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# Reduced copper salt of Wells–Dawson type heteropolyacid as a bifunctional catalyst

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#### 1. Introduction

Ono and Baba observed [1] that the silver, copper and nickel salts of Keggin type heteropolyacids, when reduced with hydrogen, became strong acidic catalysts active in methyl-tert-butyl ether (MTBE) synthesis conducted in the vapor phase. The activation of such salts includes silver cations reduction to metal clusters with the simultaneous regeneration of free heteropolyacid (HPA) [2,3] according to the equation:

$$Ag_{3}PW_{12}O_{40} + 1(1/2)H_{2} \rightarrow 3Ag + H_{3}PW_{12}O_{40}$$
(1)

Activated silver salts of Keggin type heteropolyacids was investigated for both conversion of methanol to hydrocarbons [4–6] and 1-butene isomerization [7]. Recently, the research was focused on the bifunctional catalysts based on noble metal (Pt, Pd) salts of heteropolyacids of the Keggin type and/or acid cesium salts of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>. Their catalytic performance was tested among others in skeletal isomerization of n-heptane [8,9] and n-butane [10], as well as hydroizomerization of pentane [11], and hydration of ethylene [12]. Copper salt of dodecamolybdophosphoric acid, Cu<sub>3</sub>(PMo<sub>12</sub>O<sub>40</sub>)<sub>2</sub>, was found to be active and selective catalyst in liquid phase oxidation of m-cresol [13] and oxidative dehydrogenation of isobutyric acid [14]. Kasza and Bielański [15] investigated the

#### ABSTRACT

Copper salt of Wells–Dawson type heteropolyacid when reduced in ethanol vapors at temperatures 210–290 °C becomes active bifunctional catalyst for ethanol conversion. In oxygen free atmosphere (helium), both water and ethylene are formed predominantly. Other side products include small amount of diethyl ether and traces of acetaldehyde. When air is used as a carrier gas instead of oxygen free helium, acetaldehyde, typical product of ethanol dehydrogenation, forms on redox centers. Simultaneously, the formation of ethylene and diethyl ether, the products of ethanol dehydration occurring on Brønsted acid centers, is observed.

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conversion of ethanol on reduced silver salt of Dawson type heteropolyacid,  $Ag_6P_2W_{18}O_{62}$ . They showed that the catalyst obtained by reduction of the salt with ethanol or methanol vapors contained silver clusters dispersed over microcrystallites of  $H_6P_2W_{18}O_{62}$ . In the absence of oxygen, this catalyst was active in gas-phase ethanol dehydration to ethylene and/or diethyl ether. However, when oxygen was supplied to the feed, not only the dehydration products but also acetaldehyde – the product of ethanol dehydrogenation – was obtained. The former reaction occurs typically on Brønsted acid centers while the latter one on metal redox centers.

The aim of the present study was to investigate the behavior of reduced copper salt of Dawson type heteropolyacid, which was expected to exhibit bifunctional catalytic activity. It should be observed that similar bifunctional catalytic systems containing reduced transition metal atoms or clusters finely dispersed in the crystal lattice of zeolites were also studied by a number of investigators [16]. However, our interest in studying the reduced transition metal as catalysts stems from the fact that free heteropolyacids exhibit much higher acidic strength than hydrogen forms of zeolites.

#### 2. Experimental

Copper salt of diphosphooctadecatungstic acid,  $Cu_3P_2W_{18}O_{62}$  was obtained by dissolving 2.9991 g of  $H_6P_2W_{18}O_{62}$ ·26.0 $H_2O$  in ca. 10 cm<sup>3</sup> of distilled water and slow addition of stoichiometric amount (0.3871 g) of powdered  $Cu(CH_3COO)_2 \cdot H_2O$  (p.p.a.,



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Sigma–Aldrich) under intensive mixing. The pale blue solution was evaporated on water bath and dried in the oven at 50 °C for 12 h. Subsequently, the precipitate was kept over saturated solution of  $Mg(NO_3)_2$  at room temperature.

Thermogravimetric analysis (TG) of the salt was carried out within temperature range of 25–650 °C in air flow using Netzsch STA 409PC Instrument Derivatograph. Heating rate 5°/min was applied.

Pristine unreduced and reduced copper salt samples were examined using Jeol JSM 7500 field emission scanning microscope equipped with energy dispersive X-ray (EDX) spectrometer.

The X-ray photoelectron spectroscopy (XPS) and X-ray Auger excitation spectroscopy (XAES) were applied for the samples analysis with a hemispherical analyzer SES R4000 Gamma Data Scienta.

