

Catalytic performance of chlorinated Ce/Zr mixed oxides for Cl-VOC oxidation

B. de Rivas, R. López-Fonseca, M. A. Gutiérrez-Ortiz
& J. I. Gutiérrez-Ortiz

*Chemical Technologies for Environmental Sustainability Group,
Department of Chemical Engineering,
Faculty of Science and Technology, Universidad del País Vasco/EHU,
Bilbao, Spain*

Abstract

Contamination by chlorinated volatile organic compounds (Cl-VOCs) is currently a matter of considerable concern, since these compounds are considered as dangerous for their effect on human health and the environment. Catalytic oxidation appears as an attractive approach for the destruction of these hazardous compounds. Although the development of catalysts to produce CO₂ and HCl is a topic of demanding interest, less consideration has been given to examining the catalytic stability during extended time on stream. Indeed the presence of HCl and/or Cl₂ may induce alterations in the behaviour of the catalysts. The main scope of this work is to evaluate the catalytic behaviour of a series of Ce/Zr mixed oxides in the gas-phase oxidation of 1,2-dichloroethane submitted to a previous chlorination followed by calcination (550 °C for 4 hours in air) or by reduction (550 °C with 5% H₂/Ar for 1 hour) and calcination.

Chlorination led to remarkable changes in acidity and redox properties, which were shown to be the key catalytic properties of these catalysts for this reaction. On one hand, the chlorine reinforced the acidity of the catalytic surface. In contrast, redox properties were negatively impacted. However, these alterations were partially compensated leading to a slightly lower activity of chlorinated samples. It could therefore be concluded that Ce/Zr catalysts resulted in significant resistance to deactivation by chlorine poisoning, thereby showing a great potential for this environmental application, not only in terms of low-temperature Cl-VOC conversion, but also of stability during extended periods of time on stream.

Keywords: Ce/Zr, catalytic oxidation, chlorination, 1,2-dichloroethane.



1 Introduction

Gas-phase emissions of volatile organic compounds have attracted increased attention due to their remarkable noxious effects on human health and the environment. Among VOCs, chlorine-containing compounds require a special attention on account of their toxicity, high stability and widespread application in industry [1]. Nowadays, the compliance of stringent standards on VOC emissions requires significant improvements of the efficiency of removal technologies. In the last years the reduction of their atmospheric concentration by means of preventive catalytic combustion has acquired great importance owing to its ability to destroy these pollutants at a far lower temperature than those required for thermal destruction. As a consequence there is a decreased pollution by dioxins and nitrogen oxides (NO_x), as they are usually formed under high temperature condition. Furthermore, catalytic deep oxidation is more selective and as it requires less heating, is more cost effective. However, because large gas volumes have to be treated, this must be performed at very high space velocity and thus requires very highly active catalysts. Consequently, the success of this technology mainly depends on the selection of an adequate catalyst. Indeed, the discovery of appropriate catalysts for low temperature complete oxidation of VOCs to produce CO_2 and HCl is a challenging task of ongoing interest. Numerous materials have been evaluated as catalysts for chlorinated VOC combustion. These materials are usually divided into noble metal based catalysts and transition metal oxides. Although supported noble metals are preferred in general due to their high activity, they are more expensive and less resistant to poisoning by substances such as HCl present in the reaction stream [2].

In recent years, ceria-based oxides have come under intense scrutiny as catalysts and as structural and electronic promoters of heterogeneous catalytic reactions. Concretely, CeO_2 and CeO_2 structurally doped with Zr oxides have attracted much attention as oxidation catalyst because of their unique redox properties and high oxygen storage capacity. The utilisation of this type of oxides as a key component in three-way catalysts for the treatment of exhaust gas from automobiles constitutes its most important applications from the economic and technological points of view [3].

Previous studies carried out in our research group have shown promising results of the use of Ce/Zr mixed oxides for chlorinated VOCs oxidative decomposition. Since it is believed that the presence of HCl and/or Cl_2 may induce alterations in the behaviour of the catalysts, this paper is specifically devoted to evaluate the catalytic behaviour of a series of Ce/Zr mixed oxides in the gas-phase oxidation of 1,2-dichloroethane submitted to an accelerated Cl -poisoning.

