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Communications

Behavior of Copper(II) Ion Pairs in $Cu_2PMo_{11}VO_{40}\bullet 21H_2O$ Catalysts. Electron Paramagnetic Resonance Study

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Introduction

Despite their weak thermal stability in catalytic reactions, the heteropolyacids (HPA) with anions of Keggin structure are frequently used as selective heterogeneous catalysts for several industrial reactions. Particularly, the molybdovanadophosphoric acids ($H_4PMo_{11}VO_{40}$) have been recently demonstrated to catalyze the selective oxidation of *n*-butane and *n*-pentane to maleic anhydride.[1,2] Exchange of the protons by various cations affects the redox and acidic properties and the stability of the previous solids.[3–4] The copper(II) ions, known for their strong oxidative properties, have been extensively used as catalytic active sites in the catalysts.[5,6] Generally, three types of copper species can be evinced in copper-based solids: monomers, dimers, and clusters. EPR seems to be an excellent technique for studying the morphological behavior of copper-based catalysts. In fact, the observed EPR spectrum gives detailed information concerning monomer and dimer Cu^{2+} species,[7,8] and the intensity variation of the EPR signal of these isolated monomer or dimer Cu^{2+} ions may be regarded as a measure of the formation of clusters in the catalysts.[9,10]

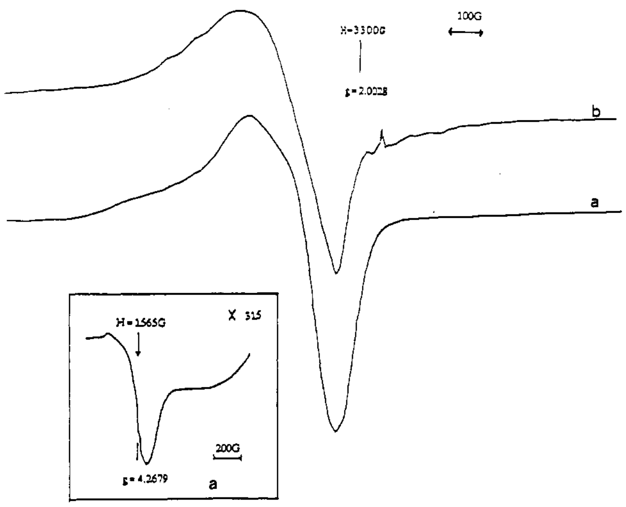

Figure 1. EPR signals (X-band) observed at room temperature with the $Cu_2PMo_{11}VO_{40}{\cdot}xH_2O$: (a) signals for $\Delta m_s = 1$ (allowed transition) and $\Delta m_s = 2$ (forbidden transition) obtained in the solid freshly prepared; (b) signal obtained after calcination of the solid at 593 K.

In the present work, we report EPR investigations to describe the behavior of copper(II) ions in $Cu_2PMo_{11}VO_{40}{\cdot}21H_2O$ and to examine the possible formation of clusters and copper oxide from monomer and dimer copper(II) ions during thermal treatments.

Experimental Part

The $Cu_2PMo_{11}VO_{40}{\cdot}21H_2O$ catalysts were obtained by simple contact exchange of the H^+ ions in the heteropolyacids (H_4P-

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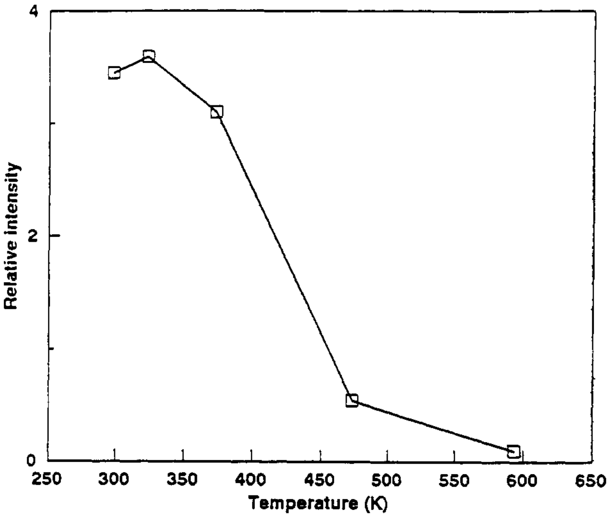

Figure 2. Variation of the relative EPR signal intensity with the calcination temperature.

