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# Simultaneous Catalytic Removal of $SO_x$ and $NO_x$ with Hydrotalcite-Derived Mixed Oxides Containing Copper, and Their Possibilities to Be Used in FCC Units

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**Hydrotalcite structures containing copper, magnesium, and aluminum have been investigated for their potential as precursors of catalysts in the decomposition and reduction of nitrogen oxides, and in the simultaneous removal of NO and $SO_2$ under conditions similar to those found in the regenerator of a fluid catalytic cracking (FCC) unit. It is shown that these catalysts are active for the decomposition of NO in the presence of low concentrations of air and for the reduction of NO by propane in the presence of up to 2% oxygen. The lower oxidation states of the copper species (0 and +1) are the active centers for the reactions. Under the conditions encountered in the regenerator of the FCC unit, there is a window in the oxygen concentration (from 0 to 1.5%), where the Cu-hydrotalcite-based catalyst can simultaneously remove $SO_2$ (by an oxidative and/or reductive reaction) and NO (by a reduction and/or decomposition reaction). When this process takes place at low $O_2$ concentrations, some copper-sulfur species are formed. These centers are more active for the NO removal than the original copper centers. We have attributed this increment of activity to the stabilization of the active centers in presence of $SO_2$ in the stream.** © 1997 Academic Press

## INTRODUCTION

Sulfur and nitrogen oxides are two major pollutants which contribute to the formation of acid rain and the depletion of the ozone layer. Power generation stations produce ca. 30% of the total $NO_x$ emissions and 65% of the $SO_x$ emissions. Another major contribution to the total emissions comes from petrochemical plants (10% of the $NO_x$ emissions and 7% of the $SO_x$ emissions), and more specifically from the fluid catalytic cracking (FCC) units (1, 2). Current regulations controlling such pollution are becoming more stringent and new processes to control these contaminants are imperative.

Some processes have been developed successfully to decrease the emissions of sulfur and nitrogen oxides (3 and references therein) from effluent gases of thermal power stations. However, these processes are not suitable for FCC units due to the higher operational temperatures needed and the many requirements associated with the FCC operation (4). In the FCC unit, between 45 and 55% of the total sulfur present in the feed, especially the nontiophenic compounds, is converted to $H_2S$, while approximately 35–45% stays in the liquid products as sulfur compounds. The remaining 5% is left on the catalyst as part of coke and results in 90% $SO_2$ and 10% $SO_3$ during the coke burn off at ca. 750°C in the regeneration unit (5). In the case of the nitrogenated compounds (6), around 50% of these compounds are converted to ammonia in the riser, while the rest (the more basic ones) remain in the feed or end up in the coke formed on the catalyst during the cracking reaction. In the regenerator of the FCC unit, the coke is burnt off in the presence of oxygen, and a mixture of nitrogen oxides (90% NO, 10% $NO_2$) is formed. Therefore, the amount of $NO_x$ and $SO_x$ emitted from a FCC unit can be controlled by lowering the concentration of nitrogenated and sulfured compounds in the feed, either by choosing appropriate petroleum sources or by hydrotreating the feed. The problem is that from the economical point of view, these alternatives are very costly and not always technologically possible. A third alternative is to develop suitable additives to the FCC catalyst that remove $NO_x$ and $SO_x$ in the regenerator unit. These additives must be able to operate at the high temperatures found in the regenerator, and in the presence of other gases such as CO, $CO_2$, $O_2$, and $H_2O$.

Some additives based on Mg–Al mixed oxides produced from hydrotalcites can be used successfully for the removal of $SO_x$ under these conditions (7, 8). These additives are able to oxidize the $SO_x$ to $SO_3$ in the regenerator of the FCC unit and to remove them as sulfate. In the reductive atmosphere of the cracking zone, the sulfate formed is decomposed giving $H_2S$ which can be recovered by available techniques.

Various perovskitic oxides have been proposed for the removal of $NO_x$, but due to the low surface areas, large amounts of additive are required to achieve high $NO_x$ conversions (9, 10). Other oxides, such as ZnO and $Co_3O_4$, have also been proposed as additives (11, 12), but they lose their

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activity in the presence of $SO_2$ or $O_2$. Recently, it has been shown that hydrotalcite structures containing copper, magnesium, and aluminum in the metal hydroxide layers are potential precursors for the formation of catalysts for the decomposition and reduction of nitric oxide (13), suggesting the possibility to use this catalyst for the simultaneous removal of $SO_x$ and $NO_x$.

The aim of this work is to study the activity of copper hydrotalcites for the removal of NO under different reaction conditions and to investigate its potential for the simultaneous removal of $SO_x$ and $NO_x$ in a single step from the FCC unit.

## EXPERIMENTAL

Cu(II)Mg(II)Al(III) hydrotalcites were prepared by coprecipitation of a solution of the appropriate metal nitrates [M(II) : Al(III) ratio of 3 : 1 and containing 10% molar Cu(II) substituting for Mg(II)] with a solution of $Na_2CO_3/NaOH$ at constant pH. The gel [$0.3Cu(NO_3)_2 : 2.1 Mg(NO_3)_2 : 0.6Al(NO_3)_3 : 2Na_2CO_3 : 6.6NaOH$] was aged under autogenous pressure conditions at 80°C for 18 h, then filtered and washed with distilled water until the pH was 7 and carbonate was not detected in the filtrate. The hydrotalcite was calcined at 750°C in air for 3 h before reaction, resulting in a mixed oxide with the molar composition $7MgO : Al_2O_3 : CuO$.

X-ray powder diffraction patterns were obtained on a Philips PW 1010 equipped with a graphite monochromator using the Cu$K\alpha$ radiation.

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 analyzer energy mode with a pass energy of 50 eV. The vacuum during spectra acquisition was better than $3\times 10^{-9}$ mbar. To avoid the X-ray-induced reduction of $Cu^{+2}$ to $Cu^{+1}$, 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 also reduced to prevent the damage of the sample. The main C1*s* peak, (BE) = 284.6 eV, was chosen as an internal standard to calibrate the energy scale.

The content of copper was calculated by using the surface area under $Cu2p_{3/2}$ peak, the effective ionization cross section (14) and the scape depth (15).

*In situ* type experiments were conducted in a high pressure gas cell (HPGC) installed in the preparation chamber of the spectrometer, so the catalysts could be moved to the analysis chamber of the spectrometer without exposing to air. The analysis 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. The different treatments were carried out into this cell at atmospheric pressure with a gas flowrate of 100 ml/min. First the catalyst was reduced *in situ* at 823 K in flowing $H_2$ (20% in $N_2$); then it was exposed to the reaction mixture $SO_x$ (550 ppm), NO (450 ppm), $N_2$ as gas balance; and finally $O_2$ (2.5%) was added to the mixture.

