

Conjugated Polymer-Supported Catalysts—Polyaniline Protonated with 12-Tungstophosphoric Acid

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New types of conjugated polymer supported catalysts were prepared from polyaniline and 12-tungstophosphoric acid. Two preparation methods were used: (i) chemical polymerization of aniline in the presence of $H_3PW_{12}O_{40}$ and (ii) protonation of polyemeraldine base with $H_3PW_{12}O_{40}$. UV-VIS, FTIR, and X-ray studies unequivocally prove the protonation of polyaniline with simultaneous incorporation of heteropolyacid (HPA) in the polymer. Molecular dispersion of HPA in polyaniline matrix via a protonation reaction results in effective blocking of acid-base centers since protonation results in the abstraction of the most acidic proton from the molecules of the acid. As a result, in the test reaction of isopropyl alcohol conversion the obtained catalyst exhibits very low acid-base activity and high selectivity (>90% in all cases) towards acetone. Redox activity depends on the preparation method and is higher for the samples prepared through protonation of polyemeraldine base because in this case heteropolyanions are bound only to the surface of the polymer. On the contrary, HPA introduced into the polymer matrix *in situ* during polymerization is evenly distributed on the surface and in the bulk, and the access of alcohol molecules to those HPA which are located in the bulk is more difficult. Redox activity of the catalyst with HPA distribution limited to the surface of the polymer is comparable to that observed in unsupported $H_3PW_{12}O_{40}$ for the highest obtainable protonation levels and decreases with the decrease of HPA surface concentration. On the other hand, activation energy derived from the Arrhenius plot for the dehydrogenation reaction drops with the decrease of the HPA surface concentration and is ca. 40 kJ/mole in these catalysts as compared to ca. 70 kJ/mole calculated for unsupported $H_3PW_{12}O_{40}$. © 1994 Academic Press, Inc.

INTRODUCTION

Conjugated polymers have been extensively studied since the discovery of polyacetylene doping in 1977 mainly due to their interesting electronic and optical properties (1, 2). In 1988 a new direction in conjugated polymers research evolved. They were used as convenient

catalytic supports on which catalytically active species could be deposited. The first application of conjugated polymers in electrocatalysis was reported by Bidan *et al.* (3–5), Keita *et al.* (6), Shimidzu *et al.* (7), and more recently by Wang and Dong (8). These authors introduced catalytically active heteropolyanions of Keggin type into polypyrrole, polythiophene, and polyaniline via electrochemical, oxidative polymerization of the corresponding monomers. In this case heteropolyanions are incorporated into the polymer matrix *in situ* during electropolymerization. The growing chains are of cationic nature and require the presence of anionic species to preserve the neutrality of the system. If heteropolyanions are the solely anionic component of the electrolytic medium they are inevitably inserted to the polymer.

Another approach has been used by Poźniczek *et al.* (9) who inserted heteropolyanions in polyacetylene. Polyacetylene is routinely prepared as a neutral polymer in the form of a solid film. Heteropolyanions can be inserted in polyacetylene only through the oxidative doping with heteropolyacids of the already-formed polymer. This is a typical solid state reaction and the doping is limited only to the surface of the polymer since the diffusivity of large size heteropolyanions in the solid matrix is very limited (10).

Structural and spectroscopic studies unequivocally show that the Keggin units inserted in conjugated polymers are bound with the matrix via quasi-ionic bonds and are molecularly dispersed. These phenomena have important consequences on the catalytic properties of the system. Due to strong chemical interactions Keggin units entrapped in conjugated polymers exhibit different catalytic selectivity than their parent heteropolyacids in, for example, alcohol conversion, whereas the molecular dispersion strongly enhances their catalytic activity (9).

Recently it has been demonstrated that heteropolyanions can be inserted in polyaniline in a simple protonation

reaction of already-formed solid polyemeraldine base (11). In this communication we extend these studies. In particular we report on physicochemical and catalytic characterization of two types of catalysts obtained via doping of polyaniline with 12-tungstophosphoric acid, namely the catalyst prepared by the protonation of solid polyemeraldine base with 12-tungstophosphoric acid and the catalyst prepared by the polymerization of aniline in the presence of this acid. In the former case the presence of heteropolyanions is limited to the surface of the polymer, while in the latter Keggin units are evenly distributed on the surface and in the bulk of the polymer. Catalytic conversion of isopropanol is used as the test reaction. This reaction has been selected mainly due to the fact that it clearly illustrates two types of catalytic activity: redox and acid–base (12).

