

Article

CuAlCe Oxides Issued from Layered Double Hydroxide Precursors for Ethanol and Toluene Total Oxidation

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Abstract: CuAlCe oxides were obtained from hydrotalcite-type precursors by coprecipitation using a M^{2+}/M^{3+} ratio of 3. The collapse of the layered double hydroxide structure following the thermal treatment leads to the formation of mixed oxides (CuO and CeO₂). The catalytic performance of the copper-based catalysts was evaluated in the total oxidation of two Volatile Organic Compounds (VOCs): ethanol and toluene. XRD, SEM Energy-Dispersive X-ray Spectrometry (EDX), H₂-temperature programmed reduction (TPR) and XPS were used to characterize the physicochemical properties of the catalysts. A beneficial effect of combining cerium with CuAl-O oxides in terms of redox properties and the abatement of the mentioned VOCs was demonstrated. The sample with the highest content of Ce showed the best catalytic properties, which were mainly related to the improvement of the reducibility of the copper species and their good dispersion on the surface. The presence of a synergetic effect between the copper and cerium elements was also highlighted.

Keywords: layered double hydroxide; catalytic oxidation; ethanol; toluene; VOC

1. Introduction

In the last few decades, extensive efforts have been focused on searching for methods of Volatile Organic Compound (VOC) abatement. VOCs produce ozone, which contributes to the formation of smog and global warming. The emission of these pollutants in the atmosphere is today, strictly regulated. For this, one of the most promising technologies is catalytic total oxidation, which represents an environmentally friendly control technology [1,2]. Studies of VOCs' catalytic oxidation have been widely reported [3–6]. Low temperatures (generally around 250–500 °C) are required compared to thermal oxidation, which requires high temperatures (650–1100 °C). VOC oxidation has been carried out over noble metal and transition metal catalysts.

Noble metals are more active at low temperatures but are costly and often have low stability [7]. However, transition metal oxides (especially for Co-, Mn- and Cu-based catalysts) [8–10] can be cheaper alternatives to this kind of catalyst, which are known to be more resistant to poisoning. Cobalt-based catalysts have been highly reported in the literature as a great economical choice compared to noble metal catalysts [7,11,12] but cause ethical problems because of their toxicity [13,14]. Manganese oxides have also been promising for the total oxidation of VOCs. However, they are most challenging to design due to having several oxidation states and multiple oxide polymorphs being found for every manganese oxidation state, each manifesting distinct catalytic performance for VOC oxidation [15,16]. Thus, a copper catalyst could be a good candidate for VOC oxidation.



Moreover, Layered Double Hydroxides (LDH), named anionic clays or hydrotalcite-like materials, have been revealed to be interesting oxide precursors for the oxidation reaction. These consist of brucite-like Mg(OH)₂ positively charged layers separated by an anionic layer compensating the positive charge, along with the water molecules trapped inside these layers. The most frequently occurring hydrotalcite (HT) compound is Mg₆Al₂(OH)₁₆CO₃,4H₂O. A wide variety of LDH compounds are available due to the substitution of divalent and trivalent cations. After calcination, oxide materials are formed and show unique properties such as high surface area, thermal stability and well-mixed oxide homogeneity [8].

CuO-based catalysts present remarkable catalytic performance and selectivity for CO₂ concerning the VOC oxidation reaction [17–19]. The feasibility of the partial substitution or total replacement of Mg^{2+} by Cu²⁺ is already described in the literature [20–22]. In previous work, Cu-based hydrotalcite-like compounds have gained significant interest, among the transition metals, due to their high efficiency as catalysts in some important processes such as the total oxidation of toluene [8]. Cerium oxide (CeO₂) is widely used as a promoter in various redox reactions due to its reducibility and its high oxygen storage capacity (OSC) [23,24], which can improve the catalytic properties. A recent study has shown that the addition of cerium in the CuAl hydrotalcite-like material improves activity and selectivity towards NO selective catalytic reduction by lowering the temperature of carbon monoxide oxidation [25]. In addition, cerium incorporation has already been studied and tends to favor the reduction of metal cations in the catalyst based on mixed oxides prepared via the hydrotalcite route, which could lead to an increase in the catalytic activity [26]. Thus, in this work, a new and original approach is to combine cerium with Cu-Al materials using the LDH synthesis approach.

