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VI Encuentro Franco-Español de Química y Física del Estado Sólido  
VI<sup>ème</sup> Rencontre Franco-Espagnole sur la Chimie et la Physique de l'État Solide

## Pt/CuZnAl mixed oxides for the catalytic reduction of nitrates in water: Study of the incidence of the Cu/Zn atomic ratio.

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### Abstract

1%wt Pt was impregnated on CuZnAl calcined hydrotalcite-type precursors with three Cu/Zn atomic ratios (2, 1 and 0.5). The calcined hydrotalcites and the Pt impregnated materials were characterized by: XRD, BET, TGA, and TPR. These materials were tested as catalysts for the nitrate reduction in water, to study the role of the Cu/Zn atomic ratio in the conversion and selectivity of the reaction. The different Cu/Zn atomic ratios led to different catalytic behaviours. In addition, support activity and adsorptive tests were performed.

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*Keywords:* Nitrate removal; hydrotalcites, CuZnAl.

### 1. Introduction

Groundwater pollution with high nitrate concentration mainly caused by the use of fertilizers in agriculture, chemical products and septic tank systems, is a cause of concern in several countries. Nitrate is a potential human health hazard, and subsequently the governments to prevent health problems like clinical cyanosis established drinking water standards. Different techniques to remove nitrates from water had received increasing attention [1]. Catalytic denitrification is one of the most promising techniques for nitrate removal considering an ecological point of view, because it transforms nitrates into nitrogen without a waste generation. The technique was first described by Vorlop and Tacke [2], and it consists in the nitrates reduction over a bimetallic catalyst using a reducing agent like hydrogen.

It was well established during the previous studies that the diffusion limitations affects the kinetics and selectivity of the reaction [3]. Selecting and adequate catalytic support like calcined hydrotalcites, these problems can be

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solved, as it was demonstrated by Palomares et al [4]. Hydrotalcites are layered double hydroxides that can be represented by the general formula:  $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[(A_{x/n}^{n-})] \cdot mH_2O$ , where  $x$  is typically between 0.25 and 0.33, and  $A^{n-}$  is a  $n$ -valent interlayer anion. A wide range of derivatives containing various combinations of  $M^{2+}$ ,  $M^{3+}$  and  $A^{n-}$  ions can be synthesized. After calcination, they form homogeneous mixed metal oxides with very small crystal size, stable against thermal treatments, which by reduction results in high dispersion of the metallic crystallites. The mixed oxides recover its initial structure when they are again hydrated, this is called the “memory effect” [5]. Recently, hydrotalcite containing copper, magnesium and alumina in its structure had been investigated for their potential as precursors of catalysts in the reduction of nitrates using Pd-Cu and Pd-Sn metallic pair [4].

The aim of this work is to prepare CuZnAl mixed oxides with different Cu/Zn atomic ratios and to characterize them by different techniques: XRD, TPR, TGA, BET. Also, the materials were used in the catalytic reduction of nitrates in water.

## 2. Experimental

CuZnAl hydrotalcite-like precursors with different Cu:Zn:Al atomic ratios were prepared by a standard coprecipitation method, using the nitrate salts as metal precursors and a solution containing NaOH 2M as precipitating agent. The (Cu+Zn)/Al atomic ratio in the starting solution was maintained at 3 and the Cu/Zn atomic ratio was theoretically fixed as 2, 1 and 0.5. The hydrotalcite precursor was calcined at 450°C overnight. The prepared materials were then wet-impregnated with 1%wt Pt using  $H_2PtCl_6$  as salt precursor.

## 3. Results and discussion

Initially, CuZnAl hydrotalcites were prepared and characterized by XRD (Fig 1.) to confirm the presence of a lamellar structure in all the samples. The thermal decomposition of the hydrotalcite precursors was also monitored by XRD and TGA. The thermal decomposition of the materials can be divided in two steps in all cases. First, from 50°C to 190°C the signal indicates emission of the weakly bonded interlayer water molecules. The second weight loss between 180°C and 450°C is assigned to dehydroxylation of the brucite-like layers and decomposition of the anions located in the interlayer space. As a result of the XRD thermal studies the formation of CuO and ZnO phases were observed, and a temperature of 450°C was fixed to calcine the materials. After calcination overnight of the hydrotalcite precursors, they were characterized by different techniques.

