Cu Mixed Oxides Based on Hydrotalcite-Like Compounds for the Oxidation of Trichloroethylene

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ABSTRACT: Different Cu/(Mg or Ni)/Al mixed oxides based on hydrotalcite-like compounds have been studied for the catalytic oxidation of trichloroethylene. The catalysts have been synthesized and characterized by different techniques such as N_2-adsorption, inductively coupled plasma (ICP), X-ray diffraction, and temperature-programmed reduction (TPR). It has been shown that the activity for the catalytic abatement of trichloroethylene depends on the presence of metals with redox properties in the catalyst composition. The best results have been obtained with containing copper mixed oxides, although there is no direct correspondence between the copper content and the catalyst activity. These catalysts are highly active and selective, CO_2 and HCl being the main reaction products. A mechanism for the reaction has been proposed.

■ INTRODUCTION

Trichloroethylene (TCE) is an organic solvent mainly used for industrial degreasing. Nevertheless, due to its low vapor pressure, during its use and storage it may be emitted to the atmosphere, generating an air pollution problem. This molecule has been classified in the European Union as a category 2 carcinogen, and as other chlorinated organic compounds, it participates in the ozone layer destruction, photochemical smog, and groundwater pollution. There are different techniques that can be used to control these emissions such as adsorption, thermal oxidation, condensation, or absorption. They are effective, but they have some problems related with the formation of new wastes or with the economic cost. A new option that is being successfully used for the control of different volatile organic compounds is catalytic oxidation.[1−3] This technique could also be an alternative for the treatment of the TCE emissions. There are different types of oxidation catalysts based on metal oxides (single or mixed oxides),[4−7] on supported noble metals,[8,9] or on zeolites[9−11] that could be used for this reaction. However, although noble metals are very active, they can be easily poisoned by chlorine.[3] On the other hand, some metal oxides, such as chromium oxide, only can be used at low temperature because they generate volatile and toxic chromium oxychlorides,[6,12] and zeolites need a high temperature to be active. Recently, the use of Mo/W-based bronzes for the catalytic oxidation of trichloroethylene (TCE) has been described, obtaining interesting results.[13] Nevertheless, it is still necessary to find more active and stable catalysts.

Mixed oxides containing transition metals derived from hydrotalcite-like compounds could be good candidates to catalyze this reaction as they are active catalysts in different oxidation reactions.[14−17] Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds, are two-dimensional layered synthetic materials with alternating positively charged mixed metal hydroxide sheets and negatively charged interlayer anions along with water molecules.[18] They are represented by the general formula $[M(II)_{1−x}M(III)_x(OH)_2]^{x+}(A^{n−})_{x/n}·mH_2O$ where M(II) is a divalent metal ion, M(III) a trivalent metal ion, and A the interlayer anion and x has values between 0.2 and 0.4.[19] The most frequent divalent metals are those whose ionic radii vary from 0.65 Å (Mg) to 0.80 Å (Mn), whereas the radius of the trivalent metal has to be comprised between 0.50 Å (Al) and 0.69 Å (Cr). As a result, different isostructural materials with widely varied physicochemical properties can be obtained by changing the nature of the metal cations, the M^{2+}/M^{3+} molar ratio, as well as the type of interlayer anions. Calcination of LDHs leads to the formation of mixed oxides with interesting properties for the catalytic removal of chlorinated volatile organic compounds (VOCs) either by oxidation or by reduction, such as small particle size, large specific area, homogeneous interdispersion of the metals, and a good resistance to sintering.[20−22] As an example, Yun Fan et al.[23] studied the dechlorination of hexachlorobenzene over $Cu_xMg_{1−x}Al_2O_4$ spinel-type catalysts obtaining a dechlorination efficiency higher than 90% at 300 °C and showing that the catalytic activity depends on the copper content. Meshesha et al.[24] studied different Pd/NiMgAl catalysts for the gas-phase hydrodechlorination of trichloroethylene, observing that the catalysts' performance was significantly influenced by the Ni/Mg/Al molar ratio, the reduction temperature, and the protocol for the noble metal deposition onto the support. They also showed that the selectivity toward ethylene formation increased with the amount of surface metallic nickel. De Rivas et al.[25] analyzed the catalytic performance of a series of Co_3O_4 catalysts prepared through several routes for the gas-phase oxidation

Table 1. Physical and Chemical Properties of Catalysts

| catalyst | S_{BET} (m^2·g^{-1}) | pore volume (m^3·g^{-1}) | ICP[a] | | | | nominal molar ratio |
			% Al	% Cu	% Ni	% Mg	
NiAl	171	0.212	5.1	-	46.1	-	Ni/Al = 4:1
CuNiAl 131	144	0.259	4.7	11.6	33.3	-	Cu/Ni/Al = 1:3:1
CuNiAl 441	106	0.267	2.7	26.2	24.5	-	Cu/Ni/Al = 4:4:1
MgAl	169	0.591	6.9	-	-	24.8	Mg/Al = 4:1
CuMgAl 131	168	0.269	13.0	19.5	-	29.9	Cu/Mg/Al = 1:3:1
CuMgAl 441	86	0.519	4.9	51.0	-	20.8	Cu/Mg/Al = 4:4:1
CuAl	92	0.228	4.9	47.1	-	-	Cu/Al = 4:1