This research work aims to synthesize $Cu_6Al_{2-x}Ce_x$ -O catalysts using the hydrotalcite precursor to generate efficient catalytic systems for VOC abatement. Additionally, the effect of Ce content within the materials will be studied in catalytic $Cu_6Al_{2-x}Ce_x$ -O systems for the total oxidation of toluene (probe molecule of BTEX) and ethanol (probe molecule of oxygenated VOCs).

2. Results

2.1. Structural Properties

The XRD profiles of the hydrotalcite precursors before the calcination process are shown in Figure 1A. All the samples show the typical diffraction patterns of hydrotalcite-like materials, $Cu_6Al_2(OH)_{16}CO_3, 4H_2O$ (JCPDS-ICDD 37-0630). This result confirms that the hydrotalcite structure is retained even after cerium addition. $Cu_6Al_{2-x}Ce_x$ -HT materials also present pure ceria (JCPDS-ICDD 01-081-0792), which can be explained by the partial oxidation of Ce^{3+} cations to Ce^{4+} during the synthesis [27]. However, the increase in ceria addition leads to a gradual decrease in the intensities of each peak, indicating the loss of crystallinity of the corresponding phase. This might be due to the distortion of the brucite layers since Ce^{3+} ions have a larger ionic radius (1.01 Å) than Al^{3+} (0.54 Å) [28]. Therefore, Ce^{3+} cations are probably not or partially incorporated in the hydrotalcite structure.

After a thermal treatment under air at 500 °C of the $Cu_6Al_{2-x}Ce_x$ -HT samples, XRD measurements were also performed on $Cu_6Al_{2-x}Ce_x$ -O samples. Following the thermal treatment, the collapse of the lamellar structure of hydrotalcite-like compounds leads to the formation of CuO oxides (JCPDS-ICDD 48-1548) and ceria (Figure 1B). For all of the samples analyzed, no peak corresponding to Al_2O_3 is observed, thus indicating that the aluminum species are in amorphous states [25]. However, no diffractions of $Cu_xAl_yO_4$ spinel-like structures are obtained for any of the $Cu_6Al_{2-x}Ce_x$ -O samples. This result could be related to the degree of crystallization of the spinel phases [21]. In fact, the evolution of X-ray diffractograms as a function of the calcination temperature (60–1000 °C) for copper-based catalysts has been studied [20]. Since high calcination temperatures (above 800 °C) are required for the formation of the $CuAl_2O_4$ spinel phase, no spinel-like structures are expected to be detected after a thermal treatment at 500 °C. Moreover, the rate of the formation of the latter is greatly reduced for hydrotalcites with high copper contents caused by the decrease in the ions' diffusion in the presence of large particles of copper oxide [20,29].



Figure 1. Diffraction patterns of the hydrotalcite precursors (**A**) and the mixed oxide samples (**B**) #: $Cu_6Al_2(OH)_{16}CO_3, 4H_2O; +: CuO; O: CeO_2; * mitigated intensity.$

In Table 1, the CuO crystallite size is reported. When adding Ce in low amounts, the CuO crystallite size is not affected, while an increase in Ce content leads to the maximum CuO crystallite size (20.7 nm) and then a decrease to 15.2 nm. Instead, the intensity of this phase decreases with an increase in the Ce content while the same amount of Cu is present in the materials. This can suggest that the addition of Ce allows the formation of amorphous Cu species instead of CuO crystals.

Samples	CuO Crystallite Size (nm) *	Experimental Atomic Ratio (Cu/Al/Ce) **	BET Surface Area (m ² /g)	Pore Diameter (nm)	Pore Volume (cm ³ /g)
Cu ₆ Al _{1.2} Ce _{0.8} -O	15.2	5.5/1.2/0.8	47	17.3	0.19
Cu ₆ Al _{1.5} Ce _{0.5} -O	20.7	5.9/1.5/0.5	37	22.7	0.22
Cu ₆ Al _{1.8} Ce _{0.2} -O	17.7	5.6/1.8/0.2	33	23.9	0.19
Cu ₆ Al ₂ -O	17.5	5.6/2.0/-	17	35.4	0.14

Table 1. Structural and textural features of the Cu₆Al_{2-x}Ce_x-O samples.

