

Preparation and Characterization of Copper-Thorium Oxide Catalysts. 1. Solid Solution of Copper(II) in Thoria: An ESR Study

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Copper-thorium oxide catalysts prepared with an atomic ratio Cu/Th < 0.01 by coprecipitation of the hydroxides and calcination under dried air up to 1073 K were mainly studied by electron spin resonance (ESR). These systems behave as a solid solution, with the thoria structure. ESR studies evidenced two well-resolved signals, A₁ and A₂. A complete simulation of these signals was carried out by taking into consideration the presence of both copper isotopes ⁶³Cu and ⁶⁵Cu. It has been shown that copper is localized in the thoria structure as isolated Cu²⁺ ions, probably both in interstitial and substitutional sites. Then 8-fold coordination has been suggested for both Cu²⁺ ions sites. In the thoria lattice, such an environment seems more probable than an octahedral symmetry.

Introduction

Copper ions associated with other cations such as zinc, aluminum, or chromium in well-defined oxide structures give very interesting catalytic systems, particularly for the selective hydrogenation of unsaturated compounds¹⁻⁴ or for carbon monoxide conversion into methanol.⁵ For many years, such systems have been extensively studied in the literature; nevertheless, the catalytic role of copper remains controversial.⁶⁻¹⁵

We have recently developed a complete structural model for CuCrO, CuAlO, and CuZnO systems, to explain the catalytic behavior of these solids.^{16,17} A major feature in this study concerns the existence, in the reduced catalysts, of unsaturated octahedral Cu⁺ ions in the bulk and on the surface of such oxide phases. These ions, bound to a hydride ion, H⁻, have been demonstrated to be active sites in dienes selective hydrogenation,¹⁸ and it is probable that this model can be extended for CuZnO system in the methanol synthesis reaction.¹⁹

In the recent years, supported copper on thoria catalysts have also been used in the methanol synthesis reaction,^{20,21} but few correlations between structural and catalytic properties could be established for this system, probably because copper was not present in the bulk. An extrapolation of our previous approach to such new systems will be attempted in the present work; copper ions will be introduced in the lattice of ThO₂ by using a coprecipitation method of copper and thorium hydroxides by ammonium hydroxide, followed by calcination. In catalytic tests^{18,19,22} catalysts are used in reduced form; however, an understanding of the state of the catalysts before reduction can be helpful.

ESR techniques mainly will be used to investigate Cu²⁺ ions interactions with the surrounding, versus the major parameters affecting the preparation of the catalysts. A determinant factor is the copper/thorium ratio. To discuss in a more comprehensive way the various observations, we shall consider in this study only ESR results concerning samples with low copper contents. Catalysts with higher copper contents will be investigated further.²²

Experimental Section

Preparation of CuThO Samples. Different solids were prepared at room temperature by precipitation of hydroxides by

2.9 M ammonium hydroxide from a mixture of 0.1 M copper and thorium nitrates up to pH = 6.0 (all reactants are of pure grade analytical quality). Thereafter, the precipitates were carefully washed, filtered, and dried at 373 K, before a calcination treatment in a flow of dried air (150 K h⁻¹ heating rate and 5 h at calcination temperature, up to 1073 K).

A complete study of different parameters, as partly detailed below, such as reactant concentrations, atomic Cu/Th ratio, pH, and temperature of precipitation, led us to select the above conditions.

Structure. Oxides structures were analyzed on a Philips PW 1008 X-ray diffractometer equipped with a copper anode and a nickel filter.

