JOURNAL OF CATALYSIS 93, 224–230 (1985)

Catalysis by Heteropoly Compounds

IX. Role of Water in Catalytic Dehydration of 2-Propanol over Copper Salts of $H_3PW_{12}O_{40}$[1]

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Received February 14, 1984; revised October 16, 1984

The catalytic and acidic properties of copper salts of 12-tungstophosphoric acid have been studied. An induction period was observed in the dehydration of 2-propanol and it became longer as the water content decreased. In addition the catalytic activity was enhanced by the addition of water to the feed gas. This catalytic behavior has been explained on the basis of the "pseudo-liquid phase" model as follows. The absorption of 2-propanol into the bulk of the copper salts was accelerated by the presence of water. Thus, the increase of the rate is ascribed to the expansion of the effective reaction zone caused by water-promoted absorption of 2-propanol. Infrared spectroscopy of adsorbed pyridine revealed that the copper salts were strong protonic acids, and the amounts of proton were about one-third that of the acid form. Based on the infrared data of absorbed pyridine and electron spin resonance of Cu^{2+}, the mechanism for the generation of acidity is discussed. © 1985 Academic Press, Inc.

INTRODUCTION

Heteropoly compounds are effective catalysts for various acid-catalyzed reactions (*1–8*). Recently, it has been reported that metal and organic salts of heteropoly acids are more active or selective than the acid form in some acid-catalyzed reactions (*5–7*).

So far, three schemes have been proposed as the mechanism for the generation of acidity of metal salts: (1) dissociation of water which is coordinated to metal cation (M^{n+}) (*3*); (2) proton generation from H_2 or H by the reduction of metal cations like Ag^+ and Cu^{2+}, where H_2 or H originates in reactions (*9*), and (3) proton formation by partial hydrolysis of anion in the preparation process (*7*).

Relationships between catalytic activity and acidity of metal salts have been reported. Niiyama *et al.* obtained a fair correlation between activity for 2-propanol dehydration and electronegativity of metal cations (*3*). Hayashi and Moffat found that the activity for methanol conversion was related to the partial charge on oxygen atom (*8b*). However, in order to fully understand the catalysis of heteropoly compounds, we consider that the "pseudo-liquid phase" behavior (*2, 4, 7*) should be taken into account in addition to the acidic properties.

In the pseudo-liquid phase, such reactants as alcohols and water are absorbed into the bulk expanding the distance between the anions, and reaction occurs in the bulk as was demonstrated in the case of dehydration of 2-propanol over $H_3PW_{12}O_{40}$ (*11*). This model has successfully explained the characteristic behavior of the catalysis of heteropoly acids, e.g., high catalytic activity at low temperatures (*2, 4, 7, 10*). Since some metal salts also absorb polar

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[1] Part of this paper was presented at the 45th National Meeting of the Chemical Society of Japan, Tokyo, April, 1982, 2K29. Part VIII: Mizuno, N., Watanabe, T., and Misono, M., *J. Phys. Chem.* **89**, 80 (1985).

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0021-9517/85 $3.00
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molecules (*7*), it is very probable that the pseudo-liquid phase model is applicable to the metal salts.

In this work, copper salts of $H_3PW_{12}O_{40}$ were chosen as a metal salt containing reducible transition metal ion, and their catalytic and acidic properties were investigated in relation to the pseudo-liquid phase. This salt shows a high catalytic activity for some reactions (*5*) and exhibits peculiar catalytic behavior like induction period (dehydration of alcohols) (*9, 12*), which seems closely related to either of the three schemes described above or the pseudo-liquid phase. Furthermore, the reduction of the Cu^{2+} ion can be followed by means of ESR (cf. Scheme (2)). As for the acidic and catalytic properties of alkali metal salts, we reported them previously (*7*).

