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Influence of the ethylenediamine addition on the activity, dispersion and reducibility of cobalt oxide catalysts supported over ZrO_2 for complete VOC oxidation

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A new and simple method for obtaining highly dispersed Co/ZrO_2 catalyst is described. The presence of ethylenediamine during the preparation of Co/ZrO_2 was studied and compared with a reference catalyst conventionally prepared. Addition of an aqueous solution of ethylenediamine to a cobalt nitrate solution had a dramatic effect on the catalytic performance of the catalyst as compared with a reference catalyst. This promotional effect was explained in terms of higher cobalt dispersion in the catalysts using ethylenediamine. The reason why ethylenediamine improves dispersion of the cobalt species was explained in terms of the size of the stable complex ions which could be formed *in situ* during impregnation. The best catalytic results were also explained in terms of Co-support interaction since new cobalt species were reducible at lower temperatures.

KEY WORDS: zirconia; cobalt oxides; ethylenediamine; propene oxidation.

1. Introduction

Volatile organic compounds (VOC) are among the main pollutants in the low atmosphere of cities and their release begins to be severely regulated. VOC coming from automobiles must decrease by 24% in Europe between 1993 and 2010 [1]. For industries, in compliance with the stringent environmental regulations, catalytic oxidation can effectively destroy VOC at much lower temperatures than thermal oxidation. The advantage of low oxidation temperature is to reduce fuel consumption particularly for large volumes of dilute VOC polluted air. Noble metals catalysts such as Pt and Pd supported on alumina or silica are conventionally used in this objective. However, attention has also been given to transition metal oxides due to the limited availability and to the price of precious metals. Metal oxides such as cobalt, copper or manganese oxides are active catalytic phases in the total oxidation of hydrocarbons (temperature range of 300–600 °C). A preliminary study in our lab reveals that among them, bulk Co_3O_4 is the best catalyst to oxidise propene or toluene into CO_2 and H_2O. The dispersion of cobalt species over a support has been studied in order to stabilize these species. The types of support generally used are oxides such as Al_2O_3 [2–4], SiO_2 [4,5], TiO_2 [6], CeO_2 [6] and ZrO_2 [2,4,6–8].

It is known that cobalt dispersion depends on the preparation method and on the type of cobalt precursors. A study by Koyano *et al.* [9] of the $CO + O_2$ reaction on CoO_x/ZrO_2 prepared by low-temperature-plasma oxidation showed the presence of Co_3O_4 particles, much smaller than those obtained by the conventional impregnation technique. J. van de Loosdrecht *et al.* [3] showed that for preparation of Co/Al_2O_3 by incipient wetness impregnation using cobalt EDTA and ammonium cobalt citrate precursors resulted in very small cobalt oxide particles. For titania-supported catalysts, the use of oxalate, acetate and acetyl acetonate as cobalt precursors resulted in an increasing cobalt dispersion compared with the reference catalyst prepared from nitrate [6]. For Co/ZrO_2, preparation using metal–EDTA complex resulted also in a higher dispersion of the cobalt species [10]. For the preparation of alumina supported Ni catalysts, Negrier *et al.* [11] shown that the employ of ethylenediamine as chelating ligand is effective to obtain finely dispersed nickel metal particles by a one-step thermal treatment. For hydrocarbons oxidation on metal oxides, a redox mechanism is often proposed to explain the catalytic results [12]. In this mechanism, the reduction step of the oxide catalyst is the rate determining step. Then, the reducibility of metal oxides particles of the catalyst have to rule the catalytic performances. But in the presence of highly dispersed cobalt species, a solid-state reaction between the support and the cobalt oxides could also result in mixed oxides,

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such as cobalt aluminate and cobalt silicate, more difficult to reduce. Therefore, a weak cobalt support interaction is required to promote high cobalt reducibility.

For VOC oxidation, ZrO_2 is a desired support because of its good mechanical properties and high thermal stability. Moreover, weaker interactions between the cobalt species and the zirconia have been observed in comparison with those observed using alumina support since the use of ZrO_2 in comparison with Al_2O_3 enhances the reducibility of the cobalt phase [2]. However with the Co/ZrO_2 catalytic system, it is difficult to reach a highly dispersed active phase. Indeed, in comparison with Al_2O_3 and SiO_2, ZrO_2 provides lower specific surface area leading to lower cobalt species dispersion.

Then, the aim of this work is to prepare Co/ZrO_2 catalyst with simultaneous high cobalt species dispersion and reducibility. For the first time, the effect of ethylenediamine addition during the preparation of Co/ZrO_2 was studied with respect to catalytic activity in the propene oxidation, Co dispersion, surface/bulk compositions and reducibility in comparison with a reference catalyst conventionally prepared by impregnation of ZrO_2 with an aqueous solution of $Co(NO_3)_2$. Propene has been chosen as VOC probe molecule because alkenes are present in the major part of the industrial and automotive emissions [13] and because propene presents an important POCP (Photochemical Ozone Creativity Potential) [14].