ESR Spectra and Simulation. X-band ESR spectra were detected on a Bruker ER 200 D spectrometer at room temperature. Spectra were taken at microwave powers that did not cause saturation of ESR signals. A modulation amplitude of 1.25 G and

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Table I. ESR g and A Anisotropic Tensor Values for Cu^{2+} ions in CuThO Polycrystalline Powders (A_1 and A_2 Signals), Compared with Monocrystals of Strontium and Calcium Compounds Doped with Cu^{2+} (8-fold Coordinated Copper II)

samples	g_{\parallel} g_{zz}	g_{\perp}		A_{\parallel}, G A_{zz}	A_{\perp}, G		ref
		g_{yy}	g_{xx}		A_{yy}	A_{xx}	
A_1 signal ($\text{Cu}/\text{Th} = 0.01$)	2.2760	2.0445	2.0445	144.0 ($^{63}\text{Cu}^{2+}$) 153.8 ($^{65}\text{Cu}^{2+}$)	15.66	15.66	this work
A_2 signal ($\text{Cu}/\text{Th} = 0.01$)	2.2470	2.0097	2.0097	155.0 ($^{63}\text{Cu}^{2+}$) 165.5 ($^{65}\text{Cu}^{2+}$)	18.36	18.36	this work
Cu^{2+} doped $((\text{C}_7\text{H}_5\text{O}_3)_2\text{Sr}, 2\text{H}_2\text{O})$	2.2961	2.0760	2.0468	140.4 ($^{63}\text{Cu}^{2+}$)	28.70	22.70	28
Cu^{2+} doped $((\text{C}_7\text{H}_5\text{O}_3)_2\text{Ca}, 2\text{H}_2\text{O})$	2.2990	2.0750	2.0490	136 ($^{63}\text{Cu}^{2+}$)	35.00	15.00	28

a modulation frequency of 100 kHz were used.

Theoretical ESR spectra were calculated by using the effective spin Hamiltonian

$$\mathcal{H} = \beta H S g u + \beta_n H I g_n u + \sum_i S A_i I_i$$

where u is the unit vector along the magnetic field direction, A_i the hyperfine interaction tensor, and β , β_n , g , g_n , S , and I have their usual meaning.

A polyoriented sample ESR spectrum was simulated by generating 120 000 random orientations of magnetic field and by summing the corresponding 120 000 absorption spectra. The final spectrum was obtained by performing a convolution (Gaussian line shape) of each transition line, adding all contributions, and calculating the first derivative of the spectrum; the line width for convolution (2 G) was optimized in order to obtain the best accordance with the observed experimental values.

Concerning the hyperfine tensor, we have tried to simulate spectra by assuming that this tensor has an axial symmetry, as observed in this work for the g tensor, and that principal axes of hyperfine tensor are aligned along g eigenvectors. Due to presence of two copper isotopes (^{63}Cu and ^{65}Cu), natural isotopic distribution has to be taken into consideration: we introduced ESR parameters determined for ^{63}Cu (69.09%), and parameters for ^{65}Cu were directly calculated to give complete simulated spectra taking into account the magnetic properties of both nuclei. Finally, we used a program of spectra addition to determine the relative proportions of the different Cu^{2+} species.

Results

CuThO samples prepared with various Cu/Th ratios (0.005–0.25) and calcined at 1073 K in air exhibit complex ESR spectra (Figure 1), which are characterized by a progressive evolution from one type (A) to another type (B):

The first (A) is obtained only at low copper contents, and it is characterized by a lot of very sharp lines, at low g values and many humps on the left side of the spectrum, at higher g values. Such narrow lines in polycrystalline solids containing copper(II) ions are not often observed; thus they need particular attention. This A spectrum totally disappears for $\text{Cu}/\text{Th} > 0.25$.

The second (B) appears at higher copper contents ($\text{Cu}/\text{Th} > 0.01$), and it is characterized by much broader lines with respect to A spectrum.

In this work, only the A spectrum will be discussed to derive information concerning the localization of corresponding Cu^{2+} ions in the CuThO system. The B spectrum will be further analyzed and discussed in ref 22.

To characterize the genesis of the copper species leading to the A spectrum, we have studied a new series of samples at low and constant copper content ($\text{Cu}/\text{Th} = 0.01$), versus the calcination temperature in air (from room temperature to 1073 K; Figure 2).