$Mo_{11}VO_{40}$) with Cu^{2+} ions present in a resin previously saturated by such ions. Thereafter, the solids freshly prepared were placed in a microflow reactor and calcined in a flow of dried oxygen (200 K h^{-1} heating rate) at a given temperature. The microflow reactor was assembled with an EPR quartz tube into which the catalyst could be transferred after a treatment.

EPR spectra were recorded with a Bruker ER 200D spectrometer operating in the X band (9.3 GHz) and using 100-kHz modulation. All spectra were recorded at 293 K at a microwave power sufficiently small to avoid saturation. The g values were measured relative to a "strong pitch" value (g = 2.0028).

Results and Discussion

Figure 1 shows the EPR spectra obtained after calcination of the $Cu_2PMo_{11}VO_{40}{\cdot}21H_2O$ catalyst under a flow of dry oxygen from 293 to 523 K. Compared with spectra of Cu^{2+} species in different matrices,[11,12] the spectrum is characteristic of a d^9-like ion and can be assigned to Cu^{2+} ions, although it is not well-resolved. Apparently, the spectrum consists of two signals: a large signal with peak-to-peak width of 280 G and $g_{iso} = 2.15$, surrounded on the low- and high-field sides by a resolved group of lines, and a half-field signal situated at $g = 4$. The intensity of the half-field signal is relatively weak. The resolved lines observed have been attributed to the presence of V^{4+} species in the solid.

The copper(II) ion pairs are generally identified[13] by the form of the signal obtained at $\Delta m_s = 1$ (allowed transitions) and the presence of a weak signal at half-field intensity, which is produced by forbidden transitions ($\Delta m_s = 2$). We deduce from the spectrum of Figure 1a and particularly, from the half-field signal that the copper(II) ion pairs signal is present in the spectrum with another intense signal probably attributed to Cu^{2+} ion monomers.

The EPR spectra obtained versus the calcination temperature from room temperature to 593 K, under a flow of a dry oxygen, are illustrated in Figure 1. The broadness of the EPR spectra is characteristic of the copper(II) ions surrounded by H_2O molecules.[14,15] Up to 373 K, the normal field signal intensity decreases before reaching a plateau (Figure 2) and the half-field signal totally disappears. This small decrease can be due to a total disappearance of the copper(II) ion pairs. From 373 to 593 K, another significant decrease of the normal field signal intensity was observed. Consequently, the variation of the spectrum intensity versus the calcination temperature clearly shows that the spectrum mentioned in Figure 1a is the superimposing of two spectra: one corresponding to copper(II) ion pairs and another to Cu^{2+} ion monomers.

The interion distance r in the dimer can be calculated from the relative intensity I_{rel} of the half field and the normal field signals characterizing the dimer spectrum:[16]

$$I_{\text{relative}} = \frac{I(\Delta m_s=2)}{I(\Delta m_s = 1)} = \frac{A}{r^6}\left(\frac{9.1}{\nu}\right)^2$$

In the equation, A is a constant with a value of 21 ± 2, r is the interion distance in angstroms, and ν is the measuring microwave frequency in gigahertz. The signal intensity corresponding to $\Delta m_s = 1$ was obtained from Figure 2 by assuming that the total decrease of the intensity between room temperature and 373 K is due only to the disappearance of the copper(II) ion pairs spectrum. The r value derived is about of 4.0 ± 0.3 Å.