2. Experimental

2.1. Samples preparation

Zirconium hydroxide was prepared by drop wise addition of an aqueous ammonium hydroxide solution (0.7 M) to a zirconium oxychloride $ZrOCl_2 \cdot 8H_2O$ solution 0.15 M keeping pH = 9.8. To obtain the ZrO_2, the precipitated hydroxide ($ZrO(OH)_2$) was filtered, washed and dried at 100 °C before calcination in a flow of dried air ($2\ l\ h^{-1}$) during 4 h at 600 °C. Two different cobalt solutions were used to impregnate ZrO_2. The first one was prepared by dissolution of the appropriate amount of cobalt nitrate $Co(NO_3)_2 \cdot 6H_2O$ in distilled water (classical method, samples named Co(N)). The second impregnation solution was obtained at pH = 7.5 by mixing an ethylenediamine–cobalt nitrate solution (1:1) with distilled water (samples named Co(en)). For each preparation, 100 ml of the impregnating solution were added to 2 g of ZrO_2 powder. After evaporating the excess of solvent at 60 °C under vacuum, the samples were dried at 100 °C for 20 h followed by an activation treatment in a flow of dried air ($2\ l\ h^{-1}$) during 4 h at 450 °C. The final cobalt contents were 5 and 10 wt% (samples respectively named Co_5(N) or Co_5(en) and Co_{10}(N) or Co_{10}(en)).

2.2. Samples characterization

The cobalt content in the catalysts was determined by atomic absorption at the "Service Central d'Analyse du CNRS" (Vernaison, France).

The specific surface areas were determined by the BET method using a Quantasorb Junior apparatus, and the gas adsorbed at −196 °C was pure nitrogen.

Differential Thermal and Thermo Gravimetric Analyses (DTA/TG) (Netzsch STA 409 equipped with a microbalance) were conducted in flowing air ($75\ ml\ min^{-1}$) at a heating rate of $5\ °C\ min^{-1}$ from room temperature to 600 °C. For the Co(en) samples, a lower amount of catalyst should be used because of the exothermicity of the decomposition reaction. Typically, a mass of about 45 and 15 mg Co(N) and Co(en) samples respectively was used.

The crystal structure of catalysts was analyzed at room temperature by X-ray diffraction (XRD) technique in a Bruker D8 Advance diffractometer equipped with a copper anode ($\lambda = 1.5418$ Å). The scattering intensities were measured over an angular range of $10° < 2\theta < 80°$ for all the samples with a step-size of $\Delta(2\theta) = 0.02°$ and a count time of 4 s per step. The diffraction spectra have been indexed by comparison with the JCPDS files. Crystallite size has been determined (Scherrer method) using a graphics based profile analysis program (TOPAS from Bruker AXS).

X-Ray Photoelectron Spectroscopy (XPS) analyses were performed at the "Laboratoire de Catalyse de Lille". Spectra, were recorded using a VG instrument (anode operated at 12 kV and 25 mA with fixed analyzer transmission mode) equipped with an aluminum anode ($h\nu = 1486.6$ eV). Charging effects were corrected using C1s peak as reference (binding energy of 285 eV). Surface atomic ratios were obtained on the basis of the peak area intensities after correction for instrumental parameters, photoionization cross sections and electron mean free paths.

Temperature-Programmed Reduction (TPR) of the activated catalysts was carried out in a conventional laboratory apparatus (Zeton Altamira AMI 200). Prior to the TPR experiments, all samples (100 or 200 mg) were activated under argon at 150 °C for 1 h. The samples were heated from ambient to 600 °C under H_2 flow (5 vol.% in argon – $30\ ml\ min^{-1}$) at a heating rate of $5\ °C\ min^{-1}$.

The activity of the catalysts was measured in a continuous flow system on a fixed bed reactor at atmospheric pressure. Before each test, the catalyst was activated in flowing air ($2l\ h^{-1}$) at 450 °C for 4 h. The flow of the reactant gases ($0.6\ ml\ min^{-1}$ of C_3H_6 and $99.4\ ml\ min^{-1}$ of air) was adjusted by mass flow controllers. After reaching a stable flow of the reactants, they passed through the catalyst bed and the temperature was increased from room temperature to 450 °C ($1\ °C\ min^{-1}$). The amount of catalysts used in all the tests was 200 mg. The feed and the reactor outflow gases were analyzed on line by a gas chromatograph (Varian 3600) coupled with TCD (CTR I column - Alltech) and Flame Ionization Detector (FID) (HayeSep R column - Alltech).