[a]Bulk composition of calcined samples determined by ICP (weight %).

of 1,2-dichloroethane. They found that all the synthetic routes led to the formation of the same structure, although substantial differences existed in terms of surface area, crystallite size, and redox properties. It was shown that reduced crystallite size along with a high surface area were the key factors to determine the activity of the bulk cobalt catalysts.

In this work we study the catalytic activity for the trichloroethylene oxidation of different mixed oxides (NiAl, CuNiAl, MgAl, CuMgAl, and CuAl) based on hydrotalcite-like compounds. The activity of a H-MOR zeolite, which is a conventional catalyst used for this reaction,[26] is used for comparison purposes. The catalysts have been analyzed by different techniques, i.e., gas adsorption (SBET), X-ray diffraction (XRD), infrared spectroscopy (FTIR), temper-ature-programmed reduction (TPR), diffuse reflectance (DR UV–vis), and elemental analysis through inductively coupled plasma (ICP), to characterize the material.

■ EXPERIMENTAL SECTION

Catalyst Preparation. CuMgAl-hydrotalcite samples were synthesized using the simultaneous coprecipitation technique at constant pH. A Cu(NO$_3$)$_2$·3H$_2$O, Mg(NO$_3$)$_2$·6H$_2$O, and Al(NO$_3$)$_3$·9H$_2$O (Panreac, >99%, Fluka, >99%, and Panreac, 98%, respectively) aqueous solution was mixed with a NaOH and Na$_2$CO$_3$ (Aldrich) solution. They were prepared to have a Cu/Mg/Al molar ratio of 1:3:1 and 4:4:1 (samples labeled as CuMgAl 131 and CuMgAl 441, respectively). Both solutions were added simultaneously with a flow rate of 20 mL·h^{-1} at room temperature and atmospheric pressure, and they were mixed under vigorous stirring. The resulting gel was dried overnight at 60 °C. The product was then filtered off and washed thoroughly with distilled water obtaining a gel with a pH of 7. The dried hydrotalcite was calcined in air at 550 °C for 6 h.

CuNiAl-hydrotalcite samples were synthesized by mixing an aqueous solution (2.5 M) of Cu(NO$_3$)$_2$·6H$_2$O, Ni(NO$_3$)$_2$·6H$_2$O, and Al(NO$_3$)$_3$·9H$_2$O (Merck 99%, Aldrich 99% and 98%, respectively) with a 1.86 M solution of NaOH (Aldrich). The precipitation was carried out adjusting both flows to obtain a constant pH of 9. Both solutions were prepared to have a Cu/Ni/Al molar ratio of 1:3:1 and 4:4:1 (samples labeled CuNiAl 131 and CuNiAl 441, respectively). The resulting gels were treated in a microwave autoclave (MIC-I, Sistemas y Equipos de Vidrio S.A. de C.V.) for 10 min operating at 2.45 GHz with a microwave irradiation power of 200 W, while the temperature was maintained at 80 °C. The solids were recovered by decantation and washed several times with distilled water until the residual solution reached a pH value of about 8. Finally, solids were dried at 60 °C for 24 h and calcined in air at 550 °C for 6 h.

CuAl, NiAl, and MgAl-hydrotalcite samples were prepared using the same procedure described in the synthesis of the CuNiAl-hydrotalcite, but adjusting the metal solutions to obtain a Me^{2+}/Al ratio of 4.

Zeolite NH$_4$-MOR (CBV 10AH with SiO$_2$/Al$_2$O$_3$ = 14 and surface area of 490 m^2·g^{-1}) was supplied by Zeolyst Corp., and it was transformed into the H-form by calcination in air at 550 °C for 3 h.

All catalysts were pelletized and then crushed and sieved to obtain grains of 0.25–0.45 mm diameter.

Catalyst Characterization. The chemical composition of the samples was measured by inductively coupled plasma. Samples (ca. 20 mg), previously calcined, were dissolved in a HNO$_3$/HCl (1:3 vol.) solution before analysis in a Varian 715-ES ICP-Optical Emission Spectrometer.

BET surface areas were determined from the nitrogen adsorption–desorption curves by the conventional multipoint technique with a Micromeritics ASAP 2020. The samples were pretreated at 200 °C for 5 h at high vacuum.

A Bruker-axs D8-advance diffractometer coupled to a copper anode X-ray tube was used for the XRD characterization. Compounds were identified in the conventional way using the JCPDS file.