The catalytic experiments were carried out in a fixed bed quartz reactor. Prior to reaction, the catalyst was activated under $H_2$ at 550°C for 30 min, simulating the reductive conditions in the riser of the FCC unit. The $H_2$ was flushed out with $N_2$ and the catalyst brought from this temperature to the reaction temperature under $N_2$. For the NO decomposition reactions 0.6 g of the calcined hydrotalcite was placed into a quartz reactor; then 300–400 ppm NO was introduced in the reactor ($N_2$ gas balance), using a total flow of 1700 $cm^3$/min. The reaction was carried out for 10 min, the usual time the catalyst remains in the regenerator. After purging out the NO with $N_2$ the catalyst was regenerated under $H_2$ at 550°C for 30 min, restarting a new cycle of reaction. For the NO reduction reactions the same activation procedure and contact time were used, but a 1 : 1 propane : NO ratio was introduced in the reactant stream. Some experiments were carried out by mixing the copper hydrotalcite additive with a commercial FCC catalyst supplied by Engelhard Co. in order to study the effect of the zeolite and the matrix components. In these experiments a 3% Cu additive was diluted in the FCC catalyst. The catalytic conditions were chosen to obtain the same contact time (referred to as the additive content) as in previous experiments.

Cracking of vacuum gasoil was carried out on the physical mixture of the FCC catalyst and the Cu additive, using a M.A.T. unit in order to study the influence of the additive in the activity and selectivity of the FCC catalyst.

The effect of potential poisons for the copper additive, such as water and oxygen, was tested by introducing 2.8% water in the feed and variable amounts of oxygen, respectively.

In the simultaneous removal of $SO_2$ and NO studies, 2 g of the additive was placed in the reactor and 450 ppm of NO, 540 ppm of $SO_2$, and variable amounts of $O_2$ and $C_3H_8$ ($N_2$ gas balance) were introduced in the system at 750°C, using a total flow of 1600 $cm^3$/min. The $NO_x$ was measured using a chemiluminiscence detector and the $SO_2$ with an infrared nondispersive analyzer connected on line to the outlet of the reactor.

## RESULTS AND DISCUSSION

*Characterization.* The XRD pattern of the calcined hydrotalcite (Fig. 1a) shows the formation of magnesium oxide poorly crystalline with peaks at $2\theta = 37$, 42.9, and 62.6°. In addition, the presence of the peaks appearing at $2\theta = 35.5$, 38.7, 48.8, 53.4, 58.2, 61.3, 66.3, and 67.6° provides evidence that CuO is also formed during calcination.

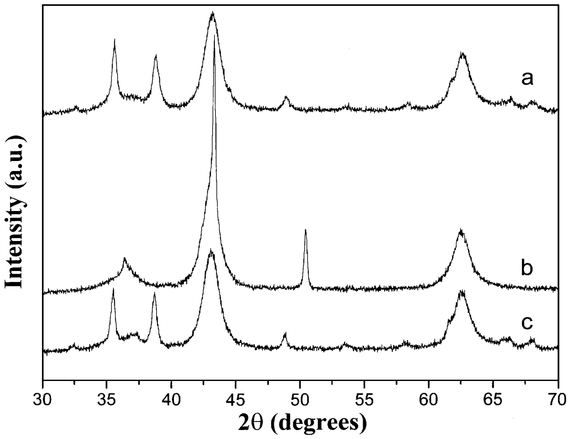

**FIG. 1.** X-ray diffraction patterns of the copper hydrotalcite additive (a) after calcination at 750°C, (b) after activation in $H_2$ at 550°C, and (c) after NO decomposition reaction.

Upon reduction the different peaks corresponding to the MgO phase remains unchanged while the peaks assigned to CuO disappear, due to the transformation to Cu metal as shown by the presence of two narrow peaks centered at $2\theta = 43.2^\circ$ (that overlaps with the peak of MgO) and 50.4° (Fig. 1b).

Finally, after NO decomposition reaction, the XRD pattern of the Cu hydrotalcite additive is similar to the catalyst before activation, indicating that CuO is formed during NO decomposition or by exposing it to the atmospheric oxygen (Fig. 1c).

Studies directed to achieve further knowledge on the active species for the simultaneous removal of NO and $SO_2$ have been carried out by XPS.

The oxidation states of copper in the additive have been assigned by using the $Cu2p_{3/2}$ transition, the associated shakeup satellite, the $CuL_3VV$ Auger transition, and the modified Auger parameter ($\alpha'$). $Cu^{+2}$ species shows a shakeup satellite at ca. 10 eV higher than the $Cu2p_{3/2}$ peak that is not shown by $Cu^{+1}$ or $Cu^0$ species, as this characteristic is normally used to distinguish between $Cu^{+2}$ and $Cu^{+1}$ or $Cu^0$. The determination of reduced copper ($Cu^{+1}$ or $Cu^0$) requires one to analyze the $CuL_3VV$ transition and the modified Auger parameter.

Figure 2 shows the $Cu2p_{3/2}$ (Fig. 2I) and $CuL_3VV$ (Fig. 2II) transitions recorded after different treatment conditions (see Table 1). After flowing $H_2$ at 823 K (Fig. 2Ia) the shakeup satellite associated to the main peak is not observed. On the other hand, the $CuL_3VV$ Auger transition (Fig. 2IIa) is coincident with that observed in copper metal (see Table 1) indicating the full reduction to $Cu^0$. On the other hand, the coincidence observed with the Auger kinetic energy of copper metal could be related to the aggregation state of copper, indicating that large particles of copper metal have been formed under reduction in $H_2$.

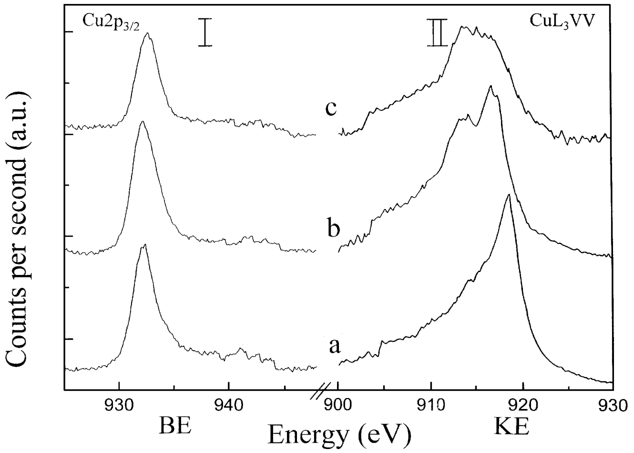

**FIG. 2.** $Cu2p_{3/2}$ (I) and CuL3*VV* (II) electron spectra of CuHT: (a) CuHT reduced *in situ* at 823 K for 3 h in flowing $H_2$ (20% in $N_2$), total flow = 100 $ml \cdot min^{-1}$; (b) CuHT exposed for 2 h to the reaction mixture: $SO_x$ (550 ppm), NO (450 ppm), $N_2$ as gas balance, total flow = 100 $ml \cdot min^{-1}$; and (c) Cu-HT exposed for 2 h to the reaction mixture: $SO_x$ (550 ppm), NO (450 ppm), $O_2$ (2.5%), $N_2$ as gas balance, total flow = 100 $ml \cdot min^{-1}$.

