JOURNAL OF CATALYSIS **172,** 243–246 (1997)
ARTICLE NO. CA971802

RESEARCH NOTE

Electron Spin Resonance Studies of CuO Supported on Tetragonal ZrO_2

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Received January 27, 1997; revised June 24, 1997; accepted June 24, 1997

The state of active phase in supported catalysts is one of the major topics relating to understanding of the intrinsic nature of catalysis. Electron spin resonance (ESR) investigations are useful in distinguishing different species coexisting in supported catalysts, and studies on copper oxide dispersed on various supports have been reported in the literature (1–6). However, very few reports have been devoted to zirconia-supported CuO system. Reported in this note are our recent results on the nature of dispersed Cu^{2+} species supported on tetragonal ZrO_2.

The tetragonal ZrO_2(t-ZrO_2) was prepared using the method reported elsewhere (7), and after calcining at 773 K for 4 h, it has a BET surface area of 60 m^2/g. Samples with different CuO contents were prepared by incipient wetness impregnation using an aqueous solution of cupric nitrate [$Cu(NO_3)_2 \cdot 3H_2O$, A.R.] with required concentration, followed by drying at 373 K and calcining at 723 K for 2 h. The characteristic properties of the samples as prepared are listed in Table 1.

X-ray powder diffraction patterns were collected by a Shimadzu XD-3A diffractometer using Ni-filtered Cu$K\alpha$ radiation (0.15418 nm). The X-ray tube was operated at 35 KV and 15 mA. α-Alumina powder was used as a reference for quantitative analysis. The dispersion capacity of CuO on the zirconia estimated by XRD quantitative analysis is about 8.7 Cu^{2+}/nm^2 t-ZrO_2. ESR spectra were recorded on a Bruker ER-200D SRC spectrometer.

Solid-state cupric nitrate does not show any ESR signal, whereas a rather complex spectrum has been detected for $Cu(NO_3)_2$ supported on t-ZrO_2. Depending on the loading of Cu^{2+} ions, the spectrum generally consists of two signals with different shapes and intensities. For the low loading sample, i.e., Cu_1Zr with 2.1 Cu^{2+}/nm^2, a single axially symmetric ESR line with $g_\perp = 2.05$, assigned as α in Table 1, while the signal in the parallel region is too weak to be resolved as shown in Fig. 1a. With the increase of Cu^{2+} loading, a new isotropic signal with $g_{iso} = 2.20$, assigned as β, is found, suggesting that two dispersed Cu^{2+} species with different local environments are coexisting on the surface of zirconia.

During the impregnation and drying steps, for samples with low cupric nitrate loading, the hydrated Cu^{2+} ions are randomly anchored to the surface OH groups of zirconia through hydrogen bonding with the formation of isolated Cu^{2+} species evidenced by the axially symmetric signal α mentioned above. With the increase of Cu^{2+} loading another species is found on the surface of zirconia, as identified by the isotropic ESR signal β, which will become dominant finally. In fact, a signal similar to that of β has been observed for Cu^{2+} ions in hydrated zeolites and assigned to the Cu^{2+} ions coordinated by six water molecules, i.e., $[Cu(H_2O)_6]^{2+}$ (8–10). From the above discussions, it is suggested that for the uncalcined samples two kinds of surface Cu^{2+} species are formed on the support, namely, one located in an axially symmetric site in close contact with the surface of the zirconia and the other, an isotropic octahedrally hydrated Cu^{2+} species less influenced by the support.

The ESR spectra of the calcined samples after evacuating at room temperature for 1 h are shown in Fig. 2. Only three samples with Cu^{2+} loading of 2.1, 4.9, and 12.1 Cu^{2+}/nm^2, assigned respectively as Cu_1Zr, Cu_2Zr, and Cu_3Zr, are listed as representatives. All the spectra can be interpreted in terms of the overlapping of at least two components. Taking Cu_1Zr as an example, the first one, assigned as γ, has a resolved hyperfine structure visible in the parallel region, and its characteristic line shape could be regarded as an unequivocal proof of the existence of randomly isolated Cu^{2+} ions in an axially symmetric environment. The second, assigned as δ, consists of a single line shape gradually broadening with the increase of Cu^{2+} loading, which can be assigned to two or more magnetically interacting Cu^{2+} ions, and their dipole broadening might cause the observed line shape. The above consideration is consistent with Deen *et al.* in their studies of copper oxide supported on alumina (2). The Hamiltonian spin parameters of the above samples are summarized in Table 1.