FTIR spectra in the region 4000–400 cm^{-1} were obtained with a Magna-IR Spectrometer 550 Nicolet, using the KBr pellet technique.

Diffuse-reflectance UV–vis spectra were collected on a Cary 5 equipped with a 'Praying Mantis' attachment from Harrick.[27]

Temperature-programmed reduction experiments were carried out on 10–20 mg of catalyst with a N$_2$:H$_2$ flow (10% H$_2$) of 50 mL·min^{-1}. The heating rate from room temperature to 800 °C was 10 °C·min^{-1}.

Catalysts Activity. Catalytic oxidation reactions were carried out in a conventional quartz fixed bed reactor under atmospheric pressure. The catalyst bed (0.68 g) was supported on a quartz plug located in the reactor. Silicon monocarbide (>0.42 mm o.d.) was placed above the catalyst bed as a preheating zone of the incoming feed stream. The temperature was measured with a K-thermocouple located inside the reactor, right before the catalyst bed. The reactor was housed in an electrically heated furnace. Before reaction the calcined catalyst was activated at 150 °C with air during 30 min.

The gas mixture, composed by trichloroethylene (1000 ppm) and dry air, was introduced into the reactor at 400 mL·min^{-1} (GHSV = 15 000 h^{-1}) and with a residence time of 0.24 s. The reaction was carried out under continuous flow of reactants, and each catalyst was tested at different temperatures, i.e., 150, 200, 250, 300, 350, 400, 450, 500, and 550 °C, during 30 min at each temperature. A blank experiment was made using the same

reaction conditions but introducing only silicon monocarbide into the reactor without the catalyst.

The reaction products were identified and quantified by a gas chromatograph Varian 3900 equipped with a flame ionization detector (FID). CO and CO_2 were separated and analyzed by a Bruker 450 chromatograph with a thermal conductivity detector. The concentration of TCE, as well as any other chlorinated hydrocarbon formed in the reaction, was determined on the FID after separation in an HP-5 column. Analysis of both Cl_2 and HCl was performed at each reaction temperature. It was made by bubbling during 12 min the effluent stream through a 0.0125 M NaOH.[28] Cl_2 concentration was determined by titration with ferrous ammonium sulfate using N,N-diethyl-p-phenylenediamine as an indicator, and the concentration of chloride ions in the solution was determined using an ion-selective electrode (Thermo scientific, Orion Products).

RESULTS AND DISCUSSION

Catalyst Characterization. Table 1 shows the specific surface area and the elemental composition of the calcined samples. Note that the chemical composition matches, within experimental error, with the synthesis gel nominal molar ratio. The BET surface area of all samples varies between 86 and 171 $m^2 \cdot g^{-1}$, obtaining the highest surface area with the NiAl and MgAl catalysts. As it can be seen, the introduction of copper results in a decrease of the surface area of the catalysts, especially at high copper content, as has been previously described.[29]

The XRD patterns of the samples before and after calcination are displayed in Figures 1 and 2. Before calcination, the MgAl
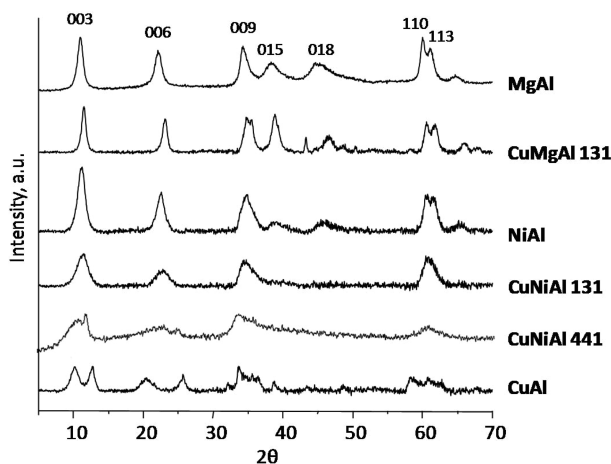

Figure 1. XRD patterns of samples before calcination. The indexed peaks correspond to a hydrotalcite phase.