* CuO crystallite size determined by the Debye–Scherrer equation based on (111) peak. ** Obtained via ICP analysis.

2.2. Textural Properties

To understand the catalytic behavior, physicochemical characterizations of the oxide samples were performed. Nitrogen physisorption isotherms for all the Cu₆Al₂-O and Cu₆Al_{2-x}Ce_x-O materials are represented in Figure 2. IV-type isotherms with H3-type hysteresis loops are observed for all samples, corresponding mostly to a mesoporous structure and narrow plate-like particles (IUPAC classification). The solids textural properties and chemical compositions are reported in Table 1. The chemical compositions are largely maintained especially the Ce and Al atomic ratio, while the Cu ratio seems slightly lower than the theoretical ratio. An increase in the Brunauer–Emmett–Teller (BET) surface area is revealed with an increase in Ce content in the materials. An increase in pore volume is observed when adding Ce to the materials, but no significant evolution is revealed upon an increase in Ce content in the materials. This observation could be explained by the progressive content of cerium oxide in the materials, which possess higher textural properties (110 m²·g⁻¹ and 0.5 cm³·g⁻¹ for CeO₂ reference obtained via hydrothermal synthesis) than CuO and Al₂O₃.

The aim of using hydrotalcite-like precursors is to obtain a very good dispersion of the resulting metal oxides. In this context, the surface morphology of $Cu_6Al_{1.2}Ce_{0.8}$ -O was analyzed and is presented in Figure 3. A non-uniform and porous structure was observed upon SEM study, confirming the N_2 physisorption results. However, the results of Energy-Dispersive X-ray Spectrometry (EDX) suggest a good dispersion of the elements (Cu, Al and Ce) based on an analysis of seven zones, randomly selected (Figure 4). These results confirm the advantages of the synthesis-by-hydrotalcite route in order to obtain homogeneous catalytic materials. It should be noted that Zedan et al. [18] synthesized Cu-Ce-O

catalysts using the combustion method but the SEM-EDX results showed that these materials had a certain heterogeneity.



Figure 2. N₂ adsorption/desorption isotherms of Cu₆Al_{2-x}Ce_x-O samples.



Figure 3. SEM image of Cu₆Al_{1.2}Ce_{0.8}-O samples.

2.3. H₂-Temperature Programmed Reduction

The H₂-TPR profiles of simple, binary and ternary oxides are represented in Figure 5. As the samples have high copper contents, only signals obtained up to a reduction temperature of 350 °C and corresponding to the reduction of copper species were analyzed. The deconvolution of the TPR signals was carried out to assign the hydrogen reduction peaks. The H₂ consumptions of α , β and γ peaks (multi-peaks fitted according to the Gaussian method) are shown in Table 2. The reduction of copper species is only taken into consideration for the theoretical H₂ consumption calculations. Copper oxide, CuO, shows only one main peak at 290 °C corresponding to the reduction of copper (from Cu²⁺ to Cu⁰) [22].



Figure 4. SEM images and element mapping of Cu₆Al_{1.2}Ce_{0.8}-O sample.



Figure 5. H₂- temperature programmed reduction (TPR) profiles of CuO and Cu₆Al_{2-x}Ce_x-O samples. **Table 2.** Reduction peak temperatures and H₂ consumption for Cu₆Al_{2-x}Ce_x-O samples.

Samples	Temperature (°C)			H ₂ Consumption (μmol/g) (T < 350 °C)		
-	Τα	Τβ	Τγ	Peak α	Peak β	Peak y
CuO	-	-	289	n.d *	n.d *	n.d *
Cu6Al _{1.2} Ce _{0.8} -O	168	206	239	942	6081	1542
Cu6Al _{1.5} Ce _{0.5} -O	187	221	249	590	4974	2866
Cu ₆ Al _{1.8} Ce _{0.2} -O	210	230	277	263	1666	6838
Cu ₆ Al ₂ -O	215	259	302	181	5235	3610

* not determined.