When this sample is exposed to $SO_x$ and NO at 823 K (Fig. 2b), the $Cu2p_{3/2}$ transition is practically unchanged (Table 1). However, the Auger transition is clearly modified showing two peaks shifted to lower kinetic energy. The kinetic energy of both peaks, together with the nonappearance of the shakeup, is consistent with the presence of $Cu^{+1}$ species (Table 1). The splitting observed in the Auger transition could be justified as due to the different location of $Cu^{+1}$ species. Thus, the peak appearing at 917 eV (KE) could be assigned to large particles of $Cu_2O$ on the surface, whereas the peak at 914 eV could be justified as due to $Cu^{+1}$ species dispersed into the hydrotalcite, possibly as copper incorporated to the mixed Cu–Al–Mg oxide. No $Cu^0$ was detected after exposure to NO and $SO_x$.

Under treatment in flowing $SO_x$, NO, and $O_2$ at 823 K (Fig. 2c), the results observed are similar to those previously described, indicating the presence of $Cu^{+1}$ species in the same aggregation states.

**TABLE 1**

**Spectral Parameters Obtained by XPS and XAES**

| Identification | Treatment | $Cu2p_{3/2}$ (eV) | $CuL_3VV$ (eV) | $\alpha'^{a}$ | Cu (%)$^b$ |
|---|---|---|---|---|---|
| Res01 | $H_2$, 823 K | 932.2 | 918.5 | 1850.0 | 0.5 |
| Res02 | NO, $SO_x$, $N_2$, 823 K | 932.3 | 914.0 | 1846.3 | 1.0 |
| | | | 917.0 | 1849.3 | |
| Res03 | $N_2$, NO, $SO_x$, $O_2$, 823 K | 932.5 | 914.1 | 1846.6 | 0.75 |
| | | | 916.9 | 1849.4 | |
| Cu (metal) | | 932.4 | 918.6 | 1851.0 | |
| $Cu_2O$ | | 932.3 | 916.8 | 1849.1 | |

[a] Modified Auger parameter = BE($Cu2p_{3/2}$) + KE($CuL_3VV$).
[b] Atomic percentage on surface.

Table 1 shows that the surface concentration of copper is dependent on the reaction conditions. Thus, under reduction in flowing, $H_2$ at 823 K, the atomic percentage of copper on surface is 0.5%, whereas when the catalyst is exposed to the reaction mixture (NO, $SO_x$ at 823 K) the level of $Cu^{+1}$ slightly increases to 1%. Finally, when 2.5% $O_2$ is added to the reaction mixture the level of copper is 0.75%. These observations may be explained on the basis of the aggregation state. If the catalyst is exposed to $H_2$, large particles of copper metal are formed and consequently, the level of copper measured on surface is low. Nevertheless, when copper metal is oxidized to $Cu^{+1}$ species, the dispersion of Cu on the particles increases justifying in this case the higher levels of copper measured on surface.

### *NO Decomposition*

The pretreatment of the copper-hydrotalcite was studied in order to achieve the most convenient activation procedure to maximize the conversion of NO. It was found that the catalyst is completely inactive for the NO decomposition after calcination under $O_2$ in the range of temperatures studied (400–750°C) where CuO is formed (see Fig. 1a). However, the catalyst becomes active upon reduction under $H_2$ or propane at 550°C. This temperature corresponds to that found in the raiser of a FCC reactor in which a reductive atmosphere is present. Thermal treatment of the Cu hydrotalcite under inert atmosphere (such as $N_2$ or Ar) gives intermediate activity. Consequently, we can conclude that the activity for the NO removal increases with the reductive power of the atmosphere during the activation process. This indicates that the active sites for the catalytic NO decomposition should be reduced species in Cu hydrotalcite, as it has been suggested by the X-ray diffraction data discussed above (Fig. 1b) and by XRD/EXAFS in our previous work (13). Consequently, we standardize the pretreatment of the Cu hydrotalcite additive reducing the sample with $H_2$ at 550°C for 30 min before starting the reaction.

A typical profile of the NO decomposition reaction at temperature similar to those used in the regenerator unit of a FCC plant (750°C) is presented in Fig. 3. In this figure, three different stages can be observed. In the first stage the catalytic activity is $7.01 \times 10^{-7}$ mol $NO \cdot g^{-1} \cdot s^{-1}$. Subsequently a fast deactivation process takes place until NO conversion is stabilized at values around $5.90 \times 10^{-7}$ mol $NO \cdot g^{-1} \cdot s^{-1}$, for a period between 50 and 200 s of reaction. Then, a slow deactivation process occurs for the following 30 min. The decrease of the catalytic activity in the first stage could be attributed to the oxidation of the Cu(0) to Cu(I) species as we have observed previously *in situ* XRD–EXAFS technique (13). Consequently, the overall stoichiometry in the initial stage of the NO decomposition reaction could be written as

$$4Cu(0) + 2NO \rightarrow 2Cu_2O + N_2.$$

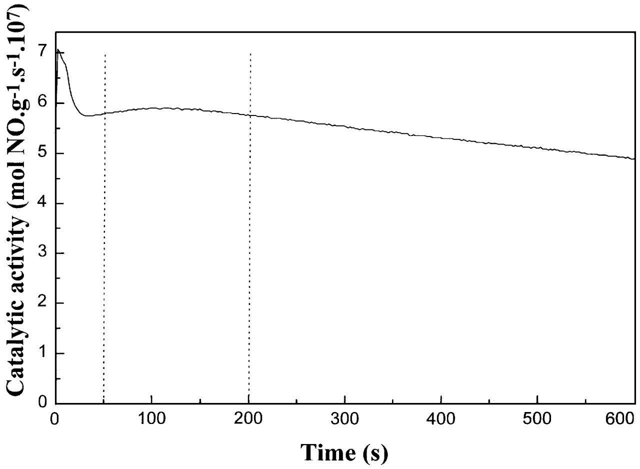

**FIG. 3.** Profile of the NO decomposition reaction at 750°C over Cu hydrotalcite additive ($7.378 \times 10^{-7}$ mol $NO \cdot s^{-1} \cdot g^{-1}_{additive}$, $N_2$ as gas balance).