and NiAl samples present the characteristic diffraction peaks of a typical nitrated hydrotalcite.[30] Instead, some differences are observed for the catalysts containing copper. As shown in Figure 1 the incorporation of copper into the MgAl and NiAl catalysts results in a decrease of the hydrotalcite crystallinity. Such modification of the peak broadening may be attributed either to a small particle size or to a strain between the crystalline planes. As the amount of copper increases (samples CuNiAl 441 and CuAl), new peaks at 10.4° and 12.5° appear: the first one is attributed to a nitrate exchanged hydrotalcite, whereas the second one corresponds to a hydroxylated
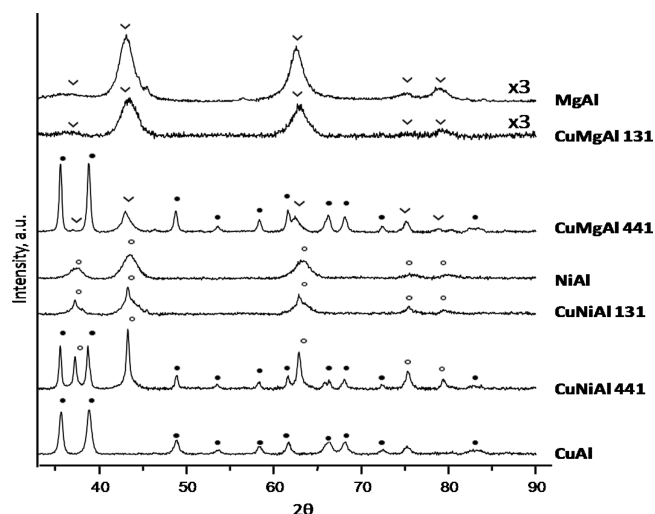

Figure 2. XRD patterns of samples after calcination ($\vee$ MgO, ● CuO, ○ NiO).

hydrotalcite. This is related with the synthesis procedure as microwave irradiation during the crystallization step produces a selective ionic diffusion depending on the size and/or charge of the ion. Thus, sample CuNiAl 441 presents an irregular distribution of copper and nickel in the hydrotalcite layers. As nickel diffuses better than copper, the nickel-enriched core is nitrated, while the periphery is copper enriched and is highly hydroxylated.[30] Similar results were obtained with other types of hydrotalcites.[31]

The calcination temperature causes several changes in the physicochemical properties of the hydrotalcites (Figure 2). For the MgAl hydrotalcite, at temperatures below 150 °C, interlamellar water molecules are ejected without altering the laminar structure. Between 300 and 500 °C the dehydroxylation of the hydrotalcite layers and the decomposition of nitrates take place, leading to the collapse of the laminar structure and giving rise to a mixed oxide. In this way, the XRD pattern of the MgAl sample after calcination shows a periclase-like structure (JCPDS-ICDD 4-0829) with the main characteristic peaks at $2\theta = 43.5°$ and 63°. The NiAl catalyst presents the typical peaks associated to NiO at $2\theta = 37.2$, 43.2, 62.8, 75.4, and 79.4°. The incorporation of a high amount of copper to the structure of the catalysts results in the appearance of new peaks at $2\theta = 35.6$, 38.8, 48.7, 53.5, 58.3, 61.5, 66.2, 68.1, 72.4, and 82.3 associated to CuO.

No changes were observed after reaction in the XRD patterns of all the calcined samples, indicating that the mixed oxide structure of the catalysts has not been modified in the reaction.

Figure 3 presents the infrared spectra of the samples before calcination. As it can be seen, the infrared spectra of the different catalysts are very similar. The broad band around 3450−3600 cm^{-1} corresponds to an elongation vibration of structural hydroxyl groups. The band around 1630−1660 cm^{-1} is due to OH groups from water molecules, and the interlayered nitrates appear around 1380−1390 cm^{-1}. The bands between 500 and 1200 cm^{-1} can be attributed to the metal−oxygen vibrations.[32]

Figure 4 shows the diffuse reflectance UV−vis spectra of samples CuNiAl 441, CuAl, NiAl, and CuMgAl 441 after calcination. The spectrum of the three Cu-containing samples corresponds to a square planar structure.[33] For the CuNiAl 441
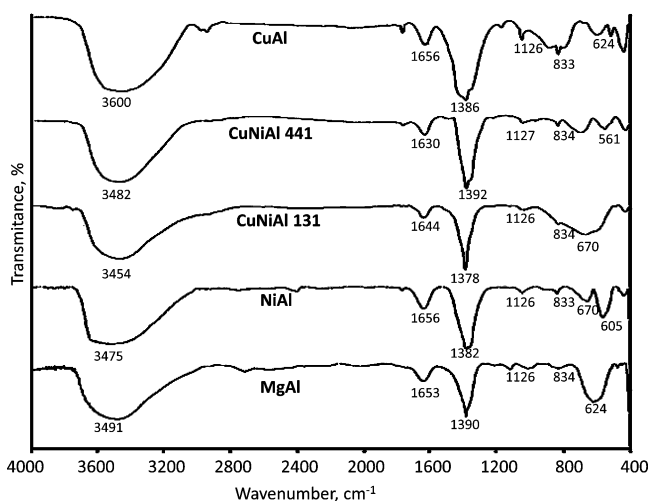
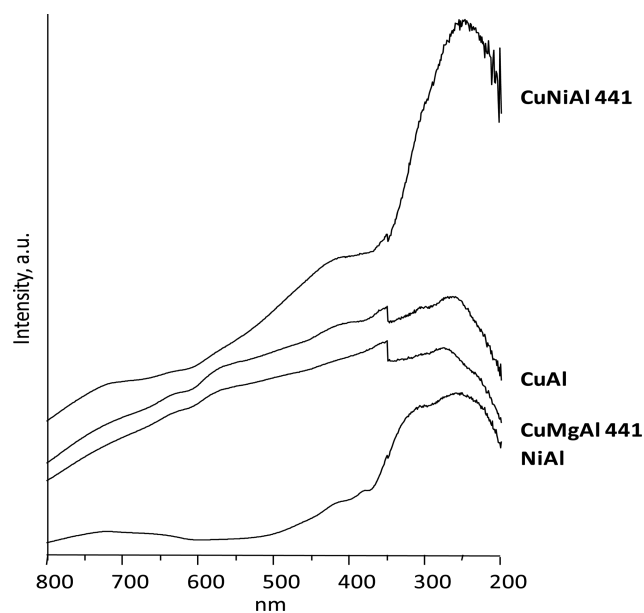**Figure 3.** FTIR spectra of samples before calcination.

