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# Reduced Silver Salt of Wells-Dawson Heteropolyacid $H_6P_2W_{18}O_{62}$ as a Bi-Functional Catalyst

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**Abstract** Silver salt preparation was obtained by neutralizing solution of $H_6P_2W_{18}O_{62}$ in water with solid $Ag_2CO_3$. In the introductory experiments the conditions of silver salt reduction with ethanol vapours were studied at 170–290 °C. At 250 °C and 2.5 h complete reduction to silver and free heteropolyacid was observed. During reduction with ethanol the initially not active salt became catalyst on which typical for free acid alcohol dehydration to ethylene occurred. In a series of experiments carried out within temperature range 210–290 °C ethanol conversion was studied on the catalyst previously reduced at 250 °C. When air was used as the carrier gas the bi-functional behavior of the catalyst was distinct, besides ethylene, diethyl ether and water, typical products of acid–base type catalytic reaction also comparable amount of acetaldehyde, the product of redox type reaction, was observed.

**Keywords** Heteropolyacid · Silver salt · Ethanol conversion

## 1 Introduction

Besides the free heteropolyacids (HPA) also their salts may exhibit some acidity and catalytic activity in the acid–base type reactions. The crystalline HPA are strong Brönsted acids the strength of which is comparable to that of the so called superacids. However, the origin of the acidity of salts may be different [1]. Lewis acidity of the metal cation, dissociation of water coordinated to the cation as e.g. $[Ni(H_2O)_h]^{2+} \rightarrow [Ni(H_2O)_{h-1}(OH)]^- + H^+$, and also protons present in the acid salts as in $Cs_{3-x}H_xPW_{12}O_{40}$ may be the source of acidity of HPA salts. Of special interest are the heteropolyacid salts containing easily reducible cations: $Ag^+$, $Cu^{2+}$ or $Pd^{2+}$. In this case protons are forming as the result of catalyst's reduction e.g. $Ag^+ + 1/2\ H_2 \rightarrow Ag^0 + H^+$. The resulting catalyst is bi-functional. It contains free solid heteropolyacid, effective acid–base type catalyst, and also reduced metal acting as the redox type catalyst.

The silver salt of $H_3PW_{12}O_{40}$ was investigated by Baba et al. [2]. They have shown that silver salts of dodecatungstophosphoric acid initially not active in *o*-xylene isomerisation became active after the treatment with hydrogen at 300 °C. Such treatment led to the formation of free heteropolyacid and reduction of $Ag^+$ to $Ag^0$. The same group of authors investigated the $Ag_3PW_{12}O_{40}$ as the catalyst for conversion of methanol to hydrocarbons [3, 4], and also gas phase formation of methyl-*tert*-butyl ether (MTBE) synthesis [5]. Physico-chemical properties and especially macropore structure of $Ag_3PW_{12}O_{40}$, $Ag_3PMo_{12}O_{40}$ and $Ag_4SiW_{12}O_{40}$ were investigated by Parent and Moffat [6]. They studied also the effect of acid strength distribution in $Ag_3PW_{12}O_{40}$ on its catalytic activity in 1-butene isomerisation [7]. Haber et al. [8] investigated a series of $Ag_xH_{3-x}PW_{12}O_{40}$ preparations and stated one phase solid solution in the whole composition range $0 \le x \le 3$. The catalytic activity in vapour phase dehydration of ethanol and hydration of ethylene was ascribed to acid protons in the salt and also the protons generated by dissociation of $H_2O$ coordinated to silver cations [8].

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The aim of the present research was to synthesize the silver salt of diphosphooctadecatungstic acid $Ag_6P_2W_{18}O_{62}$ and to test its catalytic properties in the reduced state. It was considered that such catalyst may exhibit interesting bi-functional catalytic properties. It should be here observed that in the above mentioned investigations [2–5, 7] only the typical acid–base catalytic reactions were studied and no possibility of bi-functional behaviour of the reduced catalyst was taken into account. This is why besides testing ethanol dehydration at the absence of oxygen we tested also the possibility of oxidative dehydrogenation by introducing oxygen into the feed. According to our knowledge $Ag_6P_2W_{18}O_{62}$ reduction was not investigated by any other authors.