Up to 673 K, spectra can be easily attributed to Cu^{2+} ions in identical sites with an axial symmetry.^{23,24} A good

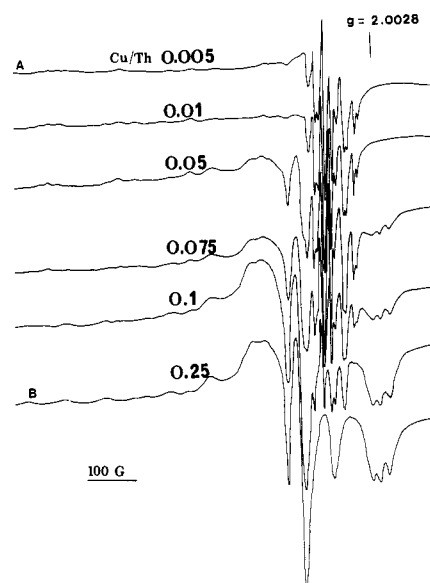


Figure 1. ESR spectra (recorded at room temperature) of CuThO oxides calcined at 1073 K, at various Cu/Th atomic ratios.

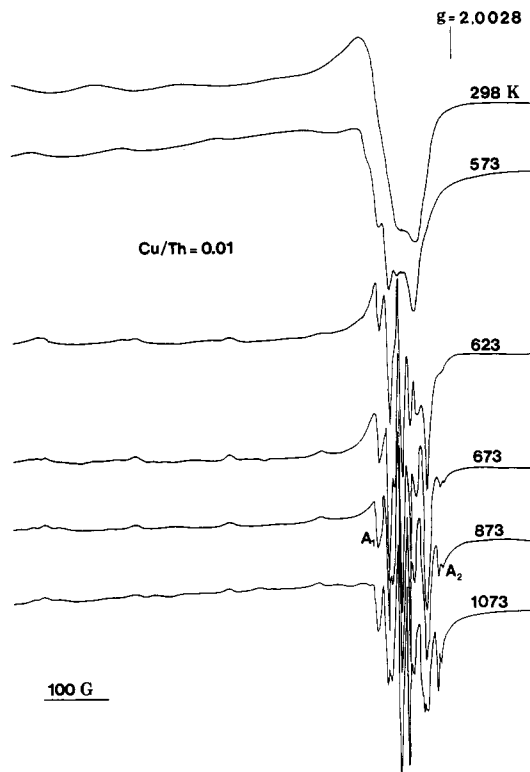


Figure 2. ESR spectra of CuThO samples with $\text{Cu}/\text{Th} = 0.01$, calcined at different temperatures. In this figure, A_1 and A_2 indicate characteristic lines of two slightly different Cu^{2+} spectra (see Figures 3 and 4).

simulation is obtained, taking into account hyperfine interactions with both ^{63}Cu and ^{65}Cu isotopes, whose nuclear

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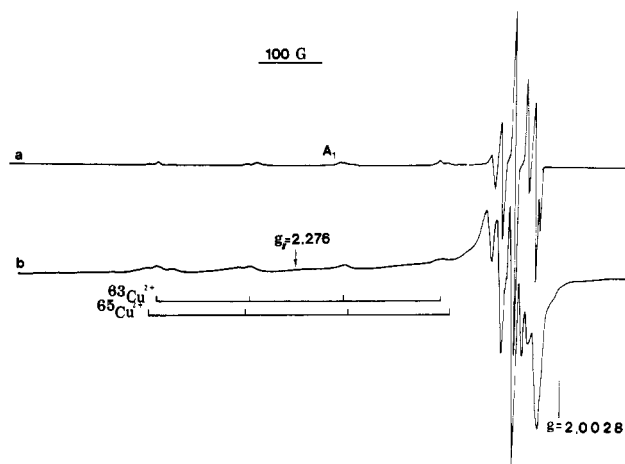


Figure 3. Simulated (a) and experimental (b) ESR spectra A_1 (Cu/Th = 0.01) for the sample calcined at 623 K. The isotopic effect of ^{63}Cu and ^{65}Cu is observed for both parallel and perpendicular components.