Figure 4. Diffuse reflectance UV–vis spectra of the catalysts calcined at 550 °C.

sample spectra, the first maximum at about 260 nm is related to charge transfer between the mononuclear Cu^{2+} ion and oxygen. The band around 355 nm can be ascribed to charge transfer between Cu^{2+} and oxygen in $[Cu-O-Cu]_n$ surface clustered species.[34] These two bands were found for all the Cu-containing samples although their relative intensities are different. On the other hand, the spectrum of the NiAl hydrotalcite presents two absorption bands at 725 and 420 nm characteristic of the octahedrally coordinated Ni^{2+} species in the NiO lattice and one band at 250 nm corresponding to the charge-transfer band.[35] These bands are more intense in the CuNiAl 441 catalyst.

The TPR profiles of the different samples after calcination are reported in Figure 5. The profile of the CuAl sample shows one main peak. This reduction peak at 232 °C is associated to the reduction[36] of Cu^{2+} to Cu^0. The shape and the maximum of this peak are very close to that of pure CuO that appears at 230 °C.[37] This result matches with that obtained with the XRD analysis, where peaks associated to CuO were the main peaks
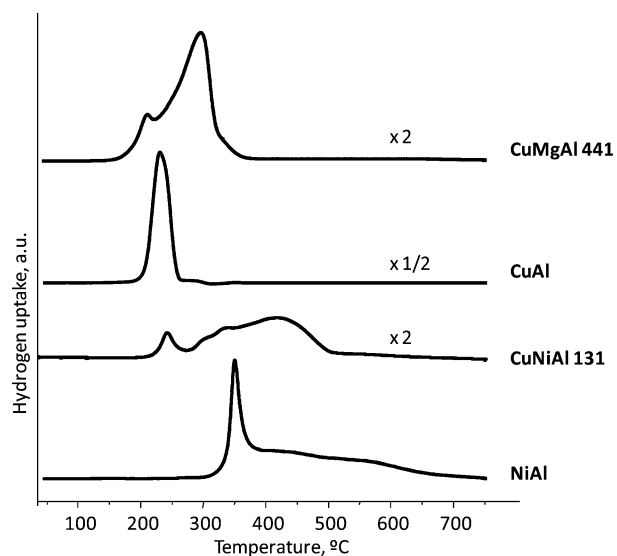

Figure 5. TPR profiles of samples NiAl, CuAl, CuNiAl 441, and CuMgAl 441.

observed in this sample. The partial substitution of some of the copper atoms by magnesium (CuMgAl 441) results in the transformation of the single peak assigned to the reduction of Cu^{2+} to Cu^0 in two peaks, one around 210 °C and a second one centered in 296 °C. The first peak is attributed to the reduction of the highly dispersed copper oxide species, which include isolated copper cations and small two- or three-dimensional clusters.[38] The second peak around 296 °C may be assigned to the reduction to Cu^0 of large bulk-like CuO particles, formed during the calcination process.[39] On the other hand, the TPR pattern of the NiAl sample shows a main peak at 351 °C and a diffuse broad band with two maxima, the first one at about 440 °C and the second one at about 570 °C. The main peak at 351 °C can be assigned to the reduction[40−42] of Ni^{2+} to Ni^0. The other peaks at higher temperatures are characteristic of nickel with different interactions with aluminum.[43] No peaks above 700 °C usually attributed to nickel aluminate are observed, indicating that aluminates are not generated in our calcination conditions as was also shown by XRD (Figure 2). The partial substitution of some of the nickel atoms by copper (sample CuNiAl 131) results in a shift to lower temperatures of the three peaks related with the nickel reduction (from 351 to 300 °C, from 440 to 335 °C, and from 570 to 420 °C), indicating that the addition of copper enhances the reducibility of the nickel species.[14] In this sample, another peak at 242 °C assigned to the reduction of Cu^{2+} to Cu^0 is also observed. The quantification of the hydrogen consumed in the TPR measurements of the different samples agrees, within experimental error, with the complete reduction of copper(II) and nickel(II) to the metallic species.