## 2 Experimental

Silver salt of diphosphooctadecatungstic acid $Ag_6P_2W_{18}O_{62}$ was obtained by adding small portions of solid $Ag_2CO_3$ to the stoichiometric amount of $H_6P_2W_{18}O_{62}$ dissolved in a small amount of water [9]. The precipitated salt and the solution was dried over a water bath.

Thermal analysis (TG, DTG and DTA) of the salt has been carried out within temperature range 22–800 °C using STD 2960 TA Instrument Derivatograph. Heating rate 25° $\mathrm{min}^{-1}$ was applied.

FTIR spectra were obtained with Bruker Equinox 55 spectrometer using KBr technique.

The X-ray microanalysis of the sample was carried out using JEOL JSM 7500F Field Emission Scanning Electron Microscope.

The X-ray Photoelectron Spectroscopy (XPS) measurements were carried out with a hemispherical analyzer (SES R4000, Gammadata Scienta).

Catalytic reaction and catalyst reduction has been carried out in a constant flow microreactor connected on line with a gas chromatograph. The mass of catalyst was the same in all experiments and equal to 0.063 g. The total flow of helium or air saturated with ethanol vapour at room temperature was always 35 mL/min. The initial concentration of ethanol was kept on the same level in all of experiments.

## 3 Results and Discussion

### 3.1 Pristine Silver Salt

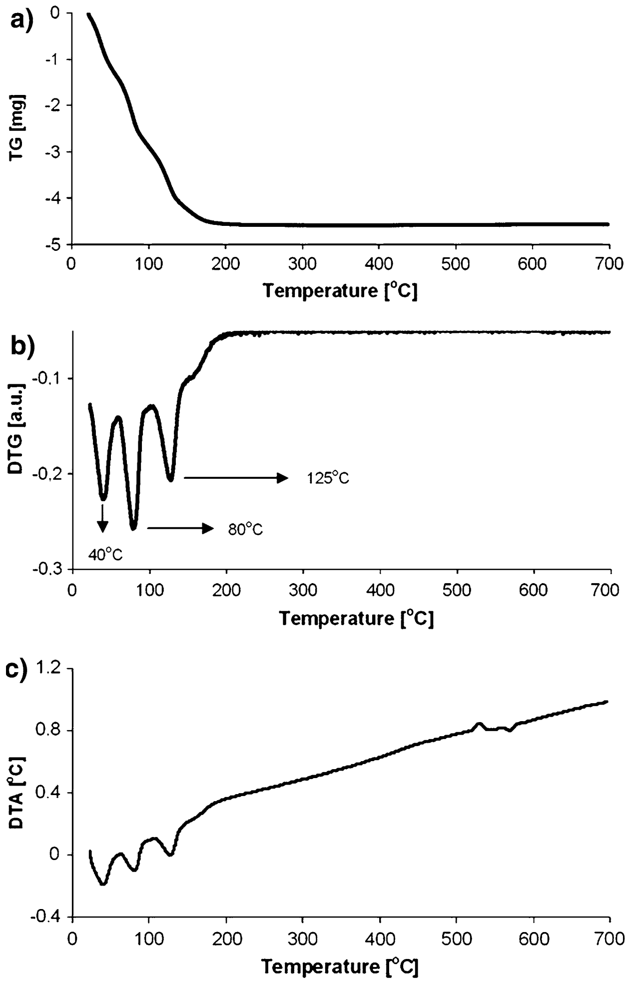

**Fig. 1** Thermal analysis of pristine heteropolyacid silver salt. **a** TG, **b** DTG and **c** DTA curves

Figure 1a–c shows the results of thermal analysis of $Ag_6P_2W_{18}O_{62}$ sample previously kept in a dessicator over the saturated solution of $Mg(NO_3)_2$ at room temperature. The weight loss 4.58% observed between room temperature and 200 °C corresponded to the loss of 13 mol of water per mole $Ag_6P_2W_{18}O_{62}$. The DTA endothermic peaks at about 40, 80 and 125 °C indicate that water vapour is adsorbed (or absorbed) in at least three different positions or forms. No any further weight loss between 200 and 700 °C nor the DTA peaks were observed thus indicating the thermal stability of silver salt.