In the second stage of the reaction, i.e., the plateau observed between 50 and 200 s, the NO is decomposed by the Cu(I) species formed in the previous step as has been found in Cu-overexchanged ZSM-5, mordenite, and beta zeolites in NO decomposition (16–19). Finally, during the last stage of the reaction, the active centers of Cu(I) are oxidized to Cu(II) species by the oxygen generated during the NO decomposition reaction, as is shown in the X-ray pattern of the recovered additive (Fig. 1c), where CuO is clearly identified. These Cu(II) species are not active in the NO decomposition producing the deactivation of the catalyst.

The influence of the reaction temperature on the catalytic activity of the Cu hydrotalcite additive in NO decomposition is represented in Fig. 4. The level of conversion at each temperature was calculated after 10 min reaction, which is a typical residence time of the catalyst in the regenerator unit. The maximum activity is achieved between 700 and 750°C,

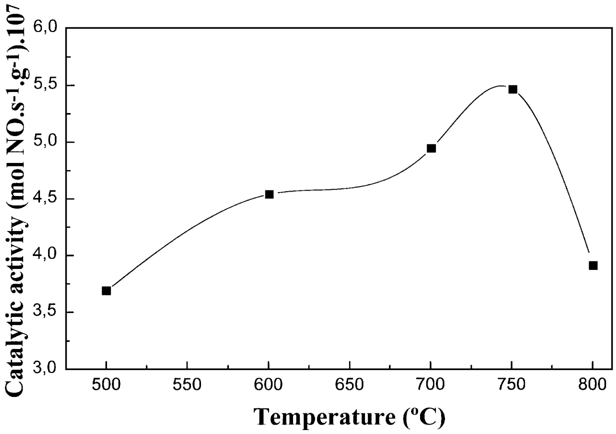

**FIG. 4.** Influence of the temperature in the NO decomposition reaction over Cu hydrotalcite additive ($7.378 \times 10^{-7}$ mol $NO \cdot s^{-1} \cdot g^{-1}_{additive}$, $N_2$ as gas balance).

which is a higher temperature than those found when transition metal exchanged zeolites are used as de-$NO_x$ catalysts. Also, this temperature range corresponds to that in which the FCC regenerator unit typically works. This suggests that the Cu hydrotalcite could be a promising additive to the FCC catalyst, for $NO_x$ removal in the cracking process.

In order to study the applicability of the Cu hydrotalcite as an additive to the FCC catalyst we have carried out several experiments to check that: (a) the catalytic activity of the additive is not affected by the presence of the FCC catalyst, (b) the activity of the FCC catalyst is not affected by the presence of the hydrotalcite additive, and (c) the additive is active in the presence of $H_2O$ and oxygen (that could poison the additive). In the first place, the Cu hydrotalcite was mixed with a FCC catalyst and the resultant mixture was used for the decomposition reaction of NO at different temperatures. The obtained results are given in Fig. 5, showing that the Cu hydrotalcite plus the FCC catalyst is more active than the additive alone (Fig. 4). The possible activity of the FCC catalyst in the NO decomposition has been excluded by carrying out a blank experiment using only FCC catalyst. It was proved that the FCC catalyst is completely inactive in the removal of $NO_x$. Therefore, the increase in the catalytic conversion has to be attributed to an interaction between both components of the mixture. These results may suggest that some Cu could migrate from the Cu hydrotalcite to the zeolitic component of the FCC catalyst (20). The solid state reaction could occur during the activation or/and reaction processes, resulting in an increase in the active surface area of the copper exposed to the reactant flow.

The effect of the additive on the gasoil cracking reaction was checked by carrying out the cracking of vacuum gasoil on the FCC catalyst and on the FCC catalyst plus the Cu hydrotalcite. The results shown in Fig. 6 indicate that there is no significant influence of the Cu hydrotalcite additive on the activity and selectivity during the gasoil cracking reaction.

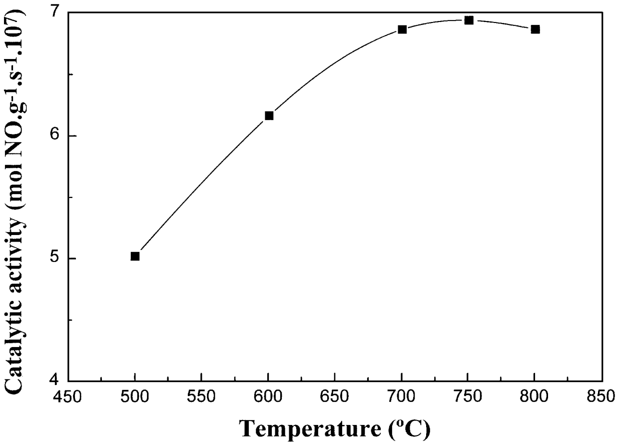

**FIG. 5.** Influence of the addition of a commercial FCC catalyst in the activity of Cu hydrotalcite additive for the NO decomposition reaction at different temperatures (3 wt.% of the additive in the FCC catalyst, $7.378 \times 10^{-7}$ mol $NO \cdot s^{-1} \cdot g^{-1}_{additive}$, $N_2$ as gas balance).

The presence of 2.8% molar of water in the reactant flow results in a loss of the 20% of activity (Fig. 7). The possible irreversibility of this effect, which could limit the applicability of the additive, was studied. The sample was regenerated under dry conditions and tested again showing a similar catalytic performance than before water exposure. Therefore, we conclude that the water is not irreversibly adsorbed on the catalyst under the reaction conditions of the FCC unit. Furthermore, the presence of 1% molar of $O_2$ in the stream results in the total deactivation of the Cu additive, as is illustrated in Fig. 8. The pernicious effect of oxygen could be due to the oxidation of the Cu(I) sites which are active in the catalytic decomposition of NO to inactive Cu(II) species. When the $O_2$ is removed from the stream the activity was partially recovered. This effect has been observed previously on Cu-exchanged zeolites (11, 19) and it has been ascribed to the spontaneous reduction of highly dispersed Cu(II) species present on the zeolitic surface to active Cu(I) centers. Based on that, we propose a similar behavior for the Cu(II) species located in the hydrotalcite additive in the NO decomposition reaction.

From the results shown above, we can conclude that we are able to prepare an additive derived from Cu-containing hydrotalcite which is active for NO decomposition at reaction temperatures similar to those found in the regenerator unit of a FCC plant. However, this additive is going to be active only in the oxygen-deficient region of the fluidized bed in the regenerator unit, where most of the oxygen is consumed by burning off the coke present on the FCC catalyst.

### *NO Reduction*

The incomplete combustion of the coke in the regenerator unit produces the formation of a reductive atmosphere in the dense phase of the fluid bed (mainly due to the production of CO and some hydrocarbons not desorbed in the striper that could be desorbed in the regenerator unit) (21). Consequently, processes of reduction of NO can also occur even in the regenerator unit. Therefore, we have studied the catalytic activity of Cu-containing hydrotalcite in the reduction reaction of NO using propane as a selective reductor. Figure 9 shows the catalytic activity of the Cu-hydrotalcite under reduction conditions at different temperatures. It can be observed that the additive starts to be active for NO removal at temperatures lower than those necessary for NO decomposition and higher activity is obtained at temperatures above 600°C. And even more important, no deactivation of the additive is observed after 30 min reaction.