Catalytic Activity Results. Catalytic activity was studied by the TCE light-off curve, monitoring the TCE conversion as a function of temperature. In Figure 6 the catalytic activity for the oxidative decomposition of trichloroethylene of different (Cu)MgAl catalysts is compared with a blank experiment and with the activity of the H-MOR zeolite, which has been used as a reference catalyst in this work because it has been already described in the literature[26] as an active catalyst for this reaction. The catalytic activity of the zeolite catalyst starts at 400 °C, and 80% of TCE conversion is obtained at 550 °C. The $T_{50\%}$ (temperature at which 50% conversion was reached) of
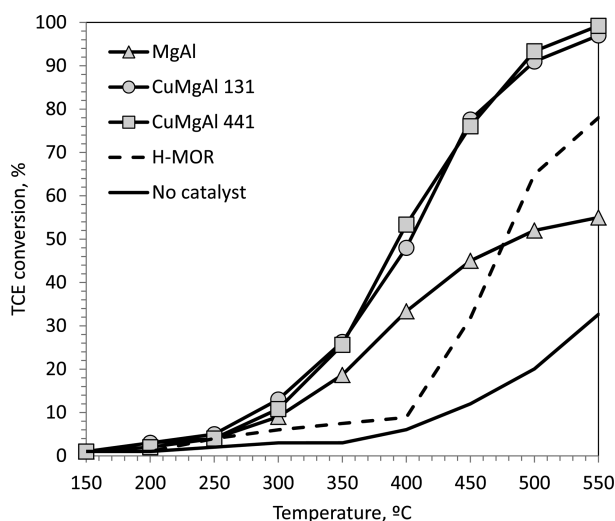
Figure 6. TCE oxidation light-off curves over MgAl, CuMgAl (with a Cu/Mg/Al molar ratio of 1:3:1 and 4:4:1), and H-MOR catalysts.

Figure 7. TCE oxidation light-off curves over NiAl, CuNiAl (with a Cu/Ni/Al molar ratio of 1:3:1 and 4:4:1), and H-MOR catalysts.

this catalyst is around 475 °C, while with the blank this conversion was not even achieved at 550 °C.

As it can be seen, the MgAl mixed oxide shows the lowest final conversion. It has been described[44] that for the TCE oxidation the presence of acid and/or oxidative catalytic sites is necessary. The basic nature and the limited redox properties of the MgAl mixed oxide result in a low mobility of surface oxygen species and therefore in low oxidative catalytic activity. A higher activity is obtained with the catalysts containing copper, due to the important redox properties of this metal that strongly improve the performance of the catalyst in the oxidative decomposition of trichloroethylene. It is shown in Figure 6 that both catalysts containing copper (CuMgAl 131 and CuMgAl 441) with a different Cu/Mg/Al molar ratio (1:3:1 and 4:4:1, respectively) present a higher catalytic activity than the MgAl catalyst and the H-MOR zeolite. Moreover, they have a similar catalytic performance independently of the Cu/Mg/Al molar ratio, with a $T_{50\%}$ around 400 °C and a $T_{90\%}$ around 500 °C. Similar results (not shown) were even obtained with a sample containing only 7% of copper. It was expected that changing the copper content of the catalysts resulted in a modification of the catalyst activity. Nevertheless, the catalytic results obtained indicate that above 5−10% of copper content the influence of copper in the catalyst activity becomes negligible. These results are in agreement with the data reported by Tanasoi et al.[29] for the methane total catalytic oxidation; they showed that in the Cu-containing samples the activity increases with the copper content up to 10% and that above this content there is no further increase of the catalyst activity.