EXPERIMENTAL

Two types of catalysts were prepared: (i) using a one-step procedure and (ii) using a two-step procedure. In the text that follows, the samples obtained in the one-step procedure will be abbreviated as S-I and those prepared via two-step procedure will be denoted as S-II.

One-Step Procedure (13)

Freshly distilled aniline, 3.9 ml (35.5 mM), and 12-tungstophosphoric acid, 37.8 g (13.1 mM), were dissolved in 250 ml of acetonitrile. The solution turned yellow almost immediately because of the formation of an aniline heteropolyacid (HPA) salt. Simultaneously 7.85 g (33.4 mM) of ammonium persulphate was dissolved in 9 ml of water and slowly added dropwise to the aniline–HPA–acetonitrile solution. The reaction was carried out at RT with constant stirring. After 24 h the reaction was terminated by precipitation of the obtained polymer in 1250 ml of methanol. In the next step the polymer was separated by centrifugation and washed with methanol until the filtrate was colourless. At this stage the polymer still contains significant amount of sulphur as shown by elemental analysis. This contamination is probably caused by co-insertion of HSO_4^- together with HPA during the polymerization. Sulphur contamination can be efficiently eliminated by extended washing with pure water which causes slow deprotonation of the centers with HSO_4^- anions while leaving HPA intact.

Elemental analysis gave %C = 39.28, %H = 3.28, %N = 7.45, %W = 40.92, %O, P (from the difference) = 9.07, which corresponds to the empirical formula $\text{C}_6\text{H}_{4.5}\text{N}(\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 21\text{H}_2\text{O})_{0.034}$.

In principle the content of HPA in polyaniline prepared by the one-step procedure can be varied by the change of the normalized aniline/oxidant ratio k which is defined

as (14)

$$k = \frac{2.5 \cdot n_{\text{an}}}{n_{\text{ox}} \cdot n_e},$$

where n_{an} = the number of moles of aniline, n_{ox} = the number of moles of the oxidant, and n_e = the number of electrons required for the reduction of one molecule of the oxidant (in the case of ammonium persulphate, $n_e = 2$). The coefficient 2.5 arises from the assumption that the withdrawal of 2.5 electrons per aniline molecule is required to obtain polyaniline in the polyemeraldine oxidation state.

Two-Step Procedure

In the two-step procedure polyemeraldine base is first prepared. In a typical preparation 10 ml (109.5 mM) freshly distilled aniline is dissolved in 125 ml of 1.5 M HCl. In the same amount of 1.5 M HCl, 12.5 g (54.8 mM) ammonium persulphate is dissolved. The solution of the oxidant is then slowly added to aniline solution previously precooled to 0°C. Since aniline polymerization is strongly exothermic the oxidant must be added over ca. 1 h. After the addition of the oxidant is terminated the reaction mixture is left with constant stirring for 4 h. Then polyaniline hydrochloride precipitate is separated by centrifugation and washed consecutively with water, methanol, and diethyl ether in order to remove oligomers and other side reaction products. The polymer is then vacuum dried until constant mass. Deprotonation of polyemeraldine hydrochloride is achieved in 3 wt% aqueous ammonia solution. Deprotonated polymer is again washed with water, methanol, and diethyl ether and dried until constant mass.

Protonation of polyemeraldine base is carried out in acetonitrile solution of 12-tungstophosphoric acid. Different protonation levels can be obtained by varying the HPA/polyemeraldine ratio. For a given ratio a partition equilibrium between the two phases (solid polymer and acetonitrile) is established. Thus the protonation level can be reproducibly varied by changing the above ratio. Three samples used in the catalytic tests gave the following empirical formulae based on the elemental analysis data (Table 1).

Specific surface area. The specific surface area of heteropolyanions containing polyaniline strongly depends on the protonation level, in general decreasing with increasing content of HPAs. The measurements were carried out by BET method on a SORPTY 1750 using nitrogen as the adsorbed gas at the temperature of liquid nitrogen and the equilibrium pressure of 135 Torr. The results are shown in Table 2.

