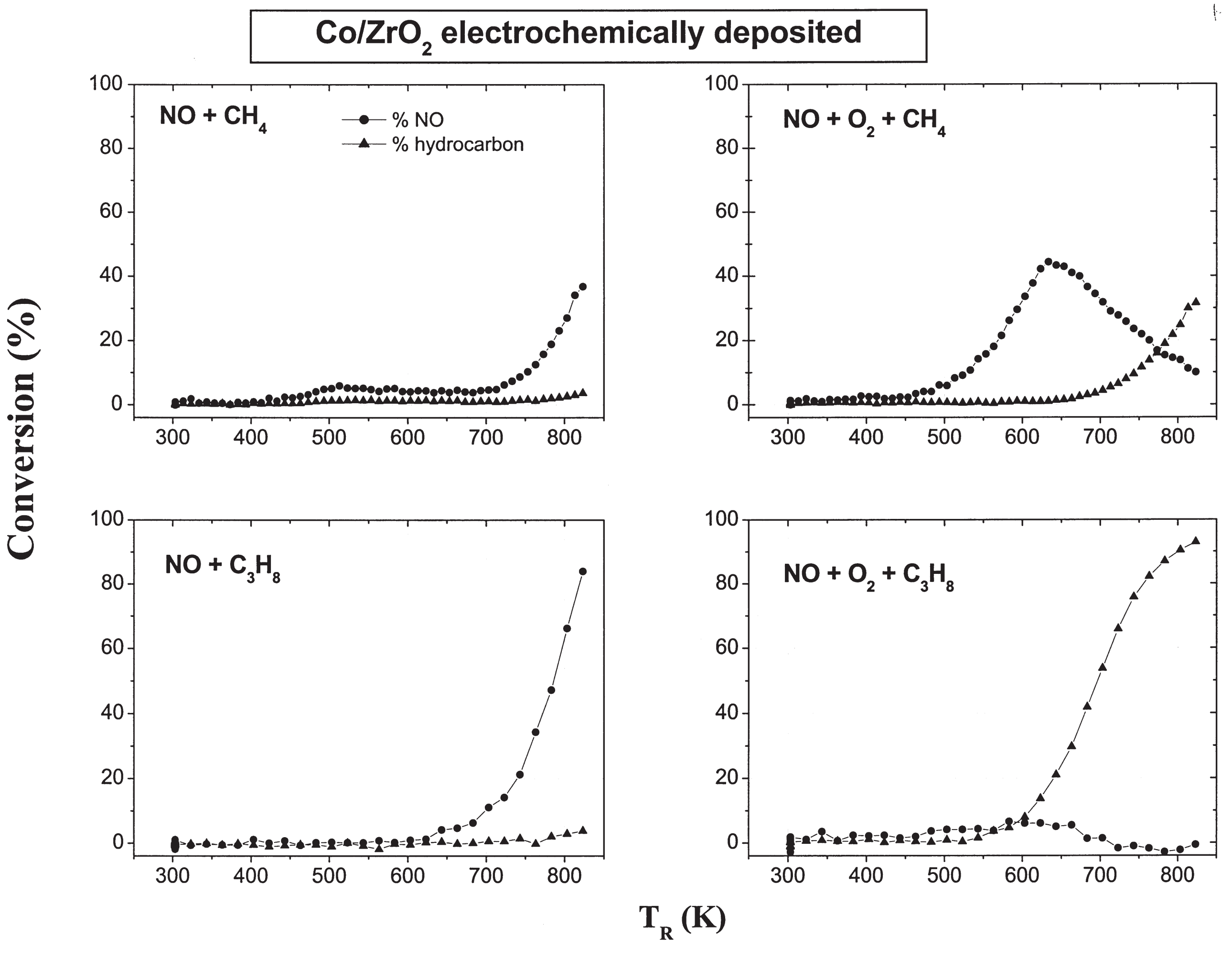

Figure 5. Percentage of conversion of NO (●) and hydrocarbon (▲) versus temperature for the SCR reaction over the Co/ZrO$_2$ thin film catalyst.