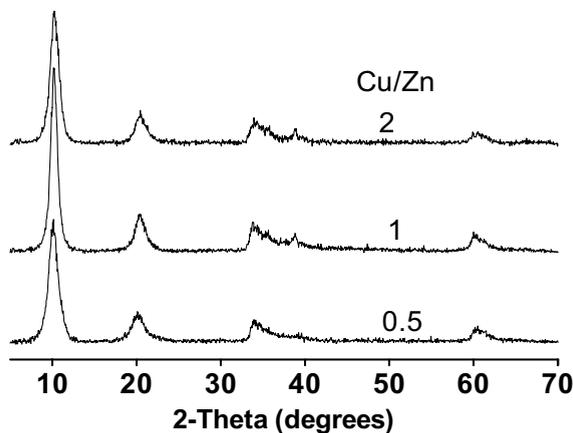


Figure 1. XRD patterns of hydrotalcite precursors with different Cu/Zn atomic ratios.

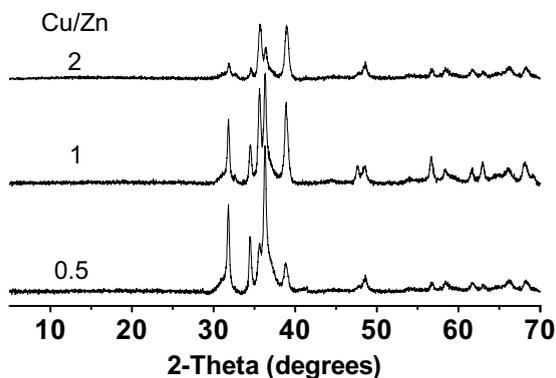


Figure 2. XRD patterns of calcined hydrotalcites with different Cu/Zn atomic ratios.

The XRD patterns of the calcined materials (Fig. 2) showed that the characteristic lamellar structure disappears and the presence of CuO phase and zincite phase are detected in all cases. The crystallinity of the calcined samples varies depending upon the elemental composition in their precursors.

The calcined precursors presented BET surface areas around 50 m<sup>2</sup>/g, and the BET area decreases linearly with the Cu/Zn atomic ratio content (see Table 1).

Table 1. BET surface area of the platinum impregnated materials with different Cu/Zn Ratios

| Cu/Zn ratio  | 0.5  | 1    | 2    |
|--|------|------|------|
| BET Surface area (m <sup>2</sup> /g) of Pt-impregnated materials | 62.9 | 52.9 | 52.0 |
| BET Surface area (m <sup>2</sup> /g) of CuZnAl supports          | 54.0 | 48.0 | 42.0 |

The samples were also analyzed by TPR (Fig. 3). The CuZnAl calcined hydrotalcites all give similar profiles consisting of a single intense peak around 300°C, and the reduction temperature increases while copper content increases.

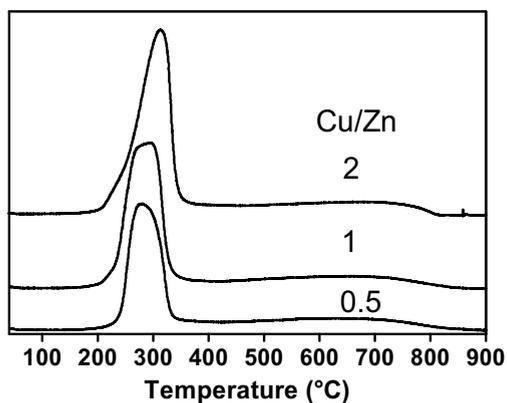


Figure 3. H<sub>2</sub>-TPR analyses of calcined precursors.

Finally, the characterized CuZnAl calcined hydrotalcite-like materials were impregnated with platinum and characterized by XRD and TPR. For none of the catalysts XRD diffraction peaks associated to platinum species are observed, because of the low Pt content (1% wt.) and its good dispersion. As for TPR analysis, the reduction temperature of CuO is affected by the Pt addition. When Pt is impregnated the peaks are shifted to lower temperatures. No reduction peaks are assignable to Pt (Fig. 4).