The catalytic performance of (Cu)NiAl mixed oxides derived from hydrotalcites was also studied, and the results are shown in Figure 7. Contrarily to what occurred with the MgAl catalyst, the catalytic activity of the NiAl sample was higher for the entire range of temperatures studied ($T_{50\%}$ = 420 °C and $T_{90\%}$ = 535 °C) than the activity obtained in the reference catalyst (H-MOR with a $T_{50\%}$ = 475 °C and $T_{90\%}$ > 550 °C). As it occurred with the MgAl catalysts, the addition of copper results in an increase of the activity at lower temperatures ($T_{50\%}$ = 340 °C and $T_{90\%}$ = 550 °C). This can be related with a synergic interaction between nickel and copper favoring the redox properties of the catalyst, enhancing its initial activity. The same effect was observed in the TPR experiments (Figure 5), where
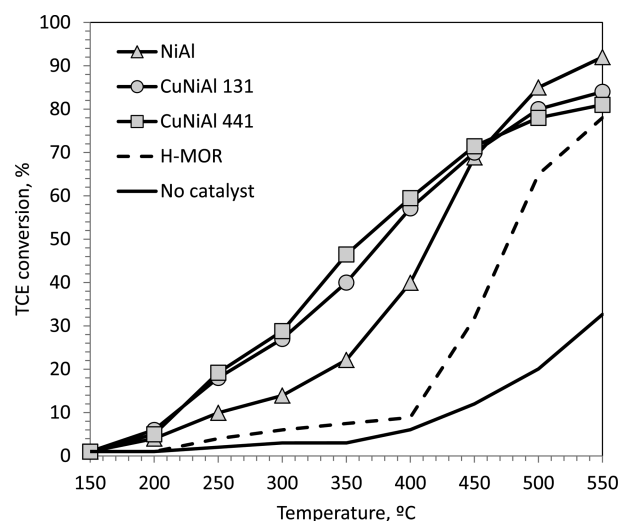
the peaks related to the nickel reduction appeared at lower temperatures in the CuNiAl catalyst than in the NiAl, indicating better redox properties for the first catalyst. On the other hand, as it also occurred with the (Cu)MgAl catalyst, there is not a direct correlation between the copper content and the catalyst activity. In fact, results were obtained with the sample containing 11% of copper (CuNiAl 131) similar to in the catalyst with 26% of copper (CuNiAl 441).

The results obtained with the Cu-containing MgAl and NiAl catalysts have shown that the copper presence improves the catalytic activity of these materials for the TCE oxidation. Nevertheless, it has been seen that the activity does not depend on the total copper content and that the other metals of the catalyst were also playing a catalytic role. In fact, comparing the activity of a catalyst where 100% of the divalent metal was Cu (sample CuAl) with that obtained with the catalysts where 75% of the copper atoms have been substituted by magnesium or nickel atoms (Figure 8), it is observed that the CuAl catalyst presents a catalytic activity that is only slightly better than that obtained with the other samples. In addition, there are some
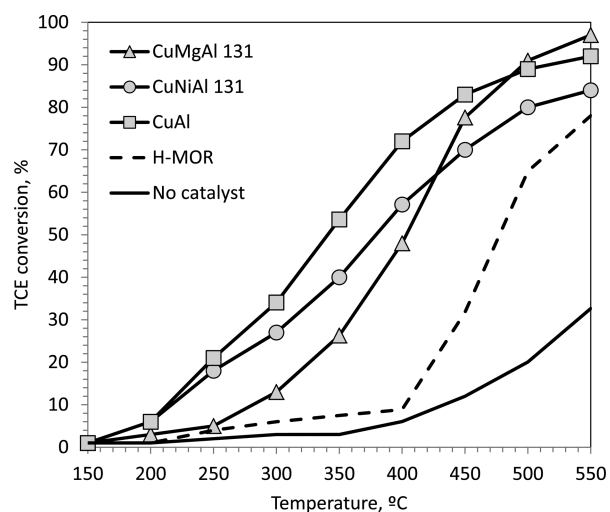

Figure 8. TCE oxidation light-off curves over CuAl, CuNiAl 131, and CuMgAl 131 catalysts.

differences at low temperatures in the activity of the CuMgAl compared with that of CuNiAl. As it can be seen, the reaction starts at lower temperature with the CuNiAl catalyst than with the CuMgAl catalyst, supporting our hypothesis that there is a synergic effect between copper and nickel sites favoring the TCE oxidation at low temperatures.

Product Distribution. Figure 9 presents the product distribution of the TCE oxidation reaction when using the
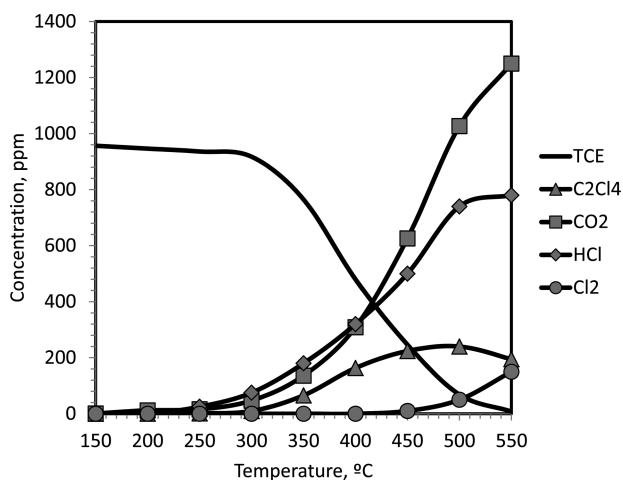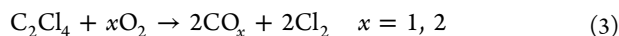

Figure 9. Product distribution of TCE oxidation over the CuMgAl 441 catalyst.

