

# Characterisation of the active copper species for the NO<sub>x</sub> removal on Cu/Mg/Al mixed oxides derived from hydrotalcites: an *in situ* XPS/XAES study

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*In situ* X-ray photoelectron spectroscopy was used to characterise Cu/Mg/Al mixed oxides derived from hydrotalcites (catalyst used for the NO<sub>x</sub> removal reaction). The active sites are the copper centres: (i) Cu(0) for NO decomposition and (ii) Cu(0) and/or Cu(I) for NO reduction with a hydrocarbon. The ability of these materials to redisperse the copper active sites without destroying the structure of the material makes them different from other catalysts such as zeolites, and is essential for suitable catalytic behaviour at high temperatures.

## Introduction

Synthetic hydrotalcite-type anionic clays, also named in the literature as layered double hydroxides (LDH), can be represented by the following formula: [M(II)<sub>1-y</sub>M(III)<sub>y</sub>(OH)<sub>2</sub>]<sup>y+</sup>[(X<sub>y/n</sub>)<sup>n-</sup>mH<sub>2</sub>O]<sup>y-</sup>, where *y* is typically between 0.25 and 0.33, and X<sup>n-</sup> is an *n*-valent anion. These compounds present positively charged brucite-like layers, Mg(OH)<sub>2</sub>, with trivalent cations substituting divalent cations in octahedral sites of the hydroxide sheet, with the compensating anions (typically carbonates, nitrates, etc.) located in the interlayer space. A satisfactory knowledge of the problems involved in the synthetic aspects of LDH phases has been achieved, thus enhancing the possibility of modelling their structure by changing the di and tri-valent cations in the brucite layer and the interlayer anion. Several reviews have been published in the last years reporting their preparation, characterisation and applications.<sup>1-3</sup> Hydrotalcites retain the layered structure up to 673 K, but at higher temperatures yield to high surface area metal mixed oxides.

Calcined hydrotalcites are potentially useful as catalysts or catalyst precursors if the advantage of their unique properties of high surface areas and basic character can be utilized.<sup>1-3</sup> Some examples of the use of Mg–Al hydrotalcites as active and selective catalysts in various base-catalysed reactions have been reported in the last few years.<sup>4-9</sup> They have also been employed as catalysts or catalyst supports for redox reactions by incorporating transition metals, with redox properties, in their structure.

These characteristics have allowed the development of new applications of hydrotalcites as environmental catalysts, especially in the field of gas purification.<sup>10-16</sup> Recently, it has been shown that mixed oxides derived from hydrotalcite structures containing copper, magnesium and aluminium can be used as catalysts for the simultaneous removal of the NO and SO<sub>2</sub> formed in the fluid catalytic cracking (FCC) unit regenerator.<sup>11,12</sup> This is only possible with this type of catalyst because other catalysts also used for NO removal, such as Cu exchanged zeolites, get poisoned in the presence of SO<sub>2</sub> and are not active at temperatures higher than 823 K.

Nevertheless, the most problematic step in the simultaneous

catalytic removal of SO<sub>2</sub> and NO<sub>x</sub> using Cu/Al/Mg mixed oxides derived from hydrotalcites is the removal of NO. Indeed, previously it has been found that Cu species active for removal of NO are quite sensitive to the presence of oxygen and to the presence of a reducing agent. We have focused our attention on identifying the exact nature of the copper species in some of these materials with different loadings of copper, since the study and characterisation of these centres are essential for an appropriate final design of the catalyst. Copper catalysts can be studied by different spectroscopic techniques such as ESR,<sup>17,18</sup> EXAFS,<sup>19</sup> luminescence,<sup>20</sup> infrared spectroscopy<sup>21</sup> and XPS/XAES,<sup>19a,22</sup> which report information about the oxidation state, coordination and distribution of copper species.

The purpose of the present contribution is to characterise Cu/Mg/Al mixed oxides derived from hydrotalcites, with different copper contents by *in situ* photoelectron spectroscopy. It is our goal to elucidate the active sites and the special characteristics of the working catalysts during NO removal under reduction and decomposition conditions. It has been found that the ability of this material to redisperse the copper active sites while preserving the structure is essential for adequate catalytic behaviour. It is this unique ability which makes it different from other catalysts such as copper exchanged zeolites.