Regarding the mixed oxide Cu₆Al₂-O, three reduction peaks (α , β and γ) are observed. The α reduction peak located at a lower temperature is attributed to the reduction of Cu²⁺ ions highly dispersed on the surface. The β reduction peak corresponds to the reduction of CuO cluster species. The γ reduction peak, located at higher temperatures, is assigned to larger CuO bulk-like particles/crystalline CuO [22,30–32]. The ceria-based samples present three reduction peaks (α , β and γ), which correspond to the zones of the reduction of the copper species in interaction with cerium species. As shown in Table 2, the reduction temperature of these three peaks shifts to lower temperatures with the increase of ceria content. The redox properties improvement is attributed to the decrease in the crystallite size shown in XRD results previously. On the other hand, researchers suggest that a synergetic interaction between CuO and CeO₂ could considerably improve the reducibility of the catalysts [33–35].

The H₂ consumption (Table 2) of the α and β peaks increases with the addition of Ce in the catalyst. Therefore, the Ce addition favors copper active species dispersion on the surface and promotes their reduction [35,36]. The decreasing consumption values of the γ peak indicate the diminution of the CuO bulk-like proportion of particles. It can be concluded that Ce addition enhanced the transition from CuO bulk-like particles into CuO clusters while promoting the high dispersion of Cu²⁺ on the surface.

2.4. X-ray Photoelectron Spectroscopy

XPS was performed in order to gain more insight into the surface composition and the chemical state of the elements existing on the surface of $Cu_6Al_{2-x}Ce_x$ -O catalysts.

The Cu 2p photopeaks are presented in Figure S1. The Cu 2p spectra exhibit the principal peaks of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ (centered at 934.4 and 954.2 eV, respectively) and shake-up satellite bands at 938–948 eV. No significant energy shift is observed with increasing Ce content. In line with the literature, it is reported that the higher Cu $2p_{3/2}$ binding energy and the satellite peak are two most important XPS characteristics of Cu²⁺ species. Meanwhile, the lower Cu $2p_{3/2}$ binding energy and absence of the shake-satellite peak are characteristic of reduced copper species (Cu⁺ and Cu⁰) [26,37,38]. Thus, Cu species initially existing in these samples are mainly in divalent oxidation states (Cu²⁺). Furthermore, the lack of band at lower apparent Cu $2p_{3/2}$ binding energy (932.4 eV) demonstrates the absence of Cu⁺ or Cu⁰ species in the catalysts. According to Table 3, an increase in the nCu/nM atomic ratio as function of Ce content is noticeable. The presence of cerium in catalyst can then increase the dispersion of copper species on the surface and therefore promote their reductions. This can be directly linked to the formation of smaller particles of CuO reported in the reduction part.

Samplas		C.III.C.IV	B.E. * O 1s/eV (%)		nCu/nM **	
Samples	D.E. Cesuu /ev	Ce/Ce	O-I	O-II	ncu/nwi	110/11/00
Cu ₆ Al _{1.2} Ce _{0.8} -O	917.1	0.11	530.2 (26.1%)	532.6 (73.9%)	0.48	0.81
Cu ₆ Al _{1.5} Ce _{0.5} -O	916.8	0.13	530.0 (23.0%)	532.0 (77.0%)	0.39	0.47
Cu ₆ Al _{1.8} Ce _{0.2} -O	916.4	0.36	529.8 (17.9%)	531.8 (82.1%)	0.33	0.57
Cu ₆ Al ₂ -O	-	-	530.3 (24.0%)	532.2 (76.0%)	0.65	0.56

Table 3. Summarized XPS results from Ce 3d, O 1s spectra and atomic ratios.

* Binding energy. ** nM = nCu + nAl + nCe. *** nTot = nO + nCu + nAl + nCe.

The Ce 3d spectra are presented in Figure S2, and the corresponding binding energies are assembled in Table 3. The Ce 3d spectra can be deconvoluted into ten peaks (Figure 6) with six components for Ce^{IV} (u^{"'}/v["]/u["]/v["]/u/v) and four components for Ce^{III} (u[']/v[']/u⁰/v⁰). This indicates a combination of Ce³⁺ and Ce⁴⁺ ions within the catalysts [26,32]. The ratio Ce^{III}/Ce^{IV} (Table 3) decreased upon increasing the amount of Ce in the composition of the mixed oxide. Therefore, a partial substitution of Al³⁺ by Ce³⁺ is possible at low concentrations of Ce. This substitution can be less significant when this concentration increases, leading to the formation of CeO₂, which can explain the abundance of the Ce⁴⁺ proportion and the improvement of the textural properties.

