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Reversible Reduction of Copper-Exchanged Zirconium Phosphate

α-Zirconium phosphate exchanged with copper(II) ions, $ZrCu(PO_4)_2$, hereinafter referred to as α-ZrCuP, has been shown to be a good catalyst for the oxidation of carbon monoxide (*1*). It was therefore of interest to examine other reactions, and indeed it was found that this catalyst is active for oxidative dehydrogenation reactions (*2*). For example, almost quantitative yields of benzene are obtained from cyclohexene–oxygen mixtures at 300°C. During these reactions a portion of the copper(II) ions was reduced to copper metal. In order to gain insight into the mechanism of this reaction, studies on the reduction of the catalyst by hydrogen were carried out. Some preliminary results are reported here.

EXPERIMENTAL

α-ZrCuP was prepared as described previously (*1, 3*) and dehydrated at 300°C. Samples containing 1.0–100% Cu(II) were prepared and had surface areas (BET) of 7–8 m^2/g after drying. The reductions were carried out in a simple tube reactor with a flowing stream of H_2 (Matheson ultrahigh purity) at atmospheric pressure. For the oxidation cycle a dilute stream of oxygen mixed with helium was passed over the catalyst at 25–300°C. EPR spectra were recorded with a Varian E-15 X-band spectrometer at both room temperature and liquid-nitrogen temperature at a frequency of 9.821 GHz.

EPR samples. Hydrated samples were dried over P_2O_5 and transferred to EPR sample tubes at room temperature and sealed without further treatment. Anhydrous samples were first dried in air at 300°C, then heated at 320°C under vacuum for 2 hr, and sealed under vacuum. Reductions with hydrogen were carried out on dried samples by heating at 320°C for different lengths of time under a hydrogen atmosphere directly in the EPR tube and sealing under hydrogen. Reoxidation was accomplished by pumping out the hydrogen followed by introduction of O_2, heating at 320°C for different lengths of time, and resealing the tubes.

RESULTS AND DISCUSSION

Reduction of copper was found to commence at 260°C as evidenced by a copper-colored coating forming on the surface and disappearance of the blue color. The color change started at the end of the sample facing the flow and slowly moved in the direction of flow until the entire sample was copper colored. An X-ray pattern of the completely reduced solid showed the presence of copper metal and λ-ZrP. The lambda phase had been obtained earlier (*4*) by the reaction

$$Zr(NaPO_4)_2(s) + HCl(g) \rightleftarrows Zr(HPO_4)_2(s) + NaCl(s). \quad (1)$$

The initial α-ZrCuP was present as phase G after dehydration (*5, 7*). Thus, the reduction may be formulated as

$$ZrCu(PO_4)_2(\text{solid-G}) + H_2(g) \rightleftarrows Zr(HPO_4)_2(\text{solid-}\lambda) + Cu^0(s). \quad (2)$$

About 12–17 hr at 260° was required to completely reduce a sample containing

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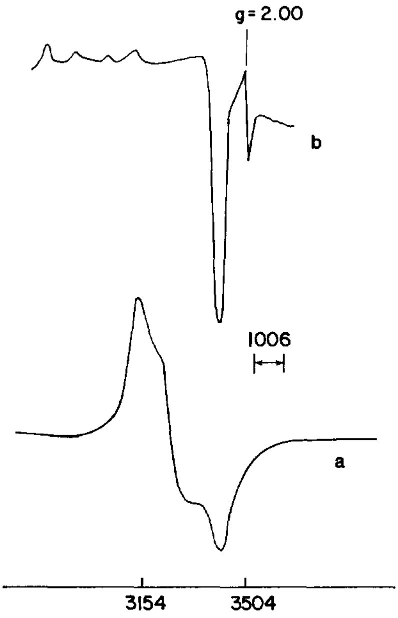

FIG. 1. EPR spectra of Cu(II)-exchanged α-zirconium phosphate: (a) hydrated sample containing Cu(II) exchanged to the 10% level, i.e., $Zr(Cu \cdot 4H_2O)_{0.1}H_{1.8}(PO_4)_2 \cdot 0.9H_2O$; (b) same sample dehydrated at 320°C yielding $g_{\parallel} = 2.39$ and $g_{\perp} = 2.07$.

98% Cu^{2+}, i.e., $ZrCu_{0.98}H_{0.04}(PO_4)_2$. At 350°C less than 1 hr was required.

Passage of an oxygen–helium (1–100) mixture over the freshly reduced sample at room temperature (25 ± 2°C) resulted in the restoration of the blue color. About 24–48 hr was required for complete oxidation. At 100°C 14–16 hr was required, and at 300°C, 1 hr. If air was used instead of the oxygen–helium mixture some CuO was also obtained. This may have resulted from the presence of excess oxygen. That is, when the rate of oxidation exceeded the rate at which diffusion of the Cu^{2+} back into the ZrP lattice can occur, CuO formed. Water was the main hydrogen-containing product of the oxidation, but no quantitative data were obtained. On the assumption that water was the only reduced form of oxygen produced, the oxidation reaction is represented as

$$Zr(HPO_4)_2 + Cu^0 + \tfrac{1}{2}O_2 \rightleftarrows ZrCu(PO_4)_2 + H_2O. \quad (3)$$

It seems remarkable that this reaction can proceed, albeit slowly, at room temperature.

