Catalytic oxidation of toluene on Ce-Co and La-Co mixed oxides synthesized by exotemplating and evaporation methods

S.A.C. Carabineiro^{1,*}, X. Chen¹, M. Konsolakis^{2,**}, A.C. Psarras³, P.B. Tavares⁴, J.J.M. Órfão¹, M.F.R. Pereira¹, J.L. Figueiredo¹

¹ *Laboratório de Catálise e Materiais (LCM), Laboratório Associado LSRE/LCM, Faculdade de Engenharia, Universidade do Porto, 4200-465 Porto, Portugal*

² *School of Production Engineering and Management, Technical University of Crete, 73100 Chania, Greece*

³ *Chemical Process & Energy Resources Institute (CPERI), Centre for Research & Technology Hellas (CERTH), 6th km. Charilaou - Thermi Rd., P.O. Box 60361, GR-57001 Thermi, Thessaloniki, Greece*

⁴ *CQVR Centro de Química –Vila Real, Departamento de Química, Universidade de Trás-os-Montes e Alto Douro, 5001-911 Vila Real, Portugal*

* - Corresponding author. Email: scarabin@fe.up.pt, Tel. +351 220414907

** - Corresponding author. E-mail: mkonsol@science.tuc.gr; Tel. +30 28210 37682;

Web: www.tuc.gr/konsolakis.html

Abstract

Ce-Co and La-Co mixed oxides were synthesised by two different methods: exotemplating and evaporation. The obtained catalysts were evaluated for volatile organic compounds (VOCs) abatement, using toluene as model molecule. The materials were characterised by N₂ adsorption at -196 °C, X-ray diffraction (XRD), scanning

electron microscopy (SEM), H₂ temperature programmed reduction (H₂-TPR) and NH₃ temperature programmed desorption (NH₃-TPD) in order to reveal the structure-activity relationship. The results obtained showed the superiority of mixed oxides compared to single oxides in toluene oxidation. Ce-Co mixed oxides were more active than La-Co samples. For Ce-Co materials, the exotemplating method produced catalysts which were more active than those prepared by the evaporation procedure. The former showed the best catalytic performances, with full conversion of toluene into CO₂ at about 250 °C. Temperatures higher than 320 °C were required with single oxides. Characterization studies revealed strong interactions between Ce (or La) and Co, leading to a fine dispersion of oxide phases in binary systems. As a result, both the surface area and reducibility of the catalysts increase, which can be accounted for the higher performance of the mixed oxides. Furthermore, NH₃-TPD studies showed a linear relationship between acidity and VOC oxidation activity. In fact, a high concentration of weak acid sites is required for high toluene oxidation activity. The results can be explained in terms of a Mars-van Krevelen type of mechanism, involving the adsorption of toluene and its subsequent oxidation by lattice and/or surface oxygen.

Keywords: Catalytic oxidation; toluene; mixed oxides; cerium; lanthanum; cobalt.

1. Introduction

Volatile organic compounds (VOCs) are environmental pollutants produced by petroleum refineries, solvent cleaning, fuel storage and loading operations, motor vehicles, printing and painting operations. Some of these compounds are malodorous or carcinogenic [1]. VOCs are responsible for the formation of secondary particulate

matter in the atmosphere, which can subsequently result in smog formation. Therefore, VOCs are worldwide regulated in many sectors of industry and traffic.

Several VOC control technologies have been developed. Catalytic oxidation is an environment friendly and promising control technology, since lower temperatures are required (around 250-500 °C), causing less NO_x formation than conventional thermal oxidation, which requires high operation temperatures (650-1100 °C) [2-9].

Metal oxides and supported noble metals can be used as heterogeneous catalysts for VOC oxidation. Metal oxide based catalysts can be either supported or unsupported. Common support materials include alumina [10], titania [11], zirconia [12], zeolites [13] and carbon based materials [14]. Platinum and palladium are the noble metals mostly used in such applications [3, 15], but gold has also been investigated [4, 16]. Common metal oxide based catalysts for oxidation reactions are: manganese dioxide [3, 4], copper oxide [13, 14], nickel oxide [13, 16], iron oxide [17], cobalt oxide [17-19], among others [9, 17]. It has been reported that, although metal oxide based catalysts are more resistant to poisoning phenomena, they generally are less active than the supported noble metals in oxidizing VOC streams [20, 21]. However, mixed oxides [16, 22-24], like perovskites [25-27] and cryptomelane type materials [21, 28, 29] have shown good activities for the catalytic oxidation of VOCs.

In order to obtain effective low cost catalysts with high resistance to poisoning, porous materials with improved textural properties are interesting. The preparation method can have a critical influence on the morphology of the resulting materials [30], consequently affecting the catalytic activities. Various procedures can be used for the preparation of nanostructured metal oxides for catalytic applications [31]. In exotemplating, also known as nanocasting, a porous solid provides a scaffold with voids which are filled up with the precursor for another solid to be obtained [32]. The template material is

removed after the target solid is formed. Carbon materials are good choices for exotemplating, due to their high surface area and porosity, low cost, as well as the simplicity of being removed by combustion [4, 21, 33-35]. Several high-surface area metal and mixed metal oxides (of Al, Ce, Cr, Fe, Mg, Mn, Ti, etc) have been synthesized using activated carbon fibers [32, 36], carbon nanotubes [37], carbon aerogels [38], activated carbon [4, 5, 21, 32-34, 36, 39, 40], and carbon xerogels [4, 5, 21, 33, 34] as templates. Co oxide templated with silica was also used for toluene oxidation [19, 41].

