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Modified Co_3O_4/ZrO_2 catalysts for VOC emissions abatement

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Abstract

The catalytic activity study of cobalt oxides dispersed on different supports evidenced first the highest performances of zirconia based catalysts in the reaction of toluene oxidation. The influence of the presence of ethylenediamine (en) during the preparation of Co/ZrO_2 and the ZrO_2 support modification by Y_2O_3 were then studied and compared with reference catalyst prepared conventionally by impregnation of ZrO_2 with an aqueous solution of $Co(NO_3)_2$. Addition of an aqueous solution of ethylenediamine to a cobalt nitrate solution led to a strong increase on the catalytic activity of the activated solids in the toluene deep oxidation as compared with the reference catalyst. The best catalytic results were explained in terms of cobalt oxides dispersion but also in terms of Co–support interaction. The generated cobalt species were reducible at much lower temperatures and then were more active in the toluene total oxidation. Finally an efficient catalyst for VOC oxidation was produced combining the modifications of ZrO_2 by yttrium and of the precursor.

Keywords: Zirconia; Cobalt oxides; Ethylenediamine; Yttrium; Toluene 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. Transition metal oxides, especially Co_3O_4, offer a low cost alternative to metal noble based catalysts which are presently the most active catalysts in the complete oxidation of VOC at low temperatures. High cobalt loading with good dispersion is required to obtain at least similar catalytic activity with that measured in the presence of noble metals. But in the case of high metal loadings, using conventional cobalt nitrates as precursor, multiple impregnations with intermediate drying and calcination steps are needed to minimize the formation of large metal oxide particles [2,3], less active in catalytic oxidation [4]. Smaller cobalt particles can be produced using other cobalt precursors such as oxalate, acetate or acetyl acetonate [5,6] or employing organic complexes such as EDTA during the synthesis procedure [2,5,7]. The active phase dispersion depends also on the support composition. For VOC oxidation, ZrO_2 is a desired support because of its good mechanical properties and high thermal stability. Moreover the thermal stability and the catalytic properties of zirconia can be enhanced by adding some dopants (La, Ca, Y, Ce, etc.) which change its structure [8]. The introduction of yttrium into the zirconia induces the formation of anionic vacancies [9] which increase the ability of the solid to accumulate oxygen and improve an oxygen exchange at low temperatures [10].

The aim of the present study is to prepare and investigate cobalt oxides catalysts, with cobalt weight content of 5%, supported on ZrO_2 and ZrO_2–(5 mol%) Y_2O_3. For comparison, a commercial alumina is also used as carrier. For the first time, the effect of ethylenediamine addition during the preparation of Co/ZrO_2 is studied with respect to Co dispersion, surface/bulk compositions and reducibility in comparison with a reference catalyst conventionally prepared by impregnation of ZrO_2 with

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an aqueous solution of $Co(NO_3)_2$. Their activity and selectivity for VOC abatement in excess oxygen are reported. Toluene has been chosen as VOC probe molecule because aromatics are present in the industrial and automotive emissions [11] and because toluene presents an important POCP (photochemical ozone creativity potential) [12].

2. Experimental procedure

2.1. Samples preparation

The synthesis method to prepare ZrO_2 (noted Zr) and ZrO_2–(5 mol%) Y_2O_3 (noted $Zr_{95}Y_5$) was previously described [13]. Alumina support (noted Al) was provided by Degussa. For impregnation, 100 mL of cobalt solution were added to 2 g of support (previously calcined at 600 °C). Solution was prepared to obtain final product containing 5 wt.% of cobalt. Different cobalt solutions were used to impregnate the support. 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-nit)/support). Other solutions were obtained by dissolution of the necessary amount of cobalt nitrate in aqueous ethylenediamine (noted "en") solution. The total amount of ethylenediamine was adjusted to reach a molar ratio of en/Co = 1, 2 and 3 (samples named (Co-en_1)/Zr (Co-en_2)/Zr (Co-en_3)/Zr and (Co-en_1)/$Zr_{95}Y_5$). After evaporating the excess of water at 60 °C under vacuum, the samples were dried at 100 °C for 20 h before an activation treatment in a flow of dried air (2 L h^{-1}) during 4 h at 450 °C. The cobalt content in the samples, determined by atomic absorption (ICP AES), is displayed in Table 1.