3. Results and discussion

Thermal analyses were performed on fresh samples for all catalysts. Table 1 shows the results obtained.

For all the studied solids, the experimental weight loss was closed to the expected and indicates total transformation of the cobalt precursor to the oxide Co_3O_4.

DTA signals obtained are quite different depending on the precursor used (figure 1). For Co(N) samples, the signal is composed of one rather small endothermic peaks at around 180 °C and has been attributed to nitrate decomposition [15] according to the following reaction:

$$3\,Co(NO_3)_2, 6H_2O \rightarrow Co_3O_4 + 6NO_2 + O_2 + 18\,H_2O.$$

For Co(en) samples, a group of exothermic peaks is observed between 150 and 300 °C. This exothermic effect could be caused by an autocatalytic oxidation leading to the formation of cobalt oxide during the ethylenediamine combustion. A similar explanation was already proposed in the case of the cobalt acetate decomposition [16].

Different explanations could be given in order to assess the origin of the different peaks: (i) non simultaneous combustion of carbon and nitrogen present in the ethylenediamine, (ii) presence of different types of Co species (iii) same Co species but exhibiting different interaction with the support and/or among themselves.

Table 1 summarizes the specific surface area results obtained. Specific surface areas of fresh samples are around 60 $m^2\ g^{-1}$ for Co(N) and less than 10 $m^2\ g^{-1}$ for Co(en). The specific surface area of the support ZrO_2 is of 70 $m^2\ g^{-1}$. The decrease observed after the impregnation is explained by the presence of cobalt precursor's molecules blocking the pores of the support. This phenomenon is emphasized with the cobalt content and especially when ethylenediamine is used during the preparation. The strong decrease observed when ethylenediamine is used could be explained by the size of the ethylenediamine itself or of that a possible Co-ethylenediamine complex. Indeed, during the preparation, Co-en $_2^{2+}$ and Co-en $_3^{2+}$ complex ions can be formed [17]. After activation at 450 °C, specific surface areas are close to that of zirconia support and indicate that pores of the support are rather free. This result is in agreement with thermogravimetric analyses which revealed a complete Co precursor decomposition at this temperature.

Figure 2 shows XRD patterns recorded at room temperature of the impregnated samples. For all the samples, the lines at $2\theta = 28.2°$ and 33.2 ° can be attributed to the presence of ZrO_2 into the monoclinic phase (JCPDS no. 65–1023), and the peak at 31.5 ° indicates the presence of zirconia in tetragonal form (JCPDS no. 50–1089). The simultaneous presence of these peaks indicates that support is constituted of a mixture of zirconia in the monoclinic and the tetragonal phases. This result was already observed on pure zirconia calcined at the same temperature [18], and suggests that addition of cobalt at the surface of zirconia does not modify its crystallographic structure. In addition a weak peak at $2\theta = 36.8°$ is also observed. This peak is assigned to Co_3O_4 in the cubic phase (JCPDS no. 42–1467). The intensity of this peak varies with cobalt content and cobalt precursor. As expected, for the same precursor, the intensity of this peak increases with cobalt loading and for the same cobalt loading, the line at $2\theta = 36.8°$ is much more narrow and intense for Co(N) than for Co(en) samples. The results of the Co_3O_4 crystallite size determination are listed in table 2. Clearly for samples containing 10 wt.% of cobalt a decrease in the crystallite size of about 33% is observed when ethylenediamine is used during the preparation. Therefore for Co_5(en) sample, the peak at $2\theta = 36.8°$ is not visible due to the detection limit of XRD analysis. This result suggests that the use of ethylenediamine during the preparation favours the dispersion of cobalt oxides at the surface of zirconia leading to smaller particles of Co_3O_4.

The reason why ethylenediamine improves the cobalt species dispersion could well be explained in terms of the size of the complex ions (Co-en $_2^{2+}$ and Co-en $_3^{2+}$) formed

Table 1

Weight losses (measured by TGA) and specific areas evolution obtained after activation treatment at 450 °C

Sample	Weight loss (%)		Specific area ($m^2\ g^{-1}$)	
	Expected	Experimental	Before activation	Activated at 450 °C
Co_5(N)	7.3	8.5	65	68
Co_{10}(N)	12.9	12.8	58	64
Co_5(en)	11.0	11.0	9	70
Co_{10}(en)	18.9	18.6	6	68

The specific surface area of the support $ZrO_2 = 70\ m^2\ g^{-1}$.