## Experimental

### Catalyst preparation

Cu(II)Mg(II)Al(III) hydrotalcites were prepared by a standard co-precipitating procedure using two solutions. The first solution contained Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and Cu(NO<sub>3</sub>)<sub>2</sub>·5H<sub>2</sub>O, having an (Al+Mg+Cu) molar concentration of 1.5. The second solution contained NaOH and Na<sub>2</sub>CO<sub>3</sub> in adequate concentrations to obtain total precipitation of aluminium, magnesium and copper in the former solution and to fix the pH at a value of 13 (see Table 1). Both solutions were added, while vigorously stirring, at a total flow-rate of 120 ml h<sup>-1</sup>, for 4 h. The gel was aged under autogenous pressure conditions at 353 K for 18 hours, then filtered and washed with distilled water until the pH was 7 and carbonate

**Table 1** Chemical composition and textural characteristics of the studied samples

Sample	Composition (molar ratio)	Surface area/m <sup>2</sup> g <sup>-1</sup>
A synthesis gel composition A mixed oxide composition	0.3Cu(NO <sub>3</sub> ) <sub>2</sub> :2.1Mg(NO <sub>3</sub> ) <sub>2</sub> :0.6Al(NO <sub>3</sub> ) <sub>3</sub> :2Na <sub>2</sub> CO <sub>3</sub> :6.6NaOH Mg/Al/Cu=67.7/21.5/10.8	200
B synthesis gel composition B mixed oxide composition	0.15Cu(NO <sub>3</sub> ) <sub>2</sub> :2.1Mg(NO <sub>3</sub> ) <sub>2</sub> :0.75Al(NO <sub>3</sub> ) <sub>3</sub> :2Na <sub>2</sub> CO <sub>3</sub> :6.75NaOH Mg/Al/Cu=69.8/25.2/5.0	260
C synthesis gel composition C mixed oxide composition	0.03 Cu(NO <sub>3</sub> ) <sub>2</sub> :2.1Mg(NO <sub>3</sub> ) <sub>2</sub> :0.87Al(NO <sub>3</sub> ) <sub>3</sub> :2Na <sub>2</sub> CO <sub>3</sub> :6.87NaOH Mg/Al/Cu =67.0/31.4/1.6	170

was not detected in the filtrate. The hydrotalcite was calcined at 1023 K in air for 3 hours before reaction, obtaining a Cu–Mg–Al mixed oxide. Cu, Mg and Al contents were determined by atomic absorption spectroscopy. The surface areas of catalysts were obtained using an ASAP 2000 apparatus, using the BET method from the nitrogen adsorption isotherms at 77 K.

### *In Situ* XPS/XAES experimental setup

The XPS and XAES spectra were recorded on a VG-Escalab-210 electron spectrometer equipped with a multichannel detector. The spectra were excited by using the Mg K $\alpha$  (1253.6 eV) radiation of a twin anode in the constant analyser energy mode with a pass energy of 40 eV. The vacuum during spectra acquisition was better than  $3 \times 10^{-9}$  mbar. To avoid the X-ray induced reduction of Cu<sup>2+</sup> to Cu<sup>+</sup>, samples were cooled at 173 K during the acquisition and the X-ray power was limited to 100 W (10 mA, 10 KV). The spectral acquisition time was reduced to prevent the damage of the sample. For calculation of the binding energies the peak of the C–(C,H) component coming from contamination carbon, 284.6 eV, was used as an internal standard. The content of copper was calculated by using the surface area under the Cu2p<sub>(3/2)</sub> peak, the effective ionisation cross section,<sup>23</sup> the electron escape depth<sup>24</sup> and transmission analyser factors. The relative amount of Cu<sup>2+</sup>/Cu<sup>+</sup> species has been obtained from the core-level satellite intensity relative to that of the Cu2p<sub>(3/2)</sub> transition, with an accuracy of *ca.* 20%.<sup>25</sup>

*In situ* experiments were conducted in a high pressure gas cell (HPGC) installed in the preparation chamber of the spectrometer, then the catalysts were transferred to the analysis chamber of the spectrometer without exposing to air. The analyses were obtained on self supporting wafers of 9 mm diameter and *ca.* 5 mg weight that were fixed on a circular sample holder, specially designed for the HPGC, in such a way that 150 ml min<sup>-1</sup> of the reactant flow passed through the catalyst. Catalyst pretreatment was carried out by flowing H<sub>2</sub> (20% in N<sub>2</sub>) during 2 h at 823 K, followed by cooling under vacuum to room temperature. Then, the catalyst was exposed, at different reaction temperatures, to one or more of the following gas components: NO (850 ppm), O<sub>2</sub> (2.5%), C<sub>3</sub>H<sub>8</sub> (470 ppm) and balanced with N<sub>2</sub>.

To study the influence of these catalyst treatments on the copper species we have monitored the Cu2p<sub>(3/2)</sub> electronic transition and the CuL<sub>3</sub>VV Auger transition (induced by Bremsstrahlung radiation), in addition to Mg2p, Al2s and O1s transitions of the framework. The oxidation states of copper have been assigned using the Cu2p<sub>(3/2)</sub> binding energies, the associated shake-up satellites, the kinetic energies of the CuL<sub>3</sub>VV Auger transitions and the modified Auger parameter ( $\alpha$ ). The shake-up satellite peaks are final state effects which arise when the photoelectron imparts energy to another electron of the atom, ending up in a higher unoccupied state (shake-up). As a result the photoelectron loses energy and appears at a higher binding energy in the XP spectrum. This effect is most pronounced in metals with d-orbitals, being clearly observed in copper. In this case, the final state effects are only observed in Cu(II), allowing one to distinguish between Cu(II) and reduced copper. The determination of Cu(I) or Cu metal is more difficult and requires careful analysis.

