Journal of Catalysis **207,** 296–306 (2002)
doi:10.1006/jcat.2002.3514, available online at http://www.idealibrary.com on IDEAL®

Potassium and Silver Salts of Tungstophosphoric Acid as Catalysts in Dehydration of Ethanol and Hydration of Ethylene

J. Haber,[1] K. Pamin, L. Matachowski, B. Napruszewska, and J. Połtowicz

Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 8, 30-239 Kraków, Poland

Received September 4, 2001; revised January 8, 2002; accepted January 14, 2002

Potassium and silver salts of tungstophosphoric acid (HPW) with varying amounts of the cations $K_xH_{3-x}PW_{12}O_{40}$ and $Ag_xH_{3-x}PW_{12}O_{40}$ have been prepared as pure or supported on silica using the incipient wetness method. Their catalytic properties in two reactions have been studied. The vapor-phase dehydration of ethanol carried out in a conventional flow-type reactor under atmospheric pressure at temperatures varying from 398 to 773 K, and hydration of ethylene in a stainless-steel batch reactor at 478 K under the pressure of 42 atm. $K_xH_{3-x}PW_{12}O_{40}$ in the range $0 < x < 2$, is composed of two phases, $H_3PW_{12}O_{40}$ and $K_2H_1PW_{12}O_{40}$; in the range $2 \leq x < 3$ the solid solution is formed. Their catalytic activity in both dehydration of ethanol and hydration of ethylene decreases with increasing x, with $K_2H_1PW_{12}O_{40}$ and $K_3PW_{12}O_{40}$ being inactive in the hydration. $Ag_xH_{3-x}PW_{12}O_{40}$ forms one phase of the solid solution in the whole composition range $0 < x < 3$. The catalytic activity in both reactions increases. It has been shown that catalytic activity is related to acid protons and protons generated by dissociation of water molecules coordinated by silver cations. At temperatures higher than 573 K the oxidative dehydrogenation of ethanol to acetaldehyde with high yield is observed on the $Ag_xH_{3-x}PW_{12}O_{40}$ series of catalysts. © 2002 Elsevier Science (USA)

Key Words: **tungstophosphoric acid; potassium dodecatungstophosphate; silver dodecatungstophosphate; ethanol dehydration; ethylene hydration.**

1. INTRODUCTION

Heteropolyacids and their metal salts are well-known acidic and oxidative catalysts. They are efficient catalysts for such reactions as hydration of olefins (1), metanol conversion to hydrocarbons (2), synthesis of MTBE (3), and oxidation of metacrolein (4). The protons in the secondary structure of the heteropolyacid can easily be exchanged, completely or partially, with different cations without affecting the primary Keggin structure. Polar molecules like water or alcohols can easily enter and exit the bulk, expanding or contracting the distance between the Keggin anions in the crystal lattice, while nonpolar molecules (i.e., hydrocarbons) cannot enter the bulk. Due to this nature of the secondary structure, some reactions may proceed in the bulk at the state called the "pseudo-liquid phase." Unlike polar molecules, nonpolar reactants are incapable of being absorbed in the bulk of a heteropolyacid. They interact only with the surface of the catalyst (5).

However, heteropolyacids are characterized also by some properties which make their use in catalysis difficult. Their good solubility in water results in the removal of heteropolyacids from the catalyst in the presence of water vapor, formed in the course of the catalytic reaction or added as a reagent, e.g., in electrophilic addition of water to olefins, resulting, in deactivation of the catalyst. A method of preventing heteropolyacids from being leached is their partial neutralization with different cations (e.g., K^+, Ag^+) to form insoluble salts. These metal salts are also active in reactions catalyzed by heteropolyacids (6–8). Generally, it is assumed that the salts of heteropolyacids of different amounts of cations are heterophase mixtures and their final formula is an average of pure heteropolyacid and a neutral salt.

The catalytic behavior of metal salts of heteropolyacids attracts considerable interest, because the formation of salts may lead to the appearance of a bifunctional or multifunctional catalysis (9). Most of the reactions proceed not only on the acidic form of the heteropoly compound but also on the neutral salts, even in the case of reactions catalyzed by acids (10).

The purpose of the present study is to explain how catalytic activity and acidity can be controlled by the incorporation of potassium and silver cations into the heteropoly structure, deposited on silica support. In the acid-catalyzed reactions in the presence of solid acid catalysts, control of the number of active centers and their acid strength is an important factor, because each reaction to proceed selectively requires proper acidity.

A series of potassium and silver dodecatungstophosphoric acid (HPW) salts $K_xH_{3-x}PW_{12}O_{40}$, where $x = 1, 1.5, 2, 2.5, 3$, and $Ag_xH_{3-x}PW_{12}O_{40}$, where $x = 1, 1.5, 2, 3$, were prepared. They are designated $K_1, \ldots, K_3$ and $Ag_1, \ldots, Ag_3$. Also samples of these salts supported on silica were synthesized. To this end the heteropolyacid was first

---

[1] To whom correspondence should be addressed. Fax: 0048-12-4251923. E-mail: nchaber@cyf-kr.edu.pl.

0021-9517/02 $35.00
© 2002 Elsevier Science (USA)
All rights reserved.

supported on the surface of silica. Two series of samples were then prepared. In the first series the heteropolyacid after deposition on silica was treated with appropriate amounts of potassium or silver salts. These samples are denoted Me_x/SiO_2, e.g., K_1/SiO_2 or Ag_1/SiO_2. In the second series the heteropolyacid after deposition on silica was washed with water to dissolve that part of the heteropolyacid which was present in the form of small crystallites and was not bound to the support, and then it was reacted with the appropriate salt. These samples are denoted as Me_x/SiO_2^w. In the case of Me_x/SiO_2 samples the bulk acidity was measured. The catalysts were tested in the vapor-phase dehydration of ethanol, which is often employed as a "test reaction" for acidic catalysts. Then their catalytic activity in high-pressure hydration was studied.

2. EXPERIMENTAL

2.1. Materials

Potassium dodecatungstophosphate (K_x) was obtained by mixing an aqueous solution of an appropriate amount of potassium carbonate with an aqueous solution of heteropolyacids. Silver dodecatungstophosphate (Ag_x) was obtained as precipitate by adding an appropriate amount of silver nitrate to an aqueous solution of heteropolyacids. The resultant salts were dried in an oven at 363 K.

Two silica supports were used. The silica having a BET surface area of ca. 306 m^2/g, a pore diameter of 90 Å, and a pore volume of 0.90 ml/g was used as support for the catalysts in the dehydration of ethanol. It was crushed and sieved into grains of 0.2–0.4 mm. In the reaction of ethylene hydration the catalysts were prepared using the silica having a BET surface area of ca. 510 m^2/g, a pore diameter of 150 Å, and a pore volume of 0.65 ml/g, crushed and sorted into grains of 0.5–2.0 mm. The silicas were then dried in a hot-air oven at 395 K. Pure dodecatungstophosphoric acid (Merck) was supported on silica by means of incipient wetness impregnation with a coverage of 30% of the monolayer, assuming the cross section of a Keggin unit to be 144 Å. These amounts corresponded to the loading of 24.2 wt% for the silica having 306 m^2/g and 33.5 wt% for the silica having 510 m^2/g. The known amount of tungstophosphoric acid was dissolved in water and the hot silica was added to the solution. The whole solution was absorbed by the silica grains. The resulting slurry was mixed for 15 min at room temperature and dried in the oven at 363 K for a few hours. The salts of tungstophosphoric acid were also prepared using the incipient wetness method. To prepare so-called "unwashed" catalysts the known amount of heteropolyacid supported on silica was reacted with the appropriate amount of potassium or silver compound, dissolved in water, to form suitable tungstophosphate salt Me_x/SiO_2. In the second series the washed samples were prepared by mixing the dried samples of supported tungstophosphoric acid with distilled water and stirring for ca. 1 h at room temperature to remove that part of the heteropolyacid which was loosely bound to the surface. The surface coverage of the samples after the water treatment decreased to $18.2 \pm 0.4\%$ of the monolayer. Heteropolyacid salts Me_x/SiO_2^w were then prepared on the surface of silica covered with heteropolyacid strongly bound to the surface by reacting the appropriate amount of potassium or silver compound with HPW/SiO_2^w. The synthesized catalysts were tested in the dehydration of ethanol and hydration of ethylene.