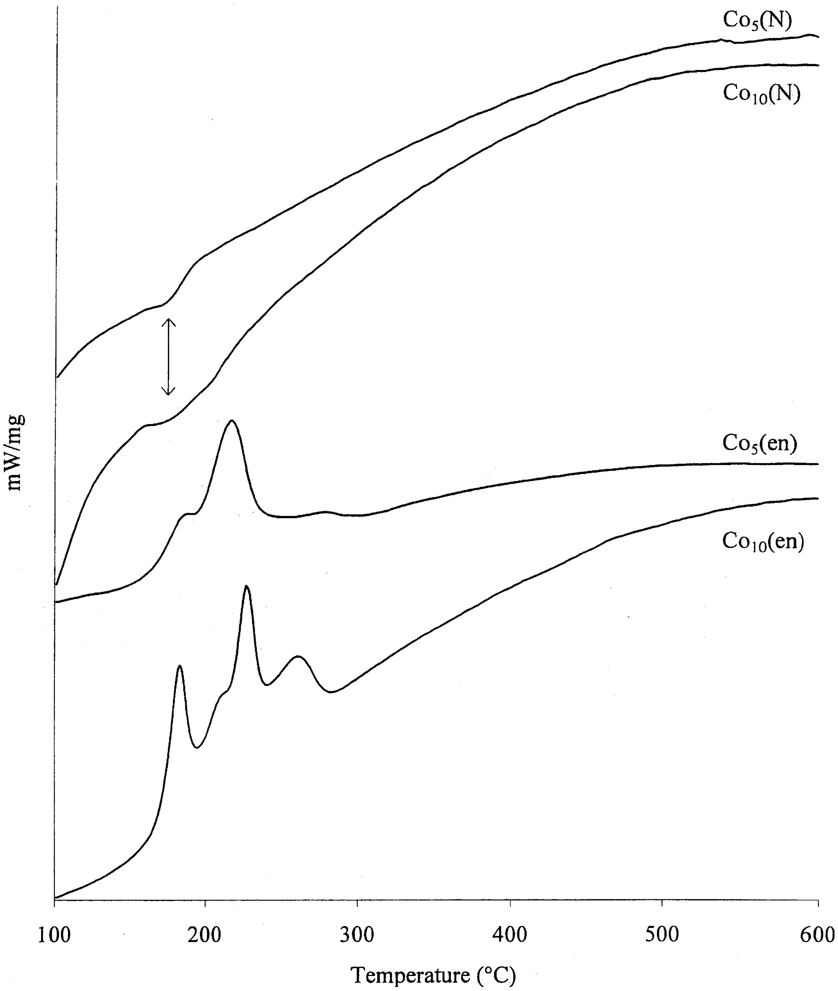

Figure 1. DTA curves obtained during the activation of fresh catalysts.

in situ during impregnation: as the cobalt atom is surrounded by the ethylenediamine ligands, cobalt atoms are forced to be far apart one from another leading to highly dispered catalyst.

Co^{2+} and Co^{3+} species, present in Co_3O_4, can be identified by XPS measurement. In the Co2p region, XPS spectra of Co(N) and Co(en) samples consist of two main peaks, $Co2p_{1/2}$ and $Co2p_{3/2}$, both exhibiting (at higher binding energy by about 6 eV) a satellite structure arising from interaction of photo emitted electrons with core vacancy and valence electrons. This result indicates unambiguously the presence of Co^{2+}. It is well known that Co^{2+} peak present a satellite structure whereas Co^{3+} peak does not. Co^{3+} ions are also present in all the samples since the I_{sat}/I_{main} ratio values are much lower than that reported for pure CoO [19].

The bulk and surface cobalt concentrations in the different samples are shown in table 2. It is notable that for a similar cobalt content, the surface I Co2p/I Zr3d ratio values is higher in a large extent for samples prepared with ethylenediamine than for conventionally synthesised samples. These results confirm the high cobalt dispersion on the zirconia support when ethylenediamine is used during the preparation. According to the spherical model proposed by Cimino *et al.* [20,21], D. Pietrogiocomi *et al.* [22] found that up to 2 atoms nm^{-2}, cobalt species are uniformly spread on the zirconia surface. In our case, for Co(N) samples, the I Co2p/I Zr3d ratio values are well below the expected value corresponding to uniform spreading on spherical ZrO_2 particles. This result points for Co(N) samples the presence of a segregated cobalt phase like Co_3O_4 identified by XRD analysis. On the contrary, for Co(en) samples, the I Co2p/I Zr3d ratio values are above the theoretical value, indicating probably a different model for cobalt species deposition.

It is generally postulated that hydrocarbons catalytic oxidation on metal oxides takes place via a redox mechanism in which the determining step would be the oxygen removal of the metal oxide to oxidise hydrocarbons. Then, the reducibility study of cobalt oxides seems to be also crucial in order to explain the catalytic results observed in propene oxidation.

