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Study of Supported Copper Chloride Catalysts by Electron Paramagnetic Resonance and X-Ray Diffraction

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Variations of catalytic properties of $CuCl_2$ supported on γ-alumina with active phase content and carrier thermal treatment were investigated by EPR and X-ray diffraction techniques. Two series of catalysts were prepared using γ-alumina, treated at 400 and 800°C, as supports. In both series the copper content ranged from 0.3 to 8 wt % of the total catalyst weight. On the basis of EPR and X-ray diffraction studies, two different types of bonds between the oxygen of the γ-alumina surface and the copper ions are considered predominant in each series of catalysts.

Catalyst activity and selectivity in the oxychlorination of benzene are discussed in terms of the chemical nature of these bonds and of the location of the copper chloride on the carrier surface.

Introduction

Among the types of alumina that have been extensively used as carriers the high-area form, γ-alumina, is perhaps of greatest catalytic interest. γ-Alumina does not behave as an inert support, but influences strongly the characteristics of the catalyst active phase. Selwood (*1*), using magnetic susceptibility data, showed that the oxidation state of a transition metal oxide could be affected by the crystalline structure of the alumina used as support; Rymer, Bridges and Tomlinson (*2*) and Tomlinson *et al.* (*3*) proposed a two-phase model, each one with different catalytic properties, for nickel or cobalt on γ-alumina, depending on the location of the metal cations; Solymosi (*4*), in his review on the electronic interaction between active species and carriers, discussed the catalytic performance of metals supported on alumina.

Lately Blanco *et al.* (*5*, *6*) reported additional evidence of such a type of interaction in the case of a salt supported on γ-alumina. They have shown that in the absence of diffusional limitations, the catalytic behavior of $CuCl_2$ on γ-alumina for the benzene oxychlorination reaction depends on the alumina pretreatment temperature and on the active phase concentration in the catalyst. The activity per gram of copper was about three times greater when the support was treated at 400°C (series A catalysts) than when the alumina thermal treatment was at 800°C (series B catalysts).

Moreover, experiments at the same level of benzene conversion, carried out with these series of catalysts, showed that those belonging to series B were roughly 15% more selective to monochlorobenzene than the corresponding ones of series A. For example, at the level of 9.3 mol % benzene conversion, the selectivity to monochlorobenzene of a series A catalyst, which contained 4.3 wt % Cu, was 81.2%, while the series B catalyst with the same copper content gave a selectivity value of 92.5%. Mean surface areas of these catalysts, measured by the BET method with N_2, were 220 and 135 m^2/g for carrier treated at 400 and 800°C, respectively.

Since EPR parameters are influenced by

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the electronic distribution and the symmetry of the electrostatic field surrounding the paramagnetic ion, the EPR spectra of the copper ion in this system could also show the location of the copper chloride molecules on the surface and the possible influence of the γ-alumina used as support. At the same time, an X-ray diffraction analysis of the catalysts can help to correlate the degree of the active phase crystallization with some characteristics of the alumina surface.

The main purpose of this study is to correlate the EPR and X-ray diffraction measurements with possible effects of the carrier on the catalytic properties of the supported catalysts.

Experimental Methods

Preparation of the catalysts. Two series of catalysts were prepared by impregnation of γ-alumina with $CuCl_2$ solutions. The $CuCl_2 \cdot 2H_2O$ (Carlo Erba) was a 99.98 wt % pure grade reagent. The two aluminas used as support were prepared by heating γ-alumina (Girdler Südchemie Katalysator GmbH, high purity T-126) for 12 hr in air at 400°C (Series A) or 800°C (Series B). After impregnation, the catalysts were heated in air at 300°C for 2 hr. In both series, the copper content ranged from 0.3 to 8 wt % of the total weight. The copper and chloride contents of each catalyst were determined using conventional methods.

EPR measurements. The signal intensity variation of the copper ion with the concentration of the active phase in the catalysts was followed with a Varian 4500 spectrometer, operating at X band frequency and with 100 kHz modulation. A JEOL-ME-3X spectrometer was used to resolve the hyperfine structure of the cupric ion. TCNQ-Li and DPPH were used as references for calibrating the magnetic field and calculating the relative intensity of the samples. Measurements were made at room temperature with dehydrated samples and at liquid nitrogen and room temperatures for the hydrated catalysts.