2.2. Nitrogen Physisorption Measurements

BET surface areas and pore size distributions of the catalysts were calculated from nitrogen adsorption isotherms at 77 K in an Autosorb-1, Quantachrome equipment.

2.3. UV–Vis Spectroscopy

Ultraviolet–visible (UV–vis) spectroscopy was performed with a Shimadzu UV-vis 160 A double beam spectrophotometer with built-in recorder, using quartz cells of 1-cm optical path.

2.4. Thermal Analysis

Thermal analysis was carried out in static air in a Paulik, Paulik, and Erdey DTA–TG thermal analyzer. Samples of about 500 mg were heated at a rate of 10 K/min up to 1273 K.

2.5. X-Ray Diffraction

X-ray diffraction (XRD) patterns were obtained with a Siemens D5005 automatic diffractometer using Cu $K\alpha$ radiation (55 kV, 30 mA) with a graphite monochromator in the diffracted beam. The samples were dried at 363 K before each measurement.

2.6. Infrared Spectroscopy

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 800 spectrometer in KBr pellets in the range of 400–1400 cm^{-1} under atmospheric conditions.

2.7. Catalytic Tests

The dehydration of ethanol was carried out in a conventional flow-type reactor under atmospheric pressure. Typically, a 0.3-ml sample was packed into a quartz reactor. Ethyl alcohol was introduced into the helium stream (5.7 mol% in He) by an evaporator–saturator set placed in a thermostat. The total flow rate of alcohol in the stream of the feed gas was 1.8 L/h. Before the test a catalyst was heated to 623 K at the rate of 100 K/h and activated in a helium flow for 2 h. All the reactions were carried out according to the same temperature and time scheme. In the catalytic tests the catalysts were heated at a rate of 2 K/min to the reaction temperature, the reaction was carried out at this temperature for 0.5 h, and then the sample was heated to the next reaction temperature. The products were analyzed by means of a Perkin–Elmer 900 gas chromatograph equipped with a flame ionization detector and Porapak S column.

The ethylene hydration reaction was performed in a stainlees-steel batch reactor system at the optimum temperature of 487 K and under a pressure of 42 atm, with the reagents molar ratio being $C_2H_4 : H_2O = 3 : 1$. Uniformity of temperature was reached by placing the reactor in the heating oven. A 4-ml sample of the catalyst fraction was encapsulated in a small space inside the reactor. The catalyst remained isolated from the reagents but was heated together with the whole system until the required temperature was obtained. In due time the catalyst was jetted into the reaction mixture by means of an overpressure of helium and the reaction started. After 3 min, the reaction was terminated by immersing the hot reactor in a cold water bath. The condensate was analyzed for ethanol content by means of the SRI 8610 B gas chromatograph equipped with a katharometer and HayeSep D column.

3. RESULTS AND DISCUSSION

3.1. *Structure of the Catalysts*

3.1.1. Bulk potassium and silver salts. The structure of salts of heteropolyacids depends on the type of countercation present. Salts with small cations have properties similar to the parent HPA: they are soluble in water, nonporous, and characterized by small surface areas. In contrast, salts with large monovalent cations such as NH^{4+}, K^+, and Cs^+ are water insoluble, have rigid micro/mezoporous tertiary structure, and show high surface areas. In this case, depending on the nature of the heteropolyacid and on the countercation-to-proton ratio $M^+ : H^+$, either a heterogeneous mixture of the solid acid and salt or acidic salts (a solid solution of acid and salt) are precipitated. On the basis of ample studies of the $K_xH_{3-x}PMo_{12}O_{40} \cdot nH_2O$ system by differential thermal analysis (DTA), XRD, ^{31}P nuclear magnetic resonance (NMR), transmission electron microscopy, electron spectroscopy for chemical analysis, and diffuse reflectance IR spectroscopy it has been claimed (11) that in this system no significant formation of solid solution takes place. A heterogeneous mixture of the acid and neutral salt $K_3PMo_{12}O_{40}$ is precipitated and at high M : H ratios an epitaxial isostructural layer of $H_3PMo_{12}O_{40} \cdot nH_2O$ becomes stabilized at the surface of $K_3PMo_{12}O_{40}$ particles. Such layers have also been obtained by impregnating this salt with the acid (12). On the other hand, it has been established (13, 14) that in the case of $Cs_xH_{3-x}PW_{12}O_{40}$ at $M^+ : H^+$ ratios surpassing the value of 2, solid solutions of $Cs_3PW_{12}O_{40}$ and $H_3PW_{12}O_{40}$ are formed after heat treatment, with compositions varying between $Cs_2H_1PW_{12}O_{40}$ and $Cs_3PW_{12}O_{40}$. Formation of such solid solutions has been confirmed by ^{31}P NMR spectroscopy. It should be mentioned, however, that also in the case of this system it has been claimed that acid salts correspond to $Cs_3PW_{12}O_{40}$ with highly dispersed $H_3PW_{12}O_{40}$ layers (15). Results obtained in the present paper seem to indicate that—as could be expected—there is an analogy between the structure of $K_xH_{3-x}PW_{12}O_{40}$ and that of $Cs_xH_{3-x}PW_{12}O_{40}$, whereas different behavior is shown by $Ag_xH_{3-x}PW_{12}O_{40}$.

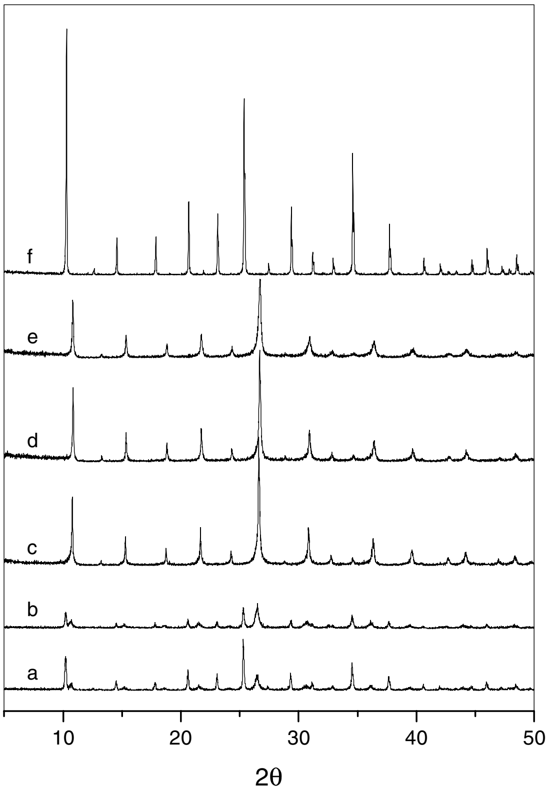

FIG. 1. Powder X-ray diffraction patterns of potassium salts: (a) K_1, (b) $K_{1.5}$, (c) K_2, (d) $K_{2.5}$, (e) K_3, and (f) HPW.

The structures of a series of bulk salts with changing stoichiometry $K_xH_{3-x}PW_{12}O_{40}$ and $Ag_xH_{3-x}PW_{12}O_{40}$ were studied by means of XRD and DTA. The diffraction patterns of K_1 and $K_{1.5}$ salts reveal the presence of additional reflexes shifted from those originating from the heteropolyacid. The intensities of these peaks, visible in Fig. 1, increase and the intensity of heteropolyacid peaks decreases when the content of potassium in the synthesized sample grows and they disappear when the composition $K : H = 2 : 1$ is reached. It may thus be concluded that in the case of potassium salts with the content of potassium ions changing in the range $0 < x < 2$ the reaction of $H_3PW_{12}O_{40}$ with K_2CO_3 resulted in the formation of mixtures of the $K_2H_1PW_{12}O_{40}$ salt and an unreacted heteropolyacid, while in the case of the $K_2H_1PW_{12}O_{40}$ salt no traces of free heteropolyacids were found. The reaction proceeds according to the following equation:

$$2H_3PW_{12}O_{40} + xK_2CO_3 \rightarrow xK_2H_1PW_{12}O_{40} + (2-x)H_3PW_{12}O_{40} + xH_2CO_3. \quad [1]$$

The amount of $H_3PW_{12}O_{40}$ decreases in the synthesized samples from unity to zero when x changes from 0 to 2. The unreacted heteropolyacid can easily be removed by washing the sample with water, as indicated by comparison of X-ray patterns of the acidic $K_{1.5}$ salt before and after the washing treatment (Fig. 2). In the case of K_2, $K_{2.5}$, and K_3 salts no traces of pure heteropolyacids were detected, proving the presence of only one phase with good crystallinity, representing a solid solution with changing composition.