EXPERIMENTAL

Catalysts. 12-Tungstophosphoric acid ($H_3PW_{12}O_{40}$, abbreviated hereafter as PW_{12}) which was obtained commercially in the form of an aqueous solution from Nippon Inorganic Colour and Chemicals Company, Ltd. was extracted with diethyl ether, recrystallized from water, and dried at room temperature in a KOH desiccator. Copper salts (abbreviated as $CuPW_{12}$) were prepared by adding $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$ powder (Koso Chemicals Co.) to an aqueous solution of PW_{12} (0.16 mol/liter). The content of Cu in $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$ was determined by chelatometric titration to be 8.856 mmol g^{-1}. The resultant solution was concentrated by evaporation and dried in a KOH desiccator for 2 days. Besides the stoichiometric salt ($CuPW_{12}$-II), two kinds of salts containing Cu by 5% excess or deficient from the stoichiometry were prepared by controlling the amount of Cu added ($CuPW_{12}$-I and -III).

Catalytic reactions. The dehydration of 2-propanol was carried out with a continuous flow reactor under atmospheric pressure. The standard reaction conditions were as follows unless otherwise noted. The catalyst (50 mg) was pretreated at 110°C in He stream for 1 h, 2-propanol (3.2% in He) was introduced onto the catalyst through an evaporator–saturator. The total flow rate was 100 cm^3 (STP)/min. The isomerization of 1-butene was carried out in a closed-circulation system (200 cm^3) at room temperature. After the catalyst (500 mg) was evacuated at room temperature for 2 h, 54 Torr (1 Torr = 133.3 Pa) of 1-butene was introduced to the catalyst. Products were analyzed by gas chromatography (*7*).

Infrared and ESR measurements. The catalysts were deposited on a thin Si plate from the aqueous solution and placed in an infrared cell which was connected to a conventional high-vacuum system. After evacuation at various temperatures, or after maintaining the reaction (27 Torr of 2-propanol) at 110°C for 1 h followed by evacuation at 110°C, the catalyst was exposed to pyridine (15 Torr) at room temperature for 30 min. Then the catalyst was evacuated at 300°C for 1 h. Infrared spectra were recorded with Fourier transform infrared spectrometer (JEOL FTIR-10) at room temperature. For the ESR measurements, the catalysts (150 mg) were pretreated at 110 or 300°C in an *in situ* reaction cell connected to the circulation system. The progress of the dehydration which was carried out at 110°C in this system was followed by observing the pressure increase. Again the catalyst was evacuated at 110°C for 30 min, and transferred to an ESR tube installed in the reaction cell. ESR spectra were recorded at room temperature on JEOL JES-PE-IX with X-band frequency using 100 kHz modulation. As the reference of static magnetic field, Mn^{2+}/MgO was used. For the quantitative measurement, the signals of Cu^{2+} were doubly integrated and compared with the doubly integrated signal of $CuSO_4 \cdot 5H_2O$.

Other measurements. Water contents of the catalysts were measured with a quartz spring balance (*13*). Absorption of 2-propanol and water was measured at room temperature with a thermogravimeter (Shimadzu TGC-30) which was connected to a

TABLE 1

List of Catalysts Used

Catalyst	Cu/anion	Surface area ($m^2 \cdot g^{-1}$)	Water content[a] (molecules · $anion^{-1}$)
PW_{12}	0	6.0	6.0
$CuPW_{12}$-I	1.43	2.4	8.0
$CuPW_{12}$-II	1.50	1.3	8.0
$CuPW_{12}$-III	1.58	1.1	9.0

[a] After evacuation at room temperature.

vacuum system. After the catalyst was evacuated at desired temperatures for 1 h, it was exposed to 2-propanol (20 Torr) or water (13 Torr). Surface area was determined by the BET method using nitrogen adsorption after the sample had been pretreated at 150°C in He flow.

RESULTS AND DISCUSSION

Surface areas and water contents of the catalysts (PW_{12} and $CuPW_{12}$-I, -II, -III) are summarized in Table 1. The surface areas of these $CuPW_{12}$ catalysts were lower than that of PW_{12}.