X-Ray diffraction. The amount of crystalline copper chloride in the catalysts was measured by the strongest reflexion intensity at $d = 5.49$ Å for $CuCl_2 \cdot 2H_2O$, where no variable orientation effect was observed. The average crystal size value was taken along its reciprocal direction; the values were estimated using the Scherrer equation (*7*), where the instrumental peak broadening was taken into account. The samples were thoroughly hydrated before the measurements were made. The diffractograms were obtained with a Philips PV 1051 diffractometer with proportional counter. CuK radiations at 40 kV and 20 mA and 1, 0.2 and 1 deg (divergence, receiving and scatter slits, respectively) were used.

Results

$CuCl_2 \cdot 2H_2O$ single crystals have an orthorhombic structure with two copper atoms per unit cell. In the EPR spectrum, because of the exchange interaction, only one line is observed, with an anisotropic g factor (*8*). The polycrystalline samples presented the spectra shown in Fig. 1. The Cu(II) spectra of the samples of copper chloride supported on γ-alumina pretreated to 400 and 800°C change strongly with the amount of copper present on the sample. In Fig. 2 the spectra of 0.5 and 4 wt % Cu(II) samples of both series, dehydrated at 300°C, are presented. The values obtained for the signal parameters of both series of dehydrated catalysts are reported in Table 1.

ΔH is taken as the distance in gauss be-

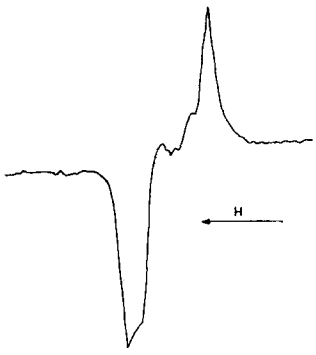

Fig. 1. EPR spectrum of polycrystalline $CuCl_2 \cdot 2H_2O$.

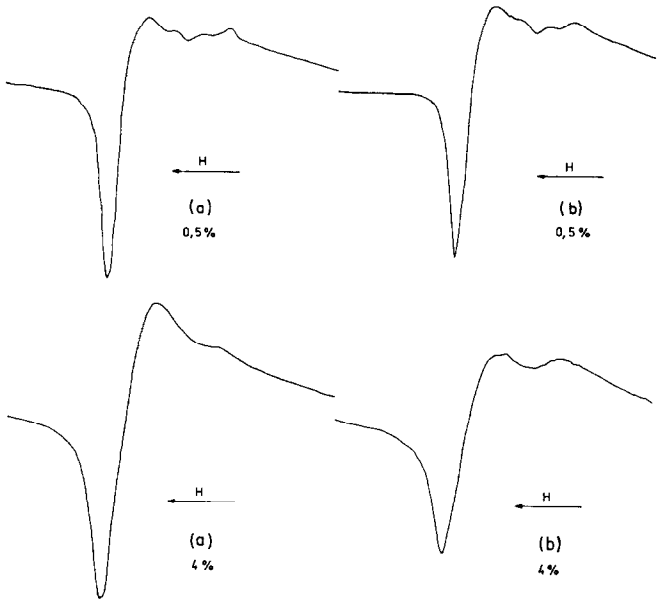

FIG. 2. EPR spectra of Cu^{2+} in dehydrated catalysts with 0.5 and 4 wt % of copper supported on γ-alumina. Series A (a) and series B (b).

tween the maximum and minimum of the line.

In the case of the hydrated samples, the signal parameters do not vary greatly with the copper concentration. In Fig. 3 the spectra of 0.5 wt % Cu(II) samples at liquid nitrogen temperature are presented. In Fig. 4, the height of the peak, taken as the vertical distance between the maximum and minimum, is plotted against copper concentration for the dehydrated samples.

The amount of crystalline $CuCl_2 \cdot 2H_2O$, measured by X-ray diffraction with a 10% accuracy, has been plotted in Fig. 5 versus copper concentration in the sample, for series A and B catalysts. As the data indicate, the presence of crystalline $CuCl_2 \cdot 2H_2O$ is shown only at copper concentrations above 1.5 wt % of copper for series A and 0.5 wt % for series B.

TABLE 1
EPR PARAMETERS

% Cu(II)	Series	$g_\perp$	$g_\parallel$	$A_\parallel$ (cm^{-1})	ΔH (G)
0.5	A	2.09	2.33	0.012	200
1	A	2.09	2.33	0.012	208
2	A	2.11	2.33	0.012	242
4	A	2.12	—	—	275
8	A	2.12	—	—	309
0.5	B	2.08	2.33	0.012	200
1	B	2.10	2.33	0.012	225
2	B	2.13	—	—	267
4	B	2.13	—	—	284
8	B	2.14	—	—	—

The mean crystal size appears to be independent of the support or active phase concentration. An average value of 460 ± 100Å was found for all the crystalline samples used. The presence in the diffractograms of peaks corresponding to the reflections of spacings 2.53 and 2.32 Å suggests the presence of small amounts of CuO in the samples.