Two synthesis procedures were used in this work for the preparation of cerium and lanthanum-containing mixed metal oxides: exotemplating (EX) and a simple evaporation method (EM). Carbon xerogels were used as template materials, due to their large surface area, highly porous structure, low cost, purity and easy removal by combustion [4, 5, 21, 33, 34]. The EM, on the other hand, is a co-precipitation method [16].

In this work, Co oxide was used as the coupling species with cerium or lanthanum in Co-Ce or Co-La mixed oxides. Cerium oxide is often used for VOC oxidation, either as a support or mixed with other metal oxides [4, 16, 42-53]; however not many studies are found in literature for lanthanum oxides [54-58]. The obtained catalysts were tested in the oxidation of toluene (C_7H_8), which has a vapour pressure of 2.734 kPa at 20°C [59]. Due to its aromatic structure, higher temperatures are required for oxidation, in comparison with other VOCs [4]. An extensive characterisation study was undertaken in order to develop a better understanding of the impact of the preparation method on catalyst activity.

2. Experimental

2.1. Catalysts preparation

2.1.1. Evaporation method (EM)

The EM preparation procedure, described by Solsona et al. [13], was adapted for the preparation of Ce-Co and La-Co mixed oxides with a Ce:Co or La:Co molar ratio of 1:2. Briefly, 2 M ethanol solutions of metal precursors (acetates) were mixed, followed by the addition of oxalic acid in a molar ratio of oxalic acid/total amount of metal cations equal to 1. The mixture was then heated up to 60 °C under stirring for the evaporation of solvent. The resulting material was dried overnight at 80 °C and then calcined in a furnace under 100 cm³/min of air flow with a heating rate of 10 °C/min up to 300 °C, and holding at that temperature for 2 h.

2.1.2. Exotemplating method (EX)

This method was based on the procedure described by Schwickardi et al. [40]. Metal nitrates were used as the precursors, as they were reported to form materials with higher surface areas [32]. Two types of carbon xerogel (CX and CXN), with a particle size between 0.05 and 0.25 mm, were used as templating materials for Ce-Co samples. Both xerogels were prepared following a procedure described by Job et al. [60]. CXN had a larger average pore size of 31.3 nm [61], whereas 24.4 nm was found for CX [21]. Surface areas were similar, 617 m²/g for CXN [61] and 633 m²/g for CX [21].

3.4 mL of precursor solution was used for impregnating 1.7 g of CX, and 3.3 mL of precursor solution for 1.7 g of CXN. These amounts were determined based on the Spv-ratio equal to 1.5, which was given by the following formula, expressing the relationship between the added volume of the precursor solution and the available pore volume of the carbon template:

$$Spv-ratio = \frac{V_{\text{solution}}}{m_{\text{CX}} \cdot v_{\text{pore}}},$$

where V_{solution} is the volume of the precursor solution (mL), m_{CX} is the mass of carbon (g) and v_{pore} the specific pore volume ($\text{cm}^3/\text{g}_{\text{CX}}$) of carbon [62]. The specific pore volume of CX was $1.32 \text{ cm}^3/\text{g}$ [21], while that of CXN was $1.30 \text{ cm}^3/\text{g}$ [61].

2 M aqueous solutions of two different metal precursors were mixed in selected volumetric proportions to achieve the desired molar ratio of metal elements in the material (1:2), prior to being impregnated into the templates. The paste-like impregnated material was then sandwiched between two sheets of filter paper with gentle squeeze applied to remove the excess solution. The material was further dried overnight in an oven at about 80°C and then calcined in a furnace. A lower temperature (220°C) was first used for the decomposition of the precursors (1 h), followed by a higher temperature (350°C) stage for the removal of the carbon templates (8 h). Calcination was carried out under $100 \text{ cm}^3/\text{min}$ of air flow, with a heating rate of $2^\circ\text{C}/\text{min}$.

2.2. Characterisation

Samples were characterised by N_2 adsorption at -196°C and temperature programmed reduction (TPR). Selected samples were further analysed with scanning electron microscopy (SEM), X-ray diffraction (XRD) and NH_3 temperature programmed desorption (NH_3 -TPD).

BET surface areas were calculated from the N_2 adsorption isotherms obtained in a Quantachrome Instruments Nova 4200e. All samples were previously degassed before analysis at 160°C , for 5 h.

TPR experiments were carried out in a fully automated AMI-200 Catalyst

Characterization Instrument (Altamira Instruments) under H_2 atmosphere, to acquire information on the reducibility of the samples. In a typical TPR experiment, ~50 mg of sample was placed in a U-shaped quartz tube located inside an electrical furnace and heated to 1100 °C at 10 °C/min under He flow of 29 cm^3/min and H_2 flow of 1.5 cm^3/min .

Surface analysis for morphological characterisation was carried out by SEM, using a FEI Quanta 400 FEG ESEM (15 keV) electron microscope. The sample powders were mounted on a double-sided adhesive tape and observed at different magnifications under two different detection modes, secondary and back-scattered electrons. EDS confirmed the nature of the components.

XRD analysis was carried out in a PAN'alytical X'Pert MPD equipped with an X'Celerator detector and secondary monochromator ($\text{Cu K}\alpha = 0.154 \text{ nm}$, 50 kV, 40 mA). The collected spectra were analysed by Rietveld refinement using the PowderCell software, allowing the determination of the grain size.