The Al 2p photoemission spectra for the studied samples are shown in Figure 7. Three peaks can be distinguished in each spectrum. Two broad-centered peaks at 84.5 and 77.5 eV are attributed to the

Cu 3p signal, while the shoulder peak at lower energy (74.2 eV) represents the Al 2p signal. The Al^{3+} cations are characteristic of the octahedral species present in alumina oxides, Al_2O_3 [39]. As expected, the signal and the appropriate atomic percentage of Al decreased with the Ce content, while the Cu signal remained approximatively the same. No modifications of Al valence occurred with the addition of Ce.



Figure 6. Fitted curve of Ce 3d spectrum for Cu₆Al_{1.2}Ce_{0.8}-O sample.



Figure 7. Al 2p photopeaks of Cu₆Al_{2-x}Ce_x-O samples.

The XPS spectra of O 1s are shown in Figure 8. Two photopeaks are distinct in the O 1s region at 530 (O-I) and 532 eV (O-II). O-II can be related to the oxygen of the surface hydroxyl or carbonate species [18,40,41], while O-I is related to the lattice oxygen of the metal oxide [19,40–42]. The binding energy and relative percentage of each photopeak are presented in Table 3. The lattice oxygen abundance increased progressively for the compounds with high Ce contents. This can be supported by the decline in the Ce^{III}/Ce^{IV} ratio presented previously and can also be attributed to the increase in the global valence of the metal oxide.



Figure 8. O 1s photopeaks of Cu₆Al_{2-x}Ce_x-O samples.

2.5. Catalytic Performance

Figure 9A shows the toluene conversion curves in the 150–400 °C range using the synthesized $Cu_6Al_{2-x}Ce_x$ -O materials. The catalytic behavior has been compared to that of CuO and CeO₂ pure oxides in terms of T₅₀, which represents the temperature when 50% conversion is obtained. It can be seen that the toluene conversion into CO₂ increased with the rise in the ceria incorporation in catalytic materials. $Cu_6Al_{2-x}Ce_x$ -O catalysts improved the reaction conversion in the following order: $Cu_6Al_{1.2}Ce_{0.8}$ -O $\cong Cu_6Al_{1.5}Ce_{0.5}$ -O > CeO_2 > $Cu_6Al_{1.8}Ce_{0.2}$ -O > Cu_6Al_2 -O > CuO. The reaction pathway of toluene oxidation is mostly initiated by an attack on the methyl group, with subsequent oxidation steps. Thus, during toluene oxidation, formation of CO and/or benzene could be observed. However, with our catalysts, no formation of those by-products was detected, except in the case of the CeO₂ catalyst as mentioned in Figure S3.



Figure 9. Light-off curves of toluene (A) and ethanol (B) total oxidation.

A similar trend is distinguished for the total oxidation of ethanol (Figure 9B). $Cu_6Al_{2-x}Ce_x$ -O achieved complete ethanol conversion at lower temperatures than the binary catalyst Cu_6Al_2 -O and the referenced pure oxides. The results on ceria-based catalysts indicate that the activity increases with an increase in Ce content, where $Cu_6Al_{1.2}Ce_{0.8}$ -O and $Cu_6Al_{1.5}Ce_{0.5}$ -O exhibit the highest catalytic activity ($T_{50} = 220 \text{ °C}$). On the other hand, the formation of acetaldehyde as a major by-product was detected in the chromatographic analysis. This latter is, however, completely oxidized at a temperature

0

250

270 T₅₀ (°C)

(A)

260

20–30 °C higher than the temperature for the 100% conversion of ethanol. After that, CO_2 and water are the main products that remain at the end of the reaction.

In order to compare the catalysts, the temperature that allows 50% of VOC conversion (T_{50}) is reported in Table 4. Moreover, the comparison of the Cu₆Al_{2-x}Ce_x-O catalysts is shown in Figure 10, as a function of the Ce^{III}/Ce^{IV} ratio (Figure 10A), percentage of O-I and O-II (Figure 10B) determined by XPS analysis, and the H₂ consumption of the α and β peaks (Figure 11) determined from H₂-TPR analysis.