Benzene oxychlorination experiments were carried out using both series of catalysts at the same experimental conditions. For each experiment a continuous fixed-bed glass tubular reactor was charged with 2 g of catalyst. Runs were made at atmospheric pressure, 270°C reaction temperature and with stoichiometric feed. The liquid benzene flow was 0.55 ml/min. Air was used as oxygen feed.

Figure 6 shows the variation of benzene conversion per gram of copper with the copper content in the catalysts. As can be

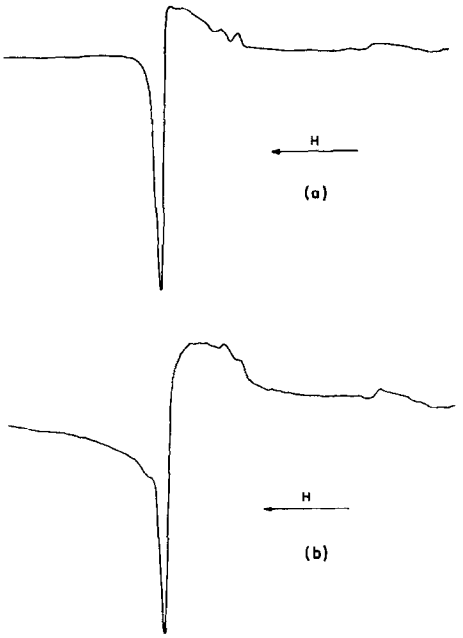

FIG. 3. EPR spectra of Cu^{2+} in hydrated catalyst with 0.5 wt % of copper, at liquid nitrogen temperature. Series A (a) and series B (b).

noted, the oxychlorination reaction rate increases with copper content up to about 1.7 wt % in series A and up to 1.0 wt % in series B. Higher copper concentrations gave lower values of the reaction rate per gram of copper.

DISCUSSION

The change in the EPR lineshape of the copper ions when $CuCl_2$ is in the polycrystalline state or when supported on alumina, shows clearly that γ-alumina is not acting as an inert carrier but is affecting the characteristics of the copper ions.

From the study of the lineshape and parameters of the spectra at different copper concentrations it is observed that the situation is similar to that of copper in zeolites (*9*). The lineshape is becoming more symmetric as the copper concentration on the γ-alumina is increased. This can be explained by superposition of a symmetric signal due to cluster formation of copper atoms, in which the ions are interacting. This line should have a g factor value close to:

$$\frac{2g_{\perp} + g_{\parallel}}{3} = 2.17,$$

which could explain the growing values observed for the g factor for increasing copper concentration. The observed linewidth will also increase, because at low

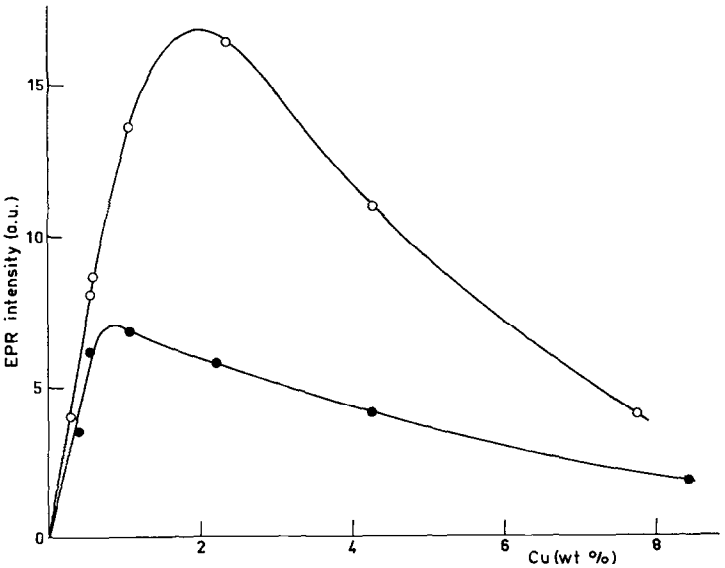

FIG. 4. Observed height of the EPR signal vs copper concentration of the series A (○) and series B (●) catalysts.