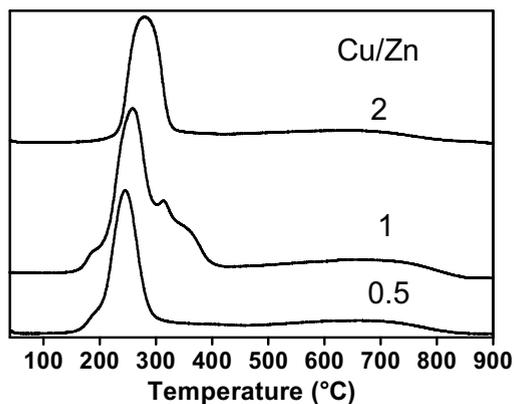


Figure 4. H<sub>2</sub>-TPR analyses of Pt-impregnated materials.

The Pt-impregnated materials were tested as catalysts for the denitrification of water. The reactions were performed in a three phase continuous reactor, operating at atmospheric conditions using hydrogen as reducing agent. Aqueous samples from the reactions were analyzed by HPLC. To determine nitrate and nitrite concentration an anion separation column Shodex IC SI-90 4E for suppressor method was used, and to analyze ammonium concentration a Shodex IC YK-421 column.

The catalytic results of the Pt-impregnated materials are shown in Fig. 5. The highest nitrate conversion was obtained for a Cu/Zn atomic ratio of 1, while the highest selectivity to nitrogen was obtained for a Cu/Zn atomic ratio 0.5. A change in the Cu/Zn ratio causes different surface metal chemistry and different types of interaction between the metals in the active supports, leading to different selectivities and conversions. Further characterization techniques should be performed (like HRTEM, acidity of the support, copper surface area, etc) in order to confirm this and to explain the catalytic activity.

Compared to results available in the literature [4] conversion achieved is lower, although ammonium selectivity is better. It has to be taken into account that this study was performed in a continuous reactor and the amount of noble metal has been reduced by 5 times. It is also worthy to remark that the catalysts were reproducible and stable in time during 1600 min of reaction.

Also, calcined hydrotalcites without Pt were catalytically tested as reference materials. They were rapidly deactivated and no ammonium formation or desorption was detected, showing that platinum is necessary to regenerate copper to increase the degradation rate of nitrate [6].

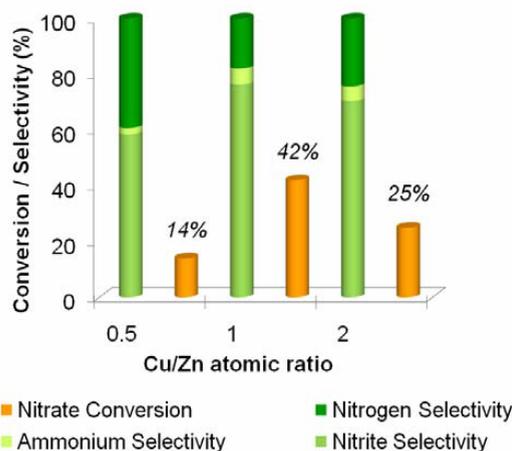


Figure 5. Catalytic results of 1%Pt impregnated CuZnAl materials

#### 4. Conclusions

CuZnAl calcined hydrotalcite materials with different Cu/Zn atomic ratios were synthesized and characterized in the present work. The surface characteristics of the materials varied with the Cu/Zn ratio. The samples are composed by CuO and ZnO phases detected by XRD. Their BET area decreases linearly with the Cu/Zn atomic ratio.

CuZnAl mixed oxides impregnated with Pt are active and stable catalysts for the catalytic reduction of nitrates, showing an important influence of Cu/Zn ratio in the catalytic behaviour. Also nitrogen selectivity is affected. Low ammonium concentrations were detected in all cases. Nitrogen selectivity should be improved in order to accomplish the European maximum admissible concentrations for nitrate, nitrite and ammonium in drinking water.

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