### Catalytic reactions

Catalytic experiments for NO decomposition and NO reduction were carried out in a fixed bed quartz reactor. Prior to reaction, the catalyst was activated by flowing H<sub>2</sub> at 823 K for 30 minutes. Then, H<sub>2</sub> was purged out with N<sub>2</sub> and when necessary the catalyst was heated up to the reaction temperature under N<sub>2</sub>. For the NO decomposition reactions, 0.6 g of the catalyst were placed into a quartz reactor and 500 ppm of NO were fed in the reactor (N<sub>2</sub> gas balance), using a total flow of 1500 cm<sup>3</sup> min<sup>-1</sup>. The reaction was carried out for 10 minutes. After purging out the NO, the catalyst was regenerated with H<sub>2</sub> at 823 K for 30 minutes before restarting a new reaction cycle. For the NO reduction reaction the same activation procedure and contact time were used, but a feed containing a mixture of propane:NO with a ratio of 1 was introduced into the reactor. The NO<sub>x</sub> was measured using a chemiluminescence detector Rosemount 951 A.

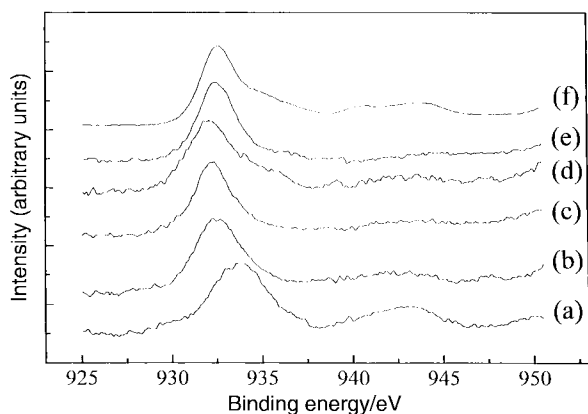
### Results and discussion

The chemical composition and surface areas of the catalysts are shown in Table 1. As can be seen, all the samples have high surface areas independently of the copper content in the sample. All the samples were characterised by electron spectroscopy before activation, after activation, under decomposition conditions and under reduction conditions and the results were compared with those obtained in the reaction studies. The spectral information corresponding to the catalysts is listed in Tables 2–4.

#### Study of the catalyst before activation: as-prepared catalysts and catalysts treated in nitrogen atmosphere

In Fig. 1(a) are shown the Cu2p<sub>(3/2)</sub> photoelectron spectra of the catalyst with the highest copper content (catalyst A) before activation. As can be seen, the presence of a shake-up satellite indicates that copper species are present as Cu<sup>2+</sup>. The presence of this species is also indicated by the binding energy of the Cu2p<sub>(3/2)</sub> transition (see Table 2), which is comparable to that observed for CuO even though the kinetic energy of the CuL<sub>3</sub>VV peak is *ca.* 0.7 eV lower in energy. Analogous results were obtained for catalysts B and C. It is also interesting to point out the low Cu/Mg and Cu/Al ratios on the surface (Tables 2–4) compared with the expected bulk ratios and the low surface copper concentration. These observations may be due to the agglomeration of copper residing on the surface hence forming large particles. In these conditions (*i.e.* before activation) the catalyst has no activity, indicating clearly that Cu(II) are not active sites for NO removal.

Under thermal treatment in flowing nitrogen at 823 K, the Cu2p<sub>(3/2)</sub> transitions were shifted to lower binding energies by *ca.* 1.3–1.9 eV and the kinetic energy of CuL<sub>3</sub>VV Auger peaks decreased by 0.2–0.9 eV. This shift was similar to that observed when Cu(II) and Cu(I) bulk oxide Cu2p<sub>(3/2)</sub> transitions are compared, as well as to that observed in other copper compounds.<sup>26</sup> The peak positions observed here are in agreement with those expected for Cu(I) species. This conclusion is also supported by the disappearance of the core level satellites associated with the main photoelectronic