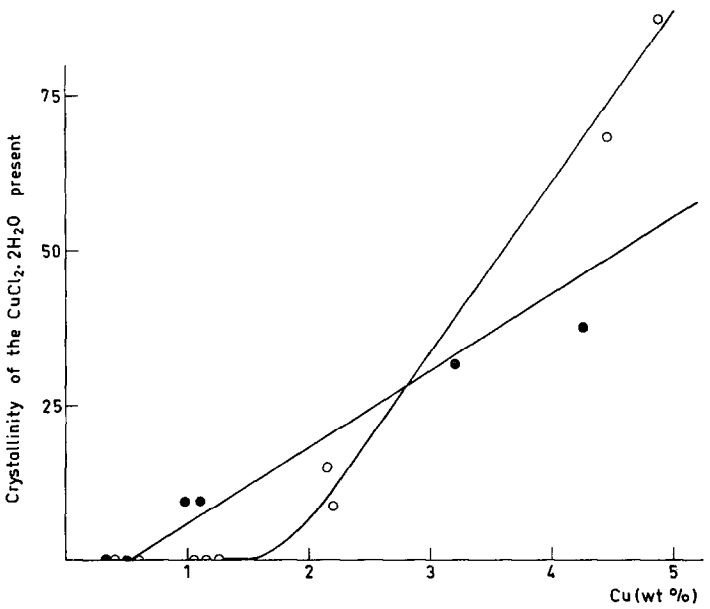

FIG. 5. Crystallinity of the $CuCl_2 \cdot 2H_2O$ present on the catalysts vs copper concentration. Series A (○) and Series B (●).

concentrations it will be the $g_\perp$ linewidth. But for high concentrations the observed linewidth will be the distance between the $g_\perp$ component and the symmetric signal. The hyperfine structure will appear less clearly resolved by the superposition of the symmetric line.

In Fig. 4 two regions are clearly differentiated. In the first, at low copper concentration, the height of the peak grows proportionally to the copper content; in the second region the height decreases with copper concentration. In this case of superposition of two signals, the height of the

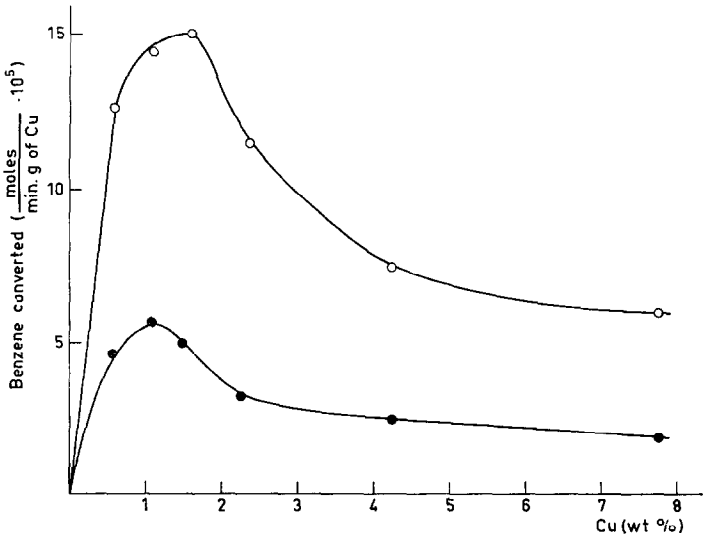

FIG. 6. Oxychlorination reaction rate vs copper concentration on the catalysts. Series A (○) and Series B (●).

peak cannot be taken as proportional to the signal intensity over all concentration ranges. However, in the region in which one of the signals is much higher than the other, the height of the peak can be correlated with the intensity. In the first region, in which the influence of the spin concentration is proportional to the copper concentration, the copper atoms are not close enough to interact. In the second region, in which the symmetric curve is the greatest, a decrease of the peak height is observed. This behavior is probably due to the interaction of copper atoms.

For all the catalysts the height of the peak of the series B samples was smaller than the corresponding samples of series A. At high copper concentrations when copper clusters are formed this effect can be correlated with the different surface areas of the supports. At low copper concentrations, even where the lineshape and signal parameters are the same, a smaller peak height must indicate a lower paramagnetism [see Ref. (*5*) for magnetic susceptibility data]. This can be explained by a smaller cupric character of the copper ions in series B.

If we consider the samples with 0.5% of copper, in which the copper atoms are isolated, it is clear that the spectra are very similar for the dehydrated samples, but for the hydrated ones, as shown in Fig. 3, the A samples have a more symmetric lineshape. This fact cannot be attributed to interaction between copper atoms, but is more due to copper atoms less rigidly bonded to the surface.