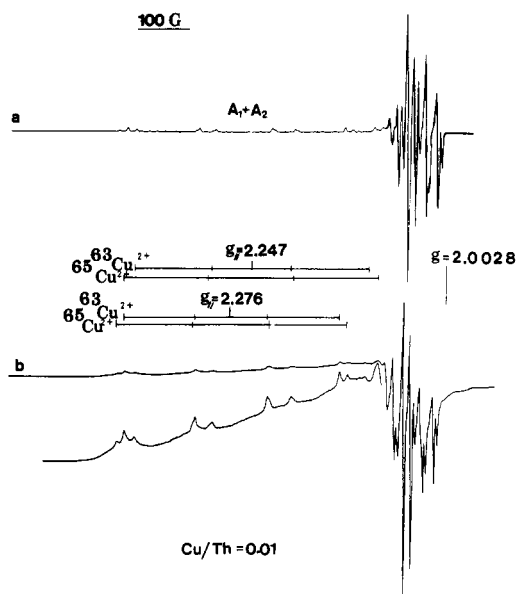


Figure 4. Simulated (a) and experimental (b) ESR spectra $A_1 + A_2$ (Cu/Th = 0.01) for the sample calcined at 1073 K (with isotopic effect of copper). Simulation corresponds to the addition of $(50 \pm 5)\%$ A_1 spectrum and $(50 \pm 5)\%$ A_2 spectrum.

spins are $3/2$ (Figure 3, Table I). The corresponding spectrum will be denoted A_1 here after. When the calcination temperature is raised from 673 to 1073 K, the A_1 spectrum resolution is slightly enhanced and, in addition a new A_2 spectrum appears. A_2 is also a well-resolved spectrum with several narrow lines, which characterizes another localized Cu^{2+} species in sites with an axial symmetry (Table I): in Figure 4, a good simulation of the $A_1 + A_2$ spectra for the Cu/Th = 0.01 sample calcined at 1073 K is obtained by the addition of $(50 \pm 5)\%$ A_1 and $(50 \pm 5)\%$ A_2 spectra.

ESR parameters determined for A_1 and A_2 spectra are independent of the calcination temperature. However, the amplitudes of the derivative signals increase with this temperature (Figure 5). A significant increase of A_2 signal intensity is observed at higher calcination temperatures.

To compare interactions of both Cu^{2+} entities leading to A_1 and A_2 signals, we have observed evolutions of the corresponding signals intensities versus the microwave power (Figure 6). Saturation of the A_2 signal occurs more easily than for A_1 .

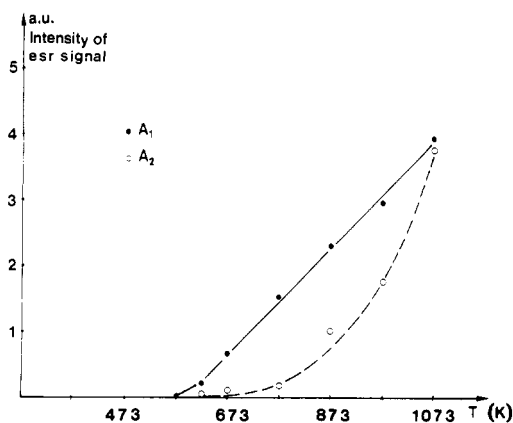


Figure 5. Variations of the relative intensities of A_1 and A_2 ESR signals, versus the calcination temperature (with arbitrary units relative to maximum amplitudes of the derivative spectra).

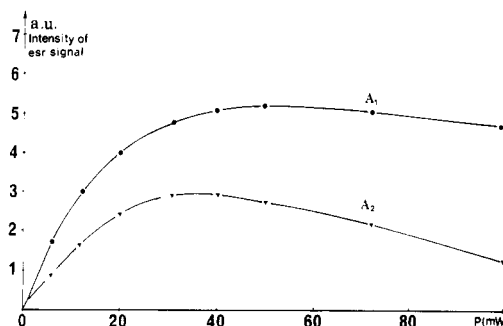


Figure 6. Variations of the relative signal intensities for A_1 and A_2 ESR signals, versus the hyperfrequency power (arbitrary units are different for A_1 and A_2).