The acidic characteristics of the mixed oxides were studied by NH_3 temperature-programmed desorption (NH_3 -TPD). In a typical experiment, 0.2 g of the sample were loaded in a plug flow quartz reactor and pre-treated at 550 °C in He (50 cm^3/min) for 1 h. Then, the sample was cooled to 100 °C under He flow and ammonia adsorption performed by admitting a flow of 5% NH_3/He (50 cm^3/min) for 1 h. Subsequently, the sample was exposed overnight to He flow (50 cm^3/min) at 100 °C to remove the physisorbed ammonia. TPD analysis was carried out from 100 to 800 °C at a heating rate of 10 °C/min and a helium flow rate of 50 cm^3/min . Quantitative analysis was carried out by continuously recording the desorbed ammonia with a mass spectrometer ($m/z = 15$) and by integrating the area under the corresponding profile. Predefined volumes of pure NH_3 were used for calibration.

2.3. Catalytic tests

The catalytic reactions were performed in a U-shaped quartz tube fixed-bed reactor with 6 mm internal diameter, placed inside a temperature controlled electrical furnace. A total air flow of 500 cm³/min (measured at room temperature and atmospheric pressure) with a VOC composition of 1000 mg_{Carbon}/m³ (~266 ppmV of toluene) was employed. The catalyst (~50 mg, particle size between 0.2 and 0.5 mm) was mixed thoroughly with an inert (SiC, carborundum) with particle sizes between 0.2 and 0.5 mm. Due to the different chemical composition and consequently different density of the mixed oxides, a different catalyst volume is obtained for the same amount of catalyst (50 mg). Therefore, the total volume of the mixture of catalyst sample and inert was always kept constant at 0.5 cm³, corresponding to a Gas Hourly Space Velocity (GHSV) of 60,000 h⁻¹. A pre-treatment at 400 °C was carried out in air before the catalytic reaction. Catalytic evaluation was performed in the temperature range of 20-400 °C at a heating rate of 2 °C/min. The extent of VOC oxidation was evaluated by continuously monitoring CO₂ formation with a non-dispersive infrared (NDIR) CO₂ sensor (Vaisala GMP222). The concentration of VOC in the effluent was also measured with a total VOC analyser, MiniRAE2000. In case of incomplete conversion of VOC into CO₂ and H₂O, a portable CO sensor was also used to obtain information on CO formation at the maximum reaction temperature during experiments. The catalytic performance was presented as conversion into CO₂, X_{CO_2} , which was obtained by the following equation:

$$X_{CO_2} = \frac{F_{CO_2}}{\nu \cdot F_{in, VOC}},$$

where $F_{in, VOC}$ is the inlet molar flow rate of VOC, F_{CO_2} is the outlet molar flow rate of CO₂, and ν is the number of carbon atoms in the VOC molecule (for toluene, $\nu = 7$).

In these comparative experiments, the activity of a given catalyst was evaluated by the

temperature required to achieve a given conversion, namely 50% conversion into CO₂ (T₅₀).

3. Results and discussion

3.1. Characterization

3.1.1. BET surface area

Table 1. BET surface areas determined by adsorption of N₂ at -196 °C; compositions, crystallite sizes and phases determined by XRD; and TPR peak maxima (plain text) and shoulders (*italic*) temperatures for Ce-Co and La-Co samples. Values from commercial [5, 33, 63, 64] and exotemplated [5, 33] single oxides are shown for comparison.

Metal oxide samples	BET area (m ² /g)	Phase detected by XRD	Composition (vol. %)	Crystallite size (nm)	TPR peaks (°C)
Ce-Co CX 1:2	131	CeO ₂ (cerianite) Co ₃ O ₄ (spinel)	47.9 52.1	7 15	201,267,322,475
Ce-Co CXN 1:2	120	CeO ₂ (cerianite) Co ₃ O ₄ (spinel)	48.1 51.9	8 16	196,273,323,489
Ce-Co EM 1:2	109	CeO ₂ (cerianite) Co ₃ O ₄ (spinel)	49.0 51.0	5 11	<i>167,200,261,326,372</i> 473
La-Co CX 1:2	92	Co ₃ O ₄ amorphous	- -	7 -	259,352,537
La-Co EM 1:2	68	Co ₃ O ₄ amorphous	- -	8 -	200,305,366,603
Commercial CeO ₂	20	CeO ₂ (cerianite)	-	54	534,865
CeO ₂ CX	96	CeO ₂ (cerianite)	-	17	490,803
Commercial Co ₃ O ₄	44	Co ₃ O ₄ (spinel)	-	32	316,382,429,471
Co ₃ O ₄ CX	64	Co ₃ O ₄ (spinel)	-	27	178,324,400
Commercial La ₂ O ₃	11	La(OH) ₃ (hexagonal)	-	23	*
La ₂ O ₃ CX	29	Mixture of oxonitrates and oxicarbonates of La	-	-	481,493,518,614,647

* - negative peaks found [63] (see text for details)

The BET surface areas of Ce-Co and La-Co mixed oxides are listed in Table 1. Values for commercial [5, 33, 63, 64] and exotemplated [5, 33] single oxides are also shown for comparison. An improvement in BET surface area was achieved with the mixed oxides, comparing with the commercial or exotemplated single oxides. This possibly indicates a rearrangement of single oxide crystals during mixed oxides preparation, which in turn results to better porosity and higher surface area. This explanation is in line with the smaller crystallite size of the oxide phases in mixed oxides, compared to that obtained in corresponding single oxides (see the XRD analysis below). The larger BET values were obtained with samples prepared by the exotemplating method, whereas important differences were not found between CX and CXN samples.