Figure 2 shows the FTIR spectra of the pristine silver salt, the sample reduced with ethanol at 250 °C and also sample on which after reduction catalytic conversion of ethanol was tested. The characteristic structural vibrations of free crystalline Wells-Dawson $H_6P_2W_{18}O_{62}$ are present also in the pristine silver salt with only the shift to the lower frequencies of the W–$O_c$–W vibration at 780 $\mathrm{cm}^{-1}$ which involves oxygen atoms $O_c$ in the $W_3O_9$ structural subunits (Table 1). This shift may be ascribed to the effect of substitution protons in the free crystalline acid by the silver ions in the salt. The spectra with only smaller shifts confirm the essentially Wells-Dawson structure of the anions in all the stages of processing the samples. They exhibit only small shifts in the reduced sample as compared with free $H_6P_2W_{18}O_{62}$ acid. The IR peak at 1,615 $\mathrm{cm}^{-1}$ corresponds to the $\delta_{H_2O}$ vibration

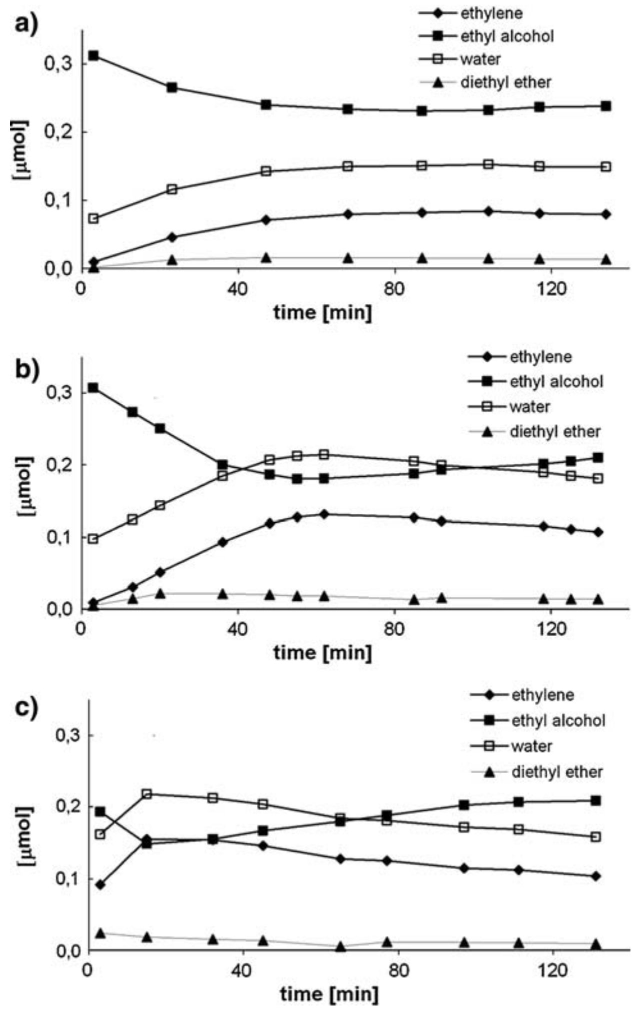

**Fig. 2** FTIR spectra of $Ag_6P_2W_{18}O_{62}$ samples: pristine, reduced and reduced after the catalytic test

of the nonprotonated water molecules [10] and a broad band at 3,570 $cm^{-1}$ typical of hydrogen bond can be ascribed to the interactions between adsorbed $H_2O$ molecules or $H_2O$ molecules and HPA anions.