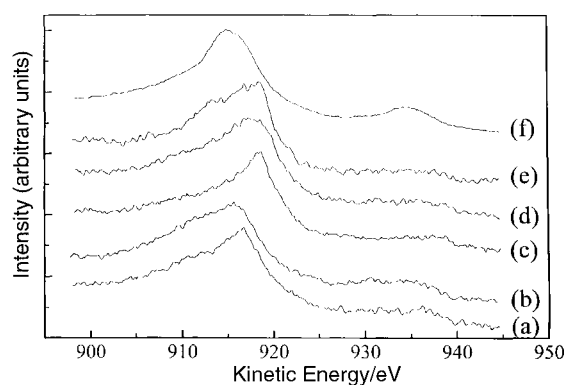


**Fig. 1** Cu<sub>2</sub>p<sub>(3/2)</sub> photoelectron spectra of Cu–Mg–Al mixed oxides derived from hydrotalcite (with 10% Cu): (a) fresh catalyst, (b) calcined *in situ* at 823 K in flowing nitrogen, (c) calcined *in situ* in flowing H<sub>2</sub> (10% in N<sub>2</sub>) at 823 K, (d) after activation *in situ* in flowing H<sub>2</sub> and subsequent exposure to NO at 823 K, (e) after activation *in situ* in a flow of H<sub>2</sub> at 823 K and exposure to the full reaction mixture at 823 K, (f) after activation *in situ* in a flow of H<sub>2</sub> at 823 K and exposure to the full reaction mixture at 623 K.

transition (Fig. 1b) indicating almost full reduction of Cu(II) to Cu(I). These results can be related to the presence of large particles of reduced copper on the surface which exhibit bulk behaviour. Apart from the partial reduction of copper, thermal treatment in flowing nitrogen is accompanied by a small decrease in the Cu/Mg ratio, possibly due to the migration of copper ions into the mixed oxide matrix.

#### Study of the catalyst after activation in hydrogen

The standard activation procedure of the samples which results in the best catalytic performance involves the treatment of the catalyst under hydrogen at 823 K. Tables 2–4 show the XPS results obtained when heating the catalysts in a flow of hydrogen at 823 K. In all samples the core level satellites disappeared (Fig. 1c) and the binding energies of the Cu<sub>2</sub>p<sub>(3/2)</sub> electronic transition experienced a substantial shift with respect to the as-received catalysts (by *ca.* 1.4–1.7 eV). The peak position observed here seems to be in agreement with that reported for Cu(0). The CuL<sub>3</sub>VV lines were shifted by *ca.* 1.8 eV towards higher kinetic energy and became sharper (Fig. 2c) compared with the non-treated samples. The kinetic energy of the Auger transitions (Table 2) was similar to that measured for Cu metal (Cu(0) bulk). All these features indicate that under hydrogen flow at 823 K the copper ions are reduced to metallic copper. In all samples this is produced together with a parallel decrease in the Cu/Al or Cu/Mg ratios at the external surface, indicating aggregation to form large particles of metallic copper species.



**Fig. 2** CuL<sub>3</sub>VV Auger spectra (X-ray induced Auger spectra) of Cu–Mg–Al mixed oxides derived from hydrotalcite (with 10% Cu): (a) fresh catalyst, (b) calcined *in situ* at 823 K in flowing nitrogen, (c) calcined *in situ* in flowing H<sub>2</sub> (10% in N<sub>2</sub>) at 823 K, (d) after activation *in situ* in flowing H<sub>2</sub> and subsequent exposure to NO at 823 K, (e) after activation *in situ* in a flow of H<sub>2</sub> at 823 K and exposure to the full reaction mixture at 823 K, (f) after activation *in situ* in a flow of H<sub>2</sub> at 823 K and exposure to the full reaction mixture at 623 K.

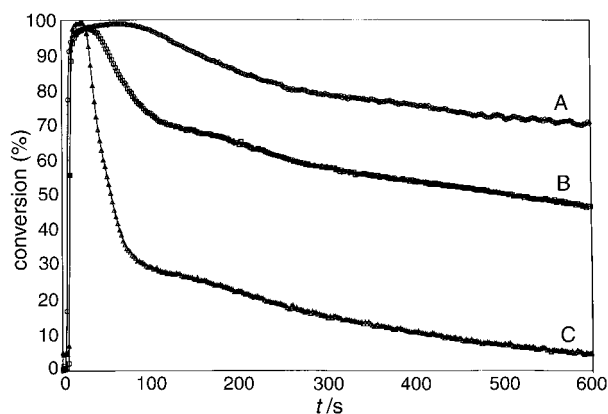
#### Study of the catalyst under exposure to NO (decomposition conditions)

Exposure of catalysts previously activated in hydrogen to NO<sub>x</sub> atmosphere at 823 K resulted in the Cu<sub>2</sub>p<sub>(3/2)</sub> electronic transitions being shifted to lower binding energies with values ranging from 932.1 to 931.8 eV. Core level satellites were not observed indicating therefore that Cu(II) species were not formed (Fig. 1d). The spectral parameters measured after reaction indicated that copper species were mainly present as metallic copper with a small amount as Cu(I). Additionally, a shoulder of higher binding energy (by *ca.* 2–3 eV) appeared after reaction in all samples. Under these conditions, the Cu/Al or Cu/Mg atomic ratios decreased in samples A and B, suggesting a possible migration of copper ions from the surface to the mixed oxide bulk. In samples A and B the measured O1s transition after exposure to NO<sub>x</sub> at 823 K shows a main peak at 530.2 eV and a small shoulder at higher binding energy (by *ca.* 2–3 eV). Nevertheless if these catalysts, previously treated in flowing NO<sub>x</sub> at 823 K, were heated in nitrogen atmosphere at 823 K the shoulders observed both in the Cu<sub>2</sub>p<sub>(3/2)</sub> and O1s transitions disappeared. This treatment did not change the oxidation state of copper ions and consequently it can be suggested that these shoulders may be induced by a change of the copper population in different spatial coordination. Similar results have been recently described in Cu-zeolites.<sup>27</sup> Thus, in Cu-ZSM-5 zeolite exposure to O<sub>2</sub> or NO/O<sub>2</sub> induced the formation of an additional Cu<sub>2</sub>p<sub>(3/2)</sub> peak at higher binding energy, which is ascribed to the coordination of copper with extra-lattice oxygen. In Cu/Mg/Al mixed oxides derived from hydrotalcites this additional component was observed upon