X-ray diffraction studies. All catalyst samples were subjected to X-ray diffraction studies using a DRON

TABLE 1

Empirical Formulae of Prepared Catalysts (Based on C, H, N, W Analysis)

Sample	Empirical formula	HPA wt%
S-I	$C_6H_{4.5}N(H_3PW_{12}O_{40} \cdot 21H_2O)_{0.034}$	48.6
S-II-1	$C_6H_{4.5}N(H_3PW_{12}O_{40} \cdot 15H_2O)_{0.018}$	35.2
S-II-2	$C_6H_{4.5}N(H_3PW_{12}O_{40} \cdot 10H_2O)_{0.010}$	23.8
S-II-3	$C_6H_{4.5}N(H_3PW_{12}O_{40} \cdot 10H_2O)_{0.005}$	13.6

TUR-M62 diffractometer with $CuK\alpha$ radiation. The main goal of these studies was to exclude the existence of the separate phase of crystalline heteropolyacids.

Spectroscopic studies. UV-VIS studies were carried out on a CARY 2315 for all catalysts, whereas FTIR measurements were performed on a Digilab FTS 60V device using a standard transmission geometry and KBr pellets.

Conductivity studies. Conductivities of HPA protonated polyemeraldine samples were measured using a standard 4-probe method in van der Pauw geometry. Disk shape samples were prepared from powders using 120 MPa pressure. Temperature dependence of the conductivity was tested in the temperature range 105–312 K and additionally at higher temperatures to verify thermal stability of the protonated samples.

Catalytic tests. The studies of catalytic conversion of isopropanol were carried out in a wide temperature range using a differential reactor which enables the determination of the true specific reaction rate (15). Neutral, oxygen free atmosphere was applied and the reactant was diluted with nitrogen to the concentration of 1.45 mole%. About 2 g of catalysts were used in the test in the case of polyaniline supported catalysts and ca. 1 g for pure, crystalline 12-tungstophosphoric acid. Care was taken to remove oxygen, water, and carbon dioxide from the carrier gas. All catalysts were thermally stabilized prior to the test reaction by heating in nitrogen flow at 120°C for 2 h. The reaction products were analyzed using a gas chromatograph

equipped with a FID detector (16). Both unreacted alcohol and the reaction products were separated in an acid-resistant column 4 mm I.D. and 4 m long packed with 4.0% Carbowax 20M on Chromosorb G, AW, DMCS mesh 80/100. The reported results refer to the steady state.

RESULTS AND DISCUSSION

The main goal of this research was to prepare a new type of catalyst in which catalytically active Keggin units would be molecularly dispersed via doping of polyaniline. It is therefore necessary to prove that the inserted heteropolyanions interact chemically with the host matrix which in turn leads to their entrapment in the polymer matrix without the formation of a separate phase. This conclusion can be proved by three complementary experiments: X-ray diffraction, UV-VIS, and FTIR. X-ray diffraction patterns of polyaniline base and HPA containing polyaniline prepared in the one-step and two-step procedures are shown in Figs. 1a, 1b, and 1c, respectively. Polyemeraldine base is amorphous, giving two broad overlapping halos centered around $d = 4.4$ and 3.7 Å. Its protonation with simple inorganic acids such as, for example, HCl leads to better ordered structure with a set of relatively distinct Bragg reflections (17). In HPA doped polyemeraldine this is not the case. Independently of the preparation method (one-step or two-step) the diffractograms are very similar and give no indication of any crystalline phase. If one takes into account that in the samples studied the wt% content of HPA is close to 50, one can immediately conclude that no crystalline heteropolyacid can be present in the system.

The next question to be answered is whether HPAs are dispersed physically or whether they form a chemical bond with the host matrix via protonation. A strong indication of the protonation reaction can be derived from UV-VIS studies. HPA protonated polyemeraldine as well as polyemeraldine base is partly soluble in *N*-methylpyrrolidone, giving a deep blue solution, essentially indistinguishable from that characteristic of polyemeraldine base. This means that in solution polyaniline is not protonated by HPA. However, upon removal of the solvent the colour changes to green and for solid films becomes characteristic of the protonated state. This is manifested by total decrease of 637 nm band in the UV-VIS spectrum, the shift of the 330-nm band to 420 nm, and the creation of a band centered at 950 nm (18). It can be therefore postulated that in the solid catalyst the polymeric chain is protonated by HPA.