3.1.2. XRD

Figure 1 and Table 1 present the information obtained by XRD on the phase identification, crystallite sizes and compositions by volume percentage for selected samples.

In the Ce-Co oxides, Ce and Co formed separated oxide phases (Co_3O_4 spinel and CeO_2 cerianite), which were the same as those found for the respective single oxides. Amorphous phases were detected for La-Co oxides and only Co_3O_4 peaks could be identified. Both exotemplating and EM methods led to the same phase compositions for both Ce-Co and La-Co oxide systems. It is worth noticing that the crystallite size of the Co_3O_4 phase found in single oxides (27-32 nm) considerably decreased (to 11-16 nm) on the Ce-Co catalysts (Table 1). A similar effect was also observed for the CeO_2 phase, resulting in crystallite sizes lower than 8 nm. These crystallite sizes were similar to those reported by Luo et al. [65] for CeO_2 -based mixed oxides prepared by EM. The XRD results obtained confirm that a more refractory rare earth oxide, such as CeO_2

(melting point 2400 °C) or La_2O_3 (melting point 2315 °C), compared to Co_3O_4 (melting point 895 °C), leads to a decrease of the crystallite sizes. That is in agreement with the textural properties, since the BET surface areas of mixed oxides are larger than those of the single catalysts. Other authors also showed that strong interactions between CuO and CeO_2 can lead to Cu-Ce mixed oxides with superior textural and structural characteristics [23].

Figure 1. XRD pattern of selected Ce-Co and La-Co samples. Miller Indices from AMCSD 0011686 for CeO_2 and from AMCSD 0007469 for Co_3O_4 .

3.1.3. TPR

The TPR profiles of the Ce-Co samples are depicted in Figure 2, whereas the main TPR peaks are summarized in Table 1. Co_3O_4 originates a multi-step profile, as the reduction of surface oxygen takes place first, and then is followed by the $\text{Co}_3\text{O}_4 \rightarrow \text{CoO} \rightarrow \text{Co}$ transitions [66-73]. Two peaks are seen in the TPR profile of CeO_2 . The high-temperature peak (~ 865 °C) corresponds to the reduction of bulk oxygen and the formation of lower oxides of cerium, while the peak at lower temperatures (~ 535 °C) is

assigned to lower temperature ceria surface shell reduction (or reduction of surface oxygen species) [33, 64].

Figure 2. TPR profiles of Ce-Co samples with commercial Co_3O_4 [5] and CeO_2 [64] shown for comparison.

The TPR profiles of Ce-Co binary oxides appeared at notably lower temperatures in relation to those of single oxides, due to the improved reduction of surface oxygen of ceria, together with the reduction of cobalt oxides. Similar profiles were obtained for exotemplated samples, with the reduction peaks of the CX-templated material appearing at slightly different temperatures from those of CXN. Larger variations were found for the EM sample. The TPR profile of Ce-Co EM 1:2 was similar to those of the exotemplated materials, yet with a larger peak at approximately 330 °C, and a smaller one at 475 °C. Unlike the exotemplated samples, the EM sample showed two peaks at ca. 170 and 200 °C. That might be due to the presence of $\text{CoO}(\text{OH})$ species (and their subsequent reduction to Co_3O_4 , as also found by Wang and co-workers [70, 73]).

Figure 3: TPR profiles of La-Co samples with La_2O_3 CX [5] and commercial Co_3O_4 [5] for comparison.

The TPR profiles of La-Co samples are plotted in Figure 3. The exotemplated sample showed three reduction peaks. The first peak, at lower temperature, could be assigned to the reduction of cobalt oxides, as the reduction of $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$ occurs in the temperature range from 150 to 450 °C [27]. Comparing with the profile of the commercial Co_3O_4 (similar to Co_3O_4 CX [5]), reduction of the single oxide occurs at higher temperature, suggesting a change in reducibility upon the formation of mixed oxides. The last peak, at higher temperature, may result from the transition of $\text{La}^{2+} \rightarrow \text{La}^0$, as no further reduction was observed until 1000 °C (the maximum temperature reached in the TPR analyses). Two peaks are observed for La_2O_3 CX. It is known from the literature that sesquioxides (like La_2O_3) are not easily reduced at low temperatures (below 1000°C), so the features at lower temperature might be attributed to the reduction of carbonate species to oxides [74, 75]. Comparing with the profile of La_2O_3 CX, it can be seen that it shifted to lower temperatures with the addition of Co. The first reduction step in La_2O_3

($\text{La}^{2+} \rightarrow \text{La}^0$) and the second in Co_3O_4 ($\text{Co}^{2+} \rightarrow \text{Co}^0$) were also possibly shifted to lower temperatures, and thus overlapped in the La-Co exotemplated profiles, originating the second reduction peak seen in the TPR spectra of these samples. The lowest onset reduction temperature of the group was found for the La-Co EM 1:2 material. It also showed a shoulder after the third peak, which might be related to the reduction of Co_3O_4 , together with the first two peaks. The third peak might be due to the reduction of La_2O_3 .

The TPR results clearly show the easier reducibility of mixed oxides, compared to single ones. These findings are also in agreement with the XRD results, which imply a notable decrease in the crystallite size of oxide phases upon the formation of mixed oxides (Table 1, Figures 2 and 3). In fact, it is well established that smaller particles are more susceptible to reduction than larger ones [8].