The presence of copper(II) ion pairs in the $Cu_2PMo_{11}VO_{40}{\cdot}21H_2O$ catalyst freshly prepared was for us an unexpected phenomenon. Indeed, in other solids such as CuTh oxide[7] or CuCe oxide,[17] the copper(II) ion pairs appear after calcination of the hydrated precursors of these above solids at high temperatures (>673 K). Then, it seems that when the Cu^{2+} ions are surrounded by H_2O molecules, which is the case for the CuTh and CuCe solids freshly prepared, the dipolar interaction between them is not important. Consequently, the formation of copper(II) ion pairs is not possible. In the case of $Cu_2PMo_{11}VO_{40}{\cdot}21H_2O$ catalyst freshly prepared, it is possible to suppose that the Cu^{2+} ions responsible of the formation of pairs are localized in sites of the solid which the region between the two Cu^{2+} ions is less accessible to H_2O molecules.

The formation of copper(II) ion pairs in the solid fresly prepared could also be correlated with the crystallographic structure of such HPA. Indeed, when the protons, localized either on H_2O molecules out of the Keggin unit[18] or near O^{2-} ions in the Keggin unit,[19] are replaced by Cu^{2+} ions, a cationic lacunar structure appears, due to substitution of singly charged H^+ by doubly charged Cu^{2+}. Then, the statistical distribution of the copper(II) ions and cation vacancies may explain the observation of different arrangements which lead to copper(II) ion monomers and pairs.

To consolidate the above hypothesis, a sample of $Cu_{0.5}H_3PMo_{11}VO_{40}{\cdot}13H_2O$, with a copper concentration weaker than the first one, was prepared. Compared to that observed in $Cu_2PMo_{11}VO_{40}{\cdot}21H_2O$, the EPR spectrum obtained at room temperature is more resolved (Figure 3), particularly the parallel components of the signal corresponding to Cu^{2+} ion monomers ($g_\parallel = 2.39$; $g_\perp = 2.07$; $A_\parallel = 140$ G). When $Cu_{0.5}H_3PMo_{11}VO_{40}{\cdot}13H_2O$ is calcined at 373 K, the normal and the half-field signals become more

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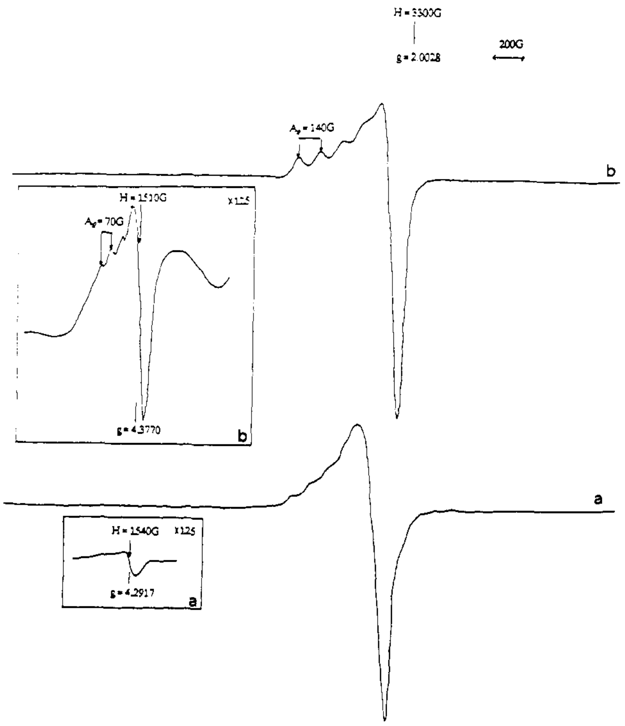

Figure 3. EPR signals (X-band) observed at room temperature with $Cu_{0.5}H_3PMo_{11}VO_{40}\cdot13H_2O$: (a) signal obtained in the solid freshly prepared; (b) signal obtained after calcination of the solid at 373 K.