The conclusion that a solid solution of $H_3PW_{12}O_{40}$ and $K_3PW_{12}O_{40}$ is formed in the range $2 \le x < 3$ is supported by a linear change in the lattice parameter with x, which follows the Vegard law. It may be mentioned here that according to the model (16) of the dehydrated $H_3PW_{12}O_{40}$ each proton is shared by four equivalent terminal oxygens, belonging to four different heteropoly anions. The same structure was suggested for $Cs_3PW_{12}O_{40}$, in which each Cs^+ ion has four equivalent terminal oxygens as closest neighbors (17). The secondary structure of acidic salt $K_2H_1PW_{12}O_{40}$ may be thus envisaged as composed of Keggin anions with H^+ and K^+ ions distributed inside between four terminal oxygens.

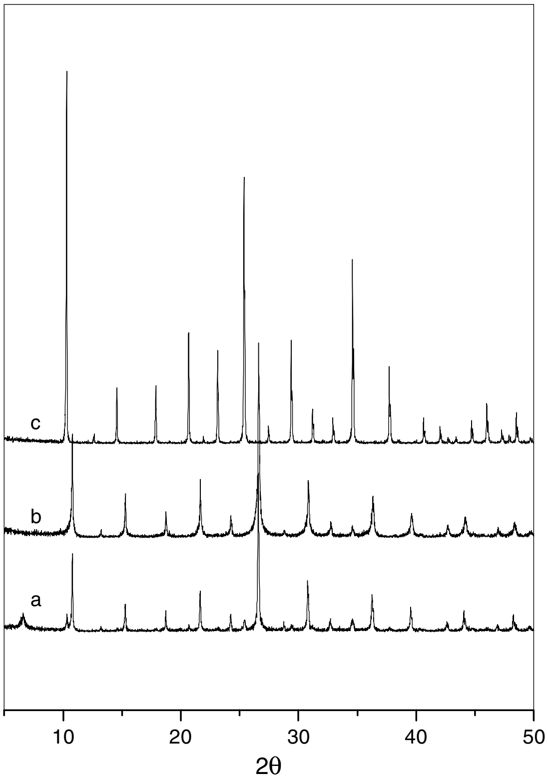

FIG. 2. Powder X-ray diffraction patterns of potassium salt: (a) $K_{1.5}$, (b) $K_{1.5}$ washed with water, and (c) HPW.

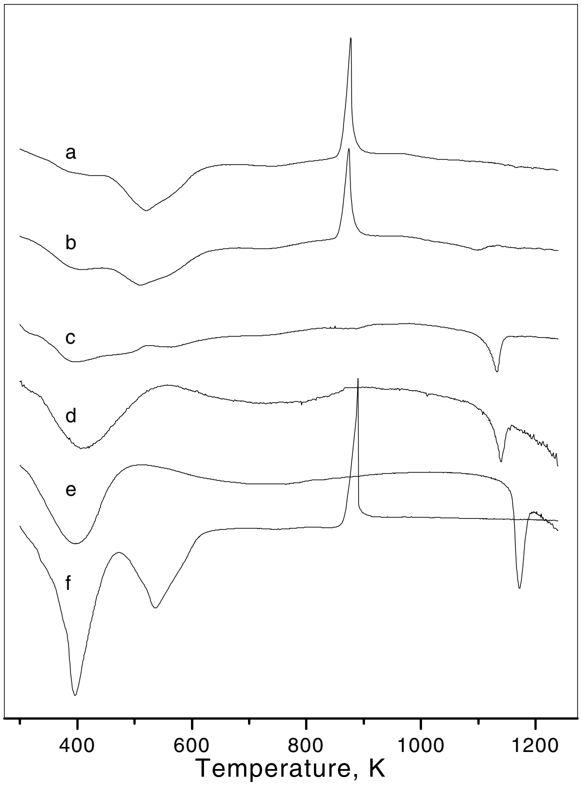

FIG. 3. DTA profiles of potassium salts: (a) K_1, (b) $K_{1.5}$, (c) K_2, (d) $K_{2.5}$, (e) K_3, and (f) HPW.

The thermal analysis fully confirms the results obtained with X-ray diffraction. In Fig. 3 DTA profiles for potassium salts were compared with those for pure heteropolyacids. In the case of HPW two large endothermic effects, at 396 and 537 K, are visible. The first one is connected with the loss of crystallization water and the other originates from the loss of water hydrating protons. The complete decomposition of the heteropolyacid with the formation of WO_3 and P_4O_{10} corresponds to the large exothermic effect at 890 K.

The two types of endothermic effects responsible for the loss of water are also observed for potassium acidic salts. The size of those effects is strictly connected with the number of potassium cations incorporated. The sample with the largest content of water hydrating protons is the K_1 sample, which has relatively low potassium content. The K_3 salt, which is neutral and has no protons, demonstrates only one small endothermic effect. The exothermic effect observed at about 873 K is the largest in the case of the K_1 salt, having the largest amount of unreacted heteropolyacids. This effect is absent in the case of K_2, $K_{2.5}$, and K_3 salts. These facts prove that the synthesis of the K_2, $K_{2.5}$, and K_3 salts leads to the formation of monophase structures.

The endothermic effect corresponding to the decomposition temperature is a characteristic value for every structure. In the case of biphasic mixtures such as K_1 or $K_{1.5}$ salts it is difficult to determine the exact temperature of decomposition. The ebulioscopic effect is responsible for those difficulties. This effect is connected with the appearance of WO_3, formed due to heteropolyacid decomposition, which disturbs the assignment of an exact decomposition temperature of these salts, shifting it considerably. For this reason as-synthesized heteropoly salts were washed with water to remove excessive heteropolyacid before DTA analysis. DTA analysis showed that decomposition temperatures of the K_1 and $K_{1.5}$ salts after washing are equal to 1143 K, characteristic for the K_2 salt. This observation indicates that in the case of K_1 and $K_{1.5}$ salts, except for unreacted heteropolyacid, the acidic $K_2H_1PW_{12}O_{40}$ salts is formed. The synthesis of K_2 salts also leads to the formation of $K_2H_1PW_{12}O_{40}$ salts. The synthesis of the $K_{2.5}$ salt results in the $K_{2.5}H_{0.5}PW_{12}O_{40}$ monophase, which decomposes at 1148 K. The K_3 salt is the most stable and decomposes at 1153 K. It may be thus concluded that the K_x salts, where $2 \leq x < 3$, are monophase solid solutions and the decomposition temperature changes from 1143 to 1153 K.

Taking into account the fact that the radius of Ag^+ ion (1.26 Å) is similar to that of K^+ (1.33 Å) it could have been expected that the silver salts of HPW will have similar properties to those of potassium salts. This is however not the case.

The formation of silver salts of tungstophosphoric acid during the synthesis of catalysts proceeds according to the following equation:

$$H_3PW_{12}O_{40} + xAgNO_3 \rightarrow Ag_xH_{3-x}PW_{12}O_{40} + xHNO_3. \qquad [2]$$

The diffraction patterns of silver tungstophosphates indicate the existence of one crystalline phase only, which means that acidic salts of heteropolyacid are formed. Figure 4 compares the XRD patterns of all synthesized silver heteropoly salts. The reflexes assigned to the Keggin salts are shifted in comparison with the pure heteropolyacid, toward lower lattice parameters, with the increase in silver cation content ranging from $a_0 = 11.9959$ for Ag_1 salts to $a_0 = 11.9242$ for Ag_3 salts. The silver salts satisfy the Vegard law (Fig. 5). As shown by thermal analysis the Ag^+ cations are hydrated. The exchange of acidic protons present in the secondary heteropoly structure in the form of dihydronium ions $H_5O_2^+$ for hydrated silver cations is responsible for the contraction of the unit-cell parameters.