### 3.2 Silver Salt Reduction

The reduction of the catalysts has been carried out in situ in the catalytic reactor in a flow of helium gas saturated with ethanol vapour. In the course of the treatment the reduced silver salt has gradually become catalytically active and the progress of this activation could be controlled by analyzing gas leaving the reactor. Examples of such run are shown in Fig. 3a–c. At 190 °C no any activity and hence no reduction was observed but it was distinct at 210 °C and a series of experiments was done within the temperature range 210–290 °C. In all cases the reduction time was 150 min. The predominant products of acid–base type reaction, ethanol dehydration, ethylene and water in the molar ratio close to 1:1 were observed thus indicating the appearance in the reduced salt of free heteropolyacid, the catalyst of ethanol dehydration. The amount of another product of ethanol dehydration, diethyl ether, was at this temperature much lower. No acetic acid, the probable product of ethanol oxidation, was detected within the investigated temperature range.

As Fig. 3a shows at 230 °C the activity of the salt being progressively reduced was increasing during 60–70 min and then stabilized on the constant level. At 250 °C (Fig. 3b) somewhat higher activity was reached after about 50 min but then it slowly decreased. The most rapid increase of reduced salt catalytic activity was observed at 270 °C. Already after 15 min maximum activity was reached and the progressing deactivation began. The most probable explanation of such observed decrease in catalytic activity is the decomposition of the segregated free heteropolyacid which already at this temperature may slowly loose its water of constitution (catalyst's dehydroxylation process). The probable explanation of such observed decrease in catalytic activity may be the formation of coke over strong acidic centers.

The progress of reduction could also be checked by the XPS investigation of the peaks Ag $3d_{5/2}$ of silver in the samples after different pre-treatments. The predominant peak in the pristine silver salt is situated at 369.1 eV (Table 2 peak C). It is attributed to the silver ions $Ag^+$ in the salt crystal lattice. Peak A at 367.2 eV according to the data base [11, 12] may correspond to silver oxide or possibly to the rests of $Ag_2CO_3$ not reacted during salt precipitation. After reduction at 250 °C the intensity of peak C distinctly decreased and a new peak (B) at 368.4 eV appeared which in all reduced samples was the predominant one. Moreover, the intensity of peak B ascribed to $Ag^0$ in comparison to other

**Table 1** FTIR vibration frequencies registered for pristine Wells-Dawson heteropolyacid and silver salt

| Vibration type | $H_6P_2W_{18}O_{62}$ devoid of crystalization water [$cm^{-1}$] | $Ag_6P_2W_{18}O_{62}$ pristine [$cm^{-1}$] | $Ag_6P_2W_{18}O_{62}$ after reduction (250 °C) [$cm^{-1}$] | $Ag_6P_2W_{18}O_{62}$ after reduction (250 °C) and catalytic test [$cm^{-1}$] |
|---|---|---|---|---|
| $P–O_a$ | 1,090 | 1,091 | 1,083 | 1,091 |
| $W{=}O_d$ | 961 | 961 | 949 | 956 |
| $W–O_b–W$ | 908 | 914 | 908 | 910 |
| $W–O_c–W$ | 773 | 780 | 801 | 793 |