Similarly to the results obtained for the NO decomposition reaction, an increase in the catalytic performance is observed when the additive is physically mixed with the

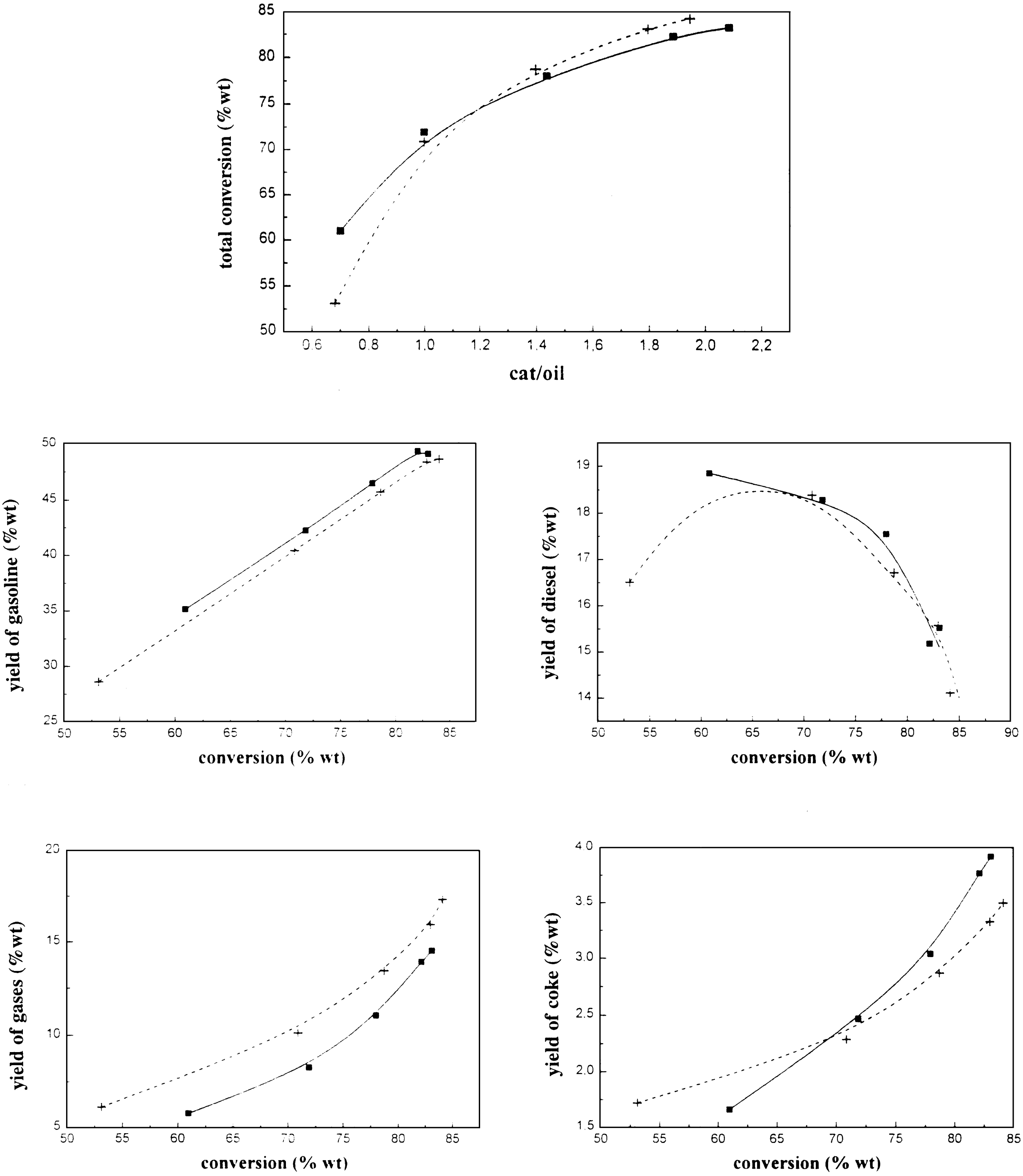

**FIG. 6.** Comparison in the activity during the gasoil cracking reaction of the commercial FCC catalyst (+) with additive (3 wt.%) and (■) without additive in a M.A.T. unit.

FCC catalyst. Taking into account that the FCC catalyst has no activity in NO removal under reduction conditions, we propose that the increase of catalytic conversion of NO could be attributed to the occurrence of some interaction between the additive and the FCC catalyst, probably due to a Cu solid ion exchange in the zeolitic component of the catalyst during the thermal treatments.

The influence of the $O_2$ concentration in the catalytic reduction of NO in presence of Cu hydrotalcite was also studied. In order to carry out this study, the concentration of $O_2$

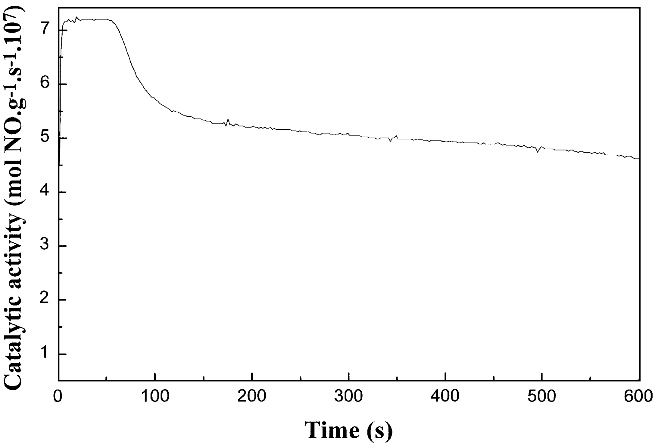

**FIG. 7.** Influence of the addition of water in the NO decomposition reaction at 750°C over a mixture of a commercial FCC catalyst and a Cu hydrotalcite additive (3 wt.% of the additive in the FCC catalyst, 2.8% molar of water, $7.378 \times 10^{-7}$ mol $NO \cdot s^{-1} \cdot g^{-1}_{additive}$, $N_2$ as gas balance).