resolved. The splitting constant of the half-field signal has been measured as $A_\parallel$ = 70 G. In this latter solid, the copper(II) ion pairs are more stable than in the $Cu_2PMo_{11}VO_{40}\cdot21H_2O$ since the disappearance of the half-field signal occurs at 473 K and not at 373 K as in the first solid. This difference in the dimers stability can be correlated either to the copper concentration or to the number of H_2O molecules coordinated with the solid. Indeed, it has been demonstrated that the intensity of the copper(II) ion pairs signal in $Cu_{0.5}H_3PMo_{11}VO_{40}\cdot13H_2O$ is weaker than in $Cu_2PMo_{11}VO_{40}\cdot21H_2O$; also, the number of H_2O molecules is less.

Furthermore, since the $Cu_{0.5}H_3PMo_{11}VO_{40}\cdot13H_2O$ spectrum (Figure 3) shows that the hyperfine splitting for the signal corresponding to monomers (140 G) is a factor 2 larger than for the half-field signal (70 G), the Cu^{2+} ion monomers must be the precursor of the copper(II) ion pairs in the solids.[20] Consequently the monomers and the dimers must have the same environment in the solids. Since in the case of $Cu_{0.5}H_3PMo_{11}VO_{40}\cdot13H_2O$ the coordination number of ligands (H_2O molecules) in the surrounding of the copper(II) ion pairs is less than in $Cu_2PMo_{11}VO_{40}\cdot21H_2O$, this phenomenon can explain why, in the first solid, the pairs are more stable than in the second one.

With the higher calcination temperature, the copper(II) ions corresponding to monomers also decrease and practically disappear at 573 K. The disappearance of Cu^{2+} ions, monomers, and dimers can be explained by the formation of clusters (wide EPR signal) and amorphous CuO (not detectable by EPR). Then, it appears that the formation of Cu^{2+} ion clusters or/and CuO amorphous oxides from $Cu_2PMo_{11}VO_{40}\cdot21H_2O$ is more important. In the oxidative dehydrogenation of isobutyric acid into methacrylic acid, performed at 593 K, $Cu_2PMo_{11}VO_{40}\cdot21H_2O$ is less active and less selective than $Cu_{0.5}H_3PMo_{11}VO_{40}\cdot13H_2O$;[21] thus the existence of Cu^{2+} (monomers and dimers) localized between the Keggin units appears necessary to obtain a catalyst with rapid and reversible redox behavior.

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Poly(ethylene oxide)/(Poly(2-vinylpyridine)/Lithium Perchlorate Blends. New Materials for Solid Polymer Electrolytes

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Considerable effort has been devoted to the development of solid polymer electrolytes with high ionic conductivity at room temperature.[1-7] Because it is generally accepted that the mechanism of ion transport through a solid polymer matrix is by a liquidlike motion through the amorphous (low T_g) phase, a number of oligo(oxyethylene)-based amorphous polymers with low glass transition temperatures have been examined.[2,5,8] For example, poly(siloxane)s with pendant oligo(oxyethylene) side chains[2,8] and poly[bis((methoxyethoxy)ethoxy)phosphazene] complexed with Li^+ salts exhibit high ionic conductivity at room temperature.[5] A major drawback of such amorphous polymer/salt complexes is the lack of dimensional stability and/or mechanical strength. These problems may be overcome by the preparation of cross-linked networks or the synthesis of block copolymers where the low T_g ionic conductive block is reinforced by a high T_g nonconductive block.[2,9-12] While these new polymer electrolytes are promising materials, the fact that their preparation requires nontrivial synthetic and/or cross-linking processes is a drawback. Therefore, the preparation of solid polymer electrolytes which exhibit high ionic conductivity by an easier process is desirable. In this communication we report on a novel polymer electrolyte, poly(ethylene oxide)/poly(2-vinylpyridine)/lithium per-

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