	6 1	(°C)			
	Samples	Toluene	Ethanol		
	Cu ₆ Al _{1.2} Ce _{0.8} -O	254	210		
	Cu ₆ Al _{1.5} Ce _{0.5} -O	261	210		
	Cu ₆ Al _{1.8} Ce _{0.2} -O	286	230		
0.4 Ce _{II} /Ce _{IA} ratio(a.u. 0.3 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	content 🔊	100 80 - 60 - ° 40 - 20 -		II	A

Table 4. Summary of catalytic properties of Cu₆Al_{2-x}Ce_x-O.

Figure 10. Evolution of XPS data ((**A**): Ce^{IV}/Ce^{III} ratio, (**B**): %O-I and %O-II) with T₅₀ for toluene oxidation reaction.

290

280

0

250

260

270

T₅₀ (°C)

(B)

280

290



Figure 11. Evolution of H_2 -TPR data with T_{50} for toluene oxidation reaction.

A correlation is noticed between the T_{50} of the catalysts in the total oxidation of toluene and the Ce^{III}/Ce^{IV} ratio obtained by XPS analysis (Figure 10A). However, no significant correlation is shown with nCu/nM ratio.

In order to determine which kind of oxygen is mainly related to the studied reactions, Figure 10B shows that an increase in the %O-I is well connected with a lower T_{50} in the toluene oxidation reaction. The %O-I increased linearly with the decrease in T₅₀, while the %O-II decreased. The reaction seems to be favored by a higher concentration of O-I at the surface. The lattice oxygen favors the reaction pathway via the Mars–Van Krevelen mechanism where it is directly involved as a reactive oxygen species. The lattice oxygen can thus positively contribute to and enhance the VOC oxidation. This finding is also related to the increase in the Ce-content that forces the lattice oxygen to migrate to the surface. Thus, despite the relatively low surface area of the synthesized catalysts, the catalytic activity will be enhanced. The correlation between the T_{50} and the H_2 -consumption of the different peak observed in the H_2 -TPR experiment is reported in Figure 11. As described above, in terms of redox properties, an increase in the consumption of H_2 of the α and β peaks (attributed to the reduction of smaller particles of CuO) is observed with increasing Ce content. The consumption of α and β peaks increased with a decrease in T_{50} , while the γ peak's consumption decreased (not presented here). The formation of a smaller cluster of CuO in interaction with ceria oxide and the diminution of larger particles of CuO seem to be the most advantageous for the activity of toluene oxidation. The presence of cerium in the copper catalyst can increase the dispersion of the copper species on the surface of the Cu₆Al_{2-x}Ce_x-O catalysts and therefore promote their reductions. It also assures a better availability and mobility of oxygen on the surface of the solid. This promotes the oxygen exchange with the well-dispersed copper species. In fact, this active phase could be reduced during the toluene oxidation and re-oxidized with oxygen released from the ceria. This synergistic effect between cerium and copper is a key factor for good catalytic activity in the toluene oxidation reaction.

Concerning ethanol oxidation, no correlation has been observed between T_{50} and the formation of CuO clusters. An optimum T_{50} in ethanol oxidation is obtained with Cu₆Al_{1.5}Ce_{0.5}-O catalysts (same T_{50} as Cu₆Al_{1.2}Ce_{0.8}-O with less Ce). It corresponds to the catalysts with the higher CuO crystallite size. It can be suggested that for the ethanol oxidation reaction, the active site is different from the toluene oxidation reaction site and present in bigger CuO crystallites.

The catalytic performances of $Cu_6Al_{1.2}Ce_{0.8}$ -O materials are compared to the performances of supported noble metals and Cu-Ce catalysts in the literature in toluene and ethanol oxidation, based on T_{50} (Table 5). Concerning the toluene reaction, the T_{50} of our catalysts is higher than the one obtained with Pd/-Al₂O₃ [43]. That was expected for supported noble metals, but in the presence of those catalysts, the formation of CO and/or by-products such as benzene is possible [43]. However, using our catalyst, no formations of CO or benzene are detected. Compared to the CoAlCe-O [43] catalyst, a similar T_{50} is obtained by replacing Cu with Co. For Cu–Ce [23,44] catalysts, the T_{50} is lower than in this work. This could be explained by the higher proportion of Ce in those materials. Concerning the oxidation of ethanol, the T_{50} of our catalyst is 210 °C. The same T_{50} has been obtained with a higher content of Ce in those materials too [23]. Thus, our materials, which contain less cerium, are just as effective.