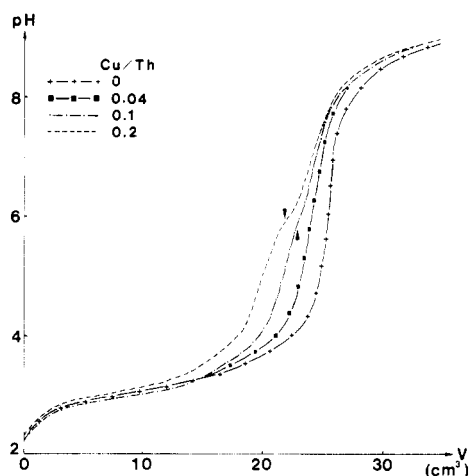


Figure 7. Variations of pH versus ammonium hydroxide volume during the thorium and copper hydroxides precipitation, for different Cu/Th ratios. The arrows correspond to the beginning of copper hydroxide precipitation.

Discussion

ESR results have to be correlated to preparation conditions, particularly to precipitation parameters. Since solubility products of copper and thorium hydroxides are very different (1.6×10^{-19} and 4×10^{-45} , respectively), a good coprecipitation is excluded. In that case, near pH 6, a visible modification of the slope relative to the pH evolution versus the ammonium hydroxide volume is characteristic of a nonhomogeneous mixture. As shown in Figure 7, such a feature is slightly visible for the Cu/Th = 0.1 ratio and becomes quite evident for Cu/Th = 0.2. For lower ratios, there is only a slight decrease in the slope

of the pH jump, as referenced to $\text{Th}(\text{OH})_4$ precipitation. This can be attributed to the introduction of copper ions in thorium hydroxide already formed. This single jump is observed for $\text{Cu}/\text{Th} < 0.1$, and X-ray diffraction analysis of the same samples calcined at high temperature (1073 K) detects only the existence of one crystallographic phase identified to be ThO_2 .

Then, from both results (pH jump and X-ray diffraction) it is very probable that copper is diluted in a thorium phase during the calcination treatment. For $\text{Cu}/\text{Th} > 0.1$, pH variations during the hydroxides precipitation undoubtedly prove the formation of a two-phase system (in Figure 7, arrows correspond to the beginning of copper hydroxide precipitation). As a matter of fact, after calcination, in addition to the previous ThO_2 phase, CuO is clearly detected by X-ray diffraction for $\text{Cu}/\text{Th} > 0.25$. Bulk CuO cannot be detected by ESR, because of the very short relaxation time of copper(II) ions in this lattice, due to strong magnetic dipolar interactions.

The narrow lines observed for A_1 and A_2 suggest that these signals correspond to isolated Cu^{2+} ions; these ions are localized in particular crystallographic sites in thorium (bulk or surface). No Cu^{2+} pairs formation^{24,25} is visible at these low copper concentrations,²² and the observed Cu^{2+} ions should be relatively distant, which would be in agreement with a simple statistic calculation of the distribution of copper in the thorium bulk at this level of concentration (i.e., the distance between neighboring copper(II) ions should exceed 1.5 nm for $\text{Cu}/\text{Th} = 0.01$).

When calcination temperature is raised, an important narrowing of all the ESR lines corresponding to both Cu^{2+} species (A_1 and A_2) is observed (Figure 2). This phenomenon can be explained by Cu^{2+} ions migrating into the ThO_2 lattice during the calcination process, then a good dispersion of these ions in the solid is obtained at high temperature, and the dipolar interactions between neighboring Cu^{2+} ions decrease. As a matter of fact, the Cu^{2+} ions ESR response factors increase with calcination temperature (Figure 5).

The A_1 ESR signal, observed alone for a low calcination temperature (673 K), must be correlated with sites more accessible to be occupied by Cu^{2+} than those attributed to A_2 spectrum, which appear at higher calcination temperatures.

ESR parameters of A_1 and A_2 spectra (Table I) show that these signals are characteristic of Cu^{2+} ions in axial symmetry. This anisotropic character is probably correlated with the fact that the Cu^{2+} ions occupy crystallographic sites in the thorium lattice. The difference between Cu^{2+} and Th^{4+} ionic radii (respectively 0.073 and 0.106 nm)²⁶ leads to a noticeable distortion of the cubic lattice.