The FT-IR spectra of the samples were obtained with Bruker Equinox 55 Spectrometer using KBr tablets.

The catalyst reduction and catalytic tests were carried out in a constant flow  $(35 \text{ cm}^3/\text{min})$  microreactor connected on line with a gas chromatograph. Helium or air, both saturated with ethanol vapors at room temperature, was used as the carrier gas. The amount of the copper salt used for the experiments was 0.063 g. The construction of the apparatus enabled to control *in situ* the sample reduction by analyzing the gas composition on outlet of the microreactor and subsequent determination of the activity of the reduced catalyst at reduction temperature or at other temperature freely chosen.

#### 3. Results and discussion

Fig. 1 shows the TG curve of the sample of copper salt of  $H_6P_2W_{18}O_{62}$  heteropolyacid previously equilibrated with water



Fig. 1. Thermogravimetric analysis of pristine heteropolyacid copper salt.

vapors over saturated solution of  $Mg(NO_3)_2$  at room temperature. It can be observed that the weight loss of the sample occurs in two stages upon heating. The first one occurring between room temperature and 201 °C is attributed to the departure of loosely bonded water. It was estimated that in this stage sample looses 16.1 H<sub>2</sub>O molecules per one heteropolyanion. The second stage observed between approximately 202 and 400 °C characterized by almost linear weight loss may be due to the departure of water coordinatively bonded to copper ions. Its amount was estimated as 9.9 H<sub>2</sub>O molecules per one heteropolyanion. Hence, the total weight loss of pristine sample corresponded to 26.0 mole of water per one mole of heteropolyanions.

Infrared spectroscopic data of the unsupported HPA, pristine copper salt and the sample reduced with ethanol at 250 °C are given in Table 1. Both spectra exhibited four characteristic peaks of the  $P_2W_{18}O_{62}^{6-}$  ion [17]. The observed shifts of bands in the spectrum



Fig. 2. Evolution of catalytic activity of Cu<sub>3</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> sample in the course of reduction period at 210 (a), 230 (b), 250 (c), 270 (d) and 290 °C (e).

#### Table 1

FTIR vibration frequencies for pristine Wells-Dawson heteropolyacid and copper salt.

Vibration type	$H_6P_2W_{18}O_{62}$ devoid of crystallization water [cm <sup>-1</sup> ]	Cu <sub>3</sub> P <sub>2</sub> W <sub>18</sub> O <sub>62</sub> pristine [cm <sup>-1</sup> ]	$\begin{array}{l} Cu_3P_2W_{18}O_{62} \text{ after} \\ reduction (250^\circ\text{C}) \\ [cm^{-1}] \end{array}$
P-O <sub>a</sub>	1090	1091	1091
W=O <sub>d</sub>	961	957	964
W-Ob-W	908	914	917
$W-O_c-W$	773	783	783

of pristine copper salt were similar to those observed by Kasza and Bielański [15] for silver salts.

As mentioned before, the reduction of the copper salt of Dawson type heteropolyacid was carried out in catalytic reactor with saturated ethanol vapors mixed with oxygen free helium as carrier gas. A series of reduction experiments were performed within the temperature range of 210–290 °C for 150 min. The progress of this activation was controlled by analyzing the gas products leaving the reactor. Fig. 2a-e shows the examples of such experiments. In all cases besides the main products, water and ethylene, the formation of small amounts of diethyl ether as well as traces of acetaldehyde were observed. The presence of ethylene and water as the products of ethanol dehydration that forms on the acid centers indicate appearance of free heteropolyacid in the reduced salt At the beginning of reduction the amount of unreacted ethanol changed rapidly achieving constant value after 90–150 min. In the prolonged time a certain deactivation (increase of amount of unreacted ethanol) of the obtained catalyst was observed. This partial deactivation was presumably due to the formation of coke on strong acid centers of recrystallized heteropolyacid forming platelet-like crystallites observed in the scanning microscope images.

The conversions of ethanol and selectivities to ethylene, water and diethyl ether at reduction temperatures of 210–290 °C are presented in Fig. 3. It shows that the effect of reduction of copper salt of Wells–Dawson type heteropolyacid was the weakest at reduction temperature of 210 °C and increased with the temperature increasing up to 270 °C. However, at temperature higher than 270 °C, the decrease of the conversion of ethanol was observed. This might be explained by the decomposition of heteropolyacid resulting from slow loss of its constitutional water at this temperature.