Further corroboration of the protonation of the polymer chain comes from FTIR studies. In Fig. 2a the spectrum of polyemeraldine base is presented, whereas in Fig. 2b the spectrum of the same material treated with HPA to

TABLE 2

Specific Surface Areas of Prepared Catalysts

Sample	Specific surface area (m ² /g)
Crystalline $H_3PW_{12}O_{40}$	5.8
S-I	15.6
S-II-1	25.0
S-II-2	48.3
S-II-3	61.2

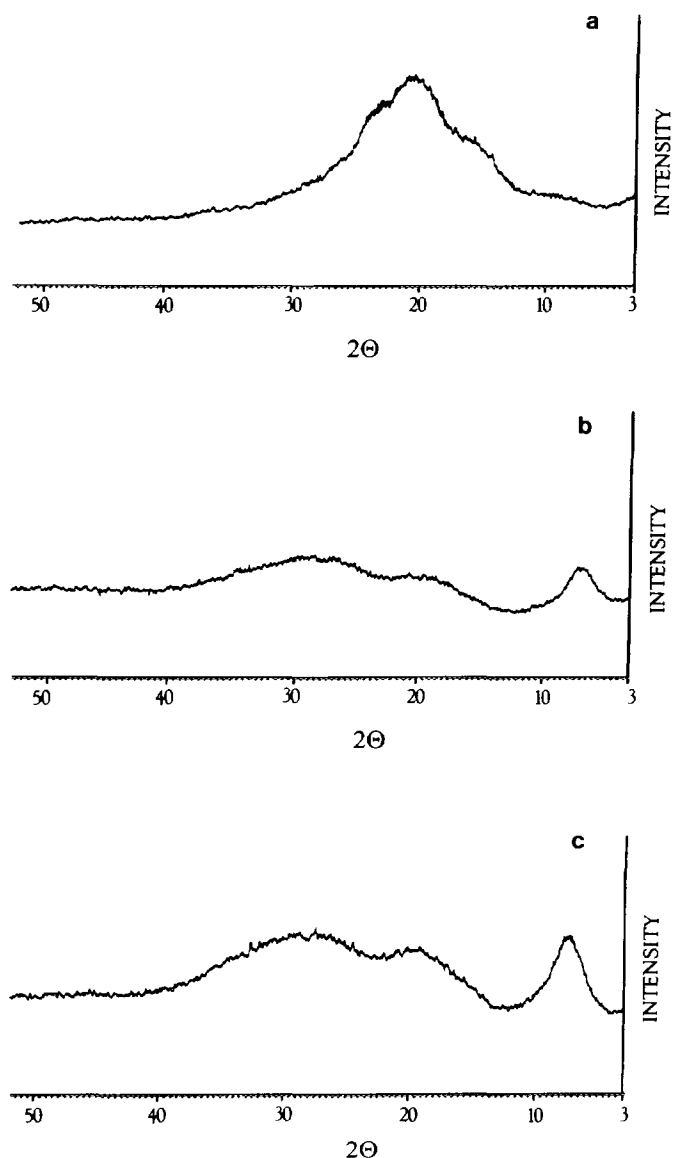


FIG. 1. X-ray diffraction spectra of (a) polymeraldine base, (b) $C_6H_{4.5}N(H_3PW_{12}O_{40} \cdot 21H_2O)_{0.034}$ prepared in the one-step procedure, and (c) $C_6H_{4.5}N(H_3PW_{12}O_{40} \cdot 21H_2O)_{0.033}$ prepared in the two-step procedure.

give $C_6H_{4.5}N(H_3PW_{12}O_{40} \cdot 21H_2O)_{0.033}$ is shown. For comparison the spectrum of crystalline $H_3PW_{12}O_{40}$ is added (Fig. 2c). Changes ascribed to protonation are clearly visible; in particular, the band at 1138 cm^{-1} characteristic of the protonated states appears in the latter spectrum. Accordingly the band at 1163 cm^{-1} , present in the first spectrum and characteristic of the base (nonprotonated form), disappears. Simultaneously the six strongest bands characteristic of Keggin structure of HPA appear in the spectrum ($527, 799, 893, 984,$ and 1080 cm^{-1}) (19). This means that during protonation heteropolyanions are introduced to the polymer matrix as charge-compensating spe-