Figure 1 shows the changes of percentage conversion with time on stream in the dehydration of 2-propanol over the catalysts pretreated at different temperatures. Only in this case, the reaction conditions were as follows: catalyst weight, 100 mg; reaction temperature, 100°C; concentration of 2-propanol, 4.7% in He; total flow rate 100 cm^3 (STP)/min. The products were propene and water with a small amount of ether (less than $\frac{1}{10}$ of propene). In the case of PW_{12}, the conversion was nearly constant from the beginning, and was almost independent of the pretreatment temperature. On the other hand, the conversion increased gradually with time in the case of $CuPW_{12}$-II, showing an induction period. Pretreatment at high temperatures made the induction period longer. The conversion continued to increase for more than 5 h over $CuPW_{12}$-II which had been pretreated at 300°C. The catalytic behavior of other $CuPW_{12}$ was very similar to that of $CuPW_{12}$-II, while the conversions at the stationary state were different. These results were reproducible.

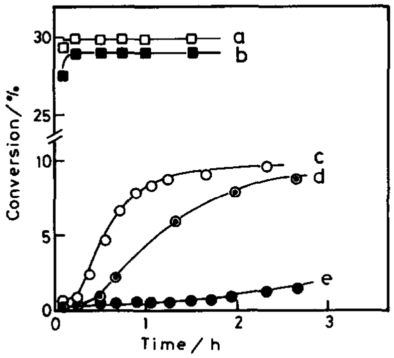

FIG. 1. Time course of dehydration of 2-propanol. Over PW_{12} pretreated at (a) 100°C, (b) 300°C, and over $CuPW_{12}$-II pretreated at (c) 100°C, (d) 150°C, and (e) 300°C.

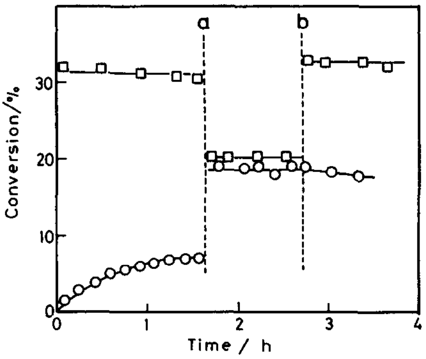

FIG. 2. Effect of water vapor on the activity of dehydration of 2-propanol. (□) PW_{12}, (○) $CuPW_{12}$-I. H_2O (1.25%) was fed during the period between (a) and (b).

Figure 2 shows the effect of water vapor added at the stationary state of the dehydration. In the case of PW_{12}, the conversion decreased from 32 to 20% when 1.25% of water was added. And the initial high conversion was regained reversibly when the supply of water was stopped. Contrary to PW_{12}, the conversion for $CuPW_{12}$-I increased immediately from 7 to 19% by the addition of water, and the high value was maintained even after the water supply was discontinued. Similar effect of water was observed for the other $CuPW_{12}$.

The promoting effect of water on the activity of $CuPW_{12}$ suggests that water

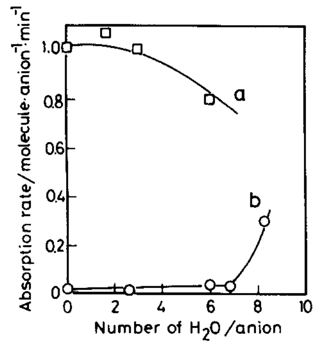

FIG. 3. Effect of water content on initial absorption rate of 2-propanol. (a) PW_{12}, (b) $CuPW_{12}$-I.

formed by the dehydration plays an important role in the increase of the catalytic activity with time as shown in Fig. 1. We considered that the concept of "pseudo-liquid phase" (*2, 7*) was a possible candidate to explain this behavior of $CuPW_{12}$, since water promoted the absorption of certain molecules into the bulk (*13*) and possibly increased the catalytic activity (*14, 15*). To verify this possibility, we performed the following experiments.