3.1.4. SEM

Figure 4 shows SEM images of selected samples. Co-Ce 1:2 CX showed a predominantly homogenous “dark” structure (Z1), with some “lighter” areas (Z2), as seen in Figure 4a. However, EDS performed in both zones showed similar results (not shown). Under the experimental conditions of analysis of this sample, the EDS beam was able to penetrate the sample surface down to at least 1 μm . It is possible that when scanning the Z2 area, a part of the Z1 material underneath was also analysed. Similar results (not shown) were obtained for the Co-Ce 1:2 CXN material. Figure 4b shows a representative SEM image of the Co-Ce 1:2 EM sample; a “dark” structure (Z1) along with a “lighter” one (Z2) is also pictured. EDS spectra revealed that the Z1 area is rich in cobalt (Figure 4c) whereas the Z2 area has more cerium (Figure 4d).

Figure 4. SEM images of samples Ce-Co 1:2 CX (a); Ce-Co 1:2 EM (b) and respective EDS spectra of zones marked as Z1 (c) and Z2 (d); La-Co 1:2 CX (e); La-Co 1:2 EM (f) and respective EDS spectra of zones marked as Z1 (g) and Z2 (h).

A SEM image of La-Co 1:2 CX material is depicted in Figure 4e, showing some “holes”

in the surface. As referred above, when the exotemplated method is employed, the template is impregnated with the oxide precursor and later removed by calcination. The “holes” observed may be related to the porous structure of the template material. Again, lighter and brighter zones are visible. The La-Co 1:2 EM sample (Figure 4f) has a more heterogeneous structure, consisting of rectangular lighter shapes and darker smaller pieces. EDS performed in several parts of both the CX and EM materials revealed similar results, i.e. the darker areas with rougher appearance are richer in Co (Z1), while the lighter smoother parts are La rich (Z2), as seen in Figures 4g and 4h, respectively.

3.1.5. TPD-NH₃

The ammonia desorption profiles of Ce-Co and La-Co catalysts prepared by EM and exotemplating are presented in Figure 5. The total amount of desorbed NH₃ and the temperature of maximum desorption ($T_{\max}$) are reported in Table 2. The amount of desorbed ammonia, determined from the area under the TPD curve, corresponds to the adsorbed ammonia on Lewis and Brønsted acid sites, whereas the temperature of maximum desorption reflects the relative strength of the acid sites [51, 76, 77]. Figure 5 and Table 2 show that there are differences in acid sites concentration and relative strength between Ce-Co and La-Co samples. In fact, the Ce-Co samples showed a sharp desorption peak in the low temperature range (238-252 °C) and presented the highest concentration of acid sites, particularly in the case of Ce-Co CXN 1:2. The amount of NH₃ desorbed from the Ce-Co CX sample is much larger (15.1 μmol/g) compared to that of La-Co CX sample (6.1 μmol/g), implying the significant effect of oxides composition on acid sites concentration. On the other hand, similar acidic characteristics were demonstrated for Ce-Co prepared by exotemplating (CX) and evaporation (EM) methods. The La-Co sample prepared by the exotemplating method originated a lower

intensity peak at high temperatures (maximum at 310 °C). However, the La-Co sample synthesized by EM exhibits similar acid characteristics to Ce-Co samples. The above results clearly reveal the significant impact of mixed oxides composition, as well as of the preparation method on the amount and relative strength of acid sites; both factors are crucial for the catalytic oxidation of toluene, as will be shown below.

Figure 5. NH_3 -TPD profiles of Ce-Co and La-Co catalysts prepared by different methods.

Table 2. NH_3 -TPD results of mixed oxide samples.

Sample	NH_3 desorbed amount ($\mu\text{mol/g}$)	Maximum temperature (T_{max}) of desorption ($^{\circ}\text{C}$)
Ce-Co CXN 1:2	15.8	238
Ce-Co CX 1:2	15.1	252
Ce-Co EM 1:2	13.8	250
La-Co CX 1:2	6.1	310
La-Co EM 1:2	12.8	252

3.2. Catalytic activity

The catalytic performance of Ce-Co and La-Co samples is shown in Figures 6 and 7, respectively. The catalytic performance of single oxides is included for comparison. Table 3 presents the VOC oxidation activity of all samples, expressed in terms of the temperature required for a certain conversion into CO₂. CO was formed only at low temperatures and always in concentrations lower than 300 ppm. At high temperatures, toluene is exclusively converted to CO₂.

The superior performance of mixed oxides compared to single ones is well demonstrated in the case of Ce-Co samples (Figure 6, Table 3), as shown by the lower temperatures required to reach a given conversion. Full conversion of toluene to CO₂ can be achieved at temperatures lower than 265 °C for all Ce-Co mixed oxides, regardless of the preparation method employed. However, much higher temperatures are required for 100 % toluene conversion over bare CeO₂ (>400 °C) and Co₃O₄ (>320 °C). Concerning the impact of the preparation method on toluene oxidation, the exotemplating procedure (CX and CXN samples) results in more active catalysts compared to the evaporation method, with CXN being the most active, allowing full conversion of toluene to CO₂ at *ca.* 15 °C lower temperature than the corresponding EM material (Figure 6 and Table 3). Surprisingly, unlike for ethyl acetate oxidation [53], exotemplated Ce-Co materials were more active for toluene oxidation than the EM samples.