After reduction at 250 °C for 150 min the catalyst was tested at temperature range of 230–290 °C in two series of experiments, one carried out in ethanol vapor with oxygen free helium gas and the other one conducted in the presence of air. Fig. 4 shows the composition (mol%) of reaction mixture registered during the former



**Fig. 3.** Ethanol conversion and selectivities to diethyl ether, ethylene and acetaldehyde reached after 150 min of salt reduction in ethanol vapor at 210–290 °C.



**Fig. 4.** Concentration of ethanol, diethyl ether, ethylene and acetaldehyde observed for the catalyst sample prereduced for 2.5 h at 250 °C. Reaction temperature 250 °C, oxygen free helium as a carrier gas (35 cm<sup>3</sup>/min).

reaction at 250 °C. It is seen that at these conditions ethanol is only partially used and about 75–85 mol% of it remains in the gas.

The effect of reaction temperature (230–290 °C) on the ethanol conversion and the selectivity of the catalysts prereduced at 250 °C is shown in Fig. 5. It is noticed that in parallel to the increase of ethanol conversion with temperature, the selectivity to ethylene, the product of an endothermic reaction, increases as well. On the other hand, the selectivity to diethyl ether, the product of an exothermic reaction, decreases with an increase of reaction temperature. Both reactions are typical for Brønsted acidity of the catalysts. Acetaldehyde, the product of ethanol oxidative dehydrogenation occurring on catalytic redox centers, was formed only in small quantities and the selectivity of the catalyst to this product was always below 1%. Some explanation should be added to the difference between conversion of ethanol in the presence of catalyst reduced at 290 °C and reaction performed at 290 °C with copper salt prereduced at 250 °C. It is well known that the temperature of reaction strongly affect the morphology, texture and dispersion of reduced metal on the surface. Our results suggest that in both cases, dispersion of  $Cu^0$  on  $H_6P_2W_{18}O_{62}$  was to some extent different. When the prereduced sample was used in reaction carried out at 290 °C, initially formed Cu<sup>0</sup> nanoparticles could migrate on the surface, agglomerate improving the accessibility of H<sup>+</sup> in heteropolyacid. The higher acidity of the prereduced catalyst may explain the higher selectivity to the products of ethanol dehydration.



**Fig. 5.** Ethanol conversion on the sample prereduced at 250 °C and selectivity to the particular products at 230–290 °C. Oxygen free helium gas used as a carrier gas.



**Fig. 6.** The concentration of ethanol, diethyl ether, ethylene and acetaldehyde observed for the catalyst sample prereduced for 2.5 h at 250 °C. Reaction temperature of 250 °C, air saturated with ethanol vapor as a carrier gas  $(35 \text{ cm}^3/\text{min})$ .

The yield of acetaldehyde distinctly increased when the atmospheric air was used as a carrier gas instead of oxygen free helium. The results of the reaction carried out under such conditions (after catalyst prereduction at 250 °C) are shown in Fig. 6. The activity of catalyst, which was first contacted with helium saturated with ethanol vapors, and then with air containing ethanol, changed



**Fig. 7.** The effect of the reaction temperature on the concentration of ethanol, ethylene, water, acetaldehyde and diethyl ether obtained on the catalysts prereduced at  $250 \,^{\circ}$ C. Air saturated with ethanol vapor was used as carrier gas ( $35 \, \text{cm}^3/\text{min}$ ).

rapidly at the beginning of reaction and after 20 min or so reached a constant value. At the beginning of catalytic test the acid–base (ethylene and water formation) type was predominant process and later on the share of redox reaction increased. Acetaldehyde, the product of redox type reaction, became the main product. On the other hand, the selectivities to ethylene and diethyl ether, the products of acid–base type reaction, were low, and the catalyst exhibited very distinct bifunctional properties.

The effect of reaction temperature on the conversion of ethanol and selectivity to acetaldehyde, diethyl ether and ethylene is shown in Fig. 7. This graph illustrates the situation when air was used as carrier gas. At first, the selectivity to acetaldehyde increased with the temperature, and then reached the maximum at 250 °C. The further increase of temperature caused reduction of selectivity to





Fig. 8. SEM image (a) and EDX maps of tungsten (b) and copper (c) distribution in pristine sample of Cu<sub>3</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>.





Cu Ka1

Fig. 9. SEM image (a) and EDX map of copper (b) and line scan of copper and tungsten distributions (c) of Cu<sub>3</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> reduced at 250 °C.

acetaldehyde in favor to ethylene. It can be seen that the temperature rise results in the increase of ethanol conversion (increasing the yield of products of acid–base type reaction) with almost constant yield of acetaldehyde (around 23%).