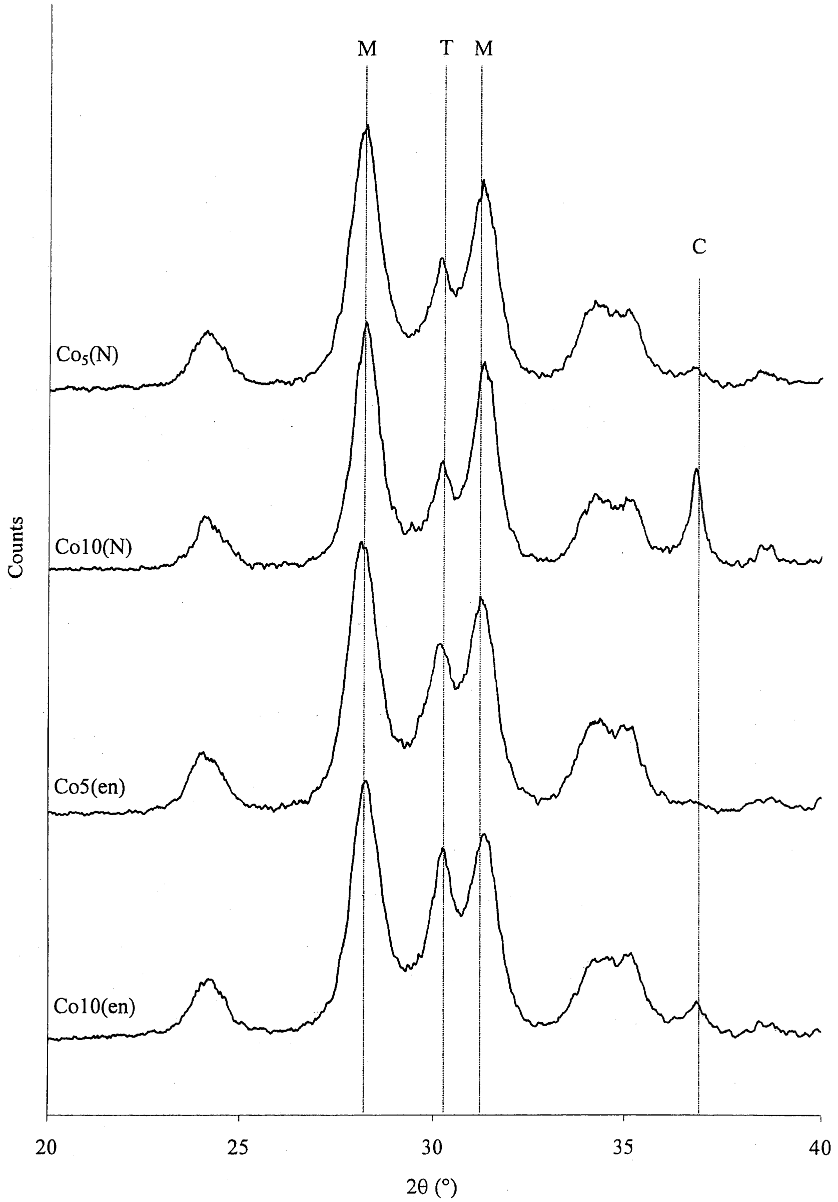

Figure 2. XRD patterns of Co/ZrO$_2$ catalysts M = ZrO$_2$ monoclinic phase; T = ZrO$_2$ tetragonal phase; C = Co$_3$O$_4$ cubic phase.

Table 2

Surface and bulk compositions of Co/ZrO$_2$ samples and quantitative results coming from XRD and H$_2$-TPR measurements

Sample	Co/Zr molar ratio		Co atoms nm^{-2}	I Co2p/IZr3d	Crystallite size (nm) (Co$_3$O$_4$)	H$_2$ consumed (μmol/g)	
	Bulb	Surface				expected	experimental
Co$_5$(N)	0.110	0.092	6.85	0.205	13	1032	1129
Co$_{10}$(N)	0.226	0.850	14.77	1.453	30	1961	2021
Co$_5$(en)	0.098	0.650	5.84	1.910	–	905	925
Co$_{10}$(en)	0.196	1.720	11.57	3.840	20	1752	1857

To facilitate H$_2$-TPR experiment assignments, standard Co$_3$O$_4$ was first measured (figure 3). TPR profiles exhibit a first maximum in H$_2$ consumption at about 318 °C attributed the Co^{3+} to Co^{2+} transformation and a second one at about 375 °C where all the Co^{2+} reduces to Co metallic. In fact, the reduction of bulk Co$_3$O$_4$ by hydrogen proceeds through the two steps denoted α and β:

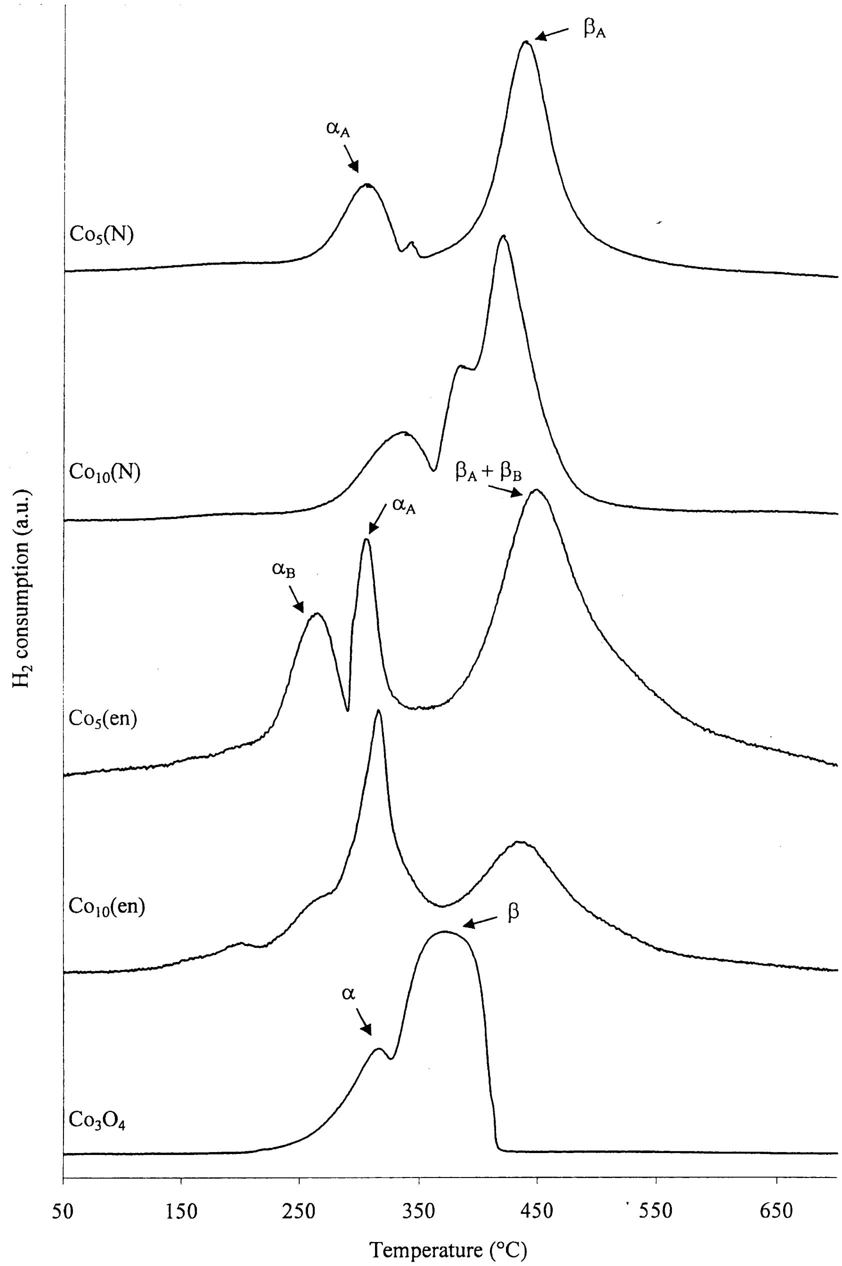

Figure 3. H_2-TPR profiles of Co/ZrO$_2$ catalysts and CO_3O_4. (Ref.).

$$Co_3O_4 + H_2 \rightarrow 3CoO + H_2O \qquad (\alpha)$$

$$3CoO + 3H_2 \rightarrow 3Co + 3H_2O. \qquad (\beta)$$

In both processes, the ratio of hydrogen consumptions is 1:3. TPR profiles of Co/ZrO$_2$ samples activated at 450 °C are also shown in figure 4. With respect to that observed on bulk Co_3O_4, the reduction of cobalt species deposited on zirconia shown significant variations. TPR profiles change with the cobalt content in the solid but also with the method of preparation. Comparison of the profile of Co supported samples with that of bulk Co_3O_4 indicates that complete reduction of cobalt species is achieved at temperatures about 100 °C higher on the supported catalysts as compared with that of Co_3O_4. Cobalt oxide particles probably present in a dispersed state on the catalyst surface are more difficult to reduce. For each sample, the experimental hydrogen consumption matches well with the theoretical one required to the total reduction of cobalt ions into metallic cobalt without reduction of the support (table 2). On the contrary, studying reduction of different Co/ZrO$_2$ samples, Milt *et al.* [23] observed the presence of hard-to-reduce species (temperature of reduction higher than 900 °C). This difference can be explained in terms of cobalt content (less than 2 wt%) but also of method of preparation. Indeed, using an epitaxial technique to incorporate cobalt on zirconia, the authors proposed that some cobalt ions migrate inside the support strongly interacting with ZrO_2.