As for the La-Co samples (Figure 7 and Table 3), the most active is the material prepared by the evaporation method (EM), full conversion of the VOC into CO₂ being achieved at about 300 °C. This temperature is lower than that obtained with commercial Co₃O₄ (327 °C) and Co₃O₄ CX (320 °C) samples, showing again the beneficial impact

of mixed oxides formation in VOC oxidation. However, the sample prepared by exotemplating required a much higher temperature for the oxidation of toluene than the single Co oxide. The worst performances were observed with the single La oxides, which are almost inactive within the temperature range studied (up to 400 °C). It is also worth noticing that La-Co samples (Figure 7) showed an inferior performance when compared to highly active Ce-Co mixed oxides (Figure 6).

Figure 6: Catalytic performances of Ce-Co samples (solid black), with commercial and CX CeO_2 and Co_3O_4 shown for comparison (dashed grey). The curves are continuous, symbols are only to facilitate identification.

Concerning the catalytic activity of commercial or exotemplated CeO_2 or Co_3O_4 bare oxides, it should be noted that the exotemplated materials exhibit better catalytic performances than the corresponding commercial materials. That can be related with the larger BET surface area (Table 1) and easier reducibility of CX samples (Table 1 and Figures 2 and 3) compared to commercial samples, as already clearly revealed in ethyl acetate oxidation [5]. Cobalt oxides are the most active among the single oxides,

followed by cerium and lanthanum oxides. The commercial Co_3O_4 sample suffered from progressive deactivation, as also shown in other works dealing with other VOCs [5, 18, 19]. Preparing this oxide by an exotemplated procedure allows much better resistance to deactivation as already shown with ethyl acetate oxidation [5]. In a similar manner, the optimum Ce-Co CXN 1:2 sample, showed also excellent stability in toluene oxidation. As seen in Figure 8, no activity loss is observed in a long term (72 h) stability test.

Figure 7: Catalytic performances of La-Co samples (solid black), with commercial and CX La_2O_3 and Co_3O_4 shown for comparison (dashed grey). The curves are continuous, symbols are only to facilitate identification.

It should be noted that CO formation is observed only during the incomplete conversion of toluene. When full conversion is achieved, toluene conversion to CO_2 is total and no other products are observed. There may be some intermediate products formed at lower temperatures (before reaching the plateau), but those were not monitored.

Table 3. Temperatures (°C) corresponding to 100 % (T_{100}), 90 % (T_{90}), 50 % (T_{50}), 20 % (T_{20}) and 10 % (T_{10}) conversion of toluene to CO_2 over Ce and La mixed oxides. Single oxides, both commercial and prepared by exotemplating with CX, are also shown for comparison.

Metal oxide samples	T_{10} (°C)	T_{20} (°C)	T_{50} (°C)	T_{90} (°C)	T_{100} (°C)
Ce-Co CX 1:2	214	222	231	246	261
Ce-Co CXN 1:2	205	213	225	241	251
Ce-Co EM 1:2	216	226	237	253	265
La-Co CX 1:2	256	273	307	350	370
La-Co EM 1:2	233	243	258	283	299
Commercial CeO_2	226	249	341	>400	>400
CeO_2 CX	215	232	285	>400	>400
Commercial Co_3O_4	241	248	266	304	327
Co_3O_4 CX	235	243	262	300	320
Commercial La_2O_3	377	>400	>400	>400	>400
La_2O_3 CX	364	394	>400	>400	>400

The correlation of catalytic performance, expressed in terms of T_{50} (required temperature for 50 % toluene conversion to CO_2), with the textural (Figure 9), redox (Figure 10) and acid (Figure 11) properties of Ce-Co and La-Co mixed oxides was attempted (similar results were obtained using other temperatures corresponding to different conversions). Such a comparison was expected to provide valuable insight into the structure-activity relationship. Figure 9 shows T_{50} as a function of BET surface area. In general, it can be seen that the increase in surface area results in an increase of activity. Nevertheless, sample La-Co CX 1:2 (depicted in open symbol in Figure 9) was not considered for the correlation. This material has the maximum of the first peak of TPR at 259 °C, while all other samples show similar values between 196 and 201 °C

(Table 1). Therefore, it can be inferred that there is a relationship with BET surface area only for samples with similar reducibility (sample La-Co CX 1:2 being out of the correlation due to its much different reducibility).

Figure 8 – Influence of time on stream on toluene oxidation at 230 °C for the Ce-Co CXN 1:2 sample.

Figure 10 presents T_{50} as a function of the maximum temperature of the first TPR peak. The latter parameter can be considered as a measure of catalyst reducibility, as the shift of TPR profiles to lower temperatures reflect a higher reactivity of the lattice/surface oxygen. Sample La-Co EM 1:2, depicted in open symbol in Figure 10, was not considered for the correlation. This material has a BET surface area of 68 m²/g, while all other samples show higher values, between 92 and 131 m²/g (Table 1). The good relationship obtained implies the key role of reducibility in toluene oxidation. Similar conclusions, concerning the relationship of catalyst activity with reducibility have been drawn for several oxides used in VOC oxidation [4, 5, 29, 53]. A Mars-van-Krevelen mechanism, involving the participation of lattice/surface oxygen species in the oxidation process can be accounted for this activity-reducibility correlation, as discussed below.

Figure 9. Correlation of the BET surface area with the VOC oxidation activity of La-Co and Ce-Co mixed oxides. T_{50} : required temperature for 50% toluene conversion into CO_2 . Bold symbols represent samples with similar reducibility (see text for details).

Figure 10. Correlation of the reducibility with the VOC oxidation activity of La-Co and Ce-Co mixed oxides. T_{50} : required temperature for 50 % toluene conversion into CO_2 . Bold symbols represent samples with similar BET surface area (see text for details).