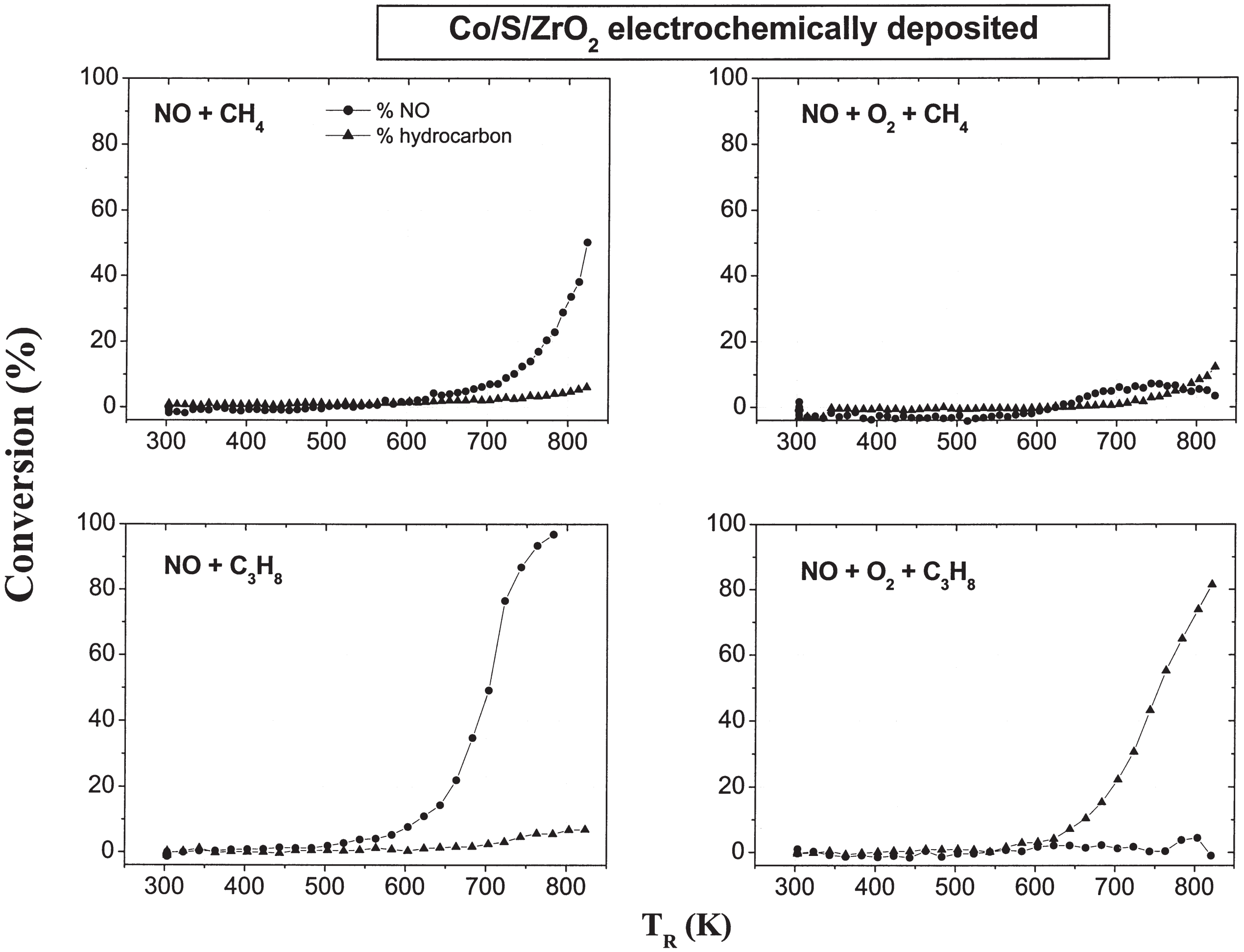

Figure 6. Conversion of NO (●) and hydrocarbon (▲) versus temperature for the SCR reaction over the electrochemically deposited Co/S-ZrO$_2$ system.

than with Co/ZrO$_2$. NO conversion was detected with the stainless-steel plates without supported ZrO$_2$.

Figure 6 illustrates the results of similar catalytic tests carried out with the Co/S–ZrO$_2$ thin film catalyst. With CH_4, the conversion of NO into N_2 at 823 K is 50%. However, in the presence of oxygen the conversion is very small (i.e., maximum conversion of 10% at 723 K). The conversion yield for the reaction of NO with C_3H_8 is high (90% at 723 K) in the absence of oxygen, but no conversion is found in the presence of oxygen. This is likely due to the direct oxidation of propane with oxygen above 673 K. This result indicates that sulfatation of the zirconia surface under our experimental conditions does not favor the NO conversion with respect to the Co/ZrO$_2$ thin film catalyst.

The previous results of the reactivity tests carried out with the Co/ZrO$_2$ thin films were very similar to those obtained with an equivalent mass of the powder Co/ZrO$_2$ catalysts in a conventional tubular reactor. Reactivity tests similar to those previously shown for the plate catalysts are shown in figure 7 for a conventional Co/ZrO$_2$ powder catalyst. The results are comparable with those obtained with the thin film samples, except for a relatively higher activity found for the powder samples in all cases. It is likely that this difference is related with the higher specific surface area in the powder ZrO$_2$ samples. In any case, the rather similar behavior found for the two types of systems indicates that thin film catalysts prepared by unconventional MS and electrochemical methods have an equivalent chemical performance than conventional catalyst samples.