EPR studies. A typical spectrum of hydrated α-$ZrCu_{0.1}H_{1.8}P$ is shown in Fig. 1a. It is similar to that given for the 100% exchanged phase (7). Indeed this spectrum did not change with Cu^{2+} loadings from 1 to 100% or with temperature, the same results being recorded at 77 K as at room temperature. It will be shown in a subsequent paper that the copper-exchanged solids can be represented by the general

TABLE 1

Experimental Conditions for Reduction and Reoxidation of Copper-Exchanged Zirconium Phosphate (T = 320°C)

Expt. no.	Percentage of Cu(II) in ZrP	H_2 pressure (mm)	O_2 pressure (mm)	Time (hr)	O_x state of Cu	Color
3	10	670	—	1.5	Cu(II) + Cu^0	Blue–gray
2	10	620	—	15	Cu^0 ~90%	Tan + gray
11	5	686	—	42	Cu^0 + Cu(II)	Tan
12	10	682	—	65	Trace Cu(II)	Tan
9	10	705	—	72	Cu^0	Tan
6-1	22	660	—	40	Cu^0	Tan
4	10	670 (17 hr)	675	16	Cu(II)	Pale blue
7	22	672 (17 hr)	690	23	Cu(II)	Pale blue
10	10	708 (66 hr)	707	96	Cu(II)	Pale blue

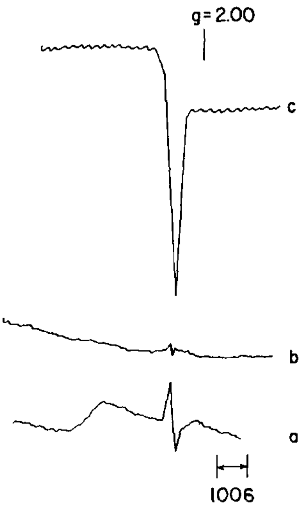

FIG. 2. EPR spectra of sample from Fig. 1b treated as follows; (a) heated under H_2 atmosphere (602 mm) at 320°C for 15 hr; (b) same sample heated at 320°C for 62 hr; (c) sample (b) heated under O_2 atmosphere (675 mm) for 77 hr ($g_\perp = 2.062$).

formula

$$Zr(Cu\cdot 4H_2O)_xH_{2(1-x)}(PO_4)_2\cdot(1-x)H_2O,$$

where x is the fraction of Cu^{2+} exchange. α-ZrP contains 1 mol of zeolitic-type cavities per formula weight (*6*). Thus, at full exchange the formula is $ZrCu(PO_4)_2\cdot 4H_2O$, and each cavity is occupied by one Cu(II) ion which is presumably surrounded by 4 mol of water and two negatively charged exchange sites (*3*, *7*). At low loads a solid solution of Cu^{2+} in the α-ZrP phase forms. At about 15% exchange, the solid solution converts to phase D (*5*) and mixtures of the α-ZrP solid solution and phase D are obtained up to 88% loading. Phase D then exists over the composition range 88–100% Cu^{2+} content or the composition range given by

$$Zr(Cu\cdot 4H_2O)_{0.88-1.0}H_{0.24-0}(PO_4)_2\cdot(0.12\text{–}0)H_2O.$$

The constancy of the EPR spectrum over the whole composition range indicates a constancy of environment for the copper(II) ions. The ions are apparently well shielded from each other by the water molecules and 24 oxygens which form the cavity. The spectrum appears to be that of a randomly oriented anisotropic powder with three g components (g_{xx}, g_{yy}, g_{zz}). Details will be presented in a subsequent publication.

Dehydration of the solid at 320°C leads to the spectrum shown in Fig. 1b. Some broadening due to Cu^{2+}–Cu^{2+} interactions was evident in the spectrum of the 100% exchanged sample. Apparently in the dehydrated state the cavity oxygens are unable to completely shield ions in adjacent cavities. No such broadening was noted with samples of less than 50% load. Thus only the 1–50% loaded solids were examined in the reduction–oxidation cycle. The spectrum for these samples (Fig. 1) resembled those recorded for Cu^{2+} in zeolites and on other supports (*8–12*) except for appearance of a relatively weak, sharp line at 3504 G. This line leads to a value of $g_\perp'' = 2.0$ and may be due to an impurity.

The conditions under which the copper ions were reduced and then reoxidized in the sealed tubes is given in Table 1. Some of the EPR spectra for the samples listed in Table 1 are shown in Fig. 2.

In the first sequence (Expt No. 3, 2, 12, and 9), more than 65 hr was required to achieve full reduction of the Cu(II) as evidenced by the disappearance of the characteristic EPR lines for this ion. Only the signal at 3504 G ($g_\perp'' = 2.003$) remained when all the Cu(II) was reduced. In the case of the 22% exchanged sample (6-1), all the bands were removed by the reduction procedure, but on long standing under hydrogen the one at 3504 G was restored. In the final experiments (4, 7, and 10) the copper-exchanged zirconium phosphates were reduced under the conditions shown and then subjected to oxygen. All of them turned pale blue, and the EPR spectrum once again showed the characteristic band at 3404 G ($g_\perp = 2.062$) but not the hyperfine lines. In the case of Expt 10, the peak at 3404 G was shifted such that $g_\perp$ was 2.122. Such shifts appear to be common (*10*). Thus the data corroborate the results of the earlier flow experiments.

At this stage of the investigation it is not known whether Cu(I) is an intermediate in the reactions as is the case for zeolites (*8*) and hydroxyapatite (*12*). If so, an exchanged phase corresponding to $ZrCu(I)H(PO_4)_2$ should have been detected in the X-ray patterns. This phase was not observed but since the X-ray reflections were quite broad it may have been obscured. Judgment on this point is reserved until quantitative evidence is available. Our tentative conclusion from this study is that hydrogen is abstracted from the hydrocarbon reducing Cu^{2+} to copper metal and taking its place in the crystal lattice. Oxygen then serves to oxidize the Cu^0 to Cu(II) and in turn become hydrogenated.

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