Table 5.	Comparison of	catalyst	performances.

Catalant	T ₅₀	D .(
Catalyst	Toluene	Ethanol	Kef.
Pd/Al ₂ O ₃	218		[43]
CoAlCe-O	249		[43]
Cu _{0.3} Ce _{0.7}	187		[44]
Cu _{0.15} Ce _{0.85}	230	210	[23]
Ce/CuCoMgAl		262	[45]
Cu ₆ Al _{1.2} Ce _{0.8} -O	254	210	This work

3. Materials and Methods

3.1. Catalyst Synthesis

The copper-based hydrotalcite-like compounds, $Cu_6Al_{2-x}Ce_x$ -HT, were synthesized by a coprecipitation method. The corresponding ratio of M^{2+}/M^{3+} used was equal to 3. A solution containing appropriate quantities of $Cu(NO_3)_2$,3H₂O (PanReac Quimica, Barcelona, Spain), Al(NO₃)₃,9H₂O (Chem Lab, Zedelgem, Belgium) and Ce(NO₃)₃,6H₂O (Chem Lab, Zedelgem, Belgium) was added dropwise, under vigorous stirring, into NaOH (PanReac Quimica, Barcelona, Spain, 98%) (2 mol.L⁻¹) and Na₂CO₃ (Thermo Fisher Scientific, New Jersey, USA, 99%) (1 mol.L⁻¹) solution. The pH was maintained at 10.5 for 18 h at room temperature. The precipitate was then filtered, washed several times with hot deionized water (60 °C) and dried at 60 °C for 48 h. Three hydrotalcite-like compounds with different ratios were synthesized: $Cu_6Al_{2-x}Ce_x$ HT with x = 0, 0.2, 0.5 and 0.8. The $Cu_6Al_{2-x}Ce_x$ -O were obtained after the thermal treatment of HT at 500 °C (1 °C.min⁻¹) for 4 h under an air flow of 33 mL.min⁻¹.

Copper oxides (99%) were purchased from Fluka Company. The coprecipitation of $(Ce(NO_3)_3, 6H_2O)$ in NaOH solution results in the formation of cerium hydroxide $Ce(OH)_4$. CuO and CeO_2 were used after calcination under air flow at 500 and 400 °C during 4 h, respectively.

3.2. Catalyst Characterization

The crystallinity of the hydrotalcite and calcined catalysts was analyzed at room temperature by X-ray diffraction analysis using a Bruker D8 Advance X-Ray Diffractometer (AXS) (Bruker, Champs-Sur–Marne, France) equipped with CuK α radiation (λ = 1.5418 Å) and a Lynx Eye Detector. The measurements were performed from 5° to 80° with a step size $\Delta(2\theta) = 0.02^{\circ}$ and a counting time of 2 seconds per step.

The textural properties of all the calcined samples were determined using N₂ adsorption/desorption isotherms carried out using Micromeritics ASAP 2020 (Micromeritics, Norcross, USA). Prior to each analysis, the samples were degassed under vacuum for 2 h at 300 °C. The specific surface area was estimated using the Brunauer–Emmett–Teller (BET) equation, while the pore diameter and specific pore volume were obtained according to the Barrett–Joyner–Halenda (BJH) model.

H₂-temperature programmed reduction (H₂-TPR) studies were carried out using an AMI-200 instrument (Labor und Analysen Technik GmbH, Garbsen, Germany) equipped with a TCD detector. First, the calcined samples (30 mg) were treated in Ar flow (30 mL.min⁻¹) at 150 °C for 60 min. After cooling, the reduction of the solid was carried out in a 5 vol.% H₂/Ar gas mixture (20 mL.min⁻¹) while heating from 150 to 900 °C (ramping rate: 5 °C.min⁻¹).