After several catalytic tests that imply heating and cooling ramps, the Co/ZrO$_2$ and Co/S–ZrO$_2$ thin films did not show any significant alteration either in its texture or in its adhesion to the stainless-steel substrate, thus supporting the good mechanical and chemical stability properties of these thin film catalysts. The absence of delamination from the stainless-steel or other physical alterations of the catalytic layers was proved by weighting the plates before and after the reaction, with ca. 0.1-mg accuracy. SEM observation of the sample surface did not show any hint of deterioration, being possible to observe a similar

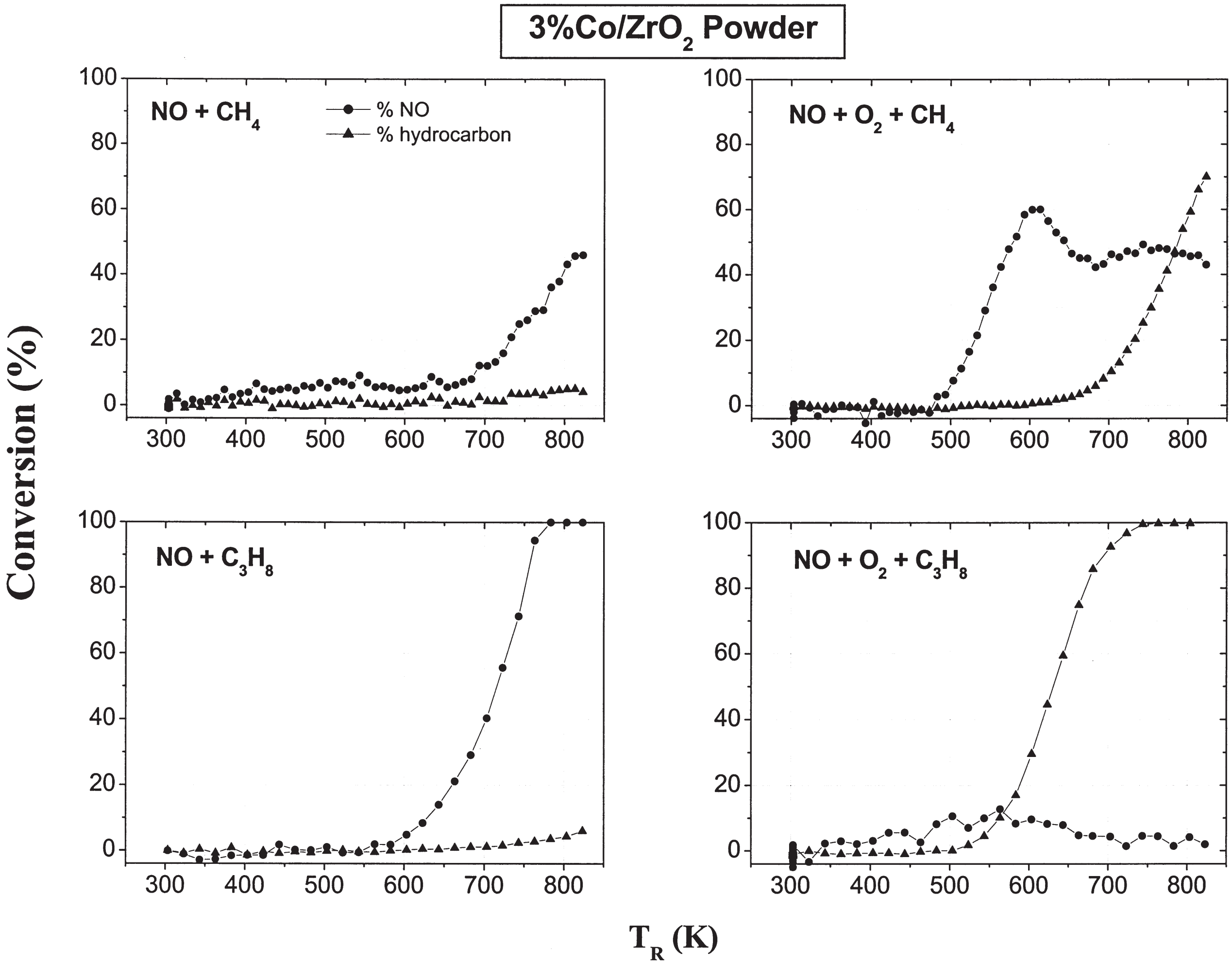

Figure 7. Conversion of NO (●) and hydrocarbon (▲) versus temperature for the SCR reaction over the Co/ZrO$_2$ powder catalyst.

microstructure than that reported in figure 1 for the virgin samples.

4. Concluding remarks

It has been shown that effective Co/ZrO$_2$ catalysts for de-NO$_x$ processes can be prepared in the form of thin films by MS and electrochemical methods. Main advantage of these procedures with respect to other classical methods of thin film preparation by wet routes (e.g., sol/gel methods) is the high stability of the film that maintains a relatively high surface area after different activation treatments. The good adhesion of the catalytic layers on the metal plates after several reaction cycles is another interesting feature that supports the use of these new types of catalysts for practical applications. Other features such as reproducibility in the preparation or the possibility of using large magnetron sputtering systems available at industrial level are additional advantages of this method of thin film.

The performance of the thin film catalysts is similar to that obtained with conventional Co/ZrO$_2$ powder catalysts, while sulfatation of the zirconia surface under our experimental conditions does not seem to improve the catalyst performance.

For certain applications, the use of catalysts prepared by means of MS or other methods relying on "dry" thin film technology may have a great interest provided that the catalyst efficiency is not altered or diminished in respect to their powder counterpart. The present paper constitutes a promising example in this direction. It is expected that further work can contribute to the improvement of the available methods of preparation of thin films and/or membranes to be used as catalysts active for de-NO$_x$ processes or other applications.

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