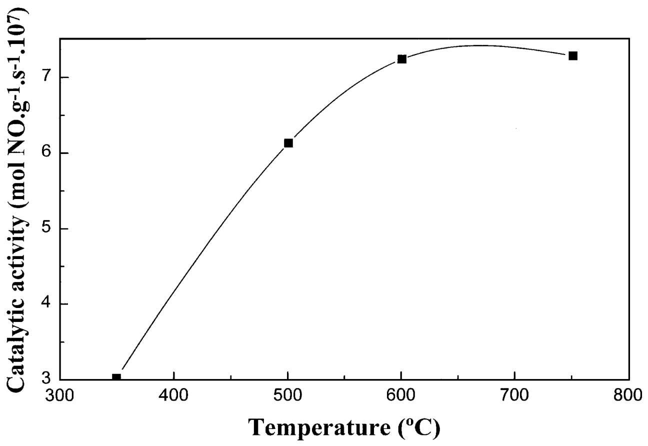

**FIG. 9.** Influence of the temperature in the removal of NO under reduction conditions over Cu hydrotalcite additive ($7.378 \times 10^{-7}$ mol $NO \cdot s^{-1} \cdot g^{-1}_{additive}$, $C_3H_8/NO$ ratio = 1 and $N_2$ as gas balance).

was increased until the catalytic conversion of NO starts to decrease, obtaining in this way the highest $O_2$/propane ratios that can be tolerated by the catalyst at different temperatures. From the results presented in Fig. 10, we conclude that (a) the catalyst is active for selective NO reduction even in presence of $O_2$, and (b) the highest $O_2$/propane ratio in which the catalyst is active depends on the temperature of reaction, as the value of this maximum ($O_2$/propane ratio) decreases as the temperature of the reaction increases. These results strongly suggest that oxygen and NO are competing in the oxidation of the propane present in the stream, in such a way that at low temperatures NO is selectively reduced by the propane (i.e., propane is oxidized by the NO), but when the temperature reaches a certain level or the concentration of oxygen becomes too high, the oxidation of propane takes place by direct reaction with oxygen.

The behavior of the mixed FCC catalyst and the Cu hydrotalcite additive in the reduction of NO in presence of $O_2$ at the working temperature in the FCC regenerator unit (700–750°C) is represented in Fig. 11, showing that when the oxygen concentration increases the catalytic activity in the NO reduction decreases, but the additive still retained 50% of activity even in presence of 2% $O_2$ in the stream.

We conclude that the Cu-containing hydrotalcites may be an active additive to the FCC catalysts for the NO removal in the regenerator unit. In the dense phase of the fluid bed, where the oxygen concentration is very low or even a reductive atmosphere could be formed due to the incomplete combustion of coke, 100% conversion of NO should be expected attending to the results obtained in this work. However, the additive becomes inactive for NO decomposition

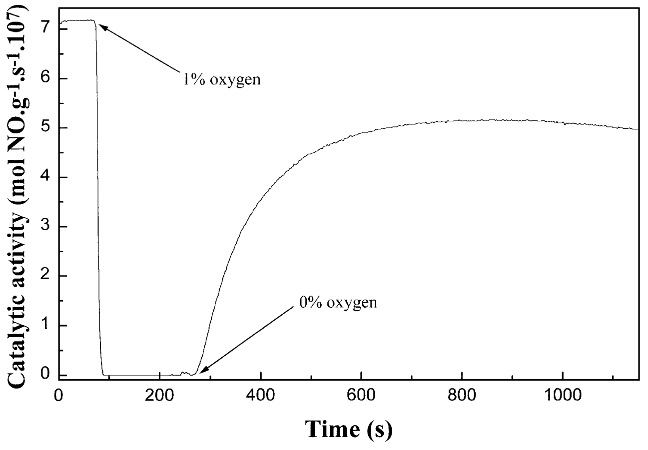

**FIG. 8.** Influence of the addition of oxygen in the NO decomposition reaction at 750°C over a mixture of a commercial FCC catalyst, and a Cu hydrotalcite additive (3 wt.% of the additive in the FCC catalyst, $7.378 \times 10^{-7}$ mol $NO \cdot s^{-1} \cdot g^{-1}_{additive}$, $N_2$ as gas balance).

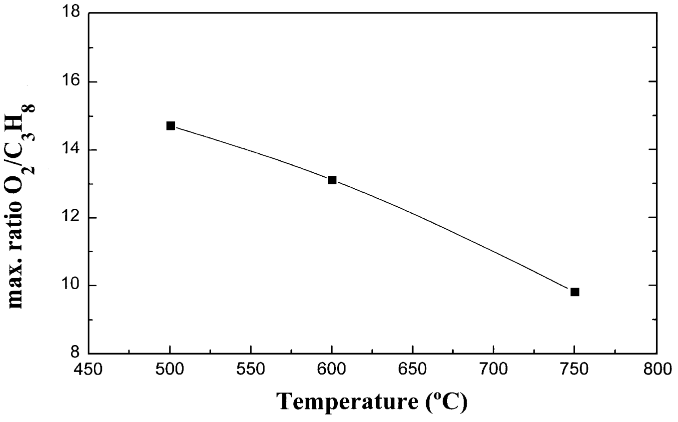

**FIG. 10.** Maximum oxygen/hydrocarbon ratio in which the CuHT additive is active for removal of NO under reduction conditions at different temperatures ($7.378 \times 10^{-7}$ mol $NO \cdot s^{-1} \cdot g^{-1}_{additive}$, $C_3H_8/NO$ ratio = 1 and $N_2$ as gas balance).

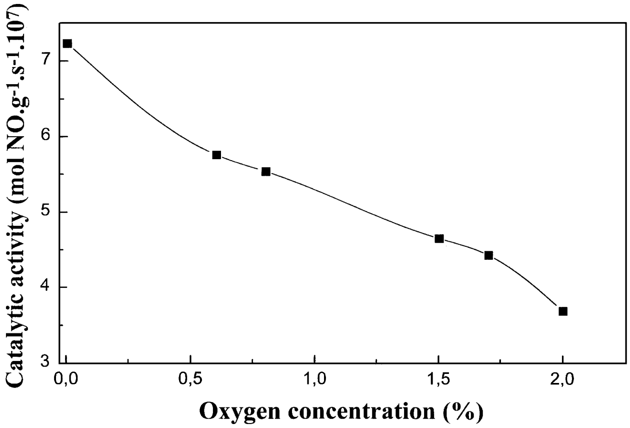

**FIG. 11.** Influence of the concentration of oxygen in the removal of NO under reduction conditions at 750°C over a mixture of a commercial FCC catalyst and 3 wt.% CuHT additive ($7.378 \times 10^{-7}$ mol $NO \cdot s^{-1} \cdot g^{-1}_{additive}$, $C_3H_8/NO$ ratio = 1 and $N_2$ as gas balance).