Figure 11. Correlation of the acidity with the VOC oxidation activity of La-Co and Ce-Co mixed oxides. (a) T_{50} versus NH_3 desorbed amount and (b) T_{50} versus maximum temperature of NH_3 desorption.

The correlations of activity, expressed in terms of T_{50} , with the NH_3 desorption amount and the maximum temperature of NH_3 desorption are depicted in Figures 11a and 11b, respectively. A correlation is found between the concentration of acid centres and the oxidation activity (Figure 11a), implying the major role of catalyst acidity in the process. In a similar manner, the superior catalytic activity of Al_2O_3 -supported chromium oxide catalysts toward trichloroethylene (TCE) decomposition was ascribed to the ability of chromium oxide to provide acid sites for TCE adsorption [78]. In addition, the activity is inversely related to the strength of the acid sites (Figure 11b); the higher the temperature of desorption, the higher the required temperature for a certain conversion of toluene. Thus, based on NH_3 -TPD studies, it can be claimed that high VOC activity requires high concentration of weak acid sites.

3.3. Reaction mechanism

The above correlations can be mainly understood by taking into account the mechanism for toluene oxidation over transition metal oxides. It is generally accepted that VOC oxidation takes place according to a Mars-van Krevelen type redox cycle, which involves adsorption of VOC, and its subsequent oxidation by lattice oxygen and adsorbed oxygen atoms [4, 5, 28, 29, 53, 79]. According to this mechanism, toluene oxidation proceeds through a two-step process involving toluene oxidation by lattice oxygen and by oxygen ad-atoms originated by O_2 . The first step, however, is a complicated process consisting of several consecutive and parallel reactions: toluene adsorption proceeds *via* interaction of methyl and phenyl groups with the catalyst surface leading to abstraction of H-atoms from the methyl group and to the formation of an adsorbed complex through a C-O bond [79]. In the above mechanistic sequence, oxygen removal from active sites, closely related with the metal oxide reducibility,

appears to be crucial for the catalytic performance. In this regard, the present results clearly show that the formation of mixed oxides notably improves the reducibility of surface oxygen (Figures 2 and 3), which in turn facilitates oxygen transfer. In a similar manner the correlation of VOC activity with the reducibility has been well established [4, 5, 29, 53].

Apart from the reoxidation/reduction of surface active centres, the adsorption of toluene could be also of major importance on VOC decomposition processes. According to the literature [79], toluene adsorption proceeds via interaction of methyl and phenyl groups with the catalyst surface, followed by H- and C-abstraction. Finally, carbon atoms react with either lattice or surface oxygen forming carbonyl compounds. The above described sequence could be notably affected by the acidity of the catalyst surface, since the latter determines the strength and consequently the extent of adsorption/oxidation. It is well known that surface acidity has a key role on hydrocarbon oxidation, since the latter is initiated by the adsorption of hydrocarbons on acid sites by proton transfer [80, 81]. In this connection, the superior catalytic activity of MnO_2 oxide supported on clinoptilolite-type zeolites (HCLT) towards toluene combustion was attributed to the pronounced effect of MnO_2 on the acidity. IR measurements of adsorbed ammonia revealed that acidity played a dominant role in catalytic activity [82].

Therefore, it can be stated that the acid-base properties of mixed oxides may have a key role towards controlling the kinetics of adsorption-desorption of reactants and/or intermediate species. Acidic centers may be involved not only in the main oxidation process but also in parallel side reactions. It should be noted, however, that the correlation of acidity with the activity in oxidation reactions is still a subject of debate [83]. Therefore, acid sites are required so that toluene is adsorbed and its decomposition can occur through subsequent oxidation, according to the Mars-van Krevelen

mechanism described above. However, these sites need to be weak so that toluene is not too strongly adsorbed, making oxygen attack more favourable.

Based on the present results and taking into account the above aspects it is difficult to judge the particular importance of each parameter on the VOC oxidation activity. The participation of lattice oxygen has been well established in VOC oxidation process. On the other hand, the importance of acid-base properties on the oxidation reactions has not been well studied. To the best of our knowledge, this work is the first attempt towards correlating the VOC oxidation activity with both the concentration and the strength of acid sites. In this regard, the use of state-of-the-art characterization techniques together with more sophisticated tools (like quantum chemical calculations) are required to properly elucidate the impact of each parameter on the reaction mechanism [83].

4. Conclusions

In the present study a series of Ce-Co and La-Co mixed oxide were synthesized by exotemplating or evaporation methods and evaluated for toluene oxidation. The catalytic evaluation of as prepared catalysts together with an extensive characterization study, revealed several important aspects, summarized as follows:

- The performance of mixed oxides towards VOC oxidation is much better than that of single oxides.
- The best performance was obtained with Ce-Co samples prepared by the exotemplating method, which allow complete oxidation of toluene at about 250°C.
- The superiority of mixed oxides can be mainly ascribed to the mutual interaction between oxides, which leads to a fine dispersion of oxide phases and consequently improves the redox/textural/structural properties.
- A close relationship between the activity and the reducibility was observed for

catalysts with similar surface areas

- A correlation was found between the total acidity and the oxidation activity, highlighting the role of acidity in the VOC oxidation process; a high concentration of weak acid sites was favourable for the catalytic activity.
- A Mars-van Krevelen mechanism involving the adsorption and subsequent oxidation of toluene by lattice and/or surface oxygen can be invoked to explain the observed acidity-activity correlations.