First, the effect of water content of the catalyst on the absorption process of 2-propanol was examined. Prior to the absorption experiments, the water content was adjusted by changing the evacuation temperature from 25 to 300°C. Results are shown in Fig. 3. The absorption into PW_{12} was rather rapid in the whole range of the water content studied. On the other hand, in the case of $CuPW_{12}$ the rate was very small at low water contents and increased sharply when the water content reached about 8 molecules per anion ($CuPW_{12}$ was preevacuated at 25°C).

Next, the effect of water vapor on the absorption of 2-propanol was measured. Typical results are given in Fig. 4. When 2-propanol or water alone were admitted over $CuPW_{12}$-I for about 30 min, the weight increases were only less than 2.5%. However, when a mixture of water (13 Torr) and 2-propanol (20 Torr) was brought into contact with $CuPW_{12}$-I, a marked increase in weight was observed (Fig. 4A). The results in Figs. 3 and 4 demonstrate that water in both the catalyst and the gas phase promotes the absorption of 2-propanol. Thus the induction period observed for $CuPW_{12}$ is probably the period in which water formed by the reaction was gradually accelerating the absorption. The increase in the activity, as shown in Fig. 2, is considered to be due to the increase of reaction zone in the pseudo-liquid phase caused by the water-promoted absorption of 2-propanol. The retention of the high conversion even after the water supply was discontinued over $CuPW_{12}$ (Fig. 2) implies that the rate of absorption–desorption which was once enhanced by water was maintained despite the decrease of the water pressure. Thus the rate of absorption–desorption process determines the effective volume of reaction zone in the "pseudo-liquid phase." If the absorption–desorption is much faster than the reaction rate, the whole bulk acts effectively as the reaction zone. But the effec-

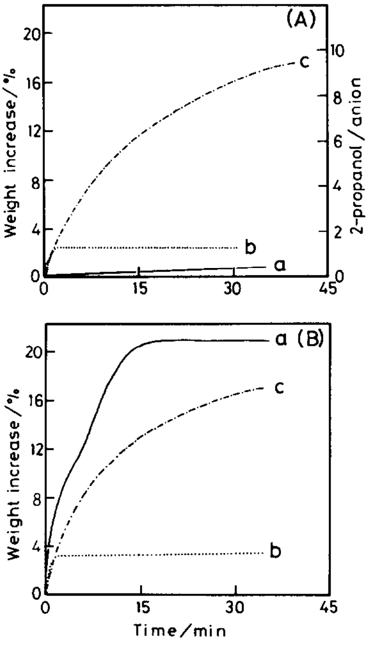

FIG. 4. Effect of water on absorption of 2-propanol. (A) $CuPW_{12}$-I, (B) PW_{12}. (a) 2-Propanol (20 Torr), (b) water (13 Torr), and (c) a mixture of 2-propanol (20 Torr) and water (13 Torr). The catalysts were pretreated at 110°C for 2 h under vacuum.

tive volume decreases as the absorption–desorption becomes slower.

In contrast, coexistence of water inhibited slightly the absorption of 2-propanol into PW_{12} as shown in Fig. 4B. In this case, water probably competes with 2-propanol for absorption, causing the reductions in the amount of 2-propanol absorption and the rate. The different effects of water on absorption of 2-propanol between PW_{12} and $CuPW_{12}$ may be due to the difference in absorptivity of these catalysts. Since the solubility of salts of heteropoly acids in water and alcohols is lower than that of the acid form (*16*), the cations, e.g., Cu^{2+} strengthen the bond between anions. This bond may be loosened by coordination of water to Cu^{2+}. By this effect, 2-propanol absorption probably proceeded more easily in the presence of water, while the absorption into PW_{12} proceeded readily in the absence of water because of its high absorptivity.