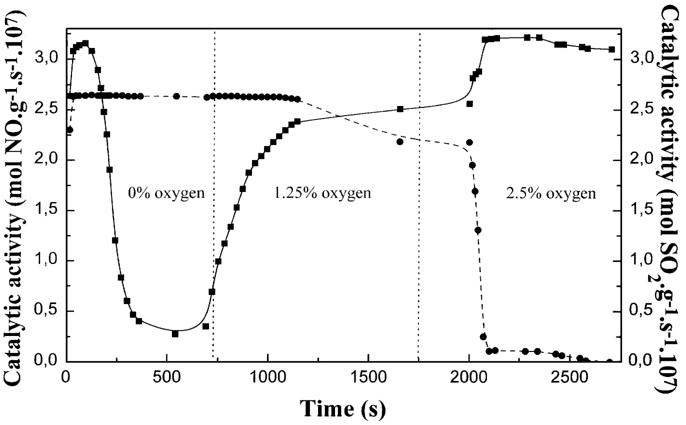

**FIG. 12.** Profile of the NO decomposition reaction (●) and the $SO_2$ removal reaction (■) at 750°C and different concentration of oxygen over Cu hydrotalcite additive. (2 g additive, 450 ppm NO, 540 ppm $SO_2$, and $N_2$ as gas balance, total flow = 1600 $cm^3$/min.)

when the $O_2$ concentration increases by going up in the fluid bed, but high elimination level of NO would still be expected due to the reduction pathway. Consequently, the overall performance of the additive along the fluid bed in the regenerator unit of FCC reactor may be acceptable for NO removal.

### *Simultaneous $NO_x$ and $SO_x$ Removal*

Previously, we have reported that the Cu hydrotalcite materials are active catalysts for the $SO_x$ removal in FCC units (8). The catalyst studied in this paper is the one showing the best absorption of $SO_x$/regenerability ratio in the $SO_x$ removal (8). Therefore, it appears feasible that this additive can be adequate for the simultaneous removal of the $SO_x$ and $NO_x$ (23). However, the elimination of $SO_x$ requires the presence of $O_2$ in order to oxidize the $SO_2$ to $SO_3$ that is adsorbed on the additive as sulfate, but an excess of $O_2$ deactivates the catalyst for carrying out the decomposition and the reduction of NO. Consequently, it becomes necessary to determine the "window" in which the catalyst can effectively remove both contaminants in one single step.

Figure 12 shows the profiles for NO and $SO_2$ conversion during reaction under conditions similar to those employed for NO decomposition (i.e., in absence of propane). Different amounts of $O_2$ were added to the stream looking for the "window" in which the content of oxygen is high enough to oxidize the $SO_2$ to $SO_3$, but not enough to deactivate the additive for the NO decomposition. As is shown, the NO is decomposed completely in absence of $O_2$ showing no deactivation with time on stream. However, $SO_2$ is removed at the beginning of the reaction, being the additive deactivated for the $SO_2$ removal after 3 min reaction. When 1.25% oxygen is added, the additive recovers some of its $SO_2$ removal capacity. At the same time, the activity for the NO decomposition starts to decrease, but under these reaction conditions still a considerable amount of NO is decomposed. Further increases in the oxygen concentration produce a complete deactivation of the catalyst for the NO decomposition reaction, but maximum removal of $SO_x$ is obtained. It is noticeable that the presence of $SO_2$ in the stream greatly increases the resistance of the additive to the poisoning by $O_2$, as is shown in Fig. 13.

In presence of propane (i.e., NO reduction conditions), the catalytic results shown in Fig. 14 indicate that complete removal of both contaminants can be achieved at concentration of oxygen lower than 2%. However, under these reaction conditions $SO_2$ is removed via a reductive pathway, instead of an oxidative process, as is made evident by the presence of $H_2S$ in the reactor outlet. Finally, when the concentration of oxygen in the stream is increased above 2%, the activity for NO reduction starts to decrease and

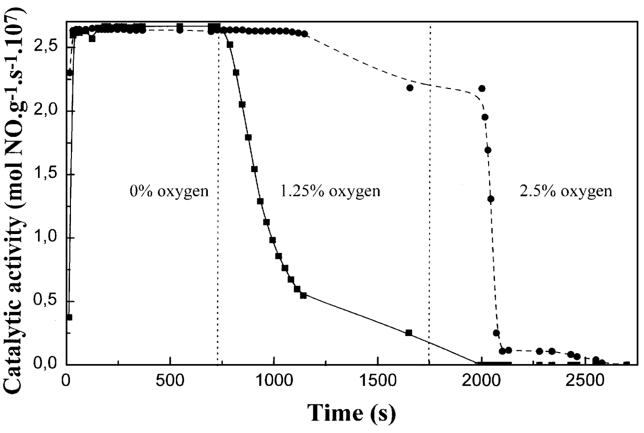

**FIG. 13.** Profile of the NO decomposition reaction in absence of $SO_2$ (■) and in presence of 540 ppm of $SO_2$ (●) at 750°C and different concentration of oxygen over Cu hydrotalcite additive. (2 g additive, 450 ppm NO, $N_2$ as gas balance, total flow = 1600 $cm^3$/min.)

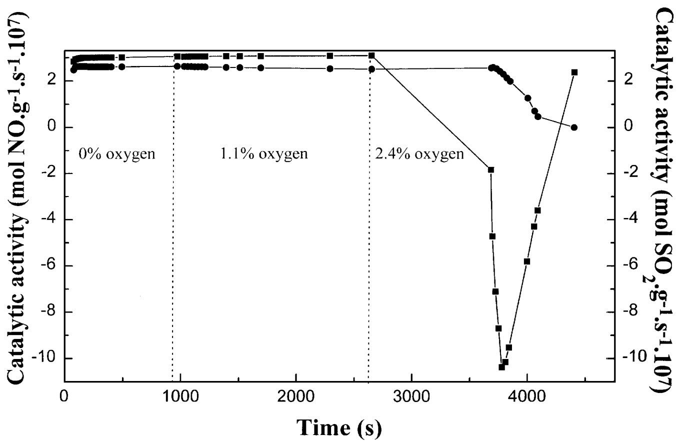

**FIG. 14.** Profile of the NO reduction reaction (●) and the $SO_2$ removal reaction (■) at 750°C and different concentration of oxygen over Cu hydrotalcite additive. (2 g additive, 450 ppm NO, 540 ppm $SO_2$, 450 ppm $C_3H_8$, and $N_2$ as gas balance, total flow = 1600 cm$^3$/min.)

$SO_2$ removal mechanism changes from a reductive pathway to an oxidative one. This is reflected by the presence of a sharp peak in the $SO_2$ conversion profile that reach values of $SO_x$ in the outlet of the reactor even higher than those that are fed, indicating that some sulfured species retained on the surface of the additive are burnt off as $SO_x$.