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0021-9517/97 $25.00

TABLE 1

Summary of ESR Spectroscopic Results

Samples and ESR signal assignment	CuO content (Cu^{2+}/nm^2 ZrO_2)	ESR signal and their features			
		Signal α^a ($g_\perp = 2.05$)	Signal β^a ($g_{iso} = 2.20$)	Signal γ^b ($g_\parallel = 2.38$, $g_\perp = 2.04$, $A_\parallel = 110G$)	Signal δ^b ($g = 2.23$)
Cu_1Zr	2.1	Yes	No	Well resolved	Weak
Cu_2Zr	4.9	Yes	Weak	Resolved^c	Medium
Cu_3Zr	12.1	Yes	Strong	Unsolved	Strong
Assignment		Isolated Cu^{2+} species anchored to the surface OH group of ZrO_2 through hydrogen bonding	$[Cu(H_2O)_6]^{2+}$, Cu^{2+} in octahedral symmetric site	Isolated Cu^{2+} ions dispersed in the surface vacant sites of ZrO_2	The paired Cu^{2+} ions dispersed in the ZrO_2 surface vacant sites

[a] Signal of the uncalcined samples.

[b] Signal of the calcined samples.

[c] In addition, a poorly resolved signal is also present in this sample.

The observed spectra of the low loading samples are partially resolved in the parallel region, and the signal becomes poorly resolved with the increase of Cu^{2+} loading. When the loading is higher than the half of the dispersion capacity of Cu^{2+} on t-ZrO_2, an overlapped and poorly resolved new signal in the parallel region can be seen from the spectrum of Cu_2Zr, showing that there are two kinds of isolated Cu^{2+} ions located in different symmetric sites of this sample. In addition, when the Cu^{2+} content increases further to higher than its dispersion capacity, the signal attributed to the isolated or nearly isolated copper ions in a distorted octahedral environment, i.e., the signal in the parallel region, is hardly to be resolved. Although the coordination of Cu^{2+} ions in various supported CuO catalysts is still a subject of controversy (11–13), with no doubt the structure of the dispersed species should be closely related to the surface structure of the support especially when the loading amount of CuO is low. As reported by Chen *et al.*, the existence of vacant sites on the surface of the support is critical for the dispersion of ionic compounds, which are not dispersed on silica due to its saturated tetrahedral structure with no vacant sites on its surface (14). As a matter of fact CuO will mostly maintain its crystalline phase on silica-supported samples with no ESR signal detected. In contrast, for γ-alumina supported CuO samples, depending on the loading amount of CuO different ESR signals have been observed as there are available vacant sites on its surface for the Cu^{2+} ions to incorporate into. For the case of tetragonal zirconia which has a slightly distorted fluorite structure, and it has been well established that (111) plane is preferentially exposed on its surface and each Zr^{4+} ion is positioned in a distorted cube of eightfold oxygen coordination (15, 16). According to Teufer (17), there are two kinds of oxygen anions, assigned as O_I and O_{II}, in the distorted cube and the average distance between them and Zr^{4+} is $Zr–O_I = 2.065$ A and $Zr–O_{II} = 2.455$ A, respectively. The

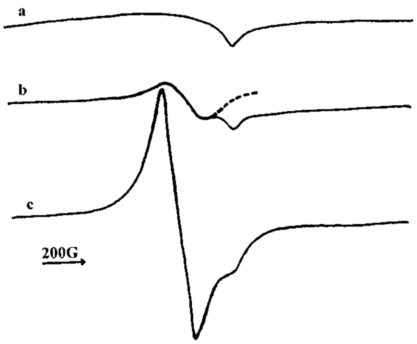

FIG. 1. ESR spectra of the uncalcined samples at room temperature (a) Cu_1Zr, (b) Cu_2Zr, and (c) Cu_3Zr with Cu^{2+} loading of 2.1, 4.9, and 12.1 Cu^{2+}/nm^2 ZrO_2, respectively.

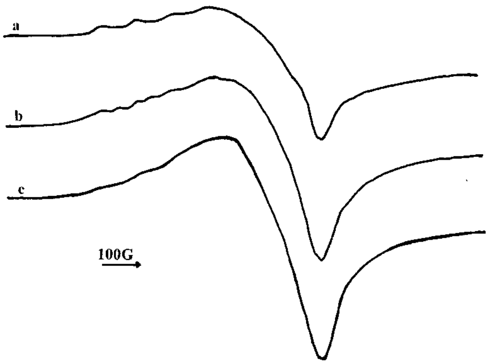

FIG. 2. ESR spectra of the calcined samples at liquid nitrogen temperature (a) Cu_1Zr, (b) Cu_2Zr, and (c) Cu_3Zr.