Baba *et al.* observed a similar induction period for the dehydration of butanol over $CuPW_{12}$ and $AgPW_{12}$ (*9*). They concluded that the acid sites were created during the reaction in the following way (Scheme (2) described in Introduction)

$$Cu^{2+} + \tfrac{1}{2}H_2 \text{ (or H)} \rightarrow Cu^{+} + H^{+} \tag{1}$$

$$Cu^{+} + \tfrac{1}{2}H_2 \text{ (or H)} \rightarrow Cu^{0} + H^{+} \tag{2}$$

If the acid sites are generated according to this scheme, the amount of acid should increase and the amount of Cu^{2+} should decrease with the progress of the reaction. This possibility in the present case was examined by the measurement of ir spectra of absorbed pyridine and ESR spectra of Cu^{2+}.

As shown in Fig. 5, in the case of $CuPW_{12}$-II, the band at 1535 cm^{-1} (pyridinium-ion band) appeared evidently and no evidence was found for the band near 1450 cm^{-1} (coordinately bonded pyridine) after evacuation at 300°C. This indicates that fresh $CuPW_{12}$ (before its use as catalyst) was a strong protonic acid. Even when $CuPW_{12}$ was pretreated at 25 and 300°C, the infrared spectra were quite similar to those of Fig. 5, showing that the acidity of $CuPW_{12}$ was almost independent of the water content (0–8 molecules/anion). The uptake of pyridine at room temperature by PW_{12} and $CuPW_{12}$ was more than 6 molecules per anion, indicating that pyridine was not adsorbed only on the surface but was absorbed in the bulk (*12, 13*).

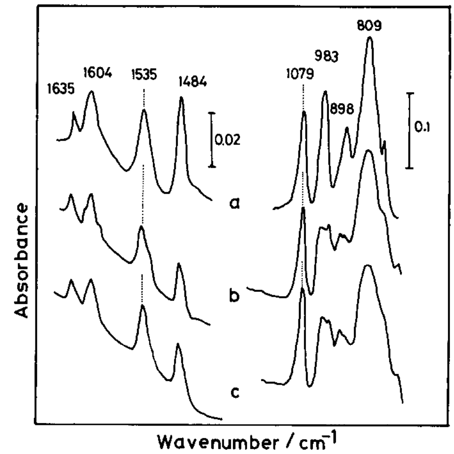

FIG. 5. Infrared spectra of pyridine absorbed in PW_{12} and $CuPW_{12}$. (a) PW_{12}, (b) $CuPW_{12}$-II, and (c) $CuPW_{12}$-II after their use in the dehydration of 2-propanol. The spectra were taken after evacuation at 300°C.

The number of protons was estimated from the relative intensity of pyridinium ion (1535 cm^{-1}) to the anion band (1076 cm^{-1}). The P–O stretching band (1076 cm^{-1}) was adopted as the reference, because the integrated intensity of this band was nearly constant. In the case of PW_{12} (3 protons/anion), the ratio of the intensity of the two bands was 9.5×10^{-2}. It was confirmed previously that 3 molecules of pyridinium ion per anion formed by the same procedure (*2, 4*). By using this value, the number of protons present in $CuPW_{12}$-II was estimated to be 1.1 per anion. This number changed little after use for dehydration reaction (compare spectra c and b).

Splitting of the bands at around 980 and 900 cm^{-1} was observed in the case of $CuPW_{12}$. The splitting is not due to the degradation of anion, since these bands split

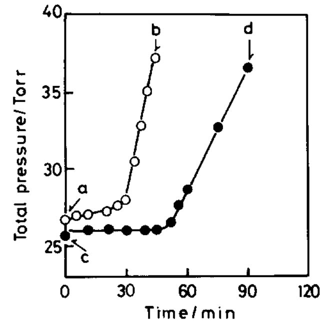

FIG. 6. Pressure changes with time in the dehydration of 2-propanol over $CuPW_{12}$-II. (○) Pretreated at 110°C, (●) pretreated at 300°C.