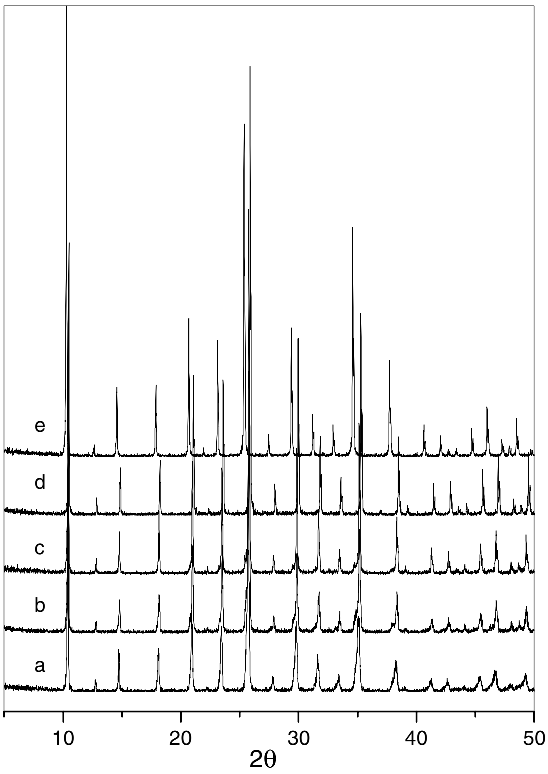

FIG. 4. Powder X-ray diffraction patterns of (a) Ag_1, (b) $Ag_{1.5}$, (c) Ag_2, (d) Ag_3, and (e) HPW.

Thermal analysis shows the presence of three types of water. The first two types are characteristic of the heteropoly structure. While the first effect observed, at about 373 K, related to the removal of crystallization water, is independent of the number of silver cations present, the second effect (361–477 K) originates from the loss of water hydrating protons and decreases with the increase in silver content in heteropoly salts. This type of water disappears completely when Ag_3 salt is formed. However, next to the water mentioned above and normally present in a heteropoly structure, another kind of water appears, which

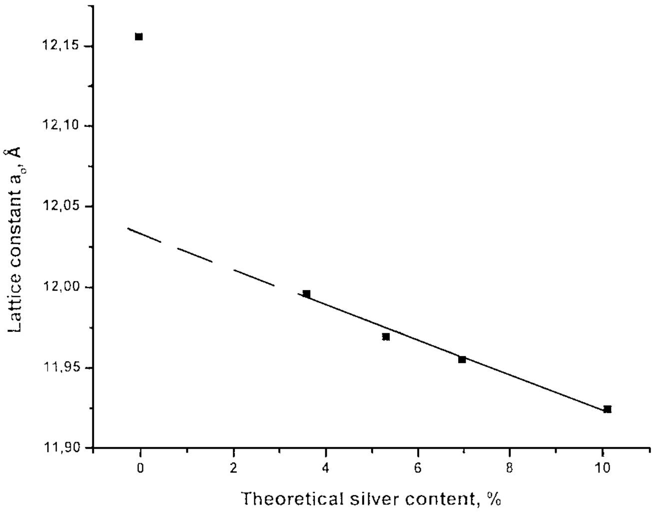

FIG. 5. Lattice constants as the function of the composition of the $Ag_xH_{3-x}PW_{12}O_{40}$ salts.

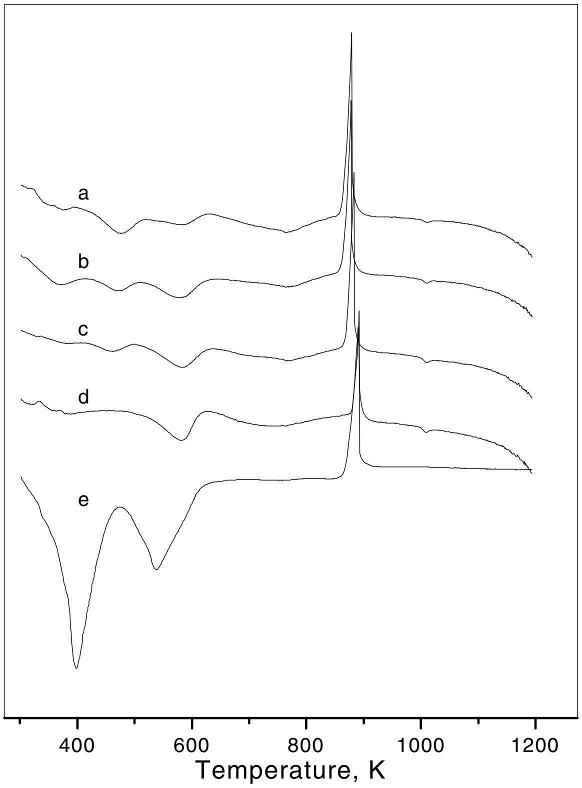

FIG. 6. DTA profiles of silver salts: (a) Ag_1, (b) $Ag_{1.5}$, (c) Ag_2, (d) Ag_3, and (e) HPW.

becomes removed between 623 and 633 K (Fig. 6). The existence of this effect can be explained by the presence of water which coordinates silver cations in the structure. It is observed that when the number of silver cations increases, the size of this effect grows.

Silver tungstophosphates are stable up to 890 K. The decomposition temperatures of the described samples are very similar, varing from 878 to 890 K. The larger the number of silver cations present in the structure, the more stable the heteropoly salt.

3.1.2. Heteropolyacid supported on SiO_2. In the studies of the structure of $H_4PMo_{11}VO_{40}$ deposited on silica (18) as a function of the coverage it has been shown by X-ray photoelectron spectroscopy and ion-scattering spectroscopy that the deposited phase forms blocks of the heteropolyacid, which cover maximally 20% of the SiO_2 surface. It could be expected that the tungstophosphoric acid will similarly form crystallites of heteropolyacid, sticking to the surface of silica, and that only the first layer at the interphase with silica will be modified by the interaction with the support. Being soluble in water the acid crystallites should be washed away by water treatment, leaving at the surface of the silica monomolecular islands. Thus, the amount of HPW taken for preparation of the catalyst was calculated under the assumption that 30% of silica should be covered with the active phase, and the excess present as crystalline phase was removed by washing with water, leaving islands of monomolecular layers of Keggin anions strongly bound to the surface of the support.

After washing away with water the loosely bound amount of heteropolyacid supported on silica, the solid was separated from the solution and dried again in the oven at 363 K. The amount of heteropolyacid dissolved in the solution was analyzed by means of UV–vis spectroscopy. The quantitative determination of the amount of tungstophosphoric acid in the solution is based on the fact that the Keggin anions have a charge transfer band at ca. 260 nm (19). The calibration curve of tungstophosphoric acid was prepared based on standards provided by our laboratory for absorbance values varying from 0.0 to 2.5. In this region the calibration curve is almost linear (Fig. 7). The monolayer coverage of heteropolyacid on silica after washing was calculated as the difference between the initial amount of HPW and the amount of HPW in the solution. To establish the efficiency of HPW removal by water from the surface of the support the following experiment was performed. Two grams of silica were dried for 5 h in the oven at 393 K. Then 0.74 g of $H_3PW_{12}O_{40}$ was dissolved in 3 ml of water and the hot SiO_2 was jetted into the solution. The slurry was stirred for about 0.5 h and was dried at 363 K for 5 h. The sample was treated with water under stirring four times, every time for 15 min, using each time a portion of 10 ml of distilled water. The obtained solutions were analyzed by UV–vis spectroscopy. The results are summarized in Table 1. The main amount of acid was removed from the surface during the first minutes of washing. The next portion of water removed 10 times smaller amounts of HPW. After 45 min only traces of acid were found in the solution. This experiment sets the time needed for washing the heteropolyacid out of the catalyst at 1 h.