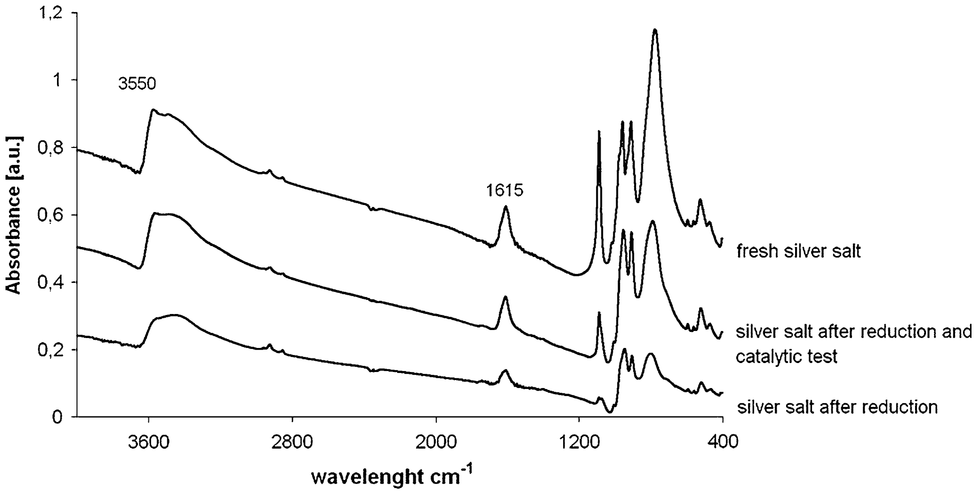

**Fig. 3** Silver salt reduction proceeding at different temperatures. **a** 230 °C. **b** 250 °C. **c** 270 °C

**Table 2** The results of XPS studies of pristine and reduced silver salt of heteropolyacid

| Sample | Ag $3d_{5/2}$ peaks | | | |
|---|---|---|---|---|
| | A | B | C | D |
| $Ag_6P_2W_{18}O_{62}$ pristine | 367.2 | – | 369.1 | 370.8 |
| | 2.1% | | 95.7% | 2.2% |
| $Ag_6P_2W_{18}O_{62}$ after reduction 0.5 h/250 °C | 367.0 | 368.3 | 369.2 | – |
| | 8.8% | 75.8% | 15.4% | |
| $Ag_6P_2W_{18}O_{62}$ after reduction 1 h/250 °C | 367.0 | 368.4 | 369.5 | – |
| | 5.7% | 82.5% | 11 .8% | |
| $Ag_6P_2W_{18}O_{62}$ after reduction 2.5 h/250 °C | 367.0 | 368.7 | 369.8 | 371.5 |
| | 3.4% | 70.2% | 20.2% | 6.1% |
| $Ag_6P_2W_{18}O_{62}$ after reduction 2.5 h+1 .5 h 1,250 °C | 367.2 | 368.2 | 369.1 | 370.9 |
| | 10.5% | 63.5% | 21.3% | 4.7% |

peaks (A, C and D) increased to 75.8–82.5% thus indicating high degree of sample reduction.

Figure 4 shows the results of scanning microscope investigation and X-ray microanalysis of the nonreduced silver salt. It is seen that the distribution of tungsten and silver over the surface of crystallites is homogeneous.

On the other hand in the case of sample reduced at 250 °C, Fig. 5. The presence of silver at the surface is limited to the areas of the order 2–5 μm. The agglomeration of silver atoms in small areas shows the mobility of reduced $Ag^o$ atoms and their migration to the areas forming there a kind of nuclei.

### 3.3 Catalysis on Reduced Silver Salt

The catalyst reduced at 250 °C for 150 min was tested at temperatures range 210–250 °C in two series of experiments. In one of them ethanol vapour were introduced in a flow of helium and in the other one the flow of air. The results of the former are shown in Fig. 6. At 230 °C diethyl ether and ethylene were produced almost in the same amounts. At higher temperatures the yield of ethylene, the product of an endothermic reaction, increased and the yield of diethyl ether, the product of an exothermic one, decreased. The same trends were observed also in [13]. Only very small amounts of acetaldehyde appear. Most probably it is the product of ethanol dehydrogenation ($C_2H_5OH \rightarrow CH_3CHO + 1/2\ H_2$) on the reduced silver atoms.

In the case when air was used as the carrier gas in the catalytic experiments the bi-functionality of the catalyst was distinct. Besides ethylene and diethyl ether, products of acid–base type reaction, also acetaldehyde, the product of redox type reaction, appeared in comparable amount and at 270 °C (Fig. 7) it was the predominant product. Considering the fact that at these conditions no any hydrogen evolution was observed, it can be assumed that the appearance of acetaldehyde is the result of oxidative dehydrogenation ($C_2H_5OH + 1/2\ O_2 \rightarrow CH_3CHO + H_2O$).