2.2. Samples characterization

The specific surface areas of solids were determined by the BET method using a Quantasorb Junior apparatus, and the gas adsorbed at −196 °C was pure nitrogen. The structure of solids was analyzed at room temperature by X-ray diffraction (XRD) technique in a Bruker D8 Advance diffractometer equipped with a copper anode (step-size of $\Delta(2\theta) = 0.02^\circ$ and count time of 12 s per step). Temperature-programmed reduction (TPR) of the calcined catalysts was carried out in a conventional laboratory apparatus (Zeton Altamira AMI 200). Prior to the TPR experiments, samples (80 mg) were activated under argon at 150 °C for 1 h. Then, samples were heated from ambient to 600 °C under H_2 flow (5 vol.% in Ar −30 mL min^{-1}) at a heating rate of 5 °C min^{-1}. X-ray photoelectron 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 C 1s 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. The activity of the catalysts (200 mg) was measured in a continuous flow system on a fixed bed reactor at atmospheric pressure. The flow of the reactant gases (0.1 mL min^{-1} of C_7H_8 and 99.9 mL min^{-1} of air) was adjusted by a Calibrage cal pc-5 apparatus constituted of a saturator and one mass flow controller. The temperature was increased from room temperature to 450 °C (1 °C min^{-1}). The feed and the reactor outflow gases were analyzed on line by a gas chromatograph (Perkin-Elmer AutoSystem XL equipped with CTR1 and Hayesep R columns from Alltech).

3. Results and discussion

Table 1 summarizes the results of BET measurements. The decrease of the specific surface area observed after the impregnation procedure is explained by the presence of cobalt precursor's molecules blocking the pores of the support. This phenomenon is emphasized when ethylenediamine is added during the preparation. The strong decrease observed when ethylenediamine is used could be explained by the size of the ethylenediamine itself or of a possible Co–ethylenediamine complex. Indeed, during the preparation, Co-en_2^{2+} and Co-en_3^{2+} complex ions can be formed [14]. After calcination at 450 °C, specific surface areas are close to that of supports 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 450 °C whatever the used support.

The results of the catalytic tests in the toluene oxidation in the presence of Co/support samples are shown in Fig. 1a. Carbonaceous selectivity towards CO_2 of 100% (no CO formation) is measured in the presence of all the catalysts whatever the used support and precursor.

Table 1
Surface specific areas (BET), bulk (ICP AES) and surface (XPS) compositions of Co/support samples

Samples	Cobalt content (wt.%)	Specific surface area (m^2 g^{-1})			$I_{Co\ 2p}/I_{Zr\ 3d}$ (XPS)
		Support (calcined at 600 °C)	Co/support (dried at 100 °C)	Co/support (calcined at 450 °C)	
(Co-nit)/Al	4.60	105	90	107	–
(Co-nit)/Zr	4.56	72	60	69	0.205
(Co-en_3)/Zr	4.07	72	6	66	4.717
(Co-en_2)/Zr	4.03	72	8	62	2.825
(Co-en_1)/Zr	4.00	72	9	67	1.453
(Co-nit)/$Zr_{95}Y_5$	4.56	82	67	77	–
(Co-en_1)/$Zr_{95}Y_5$	4.00	82	7	75	–