**Table 2** Spectral parameters obtained by XPS and XAES for sample A (10%Cu). (Cu/Mg)<sub>bulk</sub> = 0.159, (Cu/Al)<sub>bulk</sub> = 0.502

Identification	Cu/Al <sup>a</sup>	Treatment	Cu <sub>2</sub> p <sub>(3/2)</sub> /eV	CuL <sub>3</sub> VV/eV	α <sup>b</sup>	Cu/Mg <sup>a</sup>	Cu (%) <sup>a</sup>	Cu <sup>2+</sup> (%)	O1s/eV	Mg2p/eV	Al2p/eV
Res01	0.222	—	933.7	916.9	1849.6	0.060	1.8	100	530.2	49.6	73.4
Res02	0.133	N <sub>2</sub> , 823 K	932.4	916	1848.4	0.045	1.3	0	530.3	49.9	73.6
Res03	0.165	H <sub>2</sub> , 823 K	932.3	918.7	1851	0.048	1.5	0	530.5	49.9	73.7
Res04	0.121	H <sub>2</sub> , 823 K	932.1	917.9	1850	0.036	1.1	0	530.2	49.6	73.3
		+NO, 823 K	935.2						532.5 <sup>d</sup>		
Res05	0.366	H <sub>2</sub> , 823 K	932.5	918.6	1851.1	0.096	1.5	0	532.4	51.2	74.3
		+N <sub>2</sub> , O <sub>2</sub> , NO, C <sub>3</sub> H <sub>8</sub> , 823 K									
Res06	1.019	H <sub>2</sub> , 823 K	932.5	916.8	1849.3	1.346	10.5	70	530.1 <sup>d</sup>	50.9	74.5
		+N <sub>2</sub> , O <sub>2</sub> , NO, C <sub>3</sub> H <sub>8</sub> , 623 K	934.9						532.2		
Cu (metal)	—	—	932.4	918.6	1851.0						
Cu <sub>2</sub> O	—	—	932.3	916.6	1848.9						
CuO	—	—	933.8	917.6 <sup>c</sup>	1851.4						

<sup>a</sup>On surface. <sup>b</sup>Modified Auger parameter = BE(Cu<sub>2</sub>p<sub>(3/2)</sub>) + KE(CuL<sub>3</sub>VV). <sup>c</sup>Anomalous KE value. <sup>d</sup>Shoulder.



**Fig. 3** Variation of the NO decomposition conversion with the time on stream (TOS) over catalyst A (○), catalyst B (□) and catalyst C (△). Experimental conditions:  $9.301 \times 10^{-7}$  mol NO s<sup>-1</sup> g<sup>-1</sup>, N<sub>2</sub> as gas balance, reaction temperature 823 K.

exposure to NO<sub>x</sub>, suggesting that the coordination of copper with NO<sub>x</sub> is a reasonable explanation for the appearance of the small shoulder mentioned earlier.

The catalytic activity of these samples for the NO decomposition reaction is shown in Fig. 3. As can be seen, the three catalysts have initially a high activity (>90%). However, this high initial activity is not maintained with time on stream. All catalysts investigated experience a drop in their initial activity, with the extent of the drop being dependent on the copper content. A dramatic decay in activity is observed for the sample with 1% copper, where practically no activity is observed after 10 minutes on stream. This deactivation is less dramatic for the other two samples studied, within the 10 minutes limit of time on stream. The catalyst specimen with 10% copper loses only 20% of its initial activity after 10 minutes on stream. With all the catalysts, the addition of oxygen results in a fast poisoning of the catalyst.

By comparing these data with those obtained from the XPS characterisation under exposure to NO, the different activity of the Cu/Mg/Al mixed oxides derived from hydrotalcites could be related to the number of active copper species which were

characterised as Cu(0). Thus catalyst A, with the most Cu(0) on the surface (Tables 2–4), is the most active sample. On the other hand, the catalyst with the lowest copper content (catalyst C) is the one which deactivates the fastest at 823 K. This result may be due to the partial oxidation of Cu(0), which results in a decrease in the number of copper active species. In catalysts A and B this effect is not so dramatic possibly due to the higher copper content. In the presence of oxygen, reduced copper active sites are oxidised resulting in a fast deactivation of the catalysts.