Generally, similar g and A anisotropic tensors values can be correlated with Cu^{2+} ions in octahedral sites with a tetragonal distortion,²⁷ but nearly similar ESR spin Hamiltonian parameters for Cu^{2+} ions have already been observed and discussed in the case of single crystals of copper-doped strontium and calcium compounds;²⁸ these ESR parameters are also reported in Table I. In these solids, Cu^{2+} ions exhibit 8-fold coordination with oxygen anions; this coordination occurs very seldom for copper(II), due to the small ionic radius of this cation, and thus only few other examples have been reported in the literature.^{29,30}

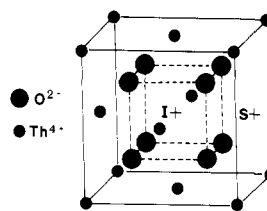


Figure 8. Crystallographic model for ThO_2 . The lattice parameter is $a = 0.56$ nm. The interstitial positions for copper ions are denoted I. S sites correspond to Th^{4+} ions (substitutional positions).

In our case, this 8-fold coordination appears more probable for copper(II) in the thorium lattice than octahedral symmetry. Furthermore, a comparison of XPS analyses of compounds with variable coordination for copper is also coherent with this 8-fold coordination of copper in thorium.^{31,32}

Following these results and discussions, the formation of a single-phase solid solution of copper(II) in thorium is now evident for the lowest contents of Cu^{2+} . It seems possible to localize the Cu^{2+} species corresponding to A_1 and A_2 spectra in interstitial (I) and/or substitutional (S) sites in the ThO_2 crystallographic model (Figure 8).

In fact, the A_1 ESR spectrum obtained at lower calcination temperatures (up to 673 K) would probably corresponds to I sites. The excess of positive charges could be balanced with some Th^{4+} vacancies in the thorium lattice. At higher temperatures, the appearance of the A_2 spectrum can be correlated with the substitution of Th^{4+} by Cu^{2+} (S). Substitution seems to be more probably at higher temperatures, for mobility reasons; under these conditions, S sites can easily balance the excess of positive charges produced by the introduction of interstitial Cu^{2+} (I) ions at lower temperatures: as a matter of fact, the quasi-equality of A_1 and A_2 signals intensities after calcination at 1073 K (Figure 4) could be significant in that way.

Furthermore, the small spectroscopic differences between A_1 and A_2 signals can be also analyzed in terms of electron localization. In the case of substitution of calcium and strontium compounds by copper(II) cations, Debuyst et al.²⁸ observed an increase of A_{\parallel} when Sr^{2+} replaces Ca^{2+} . This phenomenon is correlated with an increase of the $\text{M}^{2+}\text{O}^{2-}$ bond length ($\text{M}^{2+} = \text{Ca}^{2+}$, Sr^{2+} , or Cu^{2+}). Then, the difference between A_{\parallel} values observed for A_1 and A_2 signals in CuThO compounds (Table I) gives an important insight about the surrounding modification of Cu^{2+} in the thorium lattice: the increase of A_{\parallel} observed for the A_2 signal can be interpreted by a small increase of the average distance between copper(II) ions and the oxygen cations.

In first approximation, both sites have eight O^{2-} neighbors at $3^{1/2}a/4$ (a is the thorium lattice parameter). However, as previously noted, the electrostatic perturbation of the thorium lattice by Cu^{2+} ions is different for I and S sites:

The excess of charge (2+) that appears in the lattice in correlation with Cu^{2+} in the I site does slightly increase the bond length between the Th^{4+} nearest cations neighbors and the oxygen anions in the surrounding of Cu^{2+} (I), and thus the average $\text{Cu}^{2+}(\text{I})\text{O}^{2-}$ bond length must be smaller than $3^{1/2}a/4$.

On the contrary, the lack of charge (2+) in the thorium lattice, corresponding to Cu^{2+} in the S site, does decrease

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the bond length between the Th^{4+} nearest cations neighbors and the oxygen anions in the surrounding of Cu^{2+} (S), and consequently the average $\text{Cu}^{2+}(\text{S})\text{O}^{2-}$ bond length must appear higher than $3^{1/2}a/4$.