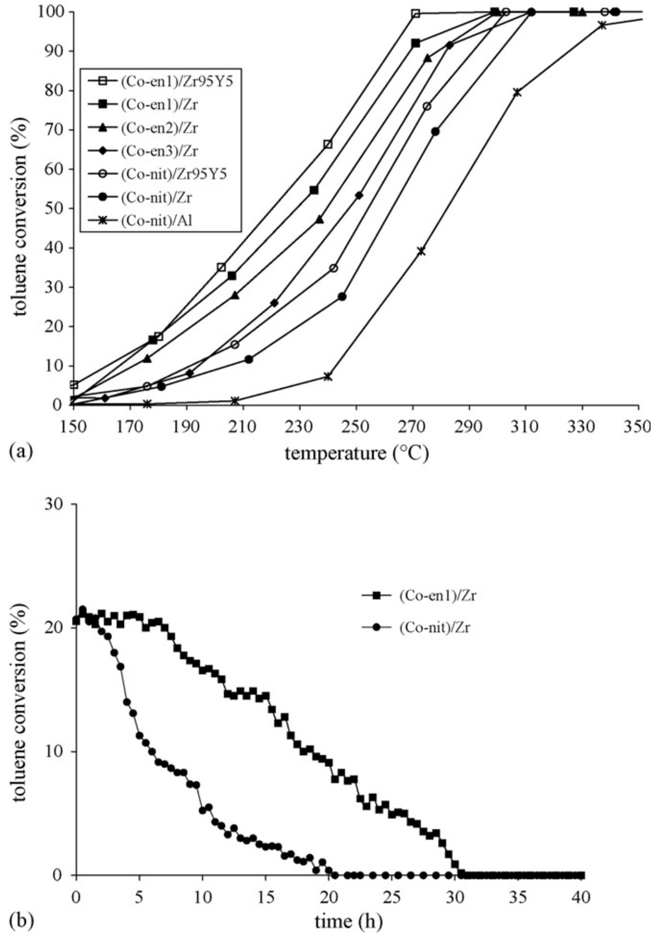

Fig. 1. (a) Evolution of the toluene conversion as a function of the temperature obtained in the presence of catalysts; (b) deactivation tests at 20% of toluene conversion in the presence of (Co-nit) ($T = 219\ ^\circ C$) and (Co-en$_1$)/Zr ($T = 197\ ^\circ C$). Space velocities = 27 000 h^{-1} for Co/Zr and Co/Zr$_{95}$Y$_5$ samples and 12 000 h^{-1} for Co/Al sample.

3.1. *Influence of the support composition*

For (Co-nit) samples, the catalytic activity depends on the support composition: (Co-nit)/Zr$_{95}$Y$_5$ > (Co-nit)/Zr > (Co-nit)/Al (Fig. 1a). In order to make clear these catalytic results, XRD measurements were performed (Fig. 2). For Co/Zr samples, a mixture of zirconia in the monoclinic (JCPDS no. 65-1023) and the tetragonal (JCPDS no. 50-1089) phases is observed (respectively noted "M" and "T in Fig. 2). According to our previous works on Cu/Zr$_{95}$Y$_5$ catalysts [13], XRD patterns obtained for Co/Zr$_{95}$Y$_5$ catalysts reveal that Zr$_{95}$Y$_5$ support only crystallizes in the tetragonal phase. A peak at $2\theta = 36.8^\circ$ is also observed for Co/Zr (noted "Co" in Fig. 2). This peak is assigned to (3 1 1) diffraction line of Co_3O_4 in the cubic phase (JCPDS no. 42-1467). For the same precursor, the intensity of this peak (zoom Fig. 2) is lower when cobalt is deposited on Zr$_{95}$Y$_5$, according to a higher dispersion of Co_3O_4 particles on higher specific surface area (Table 1). However XRD measurements do not allow estimating the cobalt oxides dispersion in Co/Al_2O_3 sample since the diffraction peaks of γ-Al_2O_3 support noted "Al" in Fig. 2 (JCPDS no. 50-0741) overlaps those of Co_3O_4 phase.

It is generally assumed 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 oxidize hydrocarbons. Then, the reducibility study of cobalt oxides seems to be also crucial in order to explain the catalytic results observed in toluene oxidation. The reduction of Co_3O_4 by H_2 proceeds through two steps denoted α and β [15]:

$$Co_3O_4 + H_2 \rightarrow 3CoO + H_2O \quad (\alpha,\ H_2\ \text{consumption} = 25\%)$$

$$3CoO + 3H_2 \rightarrow 3Co + 3H_2O \quad (\beta,\ H_2\ \text{consumption} = 75\%).$$

H_2-TPR profiles of (Co-nit)/Zr, Zr$_{95}$Y$_5$ or Al samples calcined at 450 °C are shown in Fig. 3. For (Co-nit)/Zr and (Co-nit)/Al, 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. For (Co-nit)/Zr 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 total signal intensity. The second peak (β_A) corresponds certainly to the reduction of Co^{2+} into Co^0. Using different supports, Jacobs et al. [16] found also that the ratio of the first peak to that of the second is always close to 1:3. The shoulder observed for (Co-nit)/Zr$_{95}$Y$_5$ samples at around 640 °C (in Fig. 3; noted S) can be assigned to Y_2O_3 reduction [17]. For (Co-nit)/Zr$_{95}$Y$_5$ solid, the relative intensity of the signal 1 of 33% indicates the partial formation of metallic cobalt in the temperature range 200–350 °C. Indeed, the first peak at 220 °C (α_B) can be associated to the second one at 340 °C (β_B); these two peaks correspond to the reduction in two steps of Co^{3+} species (noted "B") into metallic Co. It is well known that Zr$_{95}$Y$_5$ support presents higher quantity of anionic vacancies than that measured in undoped ZrO_2 support. Labaki et al. [13] shown that the higher quantity of Zr^{3+} in Zr$_{95}$Y$_5$ induced the formation of CuO species in a more reducing environment. In fact copper atoms can occupy the anionic vacancies associated to Zr^{3+} [18]. The same explanation can be given with "B" cobalt species which can be located near or in the anionic vacancies of the support leading to their easier reduction. Besides using pure ZrO_2 as support, "B" species are also present (Fig. 3) but in lower quantity according to the lower quantity of Zr^{3+} species in ZrO_2 [13]. For (Co-nit)/Al_2O_3 sample, the reducibility study evidences the presence of different Co-oxides species. The first peak (α_1) is assigned to the reduction process ($Co^{3+} \rightarrow Co^{2+}$) of large crystallite Co_3O_4 particles, followed by conversion of Co^{2+} into Co^0 (second peak β_1). Other peaks (α_2 and $\beta_2 > 500\ ^\circ C$) are associated with surface cobalt species highly dispersed and in strong interaction with alumina [19].