#### Study of the catalyst under exposure to NO, C<sub>3</sub>H<sub>8</sub> and O<sub>2</sub> (reduction conditions)

The results of exposing the catalysts previously activated in flowing hydrogen at 823 K to a reaction mixture of NO, O<sub>2</sub> and C<sub>3</sub>H<sub>8</sub> for 2 h at different temperatures (similar to the NO reduction reaction conditions) are shown in Tables 2–4. Fig. 1 and 2 show the results obtained in catalyst A. As can be seen, under exposure to the reaction mixture at 823 K, the Cu2p<sub>(3/2)</sub> transition was slightly shifted to higher binding energy. Core level satellites were not detected in samples A and B at this temperature indicating that copper ions were not oxidised to Cu(II). In catalyst A, peak positions corresponding to the Cu2p<sub>(3/2)</sub> and CuL<sub>3</sub>VV transitions and the modified Auger parameter ( $\alpha'$ ) were similar to those measured in metallic copper indicating that copper was fully reduced in this sample. In sample B (Table 3) the Auger transition was shifted to lower kinetic energy when compared with the catalyst previously activated in hydrogen. This observation indicates that under exposure to the gas mixture the copper ions of catalyst B were partially oxidised to Cu(I). In sample C, in contrast to the other samples under these conditions, the shake-up satellite associated with the Cu2p<sub>(3/2)</sub> transition was present indicating the oxidation of the copper species to Cu(II). Nevertheless the presence of at least a small amount of Cu(I) could not be discarded. Under these conditions the amount of copper on catalyst A surface was practically the same as after activation, being slightly increased in catalysts B and C. On the other hand, for catalysts A and B, the O1s Al2p and Mg2p binding energies (Tables 2–4) increased with respect to the measured values after activation in hydrogen, suggesting that the

**Table 3** Spectral parameters obtained by XPS and XAES for sample B (5%Cu). (Cu/Mg)<sub>bulk</sub> = 0.072, (Cu/Al)<sub>bulk</sub> = 0.198

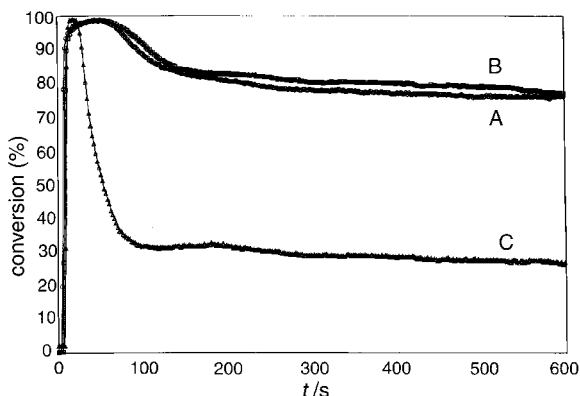
Identification	Cu/Al <sup>a</sup>	Treatment	Cu2p <sub>(3/2)</sub> /eV	CuL <sub>3</sub> VV/eV	$\alpha'$ <sup>b</sup>	Cu/Mg <sup>a</sup>	Cu (%) <sup>a</sup>	Cu <sup>2+</sup> (%)	O1s/eV	Mg2p/eV	Al2p/eV
Res01	0.036	—	933.2	916.9	1850.1	0.011	0.3	100	530.3	49.6	73.4
Res02	0.033	N <sub>2</sub> , 823 K	931.7	916.1	1847.8	0.010	0.3		530.2	49.6	73.5
Res03	0.024	H <sub>2</sub> , 823 K	931.8	918.8	1850.6	0.007	0.2	0	530.2	49.7	73.6
Res04	0.011	H <sub>2</sub> , 823 K	931.9	918.7	1850.6	0.004	0.1	0	530.2	49.5	73.5
		+NO, 823 K	934.1						532.2 <sup>c</sup>		
Res05	0.102	H <sub>2</sub> , 823 K	931.4	917.5	1848.9	0.027	0.4	0	529.8 <sup>c</sup>	50.8	74
		+N <sub>2</sub> , O <sub>2</sub> , NO, C <sub>3</sub> H <sub>8</sub> , 823 K							532.1		
Res06	0.175	H <sub>2</sub> , 823 K	932.7	917.5	1850.2	0.042	1	33	530 <sup>c</sup>	50.2	74.1
		+N <sub>2</sub> , O <sub>2</sub> , NO, C <sub>3</sub> H <sub>8</sub> , 623 K	934.7						532		

<sup>a</sup>On surface. <sup>b</sup>Modified Auger parameter = BE(Cu2p<sub>(3/2)</sub>) + KE(CuL<sub>3</sub>VV). <sup>c</sup>Shoulder.