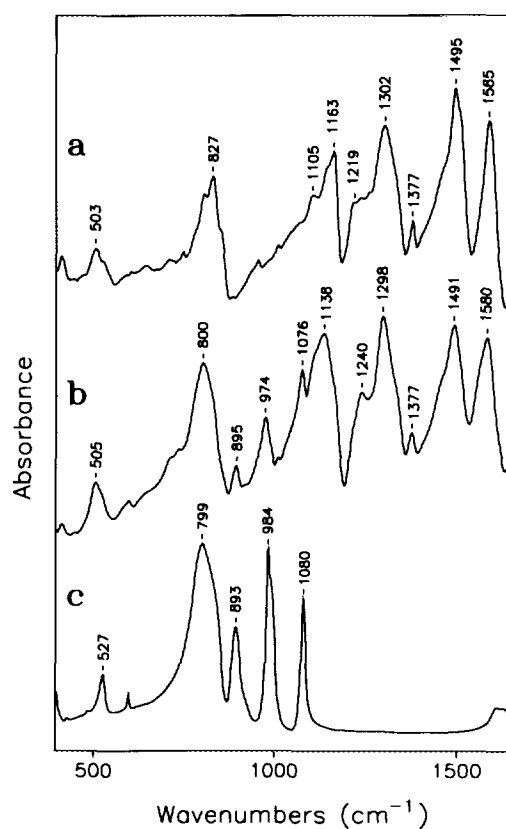


FIG. 2. IR spectra of (a) polymeraldine base, (b) $C_6H_{4.5}N(H_3PW_{12}O_{40} \cdot 21H_2O)_{0.033}$ prepared in the two-step procedure, and (c) crystalline $H_3PW_{12}O_{40}$.

cies and upon this insertion they preserve their structural identity.

Final proof of the protonation of the polymer by HPA comes from conductivity studies. It is well known that polymeraldine base is insulating with the conductivity of the order of 10^{-12} S/cm and its protonation gives rise to an increase of electronic conductivity by several orders of magnitude. HPA containing polymeraldine is conducting proving effective protonation of the polymer chains (see Table 3).

The temperature dependence of the conductivity measured in the temperature range $105\text{--}312\text{ K}$ is shown in

TABLE 3
Conductivity of HPA-Doped Polyaniline
Prepared in the Two-Step Procedure

Empirical formula	Conductivity $\times 10^3\text{ (S/cm)}$
$C_6H_{4.5}N(H_3PW_{12}O_{40} \cdot 17H_2O)_{0.033}$	1.45
$C_6H_{4.5}N(H_3PW_{12}O_{40} \cdot 21H_2O)_{0.018}$	1.37
$C_6H_{4.5}N(H_3PW_{12}O_{40} \cdot 11H_2O)_{0.005}$	0.0053

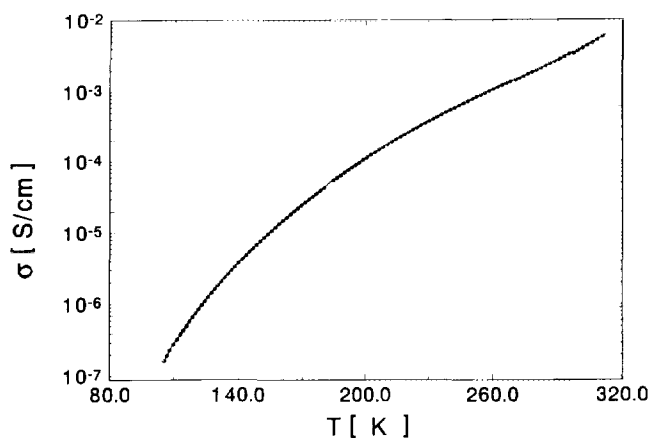


FIG. 3. Temperature dependence of conductivity for $C_6H_{4.5}N(H_3PW_{12}O_{40} \cdot 17H_2O)_{0.033}$.

Figs. 3 and 4. The results can be fitted with a variable range-hopping model which is characteristic of the majority of conducting polymers.

It should be stressed here that HPA-doped polyemeraldine shows improved thermal stability as compared to polyemeraldine protonated with a simple inorganic acid, e.g., HCl (20). Conductivity decrease upon heating is the most sensitive test for the degradation since irreversible conductivity changes appear well before any spectroscopic indication of the degradation. In Fig. 5 thermal degradation of the polymer as probed by conductivity drop is presented. The sample exhibits very high stability as compared to polyaniline protonated with other protonating agents. This is of course of extreme importance in view of catalytic applications.