CuMgAl 441 catalyst that is a representative example of all the tested samples. The main oxidation products obtained were hydrogen chloride (HCl) and carbon dioxide (CO_2). To a lesser extent tetrachloroethylene (C_2Cl_4) and chlorine (Cl_2) appeared, and traces of other chlorinated byproducts, for example, chloromethane, dichloromethane, and carbon tetra-chloride, were found at mild temperatures in the product stream. No CO was detected when testing all catalysts at any temperature. The product distribution changes with the temperature of reaction, observing that when TCE starts to decompose no Cl_2 is detected, HCl and C_2Cl_4 being the main chloride products formed. The production of HCl increases constantly with the temperature, but the formation of C_2Cl_4 has a maximum around 500 °C. At higher temperatures the formation of C_2Cl_4 decreases, and Cl_2 starts to appear, indicating that Cl_2 is a final product produced from the oxidation of C_2Cl_4. Different authors[45−47] also detected this effect in their oxidation reactions, and González-Velasco et al.[47] have proposed the next scheme of reaction that can be applied to our product distribution profiles

$$C_2HCl_3 + xO_2 \rightarrow 2CO_x + HCl + Cl_2 \quad x = 1, 2 \qquad (1)$$

$$C_2HCl_3 + Cl_2 \rightarrow C_2Cl_4 + HCl \qquad (2)$$

$$C_2Cl_4 + xO_2 \rightarrow 2CO_x + 2Cl_2 \quad x = 1, 2 \qquad (3)$$

According to eq 1, the main reaction is the oxidation of trichloroethylene forming CO_2 (as no CO is detected at any temperature), HCl, and Cl_2. Nevertheless, between 300 and 500 °C, Cl_2 reacts with TCE to form C_2Cl_4 and HCl (eq 2). At higher temperatures, the oxidation of C_2Cl_4 is produced (eq 3), and Cl_2 and more CO_2 appear in the product stream. Moreover, we cannot exclude that at these temperatures some of the Cl_2 formed was produced from the oxidation of HCl through the Deacon reaction. In addition, at high

temperatures, the chlorine balance cannot be closed, indicating that other chloride products (probably oxychlorides), that are not detected, are being formed.

Catalyst Stability. The catalyst stability was tested by doing a long-term reaction at 400 °C. The results obtained with the CuMgAl 441 catalyst are shown in Figure 10. As can be seen,
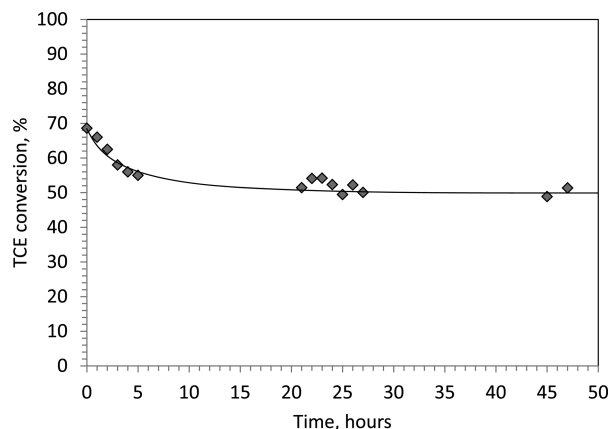

Figure 10. TCE oxidation over the CuMgAl 441 catalyst at 400 °C.

the catalyst is stable at this temperature for almost 50 h, and only a slight deactivation (around 10%) was observed at the beginning of the reaction. This deactivation cannot be related with the deposition of a carbonaceous deposit on the catalyst surface because the carbon analysis of the catalysts after reaction confirmed the absence of these compounds. Nevertheless, in some experiments with the samples with high Cu content, thin and yellow-bluish deposits appeared at the inner wall of the reactor suggesting that copper oxychlorides are formed, as occurred when chromium oxides were used as catalysts in similar reactions.[7] Although the formation of these species can be the reason for the partial deactivation of the catalyst, a high conversion (52%) and a stable product distribution were obtained after 50 h of reaction. These results indicate that Cu-containing mixed oxides based on hydrotalcite-like compounds are active and stable catalysts for the TCE oxidation.

■ CONCLUSION

CuMgAl, NiAl, CuNiAl, and CuAl mixed oxides obtained from hydrotalcite-like compounds present a high catalytic activity in the temperature range studied for the oxidative decomposition of trichloroethylene. Hydrotalcite-derived mixed oxides containing copper in their structure are more active, especially at low temperature, than those without copper, indicating that copper improves the catalytic activity of these catalysts due to its important redox properties. Nevertheless, there is not a direct relationship between the copper content and the catalyst activity, obtaining similar results when the copper content is above 10%. There is a synergic effect between copper and nickel favoring the TCE oxidation at low temperatures. The catalysts are stable at 400 °C at least for 50 h of reaction, observing only a slight deactivation (10%) that can be related with the formation of copper oxychlorides.

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