For Co_5(N)sample, the first peak (α_A) can be attributed to the reduction of Co^{3+} into Co^{2+} since its intensity corresponds to 23% of the intensity of the total signal. The second peak (β_A) corresponds to the reduction of Co^{2+} into Co^0. Using different supports, Jacobs *et al.* [24] found also that the ratio of the first peak to that of the second is always close to 1:3. Increasing cobalt content, TPR profile of $Co(N)_{10}$ sample looks like TPR profile of bulk Co_3O_4 according to a lower interaction of cobalt species with the support. Besides, for Co_5(en) sample, an additional peaks (α_B) is observed at lower temperatures (270 °C). The intensity of α_A peak decreases in comparison with that observed for Co-$(nit)_x/ZrO_2$ and the intensity of ($\alpha_A + \alpha_B$) peaks corresponds to 28% of the intensity of the total signal. These results indicates the formation of cobalt species (B) in Co_5(en) sample reducible at lower temperatures than cobalt species (A) observed in conventional Co-$(nit)_x/ZrO_2$.

The results of the catalytic tests of the calcinated samples are presented in figure 4. Introduction of cobalt to zirconia induces a promotional effect since first, the propene conversion takes place at much lower temperatures than that observed in the presence of pure zirconia [25] and second, the carbonaceous selectivity towards CO_2 of 35% in the presence of zirconia [25] becomes of 100% (no CO formation) in the presence of Co-catalysts and that whatever the reaction temperature. The presence of Co^{3+} and Co^{2+} species under the form of Co_3O_4 at the surface of ZrO_2 can explain the good activity of Co-containing solids. Indeed, it is well known that Co_3O_4 is a good catalytic phase for different oxidation reactions [12].

Increase of cobalt content in the samples (from 5 wt% to 10 wt%) leads, as expected, to an improvement of the catalytic activity although this enhancement is not proportional to the cobalt content in the catalyst and is not the same when the cobalt precursor is changed. It is clearly seen in figure 2 that, whatever cobalt content, Co(en) catalysts are much more active than Co(N) catalysts exhibiting a difference of about 60 °C at the light-off temperature. Moreover, at the same temperature, conversion is more than double when the cobalt ethylenediamine precursor is used; this beneficial effect being more pronounced in the case of low cobalt content. High cobalt oxides dispersion seems to be decisive for good propene oxidation performance of supported cobalt catalysts. In the present study, when ethylenediamine is added during the catalyst preparation (Co(en) samples) a better Co_3O_4 dispersion was evidenced by XRD and XPS analyses.