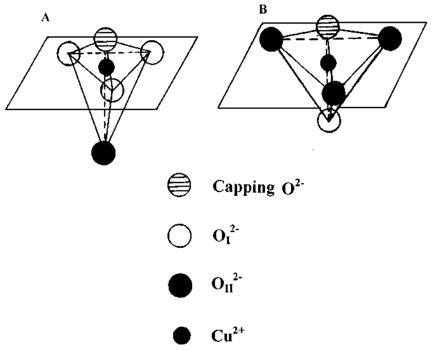

FIG. 3. A tentative model of the surface Cu^{2+} species formed on the (111) plane of t-ZrO_2.

computer simulation based on the structure factors listed in Teufer's paper has revealed that two kinds of surface vacant sites coordinated by four oxygen atoms are available on the (111) plane. According to the incorporation model proposed by Chen *et al.* (14), calcination might lead to the incorporation of Cu^{2+} ion into the available vacant sites on the surface, and the accompanying oxygen anion is capping on the top of the incorporated Cu^{2+} ion for charge compensation. As shown in Fig. 3, copper ions in these two kinds of available vacant sites have C_{3v} symmetry and can be described as distorted octahedrons with a missing corner or as trigonal bipyramid symmetry (one is elongated and the other compressed). At very low loadings, the vacant sites, as shown in Fig. 3A, are probably more favorable for the incorporation of Cu^{2+} ions since the Cu–O distance (2.09 A) is very close to that of $Zr–O_I$ (1). This expectation is consistent with the result that there is only a set of resolved ESR signal in the parallel region has been detected for Cu_1Zr sample which has a Cu^{2+} loading about one-fourth of its dispersion capacity. With the increase of the loading to a value above one half of the dispersion capacity, two sets of $g_{\|}$ signals are detected in the spectrum, as shown in Fig. 2b. The second signal is probably the contribution of the isolated Cu^{2+} ion located in the compressed trigonal bipyramid [cf. Fig. 3B]; however, as this signal is poorly resolved in the parallel region, its Hamiltonian spin parameters are rather difficult to calculate. When the Cu^{2+} loading is up to or beyond its dispersion capacity, all the available vacant sites on the support are being occupied and, in turn, the previously isolated Cu^{2+} ions are surrounded by the successively incorporated Cu^{2+} ions with the formation of Cu^{2+} ion pairs on the surface of the zirconia. It can be estimated that the distance between the nearest adjacent Cu^{2+} ions incorporated is about 3.64 A, a value less than the limit suggested by Centi *et al.* (4) for generating the dipole interaction between Cu^{2+} ions. Consequently, the broad ESR line shape (signal δ) might be due to the dipole interaction of the paired ions. Noteworthy, the fact that when the loading of Cu^{2+} is closed to its dispersion capacity no further change in both the line width and the intensity of this signal has been observed by increasing the loading of copper ions seems also in support of the above discussion. Centi *et al.* (4) have assigned signal δ to the contribution of the clustered Cu^{2+} ions which are not dispersed on the surface; however, based on our experimental results as well as the fact that Cu^{2+} ions in crystalline CuO are not ESR active, it seems reasonable to argue that signal δ of the $CuO–ZrO_2(t)$ samples should be attributed to the paired Cu^{2+} ions formed by the incorporated Cu^{2+} ions. In short, when the loadings of Cu^{2+} are low, the isolated Cu^{2+} ions are predominant and the ESR signal is relatively well resolved; with the increase of Cu^{2+} loading, the paired Cu^{2+} ions become predominant finally and the signal δ become more broad and intensive owing to the increasing dipole interaction between adjacent copper ions. Meanwhile, it is more difficult to resolve the γ signal.

It is clear that a highly dispersed precursor is necessary for the dispersion of the CuO on t-ZrO_2 surface. For the uncalcined samples, the OH groups located between the support and dispersed $Cu(NO_3)_2$ are easily eliminated during the calcination process. As a result, by the decomposition of the nitrate, CuO species are formed on the surface of zirconia, i.e., with Cu^{2+} ions incorporated into the available vacant sites and the accompanying oxygen anions sitting on the top for charge compensation. Along these lines, after the surface available sites are being occupied, i.e., the loading amount of Cu^{2+} cations reaches its dispersion capacity, an epitaxial layer consisting of oxygen anions is formed on the (111) surface of zicornia. Further increasing the loading of Cu^{2+} will lead to the formation of the bulk phase of cupric oxide which is inactive in ESR. In conclusion, the dispersed state of Cu^{2+} is relating to the surface structure of the support, the loading amount of the Cu^{2+} cations, and the nature of the precursor.

ACKNOWLEDGMENTS

We thank Professor Y. X. Xu for valuable discussions. This project was supported in part by the National Science Foundation of China under Grant 29392008.

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