This behavior of the copper in both cases can be explained by two types of bonding, the first one, mainly in the series B, being Cu·O—Al, and the second, in series A,

being Cu·O—Al. In the latter case, the Cu–O bond should be weaker because of the influence of the hydrogen atom, and the copper ion will have a weaker cupric character.

According to the X-ray measurements, the weaker type of bonding is favorable to the crystallization of the supported $CuCl_2$, allowing the incorporation of the two water molecules. So, in series A the slope of the curve (Fig. 5) is actually very close to that obtained for mechanical $CuCl_2 \cdot 2H_2O$–alumina mixtures. In series B, where the stronger type of bonding predominates, the slope of the corresponding curve is smaller.

The different behavior of the copper on the two alumina surfaces is evident when the $CuCl_2$ is extracted with distilled water. The catalysts of both series with 4.7 wt % of copper content keep different amounts of copper after complete water extraction. The series A catalyst retained 1.6 wt % of copper, while the corresponding one in series B conserved 2.7 wt %.

Therefore, all this suggests that the different activity and selectivity shown for the oxychlorination reaction between the two series of supported catalysts is related to the formation of the two bonds mentioned above.

On the other hand, the curves which relate the reaction rate with the copper content in the catalyst (Fig. 6), present a maximum at approximately 1.6 wt % copper in series A and 1.0 wt % in series B. These maxima appear at about the same copper concentration as the inflection points of the EPR intensity measurements. In the latter case the low concentration region was interpreted as due to isolated copper ions, and the region of decreasing intensity with copper concentration as being caused by cluster formation.

The change in activity for each series of catalysts in the oxychlorination of benzene, for precisely the same concentrations at which the copper atom clusters begin to be noticed, indicates a clear relationship between the activity and the dispersion degree. The clusters are less active than the dispersed copper. The cluster formation has been confirmed by X-ray diffraction measurements (Fig. 5).

Therefore, at concentrations lower than 1.6 wt % copper in series A and 1 wt % in series B, the copper ion seems to be adsorbed by the vacant surface sites of the alumina crystalline lattice. In a similar way, Rymer, Bridges and Tomlinson (*2*) discussed the catalytic behavior of nickel and cobalt oxides supported on γ-alumina.

These authors suggested that alumina has the capacity to hold transition metal ions mainly in the octahedral vacancies of its surface.

If two octahedral vacancies are considered per each 62 Å^2 (the estimated surface of a face of the γ-alumina unit cell), a 1.0 wt % of copper on the support treated to 800°C represents one copper ion per 4.6 vacancies. In the case of the support treated to 400°C a 1.7 wt % of copper is equivalent to one copper ion per 4.4 octahedral vacancies. Therefore, it appears that when about 25% of the alumina octahedral vacancies are filled, the following $CuCl_2$ molecules start to form clusters on the surface of the carrier.

It can be concluded that the change in activity per gram of copper shown in each of the series of catalysts may be assigned to the different locations of the copper chloride on the carrier surface, while the variation in the activity and selectivity between both series of catalysts can be related to the formation of the two bonds proposed.

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References

1. Selwood, P. W., *in* "Advances in Catalysis" (W. G. Frankenburg, V. I. Komarewsky and E. K. Rideal, Eds.), Vol. 3, p. 28. Academic Press, New York, 1951.
2. Rymer, G. T., Bridges, J. M., and Tomlinson, J. R., *J. Phys. Chem.* **65**, 2152 (1961).
3. Tomlinson, J. R., Keeling, R. O., Rymer, G. T., and Bridges, J. M., *Actes Congr. Int. Catal. 2nd* **2**, 1831 (1960).
4. Solymosi, F., *Catal. Rev.* **1**, 233 (1968).
5. Blanco, J., Blanco, R., Cortes, A., and Soria, J., *Nature Phys. Sci.* **232**(33), 155–156 (1971).
6. Blanco, J., Blanco, R., Cortes, A., and Soria, J., Prepr. No. 64, *Int. Congr. Catal., 5th,* Palm Beach, FL (1972).
7. Klug, H. P., and Alexaner, L. E., "X-ray Diffraction Procedures," p. 511. Wiley, New York, 1954.
8. Zimmerman, N. J., Van der Mark, F. P., and Van der Handel, J., *Physica* **46**, 204 (1970).
9. Turkevich, J., Ono, Y., and Soria, J., *J. Catal.* **25**, 1, 44 (1972).