2 Experimental

2.1 Catalyst preparation

Ceria-zirconia mixed oxides with varying molar composition were synthesised by Rhodia using a precipitation route from nitrate precursors. Rhodia also provided



the pure ceria sample whereas the pure zirconia sample was supplied from Norton. All oxides were stabilised by calcination in air at 550 °C for 4 h. Catalyst pellets with diameter from 0.3 to 0.5 mm were prepared by compressing the oxide powders into flakes by means of an hydraulic press, followed by crushing and sieving. Hereafter the samples will be referred to as CZ XX/YY where XX and YY indicate the molar percentage of CeO₂ and ZrO₂, respectively. The following oxide catalysts were used: CZ100/0, CZ50/50, CZ15/85 and CZ0/100.

In order to analyse the effect of the presence of chlorine on the catalytic performance during extended time on stream, the samples were exposed to hydrogen chloride. This pre-treatment consisted of an impregnation of the oxides with a chloridric acid solution (1 M) for 3 h under vigorous stirring. Then the Ce/Zr samples were filtered and dried in air at 110 °C overnight. Next two different stabilisation procedures were employed. The first one involved only calcination at 550 °C for 4 hours while the second one consisted of reduction with 5%H₂/Ar at 550 °C for 1 hour followed by calcination at 550 °C (4 h). In order to designate the chlorinated samples a new character was added to the nomenclature which indicated the pre-treatment employed, i.e., “C” for the oxides submitted only to calcination in air and “RC” for the samples that were reduced before being calcined.

2.2 Catalyst characterisation

The quantification of chlorine content was evaluated by energy disperse X-ray (EDX) analysis that were carried out using a JEOL JSM-6400 scanning electron microscope coupled with analysis software INCA Energy 350 from Oxford Instrument. Textural properties were determined by multi-point N₂ adsorption-desorption at -196 °C using an automatic Micromeritics ASAP 2010 equipment. Data were treated in accordance with the BET and BJH methods. The samples were previously degassed overnight at 300 °C under high vacuum. X-ray diffraction (XRD) studies were carried out on a X'PERT-MPD X-ray diffractometer with CuK α radiation (λ =1.5406 Å) and Ni filter. The X-ray tube was operated at 30 kV and 20 mA. Samples were scanned from 20° < 2 θ < 80° and the X-ray diffraction line positions were determined with a step size of 0.02° and a counting time of 2.5 s per step.

Temperature-programmed desorption (TPD) of NH₃ was performed on a Micromeritics AutoChem 2910 instrument equipped with a thermal conductivity detector (TCD). Prior to adsorption experiments, the samples (20 mg) were first pre-treated in a quartz U-tube in a 5%O₂/He stream at 550 °C. Then, they were cooled down at 100 °C in an He flow (20 cm³ min⁻¹) before the adsorption of the probe molecule started. The amount of gases desorbed was determined by time integration of the TPD-curves. The NH₃ adsorption step was performed by admitting small pulses of ammonia in He at 100 °C up to saturation. Subsequently, the samples were exposed to a flow of helium (50 cm³ min⁻¹) for 2 h at 100 °C in order to remove reversibly and physically bound ammonia from the surface. Finally, desorption was carried out from 100 to 550 °C at a heating rate of 10 °C min⁻¹ in an He stream (50 cm³ min⁻¹). This temperature was maintained for 120 min until the adsorbate was completely desorbed.



The redox behaviour was examined by temperature-programmed reduction and oxygen storage capacity experiments. Temperature-programmed reduction (TPR) experiments were conducted on a Micromeritics AutoChem 2910 instrument as well. Firstly, all samples were pre-treated in an oxygen stream (5%O₂/He) at 550 °C for 1 h, and then cooled down to room temperature. The reducing gas was 5%H₂ in Ar, with a flow rate of 50 cm³ min⁻¹. The temperature range explored was from room temperature to 950 °C with a heating rate of 10 °C min⁻¹. The water produced by reduction was trapped into a cold trap. The consumption of H₂ was quantitatively measured by time integration of the TPR-profiles.

2.3 Experimental set-up and procedure

Catalyst behaviour was determined using a lab-scale fixed-bed reactor, in which typically 0.85 g of catalyst was loaded. Catalysts were tested in powdered form (0.3-0.5 mm) using a 12-mm i.d. stainless-steel reactor tube [4]. The reaction feed consisted of 1,000 ppm of DCE in dry air. The feed stream to the reactor was prepared by delivering the liquid hydrocarbon by a syringe pump (Cole Palmer 74900-00) into dry air, which was metered by a mass flow controller (Brooks). A total flow rate of 500 cm³ min⁻¹ was used and catalysts were packed to a constant volume to give a gas hourly space velocity of 30,000 h⁻¹. Catalytic activity was measured over the range 200-550 °C, and temperatures were measured by a thermocouple placed in the catalyst bed. Conversion data were calculated by the difference between inlet and outlet concentrations. Conversion measurements and product profiles were taken at steady state, typically after 30 minutes on stream. Either product selectivity was calculated based on either chlorine or carbon atoms present in that product divided by the total chlorine or carbon atoms present in the product stream (expressed as %).