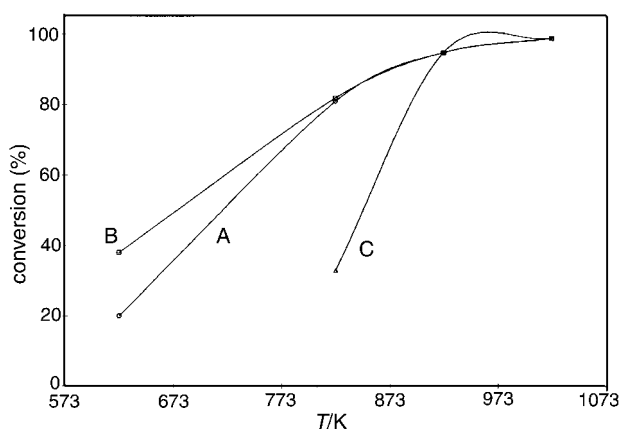
**Table 4** Spectral parameters obtained by XPS and XAES for sample C (1%Cu). (Cu/Mg)<sub>bulk</sub> = 0.024, (Cu/Al)<sub>bulk</sub> = 0.051

Identification	Cu/Al <sup>a</sup>	Treatment	Cu2p <sub>(3/2)</sub> /eV	CuL <sub>3</sub> VV/eV	$\alpha'$ <sup>b</sup>	Cu/Mg <sup>a</sup>	Cu (%) <sup>a</sup>	Cu <sup>2+</sup> (%)	O1s/eV	Mg2p/eV	Al2p/eV
Res01	0.018	—	933.6	916.7	1850.3	0.010	0.2	100	529.9	49.6	73.4
Res02	0.012	N <sub>2</sub> , 823 K	931.7	916.5	1848.2	0.006	0.1		530.2	49.6	73.5
Res03	0.006	H <sub>2</sub> , 823 K	931.9	918.5	1850.4	0.003	0.1	0	530.3	49.5	73.5
Res04	0.006	H <sub>2</sub> , 823 K	931.8	920	1851.8	0.003	0.1	0	530.3	49.5	73.6
		+NO, 823 K	934.6								
Res05	0.021	H <sub>2</sub> , 823 K	933.4	917.8	1851.2	0.011	0.3	40	530.1	49.3	73.6
		+N <sub>2</sub> , O <sub>2</sub> , NO, C <sub>3</sub> H <sub>8</sub> , 823 K									
Res06	0.013	H <sub>2</sub> , 823 K	933.2	917.6	1850.8	0.007	0.2	85	530.2	49.3	73.5
		+N <sub>2</sub> , O <sub>2</sub> , NO, C <sub>3</sub> H <sub>8</sub> , 623 K									

<sup>a</sup>On surface. <sup>b</sup>Modified Auger parameter = BE(Cu2p<sub>(3/2)</sub>) + KE(CuL<sub>3</sub>VV).



**Fig. 4** Variation of the NO reduction conversion with the TOS over catalyst A (○), catalyst B (□) and catalyst C (△). Experimental conditions:  $9.301 \times 10^{-7}$  mol NO s<sup>-1</sup> g<sup>-1</sup>, C<sub>3</sub>H<sub>8</sub>/NO ratio = 1 and N<sub>2</sub> as gas balance, reaction temperature 823 K.



**Fig. 5** Variation of the NO reduction conversion with the temperature over catalyst A (○), catalyst B (□) and catalyst C (△). Experimental conditions:  $9.301 \times 10^{-7}$  mol NO s<sup>-1</sup> g<sup>-1</sup>, C<sub>3</sub>H<sub>8</sub>/NO ratio = 1 and N<sub>2</sub> as gas balance.

chemical form of the surface aluminium, oxygen and magnesium species also depends on the treatment conditions.

The exposure of catalysts to the same gas mixture but at lower temperature (623 K) resulted in the appearance of Cu(II) species in all the studied catalysts. In these conditions, copper species detected on the surface were oxidised and metallic copper was not present. Due to the presence of only oxidised copper species it was possible to quantify the relative percentages of Cu(I) and Cu(II). In this way, the level of Cu(I) ions in catalyst A was ca. 30%, being clearly lower than that measured in catalyst B (ca. 70%). In catalyst C, all copper ions were practically oxidised to Cu(II).

Surprisingly, the level of copper measured on the surface under treatment at 623 K increased (by ca. 5 times in catalyst A and ca. 3 times in catalyst B) indicating a dramatic dispersion of copper on the surface and a possible migration of copper from the matrix.

The catalytic activity of these samples was also tested for the NO reduction reaction and it was related to the above results. If compared with the NO decomposition reaction, the catalyst activity is improved in the presence of propane, where a value close to 100% conversion at 823 K is observed during the first stages of the reaction (Fig. 4). Samples A and B, with higher copper contents, give conversions close to 100% during the first 125 seconds. After that a decrease of the activity is observed until 150 s, then conversion stabilises at ca. 85% for both catalysts. In contrast, the sample with the lowest copper

content (sample C) shows a significant deactivation after 80 seconds, after which the conversion stabilises at ca. 35%.