Then, the best activity measured in the presence of (Co-nit)/Zr$_{95}$Y$_5$ can be explained by higher cobalt oxides dispersion but also by the presence of Co^{3+} species more easily reducible into Co^{2+}. The lowest activity of (Co-nit)/Al catalyst is explained by lower quantity of Co^{3+} species available in the temperature range of total toluene oxidation reaction, despite the highest specific surface area of Al_2O_3. Therefore, the investigation of cobalt oxides catalytic properties improvement has been conducted on zirconia based support.

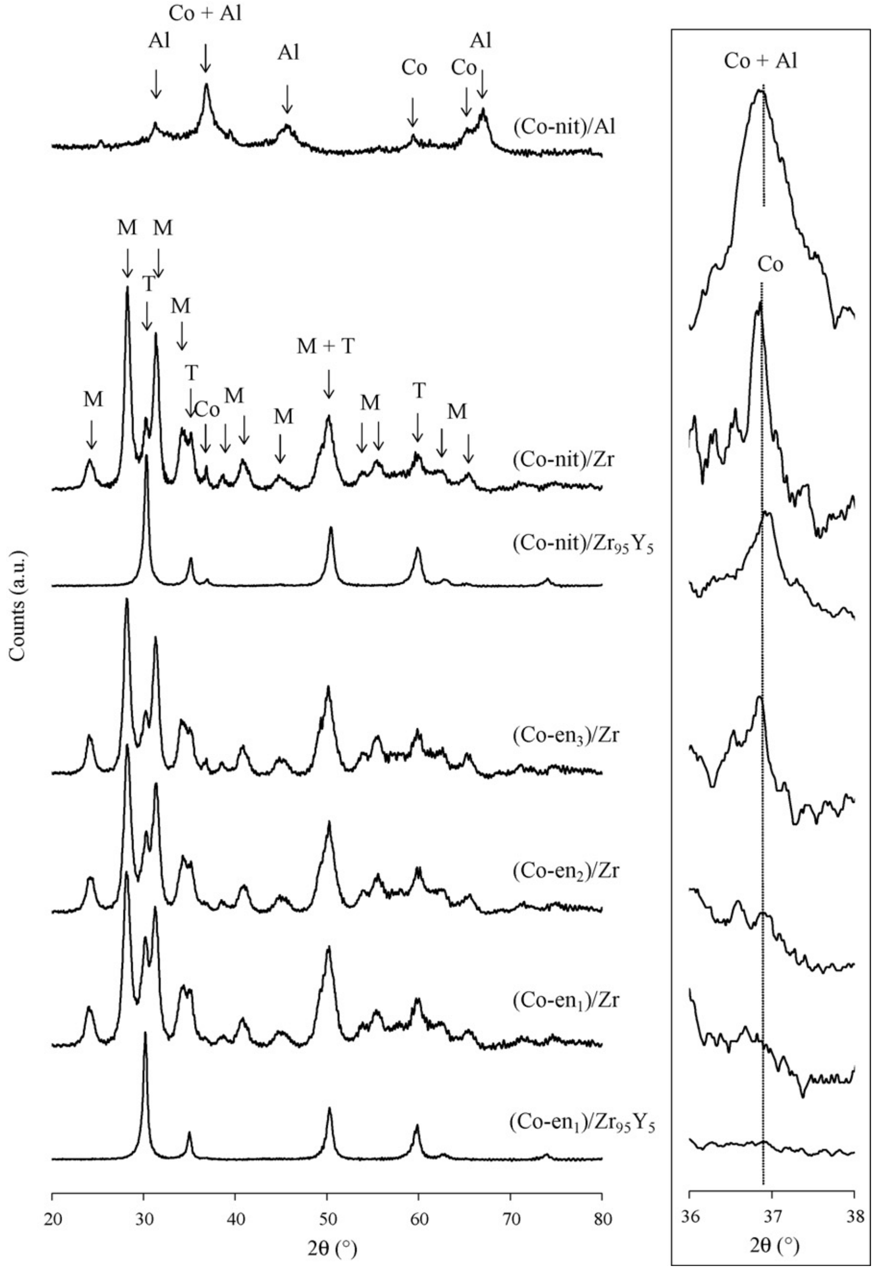

Fig. 2. XRD patterns (recorded at room temperature) of Co/Zr, Co/$Zr_{95}Y_5$ and Co/Al samples. M = ZrO_2 monoclinic phase; T = ZrO_2 tetragonal phase; Co = Co_3O_4 cubic phase; Al = Al_2O_3 γ-cubic phase.

3.2. *Influence of the ethylenediamine*

The use of ethylenediamine during the preparation leads to a large catalytic activity enhancement (Fig. 1a). Indeed, the light-off temperature is lowered of 35, 24 and 16 °C for respectively ($Co-en_1$)/Zr, ($Co-en_2$)/Zr and ($Co-en_3$)/Zr. For ($Co-en_1$)/$Zr_{95}Y_5$ sample, an additional effect of cobalt precursor and zirconia support modifications is observed since the light-off temperature is decreased of 44 °C in comparison with that measured in presence of conventional (Co-nit)/Zr catalyst (Fig. 1a).