The feed and effluent streams were analysed using an on-line gas chromatograph (Hewlett Packard 5890 Series II) equipped with a thermal conductivity detector (CO and CO₂) and an electron capture detector (chlorinated hydrocarbons). Analysis of HCl and Cl₂ was carried out by means of ion selective electrode and titration, respectively. Further details on analytical procedures are given elsewhere [4].

3 Results and discussion

3.1 Physico-chemical characterisation

As revealed by EDX analysis (table 1), it was noticed that chlorine was still present on the catalyst after whatever the thermal stabilisation treatment was. Two clear observations were evident. On one hand, ceria presented a remarkable ability to retain chlorine species and, on the other hand, a lower chlorine content was detected for reduced and calcined (RC) samples. This could be associated with a possible removal during the reduction step but also with a more complete chlorine incorporation into the samples upon reduction [5].



Table 1: Chlorine content (weight %) determined by EDX analysis.

	CZ100/0	CZ50/50	CZ15/85	CZ0/100
C	1.48	0.75	0.49	0.31
RC	0.41	0.61	0.39	–

The textural properties were determined by means of nitrogen adsorption-desorption (table 2). It is noteworthy that after the chlorination process the surface area significantly decreased (mainly for ceria pure oxide that decreased its surface area by almost 50%). The reduced impact observed on the textural properties of the rich zirconium oxides would be related to the higher resistance to chlorination as revealed by EDX analysis. In spite of the characteristics of the thermal pre-treatments no significant difference was found in the textural properties.

Table 2: Main physico-chemical properties of Ce/Zr catalysts.

	Area BET (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Average pore size (Å)	Structure	Crystal size (nm)
CZ100/0	99	0.21	59	cubic	10
CZ100/0C	49	0.18	120	cubic	16
CZ100/0R C	49	0.18	119	cubic	15
CZ50/50	99	0.21	64	tetragonal	7
CZ50/50C	65	0.18	94	tetragonal	7
CZ50/50R C	65	0.18	92	tetragonal	8
CZ15/85	86	0.28	102	tetragonal	6
CZ15/85C	71	0.23	110	tetragonal	7
CZ15/85R C	76	0.25	115	tetragonal	6
CZ0/100	51	0.25	157	monoclinic	15
CZ0/100C	43	0.21	161	monoclinic	14

The structural properties were characterised by XRD using the JCPDS files. Firstly, it was checked that the co-precipitation procedure led to the formation of homogeneous solid solutions where pure ceria and the mixed oxides exhibited a cubic and tetragonal structure, respectively. In contrast, pure zirconia showed a monoclinic pattern. As far as chlorinated samples were concerned, they maintained the original crystalline structure with the presence of small peaks assigned to CeOCl species (fig. 1) [6]. As for the crystal size no relevant modifications were observed, except for the cerium oxide that underwent a slight increase after chlorination.

The analysis of acid properties evaluated by temperature-programmed desorption of ammonia showed that the incorporation of increasing quantities of zirconium into the ceria lattice led to a marked increase in the total and strong



acidity (table 3). Therefore, the highest and strongest acidity was found for the CZ15/85 mixed oxide. Chlorination led to noticeable changes in acidity in comparison with the fresh catalysts. Hence, despite of the remarkable loss in surface area, the presence of chlorine reinforced the acidity of the catalytic surface [7]. This modification varied as a function of the catalyst composition. Hence, this improvement resulted more relevant for zirconium rich oxides and for the samples submitted to reduction + calcination treatment.

As for redox properties, they were characterised by means of temperature-programmed reduction performed with hydrogen. The redox process was found

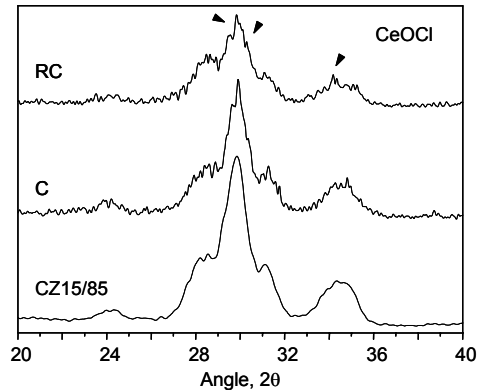


Figure 1: XRD patterns of fresh and chlorinated CZ15/85 samples.