The three catalysts were also tested at different temperatures (Fig. 5), and it was found that at temperatures around 923 K the activities of the catalysts with different copper contents are very similar and close to 100% in all cases. The main differences were observed at lower temperature (623 K), where although the activity decreases with all the catalysts, this is especially dramatic with catalyst C, which shows almost no activity in this reaction. The presence of oxygen results in a deactivation of the catalysts.

It should be pointed out that under these reaction conditions, similar results for the NO removal are obtained when the catalyst is activated under nitrogen flow instead of hydrogen flow at 823 K. The XPS results reported before show that in that case the copper species are Cu(I) but not metallic copper; for this reason it can be suggested that Cu(I) are also active sites for the reduction of NO with propane.

The results obtained indicate that in the selective catalytic reduction of NO<sub>x</sub> by propane using Cu–Mg–Al mixed oxides derived from hydrotalcite as catalyst, Cu(I) and Cu(0) species can be associated with the catalytic activity. The different activities of the catalysts tested can be related to the XPS studies. As can be seen, after exposure of catalysts A and B (the most active) to a mixture of propane, oxygen and NO, the copper species remain in the reduced form, but for catalyst C (the least active) only the inactive oxidised form, Cu(II), was detected. The results indicated that a fast deactivation occurs with this catalyst, making it inadequate for catalytic purposes. *In situ* XPS experiments carried out at 623 K show that metallic copper was not present and only a mixture of Cu(I) and Cu(II) was detected, depending on the sample. This can be correlated with the catalytic results observed: the level of Cu(I) in catalyst B is higher than that measured in catalyst A (Tables 2–4) and this could explain the high activity of catalyst B at this temperature. In catalyst C, almost all the copper species were oxidised to Cu(II), explaining the almost complete lack of activity of catalyst C for NO reduction at 623 K.

However, the most remarkable fact is that Cu/Mg/Al mixed oxides derived from hydrotalcites are very active catalysts when working at high temperatures (up to 823 K) in contrast with other catalysts such as Cu-zeolites, which are very active at low temperatures, but not at these temperatures. This must be related to the singular capacity of the Cu–Mg–Al mixed oxides derived from hydrotalcites for sintering and redispersing the copper. In Cu-ZSM-5 zeolite, reduction to form metallic copper particles was considered undesirable for the NO<sub>x</sub> removal reaction.<sup>28</sup> The low catalytic activity of the reduced catalysts was thought to be due to the substantial sintering of copper species to form particles of metallic copper. The appearance of this metallic phase would require local destruction of the zeolite and, subsequently, catalyst deactivation. On the other hand, the full reduction to metallic copper in Cu-zeolites is normally a non-reversible process<sup>25</sup> and the large particles of metallic copper cannot be redispersed under oxidative atmospheres.

In the case of Cu–Mg–Al mixed oxides derived from hydrotalcite catalysts the copper species form small clusters with bulk behaviour. These copper species can be oxidised to Cu(II) upon exposure to oxidative atmospheres, reduced to Cu(I) by flowing N<sub>2</sub> at 823 K or reduced to metallic copper under exposure to H<sub>2</sub> at 823 K. These redox treatments are normally accompanied by substantial changes in the amount of copper at the surface due in part to the migration of copper from the surface to the hydrotalcite matrix and also to sintering forming larger crystallites. The larger particles of copper are produced after full reduction to the metallic phase. Nevertheless, in contrast to what occurs in Cu-zeolites, the large particles of metallic copper can be reoxidised and redispersed under exposure to oxidative conditions. Thus, based on the

characterisation and catalytic results presented, it appears that copper clusters with bulk behaviour may be necessary to provide the optimum catalytic performance in Cu–Mg–Al mixed oxides derived from hydrotalcites. The results obtained also indicate that the redox reactions are fully reversible. This plus the possibility of using the catalyst for high temperature reactions are the main advantages of this material.

## Conclusions

From this work it can be concluded that Mg/Al/Cu mixed oxides derived from hydrotalcites and containing at least 5% Cu are adequate catalysts for the removal of NO at high temperatures. As the results of the XPS study have shown, the reduced species which are suggested to be the active sites for the removal of NO are rendered inactive after the oxidation of the copper sites. However, the copper in Cu–Mg–Al mixed oxides derived from hydrotalcites can undergo oxidation–reduction cycles without destroying its structure, in contrast to what occurs with other materials containing copper, such as for instance Cu-zeolites. This is essential in order to design a catalyst that will be able to remove NO at high temperatures. These reasons suggest that Mg/Al/Cu mixed oxides derived from hydrotalcites containing 5–10% copper could be optimal catalysts for NO removal at high temperatures.

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