For the same support, the (3 1 1) diffraction peak intensity of Co_3O_4 depends on the precursor used and on the en/Co ratio according to the following sequence (intensity decrease): (Co-nit)/Zr > ($Co-en_3$)/Zr > ($Co-en_2$)/Zr ~ ($Co-en_1$)/Zr (zoom Fig. 2). This result suggests that the ethylenediamine use during the preparation favors the dispersion of cobalt oxides at the surface of zirconia leading probably to smaller particles of Co_3O_4 less visible by XRD analysis.

Co^{2+} and Co^{3+} species, present in Co_3O_4, can be identified by XPS measurement. In the Co 2p region, XPS spectra of (Co-nit)/Zr and ($Co-en_x$)/Zr samples consist of two main peaks, Co $2p_{1/2}$ and Co $2p_{3/2}$, 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

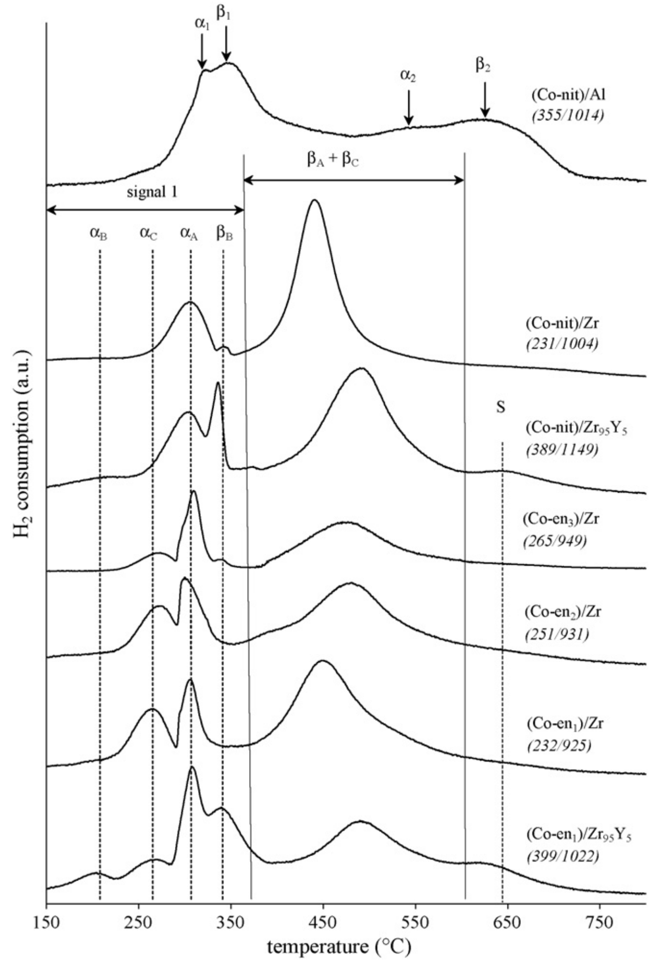

Fig. 3. H_2-TPR profiles obtained starting from calcined Co (5%)/support. The values in italic correspond to the experimental consumed H_2 quantities in μmol g^{-1}: first value assigned to the signal 1 and the second value to the total H_2 consumption.

pure CoO [20]. The surface $I_{Co\ 2p}/I_{Zr\ 3d}$ ratio values are higher in a large extent for samples prepared with ethylenediamine than for conventionally synthesized samples (Table 1). This result confirms the highest cobalt dispersion on the zirconia support when ethylenediamine is used during the preparation.