The surface coverage of the samples after water treatment decreased to 18.0%, which is in very good agreement

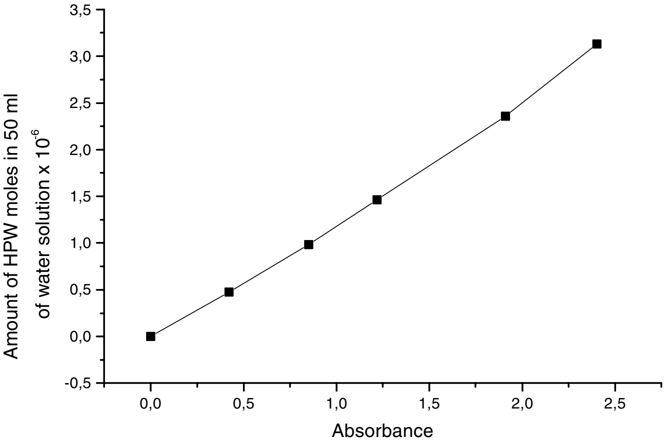

FIG. 7. Calibration curve of HPW solutions prepared by UV–vis spectroscopy.

TABLE 1

Efficiency of the Removal of Tungstophosphoric Acid from the Surface of Silica by Washing with Water

Time of water treatment (min)	Amount of HPW removed from SiO_2 (g)
15	0.2342
30	0.0235
45	0.0034
60	0

with the above-described observation (18) that the blocks of the vanadomolybdophosphoric acid cover maximally 20% of SiO_2.

This model is consistent with the results of other experiments described in the literature. Supporting HPW on silica was found to result in a shift and a line-broadening in the P^{31} NMR spectrum, indicating the distortion of the HPW structure in comparison with the bulk (20). The two detected peaks, one at −15.1 nm and the other at −14.5 nm, were assigned to the bulk crystalline phase and to the "interacting form," respectively (21). The interacting species could be formed by proton transfer according to the equation

$$H_3PW_{12}O_{40} + Si{-}OH \rightarrow (Si{-}OH_2)^+(H_2PW_{12}O_{40})^-. \quad [3]$$

The formation of a new type of proton site on the silica surface results in a decrease in HPW acid strength. According to Kozhevnikov *et al.* (22) interaction with the surface occurs very readily for samples with loadings lower than 30 wt%. In our case the layer strongly interacting with the surface corresponds to the coverage of 18.0%, equivalent to a loading of 14.4 wt%.

The BET measurements confirm the existence of the monolayer after the water treatment (Table 2). The BET surface of SiO_2 (306 m^2/g) after impregnation with heteropolyacid decreases by about 100 m^2/g to a value of 211 m^2/g for the loading amounting to 30% monolayer coverage in the sample HPW/SiO_2. This is due to blocking of the pores of silica support by the crystallites of HPW. After water treatment the surface area grows, approaching the value (278 m^2/g) which is close to the area of the silica support. The removal of heteropolyacid excess from that sample causes the increase in pore volume to the value which is close to pure SiO_2 (see Table 2).

TABLE 2

Changes in Silica Porosity Due to Heteropolyacid Deposition

Sample	BET surface area (m^2/g)	Total pore volumne (cm^3/g)
SiO_2	306.03	0.89
30% HPW/SiO_2	211.81	0.56
18% HPW/SiO_2	287.02	0.8

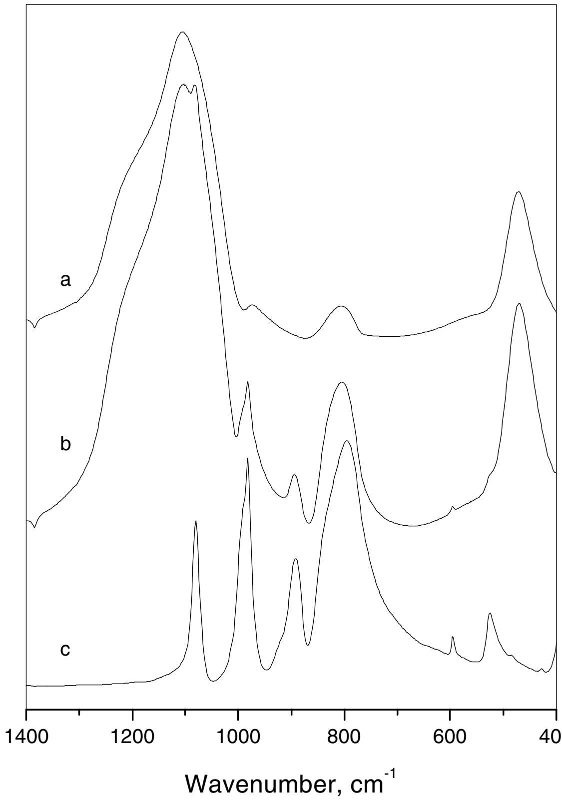

FIG. 8. FT-IR spectra of (a) 18% HPW/SiO_2, (b) 30% HPW/SiO_2, and (c) HPW.

The FT-IR spectra of heteropolyacid supported on silica are presented in Fig. 8. The tungstophosphoric acid shows five characteristic bands in the region 1100–400 cm^{-1}, observed at 1080, 982, 893, 812, and 595 cm^{-1}, which can be assigned to the stretching vibrations of P–O, W=O, and W–O–W and the bending vibration of P–O, respectively (23). Supporting heteropolyacid on silica results in lowering the intensities of characteristic IR vibrations, while their positions do not change. The spectrum of 30% HPW/SiO_2 contains all the characteristic bands. The removal of bulk heteropolyacid from the silica surface by water treatment results in a further reduction of the band intensity and in the disappearance of W–O–W vibration at 893 cm^{-1}. The vanishing of this band may be due to the hydrolysis of the W–O–W bonds linking the triads of octaedra, as postulated for the case of the HPMo/SiO_2 system, in which the Mo–O–Mo bonds undergo hydrolysis (24). It may be taken as an indication that Keggin anions are present at the silica surface in molecular dispersion. P–O vibration, normally observed at 1080 cm^{-1}, disappears, most probably screened by a very strong absorption band of SiO_2 present exactly in this region.

3.2. Catalytic Activity in Dehydration of Ethanol

3.2.1. Potassium salts supported on SiO_2. The catalytic tests were performed for the K_x/SiO_2 and K_x/SiO_2^w samples, where $x = 1, 2, 3$. For comparison, the catalytic activities of the HPW/SiO_2 and HPW/SiO_2^w catalysts were also measured. In the case of the Me_x/SiO_2 samples the heteropolyacid crystal phase is present on the surface. Because of the high absorptivity of heteropolyacid crystals toward ethanol the reaction takes place in the bulk (25, 26). In the case of the Me_x/SiO_2^w catalysts, the reaction is carried out on the surface of the monolayer.

In order to distinguish the catalytic activity of the Keggin anions in monolayer dispersion from that of the bulk of the heteropolyacid supported on silica two samples with the same heteropolyacid concentration of 18% HPW/SiO_2 were prepared and tested in the dehydration of ethanol. The first one was obtained by water treatment of the parent sample, 30% HPW/SiO_2, after which only Keggin anions in monolayer dispersion were left at the surface, and the other was prepared by depositing the amount of heteropolyacid corresponding to 18% of the monolayer (Fig. 9). Although the concentrations of HPW were in both cases the same, their catalytic activities were different. The catalyst covered with the bulk heteropolyacid is far more active than the one with monolayer dispersion. When the bulk heteropolyacid is present on the silica surface the reaction may proceed according to the pseudoliquid-type catalysis. In the bulk HPW all protons are easily available for the reagents except those directly bound to the surface. When the monolayer of HPW is formed on the silica surface, some protons linking the Keggin anions become engaged in protonation of the surface Si–OH groups and fewer protons are available for the catalytic reaction.