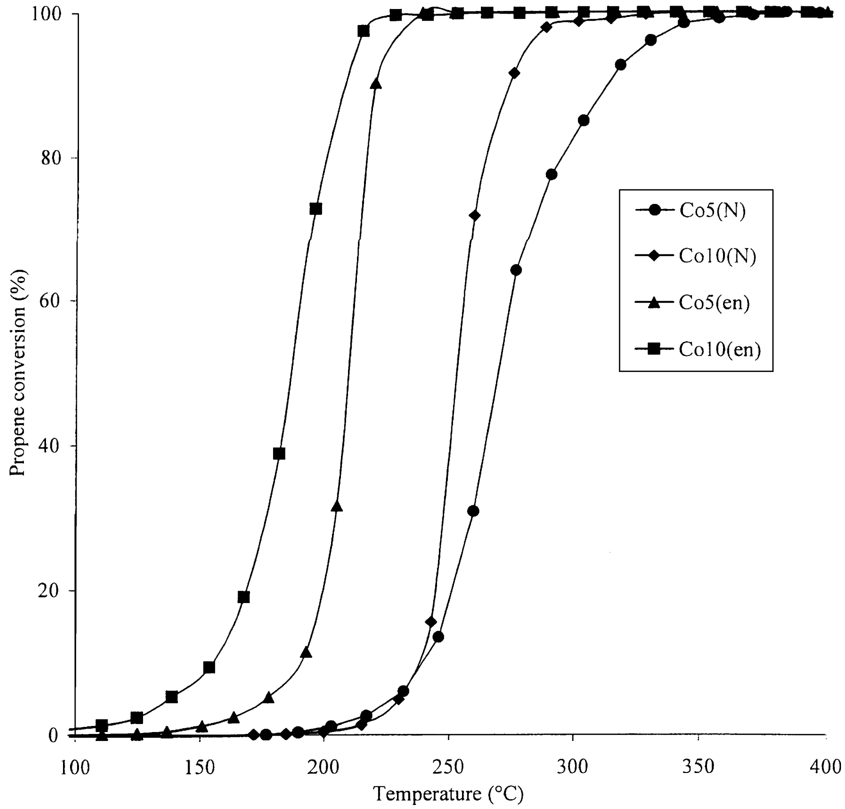

Figure 4. Cobalt precursor and cobalt content effects on the $C_3H_6+O_2$ reaction over Co/ZrO_2 catalysts: % C_3H_6 conversion as a function of temperature.

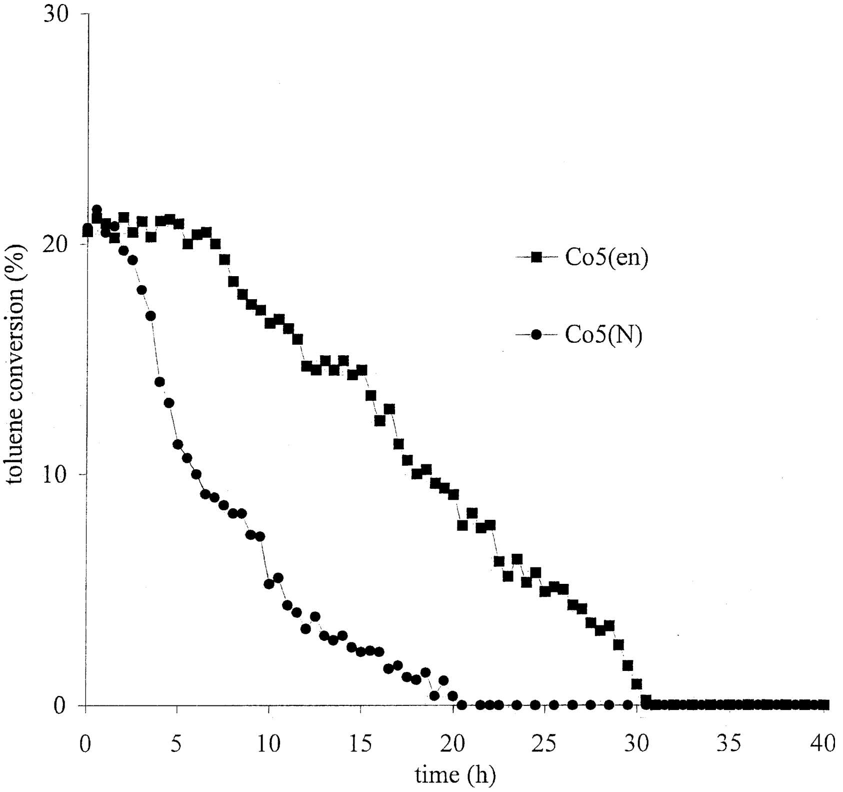

Figure 5. Deactivation tests at 20% of toluene conversion in the presence of $Co_5(N)$ and $Co_5(en)$ catalysts.

The TPR results also explain well the catalytic results. Indeed a redox mechanism is often proposed to clarify the catalytic results for total oxidation reactions. In this mechanism, the step of the removal of oxygen from the transition metal oxides is often considered as the rate determining step. The easier reducibility of cobalt species or the higher reducible quantity of transition metal oxides, observed for Co(en) samples in comparison with Co(N) solids, allows to explain the best performance of Co(en) catalysts in the reaction of propene oxidation. In these solids, the cobalt species Co^{3+} and/or Co^{2+} are more easily reduced by the propene.

Deactivation of $Co_5(en)$ and $Co_5(N)$ catalysts has been studied at 20% of toluene conversion (figure 5). Clearly $Co_5(en)$ catalyst presents a higher stability than $Co_5(N)$ solid since $Co_5(en)$ is deactivated 10 h after the second. The deactivation can be partially explained by a change in cobalt dispersion by crystal growth due to sintering. Then the best stability can be explained by a delay in the sintering due to the initial presence of much smaller cobalt species in $Co_5(en)$. Further characterization should be conducted in order to better understand the deactivation process.

4. Conclusion

In this study, a new and simple method for obtaining a highly disperse Co/ZrO_2 catalyst is described. The catalysts prepared using ethylenediamine are much more active in the propene oxidation than the one obtained using the classical wet impregnation method using cobalt nitrates. The higher cobalt oxides dispersion associated with a low interaction of these species with the zirconia are the common features of these catalysts, more active but also more stable under the reaction conditions used in the present work.

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