From the results exposed above we are able to infer the presence of different active sites for the removal of NO when $SO_2$ is present in the stream. In absence of $O_2$ and under NO reduction conditions it has been shown that $H_2S$ evolves due to the reduction of $SO_2$. Then, it is reasonable to propose that under these reactions conditions, sulfured copper species could be formed. It is well established that the most stable copper sulfides are those in which copper has the +1 oxidation state. For instance, $Cu_2S$ is formed when Cu is heated in presence of $H_2S$ (22); even CuS contains Cu(I) species and should be formulated as $Cu^{I}_{2}Cu^{II}(S_2)S$. Considering that Cu(I) species have been widely proposed as the active species in NO reduction (24–27), the presence of $H_2S$ into the stream favors the formation of sulfur-based Cu(I) species active for the reduction of NO. The formation of these species is evidenced by the generation of $SO_2$ observed when 2.5% of $O_2$ is introduced, showing that some sulfured compounds are oxidized and $SO_2$ is produced.

The same sulfur species could be claimed to be responsible for the catalytic decomposition of NO on the Cu hydrotalcite additive in presence of $SO_2$. Indeed, as is shown in Fig. 12, both contaminants are removed from the stream at the beginning of reaction (0–100 s). Under these conditions (i.e., under absence of $O_2$) and assuming that all the oxygen produced by the NO decomposition is consumed in the oxidation of $SO_2$, only a maximum of 83% conversion should be expected. However, total $SO_2$ conversion is obtained in these first seconds, indicating that processes other than simple oxidation are occurring. A possible explanation for this is that $SO_2$ is eliminated via a reductive process such as

$$2Cu(0) + SO_2 \rightarrow Cu_2S + O_2.$$

This is supported also by XPS results which show the presence of Cu(0) at the beginning of reaction, which is converted to Cu(I) in presence of NO and $SO_x$. Also, the presence of S is detected on the surface of the additive. However, it is not possible to establish the oxidation state of the S linked to Cu due to the presence of other sulfur species absorbed on the surface of the Cu hydrotalcite. The activity of the sulfur–copper species for NO decomposition was proved by carrying out an experiment in which the sample was presulfured flowing $H_2S$ through the catalyst before starts the NO decomposition reaction. In this case we observe that the sulfur species formed are active in the removal of NO, achieving a conversion similar to that obtained when we study the catalytic performance of the nonsulfured additive under the same conditions, but in presence of $SO_2$. This indicates that the copper-sulfured species formed are also active for the decomposition of NO, probably because the adequate oxidation state of the copper species (+1) is stabilized.

When the copper is completely sulfured, the additive becomes inactive for the $SO_2$ removal. However, the NO is completely eliminated under these conditions, even in the presence of small amounts of oxygen. Upon increasing the oxygen concentration in the stream, the copper sulfide species decompose and the additive becomes inactive for NO decomposition but active for the $SO_2$ catalytic removal.

Finally the influence of coke was tested by using a FCC catalyst containing the Cu hydrotalcite additive and which was precoked by carrying out the cracking of vacuum gasoil feed at 520°C. It was found that the activity for the removal of $SO_2$ and $NO_x$ was not affected by the presence of coke. We can thus conclude that working under conditions similar to those found in the regenerator of the FCC unit, there is a range in the $O_2$ concentration (from 0 to 1.5%) where the Cu hydrotalcite can simultaneously remove $SO_2$ (via an oxidative or reductive reaction) and NO (via a reduction and/or decomposition reaction) in the regenerator of the FCC unit. We have found that the sulfured copper species formed during reaction are more active for the removal of NO than the Cu species present in the original Cu hydrotalcite. Finally the presence of the steam generated during the catalyst regeneration does not negatively affect the catalytic activity of the Cu-hydrotalcite-derived catalyst.

## ACKNOWLEDGMENT

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## REFERENCES

1. Cusumano, J. A., *Chemtech* **22**, 482 (1992).
2. Seinfeld, J. H., *in* "Atmospheric Chemistry and Physics of Air Pollution," Wiley, New York, 1986.

3. Armor, J. N., *Appl. Catal. B* **1**, 221 (1992).
4. Corma, A., and Kluger, E. L., *in* "Progress in FCC Catalysts," Catalytica Studies Division, 1992.
5. Anonymous, *Intern. Petrol.* **Jan.-Feb.**, 15 (1988).
6. Mann, R., *Catal. Today* **18**, 509 (1993).
7. Yoo, J. S., Bhattacharyya, A. A., Radlowski, C. A., and Karch, J. A., *Appl. Catal. B* **1**, 169 (1992).
8. Corma, A., Palomares, A. E., and Rey, F., *Appl. Catal. B* **4**, 29 (1994).
9. Teraoka, Y., Fukuda, H., and Kagura, S., *Chem Lett.* **1**, 1 (1990).
10. Yasuda, H., Mizuno, N., and Misoni, M., *J. Chem. Soc. Chem. Commun.* **19**, 104 (1990).
11. Iwamoto, M., and Hamada, H., *Catal. Today* **10**, 57 (1991).
12. Hamada, H., *Catal. Today* **22**, 21 (1994).
13. Shannon, I. J., Rey, F., Sankar, G., Thomas, J. M., Maschmeyer, T., Waller, A. M., Palomares, A. E., Corma, A., Dent, A. J., and Greaves, G. N., *J. Chem. Soc. Faraday Trans.* **92**, 4331 (1996).
14. Scofield, J. H., *J. Electron. Spectrosc. Relat. Phenom.* **8**, 129 (1976).
15. Vulli, M., and Starke, K., *J. Phys. E* **10**, 158 (1978).
16. Inui, T., Iwamoto, M., Kojo, S., and Yoshida, T., *Catal. Lett.* **13**, 87 (1992).
17. Li, Y., and Hall, W. K., *J. Catal.* **129**, 202 (1991).
18. Burch, R., and Millington, P. J., *Appl. Catal. B* **2**, 101 (1993).
19. Corma, A., Palomares, A. E., and Fornes, V., *Appl. Catal. B* **11**, 233 (1997).
20. Karge, H. G., and Beyer, H. K., *Stud. Surf. Sci. Catal.* **69**, 43 (1991).
21. Rheaume, L., Ritter, R. E., Blazek, J. J., and Montgomery, I. A., *Oil Gas J.* **74**, 103 (1976); **74**, 76 (1976).
22. Greenwood, N. N., and Earnshaw, A., *in* "Chemistry of the Elements," p. 1373. Pergamon Press, Oxford, 1984.
23. Corma, A., Palomares, A. E., and Rey, F., European Patent 9301712 (1993).
24. Iwamoto, M., Mizuno, N., and Yahiro, H., *Stud. Surf. Sci. Catal.* **75**, 1285 (1993).
25. Sasaki, M., Hamada, H., Kintaichi, Y., and Ito, T., *Catal. Lett.* **15**(3), 297 (1992).
26. Gopalakrishnan, R., Stafford, P. R., Davidson, J. E., Hecker, W. C., and Bartolomew, C. H., *Appl. Catal. B* **2**, 165 (1993).
27. Li, Y., and Armor, N., *Appl. Catal. B* **2**, 239 (1993).