TABLE 2

Effect of Cu Content on Catalytic Activity

Catalyst	Acid amount[a] (number of H^+/anion)	Catalytic activity[b] (ml (STP)/g · min)	
		Dehydration	Isomerization
PW_{12}	3.0	18.6 (11.6)	12.5
$CuPW_{12}$-I	1.2	4.7 (11.0)	5.7
$CuPW_{12}$-II	1.1	2.9 (7.5)	6.3
$CuPW_{12}$-III	1.1	0.6 (2.3)	5.2

[a] Estimated from the integrated ir absorbance of pyridinium ion (1515–1550 cm^{-1}) after evacuation at 300°C.

[b] Values in parentheses represent the rates obtained when the feed gas contained 1.25% of H_2O.

when the water of crystallization was removed, but the splitting disappeared after rehydration (reversible and reproducible). However, there is no experimental problem in quantitative analysis in spite of the splitting of the band at around 900–980 cm^{-1}.

ESR signals were measured before and after the reaction. Figure 6 shows the progress of the reaction. ESR signals were measured at a, b, c, and d in Fig. 6. The ESR signals are shown in Fig. 7, where a, b, c, and d correspond to those in Fig. 6. The concentration of Cu^{2+} in $CuPW_{12}$-II after pretreatment at 110°C corresponded to about 80% of Cu in $CuPW_{12}$-II. This indicates that most of the Cu in the catalyst is probably present as Cu^{2+}. The amount of Cu^{2+} decreased by only 20% (band d in Fig. 7) even after the activity of the catalyst became very high. If 20% of Cu^{2+} is reduced to Cu^+, the amount of proton created is only 0.3 per anion which is a minor part of the protons present under reaction conditions. In other words, the reduction can explain only a small part of the increase of catalytic activity with time. Thus, both ir and ESR studies suggest that Scheme (2) does not operate mainly under the reaction conditions. However, as considered by Baba *et al.* (*9*), Scheme (2) may be applicable to more easily reducible silver salt even at low temperatures, and copper salt when used at high temperatures. Since the stoichiometric Na salts, to which Scheme (1) is not applicable (*3*), also exhibits acidity (*7*), Scheme (3) in addition to Scheme (1) may contribute mostly to the generation of the acidity of $CuPW_{12}$ under the present reaction conditions.

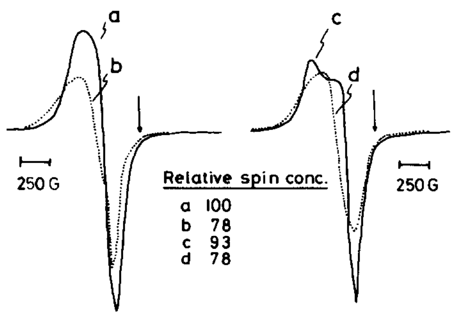

FIG. 7. ESR signals of $CuPW_{12}$-II. Before the reaction (a, c) and after the reaction (b, d). Positions of the free-electron signal (g = 2.0023) are indicated by arrows.

The effects of Cu content on the amount of acid and the catalytic activities for dehydration of 2-propanol and isomerization of 1-butene are summarized in Table 2. The activity for the dehydration decreased with the increase in the Cu content. On the other hand, the activity for the isomerization of 1-butene was nearly independent of the Cu content. The *cis*/*trans* ratio of 2-butene was 0.9 over PW_{12} and about 1.7 over $CuPW_{12}$. The acidity of the bulk, which was determined by infrared spectroscopy of absorbed pyridine, decreased slightly as the Cu content increased. The different dependences on the Cu content between the dehydration and the isomerization may be explained as follows. We classified previously the reactions which take place over heteropoly compounds into two types, "surface-type" (e.g., isomerization of butene) and "bulk-type" (e.g., dehydration of alcohols) reactions (*7*). A small dependence of the rate of butene isomerization on the Cu content suggests that the acidity on the surface remained nearly constant. On the other hand, in the case of the bulk-type reaction, the activity may depend on the effective volume of the reaction zone in the bulk as well as the bulk acidity. The decrease of the activity for the dehydration of 2-propanol with the Cu content is due to both the decrease in acidity and absorptivity of the catalysts.

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