Table 3: Acidity and redox properties of Ce/Zr samples.

	Total acidity (mmol NH ₃ g ⁻¹)	Strong acidity (mmol NH ₃ g ⁻¹)	H ₂ consumption (650 °C) (mmol g ⁻¹)	Reducibility up to 650 °C (%)
CZ100/0	0.19	0.08	0.39	14
CZ100/0C	0.29	0.05	0.20	7
CZ100/0R C	0.36	0.070	0.22	8
CZ50/50	0.38	0.11	1.28	79
CZ50/50C	0.58	0.14	1.14	70
CZ50/50R C	0.59	0.17	1.17	71
CZ15/85	0.51	0.21	0.48	85
CZ15/85C	0.61	0.28	0.41	72
CZ15/85R C	0.69	0.34	0.68	100
CZ0/100	0.35	0.16	—	—
CZ0/100C	0.50	0.29	—	—

to be promoted for the mixed oxides with respect to the pure cerium oxide. Thus, insertion of ZrO_2 into the cubic CeO_2 resulted in a distortion on the mixed oxide which led to a higher mobility of the lattice oxygen, and consequently the reduction was no longer confined to the surface but extended deep into the bulk (Fig. 2) [8]. Thus, the extent of the reduction was larger for the CZ50/50 sample.

The redox properties were also affected by chlorination + thermal treatment. Although the total hydrogen consumption generally decreased for the chlorinated samples with respect to the chlorine-free ones this difference was less evident with Zr content and also for pre-reduced samples (table 3). Only the sample CZ15/85RC exhibited promoted redox properties. At low temperatures ($< 400^\circ\text{C}$) was clearly noted a new peak attributed to the presence of easily reducible CeOCl species (fig. 2).

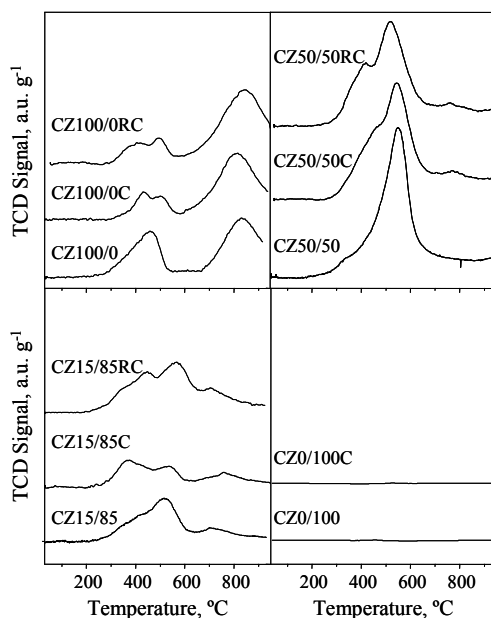


Figure 2: H_2 -TPR profiles of fresh and chlorinated Ce/Zr samples.

3.2 Catalytic performance and product selectivity of DCE decomposition

The destruction of DCE over Ce/Zr oxides was examined by means of the corresponding ignition or light-off curves, characterised by T_{50} and T_{90} parameters (temperatures needed to attain 50% and 90 % conversion, respectively) (table 4). Note that these results are described in detail in elsewhere [9]. Briefly, a noticeable catalytic performance was observed for the CeO_2 and the mixed oxide catalysts, as revealed by the low temperatures required for the deep decomposition of the chlorinated compound. In this sense, it was observed that the mixed oxide with an equimolar composition, CZ50/50, showed the highest activity. This result highlighted the beneficial synergy that could be

achieved by structural doping CeO_2 by ZrO_2 . Hence, the higher activity observed with respect to the pure oxides was associated with a suitable combination of surface acidity with relatively accessible lattice oxygen species. Accordingly, it is suggested that the first stage of the oxidation process is the adsorption of the chlorinated molecule on an acid site, which subsequently could be attacked by mobile oxygen species from the solid solution through a Mars-van Krevelen mechanism [9]. Additional experiments carried out in the absence of oxygen in the feed stream revealed the key role played by oxygen species from the catalyst as a significant activity of mixed oxides was found under these conditions. The function of surface acidity in chlorocarbon destruction was consistent with previous reports that point out that the promoting effect of acid sites was basically related to the composition of the mixed oxide [10].

Table 4: T_{50} and T_{90} values over Ce/Zr samples in the oxidation of DCE.