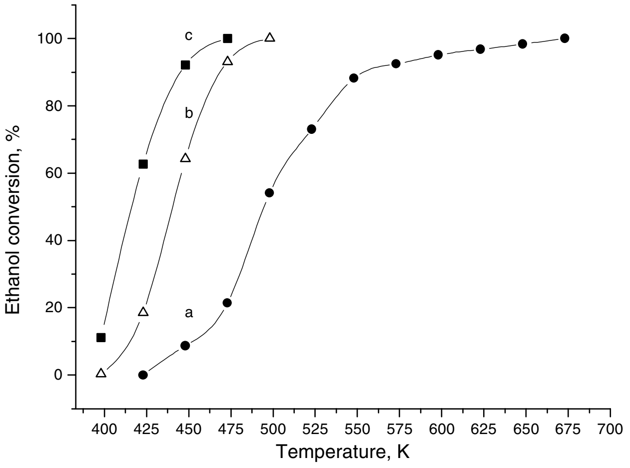

FIG. 9. Difference in catalytic activity between the bulk heteropolyacid supported on silica: (a) the monolayer catalyst 18% HPW/SiO_2^w, (b) 18% HPW/SiO_2, and (c) 30% HPW/SiO_2.

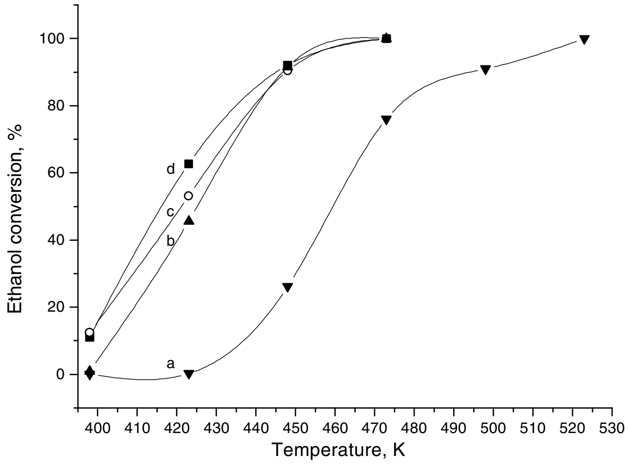

FIG. 10. Activity of the series of K_x/SiO_2 catalysts, (a) K_3/SiO_2, (b) $K_{2.5}/SiO_2$ and K_2/SiO_2, (c) K_1/SiO_2, and (d) HPW/SiO_2, in the dehydration of ethanol.

Figure 10 compares catalytic activities of HPW/SiO_2, K_1/SiO_2, K_2/SiO_2, and K_3/SiO_2 catalysts. No difference in overall conversion was observed in the case of the HPW/SiO_2, K_1/SiO_2, and K_2/SiO_2 samples. Apparently, at the surface composed of deposited blocks of HPW and K_2 salt the properties are determined by the acidity of HPW. Surprisingly, the K_3/SiO_2 catalyst is also active in this reaction, although its activity is markedly lower. Since the K_3 salt is neutral and has no acidic protons, its catalytic activity must have a different origin. Two explanations may be offered: the acidic properties of this salt may come from the Lewis acidity (26), or the K_3 salt may also contain the residual protons in the solid lattice (27). The pure, unsupported K_3 salt was also active in this reaction. On the other hand, the K_3 salt supported on silica was easily separated mechanically from the surface simply in the course of washing the sample with water, so that the catalyst was composed of a heterogeneous mixture of two solids. After their separation, the catalytic activity of the catalyst dropped down to the activity of pure silica (Fig. 11). This fact indicates that the K_3 salt formed by reacting the bulk heteropolyacid deposited at the surface of silica is only weakly bound to this surface.

Generally, the catalytic activities of the K_x/SiO_2^w samples in dehydration of ethanol are considerably lower than those of salts of the K_x/SiO_2 series. In case of the salts of the K_x/SiO_2^w series, the highest catalytic activity is observed for the samples with the lowest potassium contents (Fig. 12). The activity of K_2/SiO_2^w and K_3/SiO_2^w catalysts is close to the activity of silica.

In the course of the preparation of the K_1/SiO_2 sample, only 50% of the total amount of heteropolyacid reacts, forming $K_2H_1PW_{12}O_{40}$ salt. The second half of heteropolyacid does not participate in the reaction, proceeding according to Eq. [1]. Thus, in the case of the K_1/SiO_2^w catalyst

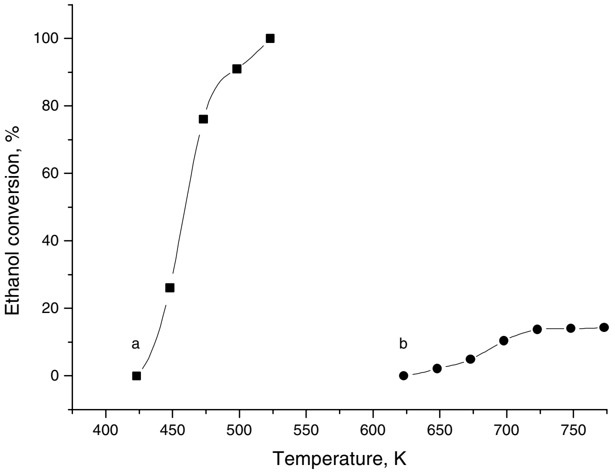

FIG. 11. Activity of the catalysts: (a) 30% K_3/SiO_2 and (b) SiO_2 after separation of K_3.

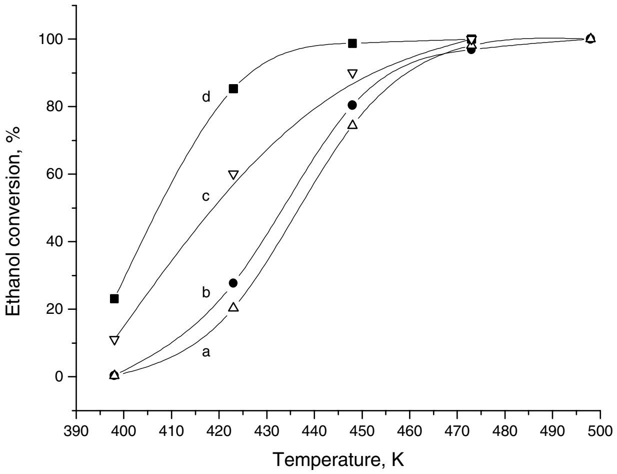

FIG. 13. Catalytic activity of the series of Ag_x/SiO_2 catalysts: (a) Ag_3/SiO_2, (b) Ag_1/SiO_2, (c) HPW/SiO_2, and (d) Ag_2/SiO_2.

the concentration of unreacted HPW amounts to 9% of the monolayer, compared with the initial concentration of HPW/SiO_2^w, which was equal to 18%. Taking into account this concentration of unreacted heteropolyacid a catalyst having 8.3% surface coverage of heteropolyacid was prepared. Its catalytic activity appeared to be very similar to the activity of the K_1/SiO_2^w catalyst (equimolar mixture of $K_2H_1PW_{12}O_{40}$ and $H_3PW_{12}O_{40}$). This proves that catalytic activity of K_1/SiO_2^w is due to the presence of unreacted HPW. The K_2/SiO_2^w catalyst is inactive in this reaction because no unreacted heteropolyacid is present in the sample. The salt, while being supported on SiO_2, transfers one proton to the silica surface (21) and, as a consequence, it has no strong Brønsted acid sites which could be responsible for that reaction.

3.2.2. Silver salts supported on SiO_2. The catalytic tests were performed for silver salts supported on silica Ag_x/SiO_2 and Ag_x/SiO_2^w, where $x = 1, 2, 3$. For comparison, the catalytic activities of the HPW/SiO_2 and HPW/SiO_2^w catalysts were also measured.

In the series of silver salts of tungstophosphoric acid Ag_x/SiO_2 the catalytic activities of Ag_1 and Ag_3 are similar. The activity of the Ag_2 salt is much higher, even higher than the activity of pure heteropolyacid (Fig. 13). A similar phenomenon observed for $Cs_{2.5}$ salts is primarily considered a result of its high surface area (28).