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Table 1. BET surface areas determined by adsorption of N₂ at -196 °C; compositions, crystallite sizes and phases determined by XRD; and TPR peak maxima (plain text) and shoulders (*italic*) temperatures for Ce-Co and La-Co samples. Values from commercial [5,33,63,64] and exotemplated [5,33] single oxides are shown for comparison.

Metal oxide samples	BET area (m ² /g)	Phase detected by XRD	Composition (vol. %)	Crystallite size (nm)	TPR peaks (°C)
Ce-Co CX 1:2	131	CeO ₂ (cerianite) Co ₃ O ₄ (spinel)	47.9 52.1	7 15	201,267,322,475
Ce-Co CXN 1:2	120	CeO ₂ (cerianite) Co ₃ O ₄ (spinel)	48.1 51.9	8 16	196,273,323,489
Ce-Co EM 1:2	109	CeO ₂ (cerianite) Co ₃ O ₄ (spinel)	49.0 51.0	5 11	<i>167,200,261,326,372</i> 473
La-Co CX 1:2	92	Co ₃ O ₄ amorphous	- -	7 -	259,352,537
La-Co EM 1:2	68	Co ₃ O ₄ amorphous	- -	8 -	200,305,366,603
Commercial CeO ₂	20	CeO ₂ (cerianite)	-	54	534,865
CeO ₂ CX	96	CeO ₂ (cerianite)	-	17	490,803
Commercial Co ₃ O ₄	44	Co ₃ O ₄ (spinel)	-	32	316,382,429,471
Co ₃ O ₄ CX	64	Co ₃ O ₄ (spinel)	-	27	178,324,400
Commercial La ₂ O ₃	11	La(OH) ₃ (hexagonal)	-	23	*
La ₂ O ₃ CX	29	Mixture of oxonitrates and oxicarbonates of La	-	-	481,493,518,614,647

* - negative peaks found [63] (see text for details)

Table 2. NH₃-TPD results of mixed oxide samples.

Sample	NH₃ desorbed amount (μmol/g)	Maximum temperature (T_{max}) of desorption (°C)
Ce-Co CXN 1:2	15.8	238
Ce-Co CX 1:2	15.1	252
Ce-Co EM 1:2	13.8	250
La-Co CX 1:2	6.1	310
La-Co EM 1:2	12.8	252

Table 3. Temperatures (°C) corresponding to 100 % (T_{100}), 90 % (T_{90}), 50 % (T_{50}), 20 % (T_{20}) and 10 % (T_{10}) conversion of toluene to CO_2 over Ce and La mixed oxides. Single oxides, both commercial and prepared by exotemplating with CX, are also shown for comparison.

Metal oxide samples	T_{10} (°C)	T_{20} (°C)	T_{50} (°C)	T_{90} (°C)	T_{100} (°C)
Ce-Co CX 1:2	214	222	231	246	261
Ce-Co CXN 1:2	205	213	225	241	251
Ce-Co EM 1:2	216	226	237	253	265
La-Co CX 1:2	256	273	307	350	370
La-Co EM 1:2	233	243	258	283	299
Commercial CeO_2	226	249	341	>400	>400
CeO_2 CX	215	232	285	>400	>400
Commercial Co_3O_4	241	248	266	304	327
Co_3O_4 CX	235	243	262	300	320
Commercial La_2O_3	377	>400	>400	>400	>400
La_2O_3 CX	364	394	>400	>400	>400

Figure captions

Figure 1. XRD pattern of selected Ce-Co and La-Co samples. Miller Indices from AMCSD 0011686 for CeO_2 and from AMCSD 0007469 for Co_3O_4 .

Figure 2. TPR profiles of Ce-Co samples with commercial Co_3O_4 [5] and CeO_2 [64] shown for comparison.

Figure 3: TPR profiles of La-Co samples with La_2O_3 CX [5] and commercial Co_3O_4 [5] for comparison.

Figure 4. SEM images of samples Ce-Co 1:2 CX (a); Ce-Co 1:2 EM (b) and respective EDS spectra of zones marked as Z1 (c) and Z2 (d); La-Co 1:2 CX (e); La-Co 1:2 EM (f) and respective EDS spectra of zones marked as Z1 (g) and Z2 (h).

Figure 5. NH_3 -TPD profiles of Ce-Co and La-Co catalysts prepared by different methods.

Figure 6: Catalytic performances of Ce-Co samples (solid black), with commercial and CX CeO_2 and Co_3O_4 shown for comparison (dashed grey). The curves are continuous, symbols are only to facilitate identification.

Figure 7: Catalytic performances of La-Co samples (solid black), with commercial and CX La_2O_3 and Co_3O_4 shown for comparison (dashed grey). The curves are continuous, symbols are only to facilitate identification.

Figure 8 – Influence of time on stream on toluene oxidation at 230 °C for the Ce-Co CXN 1:2 sample.

Figure 9. Correlation of the BET surface area with the VOC oxidation activity of La-Co and Ce-Co mixed oxides. T_{50} : required temperature for 50% toluene conversion into CO_2 . Bold symbols represent samples with similar reducibility (see text for details).

Figure 10. Correlation of the reducibility with the VOC oxidation activity of La-Co and Ce-Co mixed oxides. T_{50} : required temperature for 50 % toluene conversion into CO_2 . Bold symbols represent samples with similar BET surface area (see text for details).

Figure 11. Correlation of the acidity with the VOC oxidation activity of La-Co and Ce-Co mixed oxides. (a) T_{50} versus NH_3 desorbed amount and (b) T_{50} versus maximum temperature of NH_3 desorption.