Catalyst	T_{50} (°C)	T_{90} (°C)
CZ100/0	320	395
CZ100/0C	350	420
CZ100/0RC	335	410
CZ50/50	300	375
CZ50/50C	315	385
CZ50/50RC	305	380
CZ15/85	320	380
CZ15/85C	320	380
CZ15/85RC	310	370
CZ0/100	360	400
CZ0/100C	345	390

The differences between the efficiency of the non-modified and chlorinated catalysts allowed to evaluate the resistance to poisoning by chlorine during extended time on stream, or, in other words, the chemical stability of Ce/Zr mixed oxides. As a general behaviour, it was found that the investigated samples were negatively affected but in a limited way when they were in contact with HCl. Besides, this impact become less noticeable as the zirconia content was increased and for the samples submitted to a previous reduction before the calcination process. In fact, for ceria catalysts the increase in the T_{50} value was around 15 °C for RC sample and 30 °C for C sample. This increase in T_{50} values diminished with the incorporation of zirconia into the ceria lattice. Interestingly, the chlorinated CZ15/85 samples even showed a slightly promoted activity, more relevant for CZ15/85RC. Therefore, unexpectedly, instead of leading to a certain decrease in catalytic activity due to Cl-poisoning, it was found that a previous treatment of the CZ15/85 sample with a concentrated solution of HCl followed by reduction + calcination induced a positive effect on the catalytic activity. In contrast, a negative impact on conversion was observed for CZ50/50 (limited) and CZ100/0 (more evident). As stated earlier, a combination of acidic and redox properties was a key parameter in controlling the catalytic oxidation of Cl-VOCs over Ce/Zr mixed oxides. Therefore, the catalytic activity of the reduced

samples, which presented a better acidity and reducibility properties than the calcined ones due to the presence of CeOCl species, required lower temperatures for DCE decomposition.

As far as product selectivity was concerned, the main oxidation products were CO₂, HCl and Cl₂ along with small quantities of CO. Besides, significant amounts of vinyl chloride, 115-300 ppm, were identified at mild temperatures (250-450 °C) as a chlorinated intermediate. This by-product was presumably formed by dehydrochlorination of DCE, and completely oxidised at high temperatures [11].

Table 5: Selectivity values (%) towards CO, CO₂, HCl and Cl₂ at 550 °C.

	CO	CO ₂	HCl	Cl ₂
CZ100/0	6.3	93.7	60.4	39.6
CZ100/0C	20.3	78.5	58.8	41.2
CZ100/0RC	12.2	87.7	53.3	46.7
CZ50/50	22.2	77.8	69.6	30.4
CZ50/50C	24.5	74.5	76.2	23.8
CZ50/50RC	23.4	76.6	74.7	25.3
CZ15/85	24.8	75.2	77.5	22.5
CZ15/85C	20.1	79.9	78.8	21.2
CZ15/85RC	19.4	80.6	75.3	24.7
CZ0/100	32.7	67.3	95.7	4.3
CZ0/100C	26.4	71.1	89.0	9.4

Table 5 shows the selectivity values at 550 °C to the main oxidation products. Chlorine formation was associated with the occurrence of the oxidation of HCl to form Cl₂ (Deacon Reaction). The extent of this reaction was larger as the cerium content was higher. Hence, selectivity to Cl₂ at 550 °C increased from 4% over ZrO₂ to 40% over CeO₂. In addition to chlorinated reaction products, carbon dioxide was found to be the major non-chlorinated reaction product. Nevertheless, CO was also observed in the 250-450 °C temperature range but as reaction temperature increased lower concentrations were detected. Hence, the CO₂ selectivity values were in the order of 70-95% over mixed oxides and pure ceria. The CO/CO₂ ratio was found to be the lowest for CeO₂. It is highly accepted that CeO₂ in its pure form is a complete oxidation catalyst. Conversely, pure zirconia, which is a relatively poor deep oxidation catalyst, gave rise to significant amounts to carbon monoxide (70% CO₂ selectivity) [9]. As regards chlorinated samples, no significant differences were noticed in reference with fresh samples.

4 Conclusions

The catalytic behaviour of Ce/Zr mixed oxides submitted to an accelerated Cl-poisoning in the catalytic oxidation of 1,2-dichloroethane was affected but to a relatively small extent. Chlorination resulted in a partial modification of the



acidic and redox properties, the key catalytic properties, due to the formation of CeOCl species. These changes (positive effect for acidity and negative for reducibility) were observed to be mutually compensated leading to a reduced impact on activity.

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