The plot of overall conversion against the reaction temperature for the series of Ag_x/SiO_2^w catalysts and HPW/SiO_2^w is shown at Fig. 14. In this case, the catalytic reaction proceeds on the surface of the catalysts populated with both Brønsted acid sites and the redox centers. The products of ethanol dehydration proceeding on the first type of site are ethylene and diethyl ether, while the product of dehydrogenation on redox sites is acetaldehyde (Fig. 15).

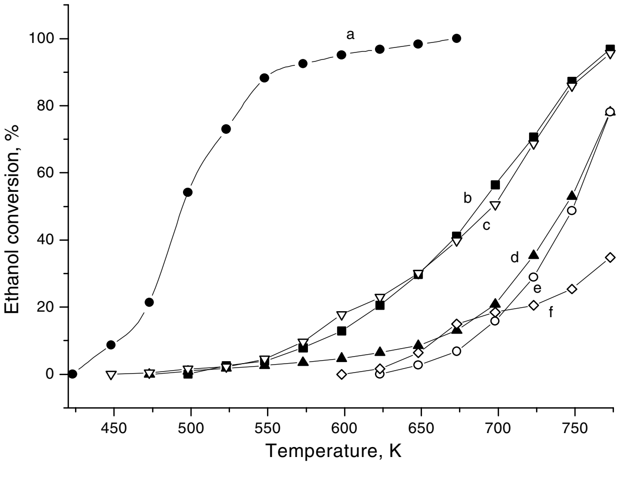

FIG. 12. Catalytic activity of the catalysts: (a) 18% HPW/SiO_2^w, (b) K_1/SiO_2^w, (c) 8.3% HPW/SiO_2^w, (d) K_2/SiO_2^w, (e) K_3/SiO_2^w, and (f) SiO_2.

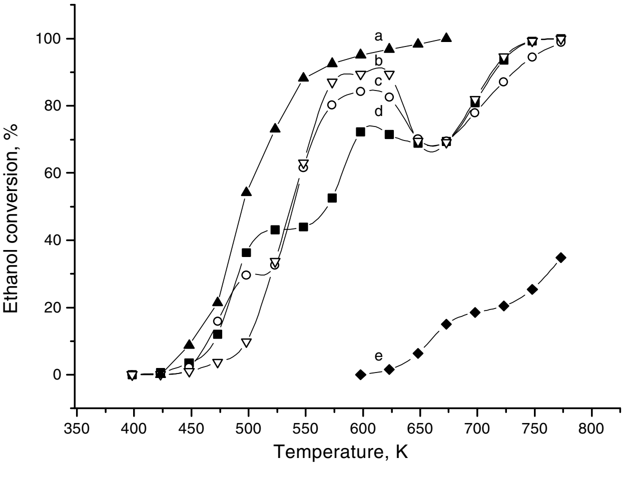

FIG. 14. Catalytic activity of (a) 18% HPW/SiO_2^w, and the silver salts (b) Ag_3/SiO_2^w, (c) Ag_2/SiO_2^w, (d) Ag_1/SiO_2^w, and (e) SiO_2.

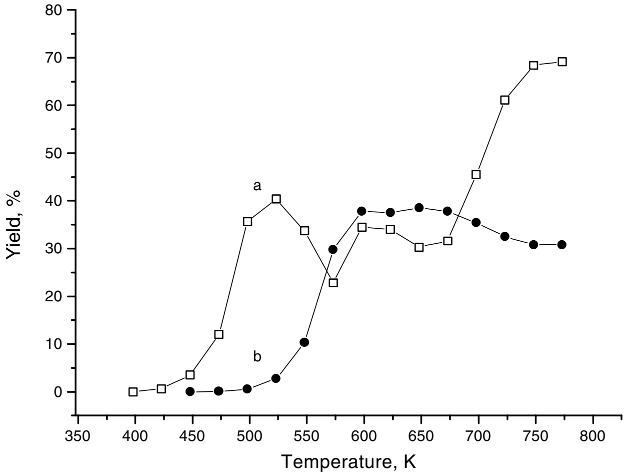

FIG. 15. Changes in catalytic activity of the Ag_1/SiO_2^w catalyst (a) in dehydration and in (b) oxidative dehydrogenation.

The conversion along the dehydration pathway is clearly connected with the presence of protons of the HPW and protons generated from water coordinated to the silver cations. On heating, the water hydrating protons is removed from the $Ag_xH_{3-x}PW_{12}O_{40}$ salts at about 523 K and the water coordinated to the silver cations vanishes above 623 K (see Fig. 6). As more and more silver cations become incorporated, the number of water hydrating protons decreases while the amount of water coordinated to silver cations increases. Niiyama *et al.* (29) suggested that water coordinated to the metal cation generates additional protons according to the following reaction:

$$\begin{aligned} M^{n+} + mH_2O &\rightarrow [M(H_2O)_m]^{n+} \\ &\rightarrow [M(H_2O)_{m-1}(OH)]^{(n-1)} + H^+. \end{aligned} \quad [4]$$

The protons of the heteropolyacid and the protons generated by dissociation of water coordinated to the silver atoms influence the yield of ethylene, and the more water present in the Ag_x/SiO_2^w samples, the more ethylene formed.

The second mechanism of proton generation consists of the reduction of the metal cation (6, 30):

$$Ag^+ + \frac{1}{2}H_2 \rightarrow Ag^0 + H^+. \quad [5]$$

XPS analysis of our Ag_3/SiO_2 samples before and after the catalytic reaction did not reveal any reduction in silver cations, which seems to exclude the redox mechanism of the generation of protons.

In the temperature range up to 523 K the influence of acid protons on the conversion of ethanol is visible (Fig. 14). The largest effect is observed for the Ag_1/SiO_2^w catalyst and a smaller one for Ag_2/SiO_2^w for the Ag_3/SiO_2^w sample, which has no acid protons, this effect does not occur. On further increase of the reaction temperature above 523 K the catalytic activity of the catalysts changes. The Ag_3/SiO_2^w sample becomes the most active catalyst in the dehydration reaction. The Ag_3/SiO_2^w catalyst with the largest amount of coordinated water shows the highest conversion of ethanol. This influence is lower for the Ag_2/SiO_2^w catalyst and, finally, for the Ag_1/SiO_2^w sample it is smallest. Apparently, conversion of ethanol is strictly connected with the amount of water coordinated to the silver cations. The catalytic activity is constantly growing up to 623 K and at that temperature the sudden breakdown is observed. The cause of such behavior is the loss of water coordinating the silver cations. This effect is most significant for the Ag_3 salt. At about 648 K all three salts exhibit almost the same catalytic activity and from that moment on their activities again slowly grow.

Figure 15 shows the yield of ethylene and acetaldehyde observed in the reaction of ethyl alcohol on the Ag_1/SiO_2^w catalyst. At temperatures lower than 523 K dehydration of ethanol to ethylene is the main reaction, the yield increasing strongly with temperature. In the temperature range 523–573 K, when dehydration of acid protons takes place, selectivity changes dramatically and oxidative dehydrogenation of ethanol to acetaldehyde becomes the most important reaction. The yield attains at 623 K the value of about 40% and remains at this level on further increase in the reaction temperature. Above 673 K an increase in the yield to ethylene is simultaneously observed. As the removal of water coordinating silver cations is observed at 623 K some other mechanism must be responsible for the dehydration of ethanol.

3.3. Catalytic Activity in Hydration of Ethylene

Catalytic activities were measured for the samples of potassium K_x/SiO_2 and silver Ag_x/SiO_2 salts supported on silica, where $x = 0.5, 1, 1.5, 2, 3$, and were compared with the activity of the parent heteropolyacid, HPW/SiO_2, in the reaction of ethylene hydration.

3.3.1. Potassium salts supported on SiO_2. As shown in Table 3 the catalytic activity of the K_x/SiO_2 catalysts decreases stepwise when x changes from 0 to 2. The K_2/SiO_2 and K_3/SiO_2 catalysts were not active in that reaction.