The reason why ethylenediamine improves the cobalt species dispersion could be well explained in terms of the size of the complex ions (Co-en_2^{2+} and Co-en_3^{2+}) formed in situ during impregnation [14]: as the cobalt atom is surrounded by the ethylenediamine ligands, cobalt atoms are forced to be far apart one from another leading to highly dispersed catalyst. The higher cobalt oxides dispersion leads to catalytic activity improvement.

H_2-TPR profiles of (Co-en_x)/Zr samples calcined at 450 °C are shown in Fig. 3. Additional peak (α_C) is observed at lower temperature (270 °C) in comparison with that observed for (Co-nit)/Zr (α_A). Intensity of the signal 1 represents 25%, 27% and 28% of total intensity of H_2-TPR signal for respectively (Co-en_1)/Zr, (Co-en_2)/Zr and (Co-en_3)/Zr. New "C" cobalt species reducible at lower temperatures are formed when ethylenediamine is used during the preparation to the detriment of "A" cobalt species. Clearly, the α_C peak intensity depends on x value and increases from $x = 3$ to 1.

An evident relation between the reducibility study of cobalt oxides species and their reactivity in the toluene oxidation can be done: the more is the reducibility, the more is the activity. Indeed additions of yttrium to the support and of ethylenediamine during the preparation leads to the formation of respectively "B" and "C" species reducible at lower temperatures than "A" species conventionally formed in (Co-nit)/Zr solid (Fig. 3). Studying the en/Co ratio value effect, the catalytic activity results are in straight line with H_2-TPR results since the catalytic activity increases with the α_C peak intensity. The additional catalytic effect observed in the presence of (Co-en_1)/$Zr_{95}Y_5$ is well explained by the simultaneous presence of "B" and "C" species, arising from respectively the modifications of the support and of the precursor, leading to higher quantity of cobalt species reducible at lower temperatures.

Deactivation of (Co-nit)/Zr and (Co-en_1)/Zr catalysts has been studied at 20% of toluene conversion reached respectively at 219 and 197 °C (Fig. 1b). Clearly (Co-en_1)/Zr catalyst presents a higher stability than (Co-nit)/Zr solid since (Co-en_1)/Zr is deactivated 10 h after the second. The deactivation does not seem caused by coke deposition since XPS study of C 1s level does not evidence additional carbon formation. However the deactivation can be partially explained by a change in cobalt dispersion by crystal growth due to sintering since XPS intensity ratios ($I_{Co\ 2p}/I_{Zr\ 3d}$) of the used catalysts decrease from 0.205 to 0.180 and 1.453 to 1.040 for respectively (Co-nit)/Zr and (Co-en_1)/Zr catalysts. 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-en_1)/Zr. Further characterization should be conducted in order to better understand the deactivation process.

4. Conclusion

In this work, a new and simple synthesis method for obtaining a highly disperse Co/ZrO_2 catalyst is described. Introduction of yttrium (5 mol%) into the support and addition of an aqueous solution of ethylenediamine to a cobalt nitrate solution during the catalyst preparation lead to an important increase of the catalytic performance of these new solids in the toluene total oxidation. The en/Co molar ratio influences significantly the catalytic activity, the lower ratio of 1 leading to the best catalyst. The catalytic results have been explained in terms of cobalt oxides (Co_3O_4) dispersion, strongly improved when support and/or cobalt precursor are modified. Besides, this higher cobalt oxides dispersion has been associated with a low interaction of these species with the zirconia support. Indeed studying the reducibility of cobalt oxides, we have evidenced two new types of cobalt species reducible at lower temperatures. Higher cobalt oxides dispersion associated with a low interaction of these species with the zirconia lead to a more active but also a more stable catalyst in the toluene deep oxidation. Finally, the modifications of the support by yttrium and of the precursor (ethylenediamine) result in a very efficient catalyst since the two effects combine to generate higher quantity of cobalt species reducible at lower temperatures.

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