Catalytic conversion of isopropanol may lead to two reaction products:

(i) propene, which is the product of dehydration and is formed on acid-base centers;

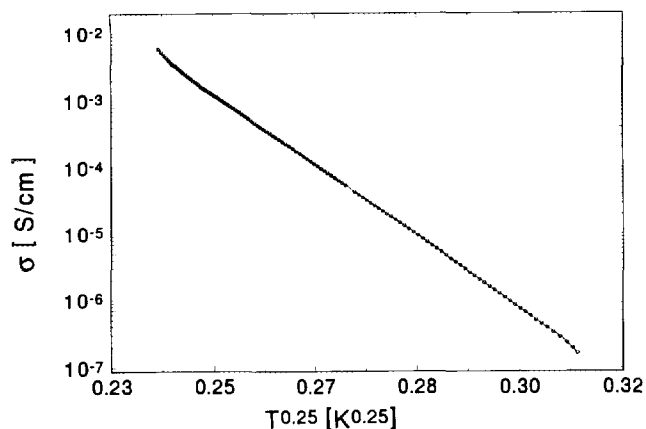


FIG. 4. Fitting of the conductivity data to Mott's equation for $C_6H_{4.5}N(H_3PW_{12}O_{40} \cdot 17H_2O)_{0.033}$.

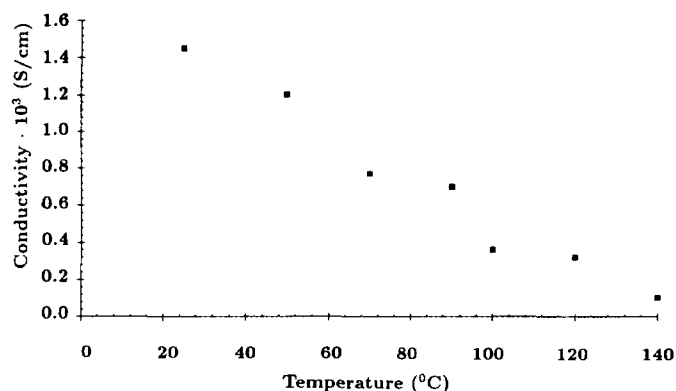


FIG. 5. The effect of thermal treatment on the conductivity of $C_6H_{4.5}N(H_3PW_{12}O_{40} \cdot 17H_2O)_{0.033}$ (samples heated for $t = 24$ h in air).

(ii) acetone, which is the product of dehydrogenation formed on redox-type centers.

In general crystalline heteropolyacids containing tungsten exhibit predominantly acid-base activity, whereas those with molybdenum show both acid-base and redox-type activity. In Table 4 the selectivities of polyaniline supported catalysts and unsupported crystalline 12-tungstophosphoric acid studied in the same experimental conditions are shown. It should be stressed that polyaniline in its base form, i.e., without heteropolyanions is catalytically inactive in the temperature range studied.

As expected the polyaniline protonation reaction involving HPA as the protonating agent drastically changes the selectivity of the catalyst. Polyaniline supported catalysts show extremely high selectivity towards acetone formation, which in all cases studied exceed 90%. This result can be easily rationalized taking into account that HPA acting as a Brønsted acid in the polyaniline protonation process loses its most acidic proton which is then bound to the polymer host matrix. With an increase of temperature the content of propene in the reaction products increases indicating a small enhancement in the acid-base activity. It is known that acid dissociation con-

TABLE 4
Selectivity of the Catalytic Isopropanol Decomposition Reaction

Catalyst unsupported	Selectivity %			
	382 K		406 K	
	Propene	Acetone	Propene	Acetone
$H_3PW_{12}O_{40}$ unsupported	96.4	3.6	—	—
S-I	3.1	96.9	17.2	82.8
S-II-1	1.0	99.0	5.6	96.4
S-II-2	6.3	93.7	10.1	89.9
S-II-3	—	—	6.9	93.1

starts increase with temperature, and thus heteropolyanions incorporated into a polymer matrix become more acidic at higher temperatures and the second proton becomes more accessible.

The results of kinetic studies of the catalytic conversion of isopropanol are presented in Figs. 6–8 where the logarithm of the observed reaction rate vs the reciprocal of the absolute reaction temperature is shown. For comparative reasons all data have been normalized to 1 g of heteropolyanions so that contribution of catalytically inactive polymer matrix to the mass of the catalyst has been eliminated.