As discussed above, the X-ray diffraction pattern and the thermal analysis of potassium tungstophosphates clearly show that K_x salts, where $0 < x < 2$, are mixtures of unreacted heteropolyacids and $K_2H_1PW_{12}O_{40}$ salts. The K_2 and K_3 salts were found to be single-phase materials. Obviously, when the number of potassium cations in the heteropolyacid supported on silica is increased, going from the $K_{0.5}$ to the K_2 salt, the acidity of the catalyst originating from the heteropolyacid decreases, resulting in lower catalytic activity. The reaction proceeds through the formation of carbenium ion as the intermediate, which probably interacts with the catalyst surface, in analogy to the mechanism of

TABLE 3

Catalytic Activity of K_x and Ag_x Salts of Tungstophosphoric Acid Supported on SiO_2 in Ethylene Hydration

Catalyst supported on SiO_2	Ethylene conversion (%)
SiO_2	0
$H_3PW_{12}O_{40}$	5.61
$H_3PW_{12}O_{40}$—washed	Traces
$K_{0.5}H_{2.5}PW_{12}O_{40}$	4.32
$K_1H_2PW_{12}O_{40}$	2.53
$K_{1.5}H_{1.5}PW_{12}O_{40}$	0.57
$K_2HPW_{12}O_{40}$	0
$K_3PW_{12}O_{40}$	0
$Ag_{0.5}H_{2.5}PW_{12}O_{40}$	2.76
$Ag_1H_2PW_{12}O_{40}$	3.94
$Ag_{1.5}H_{1.5}PW_{12}O_{40}$	4.95
$Ag_2HPW_{12}O_{40}$	5.74
$Ag_3PW_{12}O_{40}$	6.42

isobutylene hydration, as proposed by Izumi and coworkers (31). The mechanism involves the formation of a complex of heteropolyanion with the carbenium anion, which is assumed to be responsible for promoting the reaction by stabilizing the intermediate carbenium ion.

3.3.2. Silver salts supported on SiO_2. Quite an opposite situation is observed for the Ag_x/SiO_2 catalysts. The XRD pattern revealed the formation of monophase acidic silver salts. Similarly to the case of dehydration of ethanol the growing number of silver cations in the discussed samples is accompanied by an increase in their catalytic activity despite a decrease in acid proton content. These facts confirm the suggestion that silver cations must be responsible for the generation of additional protons, which are formed by dissociation of water molecules coordinated to these cations.

In our case, the water is present in the reaction mixture as a reactant for the hydration of ethylene. Therefore, it is probable that in our reaction system the high activity of silver salts is due to the generation of acid sites according to Eq. [4]. The strength of acidic sites in silver salts was examined in the decomposition of isopropanol, the model reaction (32) for the characterization of acid and redox centers in catalysts. It was observed that with an increase in silver content the amount of acetone formed in the reaction decreases while the amount of propene formed grows.

ACKNOWLEDGMENTS

The authors thank Miss Z. Czula for performing BET measurements. The financial support of the Polish Committee for Scientific Research within Grant 3 T09A 107 16 is also gratefully acknowledged.

REFERENCES

1. Izumi, Y., *Catal. Today* **33**, 371 (1997).
2. Ono, Y., Mori, T., and Keii, T., *in* "Proceedings, 7th International Congress on Catalysis, Tokyo 1980" (T. Seiyama and K. Tanabe, Eds.), p. 755. Elsevier, Amsterdam, 1981.
3. Kim, J. S., Kim, J. M., Seo, G., Park, N. C., and Niiyama, H., *Appl. Catal.* **37**, 45 (1988).
4. Misono, M., Sakata, K., Yoneda, Y., and Lee, Y., *in* "Proceedings, 7th International Congress on Catalysis, Tokyo 1980" (T. Seiyama and K. Tanabe, Eds.), p. 1047. Elsevier, Amsterdam, 1981.
5. Furuta, M., Sakata, K., Misono, M., and Yoneda, Y., *Chem. Lett.* **31**, (1979).
6. Baba, T., Watanabe, H., and Ono, Y., *J. Phys. Chem.* **87**, 2406 (1983).
7. Ono, Y., Baba, T. , Sakai, J., and Keii, T., *J. Chem. Soc., Chem. Commun.* 400 (1982).
8. Ai, M., *J. Catal.* **71**, 88 (1981).
9. Suzuki, S., Kogai, S., and Ono, Y., *Chem. Lett.* 699 (1984).
10. Niiyama, H., Saito, Y., Yoshida, S., and Echigoya, E., *Nippon Kagaku Kaishi* 569 (1982).
11. Black, J. B., Clayden, N. J., Gai, P. L., Scott, J. D., Serwicka, E. M., and Goodenough, J. B., *J. Catal.* **106**, 1 (1987).
12. Brückman, K., Haber, J., and Serwicka, E., *Faraday Discuss. Chem. Soc.* **87** (10), 1 (1989).
13. Mizuno, N., and Misono, M., *Chem. Rev.* **98**, 199 (1998).
14. Misono, M., *Chem. Commun.* 1141 (2001).
15. Essayem, N., Coudurier, G., Fournier, M., and Vedrine, J. C., *Catal. Lett.* **34**, 223 (1995).
16. Kozhevnikov, I. V., Sinnema, A., Jansen, R. J. J., and van Bekkum, H., *Catal. Lett.* **27**, 187 (1994).
17. Brown, G. M., Noe-Spirlet, M.-R., Bushing, W. R., and Levy, H. A., *Acta Cystallogr. Sect. B* **33**, 1038 (1977).
18. Prevost, M., Barbaux, Y., Gengembre, L., and Grzybowska, B., *J. Chem. Soc., Faraday Trans.* **92**, 5103 (1996).
19. Weakley, T. J. R., and Malik, S. A., *J. Inorg. Nucl. Chem.* **29**, 2935 (1967).
20. Mastikhin, V. M., Kulikov, S. M., Nosov, A. V., Kozhevnikov, I. V., Mudrakovsky, I. L., and Timofeeva, M. N., *J. Mol. Catal.* **60**, 65 (1990).
21. Lefebvre, F., *J. Chem. Soc., Chem. Commun.* 756 (1992).
22. Kozhevnikov, I. V., Kloestra, K. R., Sinnema, A., Zandbergen, H. W., and van Bekkum, H., *J. Mol. Catal. A* **114**, 287 (1996).
23. Okuhara, T., Mizuno, N., and Misono, M., *in* "Catalytic Chemistry of Heteropoly Compounds in Advances in Catalysis" (D. D. Eley, W. O. Haag, and B. Gates, Eds.), Vol. 41, p. 113. Academic Press, San Diego, 1996.
24. Brückman, K., Che, M., Haber, J., and Tatibouet, J. M., *Catal. Lett.* **25**, 225 (1994).
25. Bielański, A., Poźniczek, J., and Malecka, A., *React. Kinet. Catal. Lett.* **41**, 127 (1990).
26. Misono, M., *Catal. Rev.–Sci. Eng.* **29**, 269 (1987).
27. Highfield, G., and Moffat, J. B., *J. Catal.* **88**, 177 (1984).
28. Misono, M., *in* "New Frontiers of Catalysis—Proceedings, 10th International Congress on Catalysis, Budapest 1992" (L. Gueri, F. Solymosi, P. Tetenyi, Eds.), p. 69. Elsevier, Amsterdam, 1993.
29. Niiyama, H., Saito, Y., and Echigoya, E., *in* "Proceedings, 7th Inter national Congress on Catalysis, Tokyo 1980," (T. Seiyama and K. Tanabe, Eds.), p. 1416. Elsevier, Amsterdam, 1981.
30. Baba, T., Sakai, J., and Ono, Y., *Bull. Chem. Soc. Jpn.* **55**, 2633 (1982).
31. Urabe, K., Fukita, K., and Izumi, Y., *Shokubai (Catalyst)* **22**, 223 (1983).
32. Grzybowska-Świerkosz, B., Coudurier, G., Vedrine, J. C., and Gressel, I., *Catal. Today* **20**, 165 (1994).