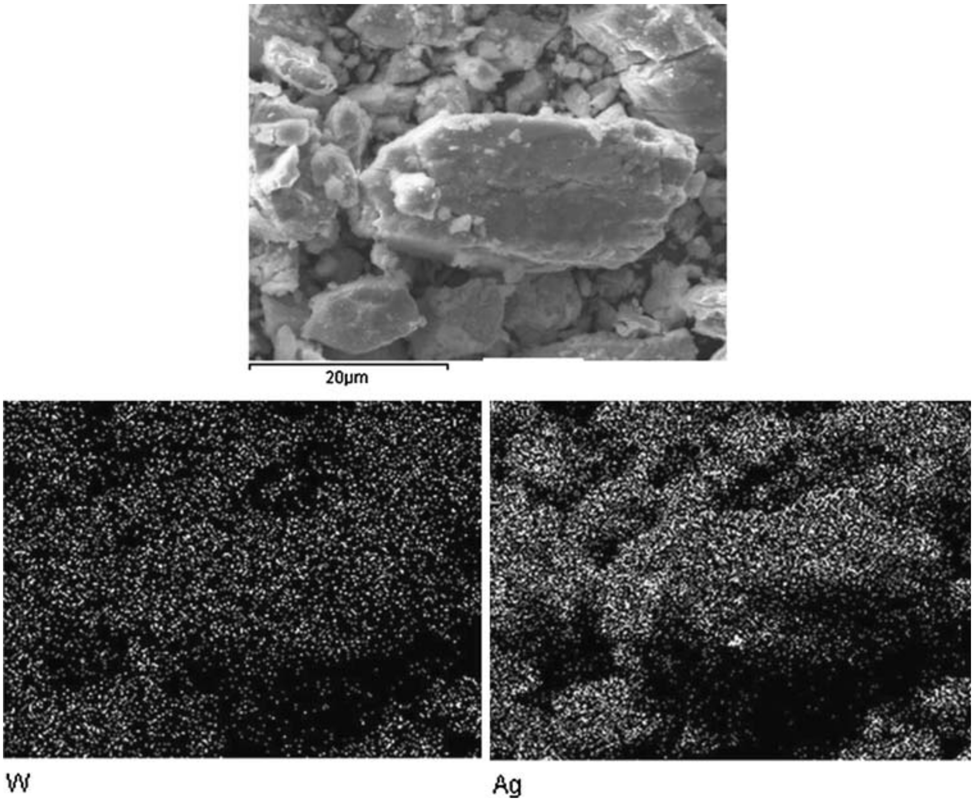

**Fig. 4** Microphotograph and maps of silver and tungsten distribution in pristine $Ag_6P_2W_{18}O_{62}$

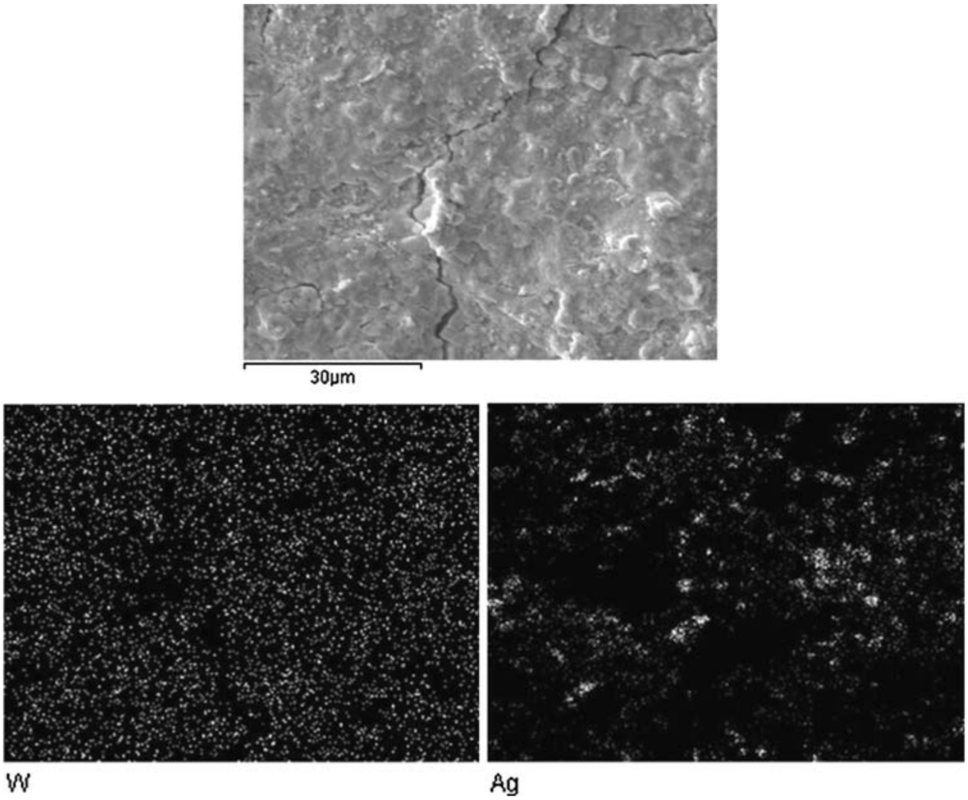

**Fig. 5** Microphotograph and maps of silver and tungsten distribution in reduced $Ag_6P_2W_{18}O_{62}$

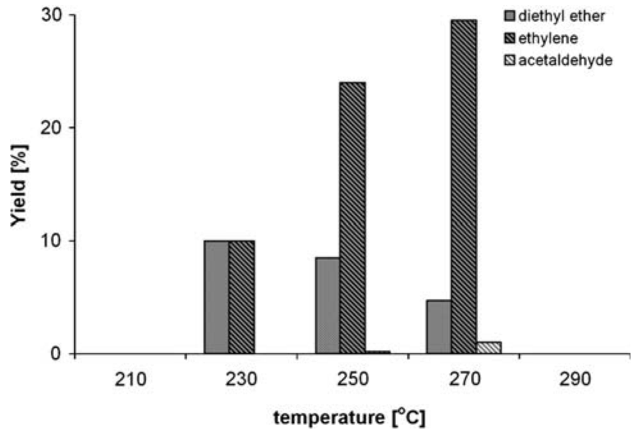

**Fig. 6** The yield of products in ethanol conversion without air

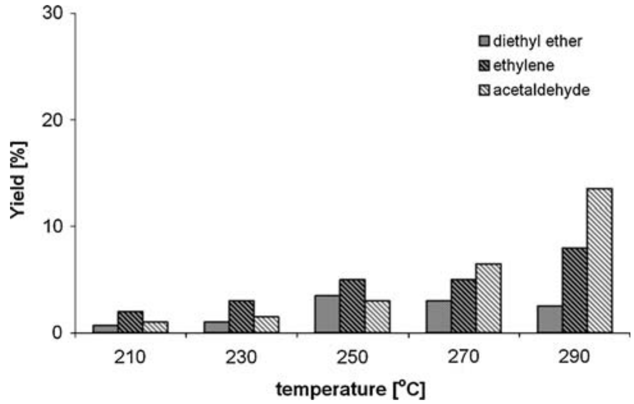

**Fig. 7** The yield of products in ethanol conversion reaction with air conditions

## 4 Conclusions

Silver salt of Wells-Dawson type heteropolyacid $Ag_6P_2W_{18}O_{62}$ can be easily reduced by ethanol vapour at temperatures above 210 °C. The reduced product contains free heteropolyacid and silver forming at the surface of heteropolyacid crystallites agglomerations of the diameter of several micrometre. The reduced salt exhibits the properties of the bifunctional catalyst in the conversion of ethanol. At the presence of oxygen besides ethylene and diethyl ether, the products of acid–base type reaction, also comparable amounts of acetaldehyde, the product of redox type catalytic reaction, appear at temperatures above 210 °C.

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