X-ray Photoelectron Spectroscopy (XPS) (Kratos, Manchester, U.K.) spectra were recorded using monochromatic Al K α (1486.6 eV) radiation at an operating source power of 13 kV and 10 mA. The hemispherical energy analyzer with a constant pass energy mode Ep = 50 eV was used in all measurements. The binding energy (BE) was calibrated based on the line position of C 1s (284.8 eV). The core-level spectra were decomposed into components with mixed Gaussian–Lorentzian lines using a subtraction of the Shirley-type background using the CasaXPS software (Casa Software Ltd. Teignmouth, UK).

The elemental compositions of the samples were analyzed using an Inductively Coupled Plasma-Optical Emission Spectrometer, ICP-OES (Thermo fisher, iCAP 6300 DUO) (Waltham, MA, USA), equipped with a charge injection device. Prior to the analysis, 50 mg of catalyst was dissolved into aqua regia (HNO₃/HCl 1:2) under microwaving for 30 min. The solution was then topped up to 50 mL with ultrapure water, diluted to 10% and filtered with a 0.45 μ m cellulosic microfilter.

Scanning Electron Microscopy was performed with a JEOL JSM-711F (JEOL, Tokyo, Japan) apparatus equipped with an Energy-Dispersive X-ray Spectrometer (MEB-EDX). The calcined samples were adhered on aluminum stubs and then coated with a thin film of chromium.

3.3. Catalytic Activity Tests

Toluene and ethanol oxidations were carried out in a continuous-flow fixed-bed reactor loaded with 100 mg (35–45 mesh) of catalyst at atmospheric pressure. The gas mixture composed of 1000 ppm of VOC in air was passed through the reactor with a flow rate of 100 mL.min⁻¹, which corresponds to a gas hourly space velocity (GHSV) of about 30.000 h⁻¹. Before each test, the catalysts were preactivated at 300 °C for 1 h under flowing air (33 mL.min⁻¹).

For the toluene oxidation, the inlet and outlet gas stream concentrations were analyzed with a micro-gas chromatographer (Agilent 490MicroGC) coupled to an infrared analyzer (ADEV CO₂-CO Analyzer Model 4400IR) for CO₂ and CO analysis.

However, the reactants and the products of the oxidation of ethanol were analyzed using a micro-gas chromatographer (Varian CP- 4900) coupled to a Pfeiffer Vacuum OmniStar Quadrupole Mass Spectrometer (QMS-200).

4. Conclusions

A Cu₆Al_{2-x}Ce_x-O catalytic system with different Ce contents was successfully synthesized via a hydrotalcite route. The characterization of the products showed favorable physico-chemical and catalytic properties of the $Cu_6Al_{2-x}Ce_x$ -O materials with Ce contents starting from x = 0.5. A homogeneous dispersion of Cu, Al and Ce species was distinguished for these materials. H₂-TPR suggests that combining Ce with the copper-based catalysts favors the dispersion of copper active species on the surface and promotes their reduction. XPS analysis confirmed the presence of Ce^{3+} , Ce^{4+} and Al^{3+} species on the surface of the Cu₆Al_{2-x}Ce_x-O samples, as well as the formation of copper Cu²⁺ species that would interact with cerium. The addition of Ce can favor a better dispersion of CuO particles on the surface of the materials. The catalyst with the best catalytic performance was found to be the one with the highest Ce content. The good catalytic activity for the total oxidation of toluene and ethanol of $Cu_6Al_{1,2}Ce_{0,8}$ -O can be attributed to the high surface area, the good metal dispersion, the high proportion of Ce^{IV} and the high reducibility of the copper species on the surface. Thus, combining cerium with CuAl oxides using the LDH synthesis approach permits efficient catalysts to be obtained. A synergetic effect between copper and cerium species occurs and is favorable for the abatement of VOCs. The improvement of the textural, structural and redox properties of the oxides can lead to the enhancement of the catalytic performance for VOC oxidation.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/8/870/s1. Figure S1: Cu 2p photopeaks of $Cu_6Al_{2-x}Ce_x$ -O samples. Figure S2: Ce 3d photopeaks of $Cu_6Al_{2-x}Ce_x$ -O samples.

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