Fig. 8b and c shows the distribution of copper and tungsten on the surface of the unreduced copper salt, and Fig. 8a presents its microphotograph. It is seen that both distributions are distinctly homogeneous. However, after reduction, the local enrichments in copper can be seen in Fig. 9b, where patches of needle-like crystallites appear at the salt surface. The graph in Fig. 9c shows the results of the EDX line scan. The concentration of copper, proportional to number of X-ray counts, shows distinct increase along the line when crossing the patch. It is clear that copper uniformly distributed over the surface of pristine copper salt in the case of unreduced sample is migrating during reduction. Moreover, it forms separate clusters or patches of the size of about 1  $\mu$ m composed of nanometric needle-like crystallites.

The surface state of  $Cu_3P_2W_{18}O_{62}$  prereduced in ethanol at 250 °C and after reaction with ethanol was analyzed by XPS and XAES techniques. The lack of changes in the values of electron binding energies for W  $4f_{7/2}$ , P  $2p_{3/2}$  and Cu  $2p_{3/2}$  (Table 2) suggests that the surfaces of both studied samples are qualitatively the same although the atomic ratios indicate surface local enrichment with

copper for the reduced sample. This feature agrees well with EDX analysis of the SEM images.

The analysis of Cu 2p core excitation (BE value and lack of shakeup satellites) allows exclusion of Cu<sup>2+</sup> presence at the surface layer of both samples [18,19]. The values of Cu  $L_3M_{45}M_{45}$  excitation maximum and the Auger parameter ( $\alpha'$ ) obtained from XPS and XAES spectra may indicate the presence of Cu<sup>+</sup> ions in both samples (Fig. 10). However, the shape of the Cu  $L_3M_{45}M_{45}$  XAE spectra can be rather assigned to the system containing metallic copper [20]. Taking into account the specific electrophilicity (electronegativity) of the Wells–Dawson unit, it can be assumed that copper in the ethanol reduced salt, is present in metallic state but the Auger parameter is shifted to lower value mainly due to a substrate effect.

According to scanning electron microscopy images the second component of reduced catalyst, free heteropolyacid, forms platelike microcrystals, which are the support of copper containing aggregates. The infrared spectrum of the reduced salt corresponds to the spectra of Wells–Dawson type anions in the salt and in the free crystalline heteropolyacid (Table 1). It can be assumed that such free acid liberated from the copper salt plays the role of acid component in the bifunctional catalyst. Similarly, it is believed that the aggregates of reduced copper are the catalytic redox centers.

Table 2	
XPS and XAES data for $Cu_3P_2W_{18}O_{62}$ prereduced in ethanol at 250 °C (Et) and after reaction with ethanol at 250 °	C (EtEt).

Sample	Binding energy (eV)			Kinetic energy (eV)	Auger parameter (eV)	Atomic su	Atomic surface ratio	
	W 4f <sub>7/2</sub>	P 2p <sub>3/2</sub>	Cu 2p <sub>3/2</sub>	Cu L <sub>3</sub> M <sub>45</sub> M <sub>45</sub>	$\alpha'$	Cu/P	Cu/W	P/W
Et	35.8	133.9	932.8	915.0	1847.8	1.36	0.15	0.11
EtEt	35.9	133.9	932.9	915.1	1848.0	0.65	0.12	0.17



Fig. 10. XAES Cu  $L_3M_{45}M_{45}$  spectra for  $Cu_3P_2W_{18}O_{62}$  prereduced in ethanol at 250 °C (a) and after catalytic reaction with ethanol at 250 °C (b).

#### 4. Conclusions

X-ray microanalysis shows that both tungsten and copper are uniformly distributed on the surface of pristine copper salt of Wells–Dawson heteropolyacid  $H_6P_2W_{18}O_{62}$ . However, after the reduction in ethanol vapors at 250 °C the form of patches composed of needle-like crystallites appear at the surface leading to local enrichments in copper. The XPS measurements indicate the presence of both metallic copper and copper Cu<sup>+</sup> ions. The formation of metallic copper allows accepting that reduction is accompanied by the formation of free heteropolyacid in the process analogous to that shown by Eq. (1). In the oxygen free helium, the main products of catalytic ethanol conversion are ethylene, diethyl ether and water. Furthermore, the typical products of reactions are formed on Brønsted acid centers. In the present case the latter are supplied by free heteropolyacid. On the other hand, in the presence of air, acetaldehyde is predominantly obtained in catalytic reaction. Such reaction occurs on redox centers and is ascribed to the presence of catalytic redox centers formed by reduced copper.

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