Thus, taking into account this electrostatic perturbation of the thorium lattice by copper, the crystallographic model (with I and S sites) is clearly coherent with the observed variation of A_{\parallel} ESR parameter. Furthermore, this model shows that Cu^{2+} S ions appear slightly more "isolated" than Cu^{2+} I ions. This conclusion is also in good accordance with the ESR saturation measurements (Figure 6).

Conclusion

Copper-thorium oxides prepared by coprecipitation of thorium and copper hydroxides by ammonium hydroxide, at low copper contents ($\text{Cu}/\text{Th} < 0.01$), are single-phase systems, with the thorium structure. Cu^{2+} ions are present in this structure, probably with an 8-fold coordination in interstitial (I) and in substitution (S) positions; I Cu^{2+} species can be introduced in the ThO_2 lattice at a low

calcination temperature (below 673 K), whereas S Cu^{2+} species appear only after calcination at higher temperatures. This information was deduced from ESR spectra of both species, which showed that both Cu^{2+} ions are isolated in the thorium lattice. The introduction of copper into I and S crystallographic sites produces a small axial distortion of the thorium cubic symmetry. From the g tensor and A tensor values, the paramagnetic electron appears a little more localized on the S copper ion than on I one.

When Cu/Th ratio is higher than 0.01, a new ESR signal (B) appears, and copper ions can no longer be considered as isolated ions. These results will be discussed in the following article.²²

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Preparation and Characterization of Copper-Thorium Oxide Catalysts. 2. ESR Study of Copper(II) Ion Pairs and Correlation with the Selective Hydrogenation of Isoprene

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CuThO oxides prepared with an atomic ratio $\text{Cu}/\text{Th} > 0.01$ were extensively studied by electron spin resonance (ESR) and X-ray photoelectron spectroscopies (XPS). The XPS analysis of these solids showed that the thorium surface is enriched with copper. The X-ray diffraction patterns for $\text{Cu}/\text{Th} > 0.25$ revealed two distinct phase systems, ThO_2 and CuO . ESR studies evidenced two signals of monomeric Cu^{2+} species (M_1 and M_2) and a well-resolved D signal ($\Delta m_s = 1$) of Cu^{2+} ion pairs, accompanied by a weak signal at half magnetic field intensity ($\Delta m_s = 2$). From the $\Delta m_s = 2/\Delta m_s = 1$ intensities ratio and from the fine splitting observed for the D signal, the distance between the Cu^{2+} ions in the pair have been calculated. These copper-thorium oxide catalysts are active for selective hydrogenation of isoprene at 373 K after reduction of the oxide phase at 523 K. A correlation between this activity and the relative intensities of M_1 , M_2 , and D signals was established.

Introduction

Solid solutions of isolated Cu^{2+} ions in the thorium lattice can be prepared by coprecipitation of the hydroxides by aqueous ammonium hydroxide, followed by a calcination treatment in air.¹ This single-phase system had been characterized at very low copper contents (below $\text{Cu}/\text{Th} = 0.01$), mainly by ESR techniques.

At higher copper contents, we had observed noticeable modifications in the ESR spectra of the Cu^{2+} ions with respect to those obtained at low copper contents. All these phenomena will be discussed and achieved with XPS characterization of the solid surface, after calcination in air, to study the copper distribution on the surface of the catalysts.

This work is a part of a larger study of copper-based catalysts in which the Cu^{2+} ions were associated with other cations (Zn^{2+} , Al^{3+} , or Cr^{3+}).²⁻⁴ Then, the present purpose is to extrapolate our previous approach to the new and relatively well characterized copper-thorium system. In that way, some catalytic results concerning the selective hydrogenation of isoprene by the reduced CuThO catalysts, at low and high copper contents, have been also reported, to demonstrate the different catalytic behavior of the various copper species characterized by ESR in the calcined compounds. Further ESR and XPS investigations

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