In crystalline, unsupported HPA the acid–base activity strongly overwhelms the redox one (ca. 2 orders of magnitude). Due to the high activity of acid–base centers at increased temperatures the dehydration reaction reaches its diffusion limit, which is clearly manifested by the continuous change in the slope of the Arrhenius plot. As seen from Figs. 6–8 the incorporation of HPA into polyaniline matrix drastically changes relative redox to acid–base activities. Now the redox activity is dominant.

It is interesting to compare the activity of the sample prepared in the one-step procedure (S-I) with that measured for the sample prepared in the two-step procedure (S-II-1). The acid–base activity is very similar for both samples and is rather low. On the contrary the redox activity differs significantly and is ca. 4–5 times higher for the S-II-1 sample. This difference can be rationalized if one takes into account different preparation methods used for the fabrication of both catalysts. The one-step procedure results in the product in which heteropolyanions are distributed both in the bulk of the polymer and on its surface. This type of distribution leads, in turn, to

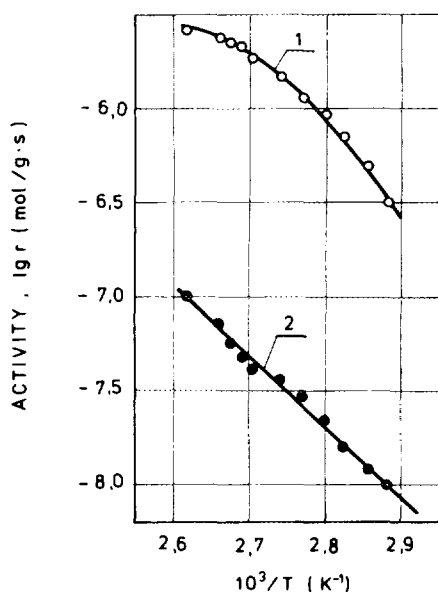


FIG. 6. Arrhenius plots of isopropanol decomposition over unsupported, crystalline $H_3PW_{12}O_{40}$. (1) Propylene; (2) acetone.

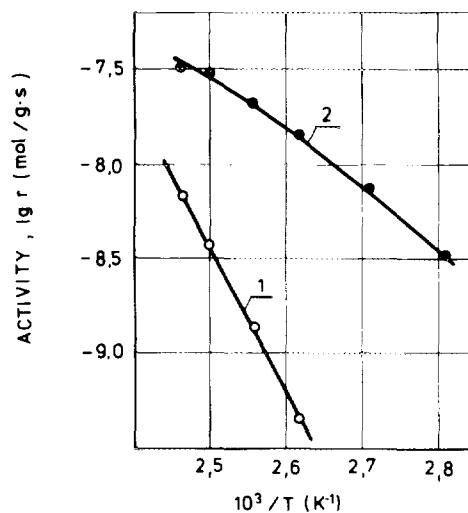


FIG. 7. Arrhenius plots of isopropanol decomposition over S-I catalytic sample. (1) Propylene; (2) acetone.

more difficult accessibility of those Keggin units which are located in the bulk. As a result a smaller fraction of HPA participates in the catalytic process. The two-step procedure produces the catalysts with HPA entrapped only on the surface of the polymer and all Keggin units are more easily accessible.

The two-step procedure enables rather easy control of the surface concentration of entrapped Keggin units. This can be done by varying the conditions of the polyaniline protonation process (vide supra). It is therefore interesting to explore the effect of surface concentration of HPA on the catalytic properties of the two-step (S-II) series of the catalyst samples. The comparison of the curves collected in Fig. 8 leads to two evident conclusions:

- (i) the normalized redox activity (per gram HPA) decreases with the decrease of the concentration of HPA entrapped on the surface;
- (ii) in the kinetic range the activation energy decreases with the decrease of HPA concentration on the polymer surface.

The catalysts from the S-I and S-II series differ in their activity, and different temperature ranges for the catalytic tests have to be selected. Thus in some cases only small temperature range overlap was possible. The calculated activation energies for all catalysts studied are collected in Table 5.

In the Arrhenius plot of the dehydration reaction two temperature ranges with distinctly different activation energies can be distinguished in the samples S-II-2 and S-II-3. Up to ca. 460 K the activation energy is ca. 65 kJ/mole and above this temperature it abruptly increases to ca. 120–140 kJ/mole, i.e., to the value close to the activation energy measured for crystalline unsupported HPA or for S-I and S-II-1 samples which exhibit higher

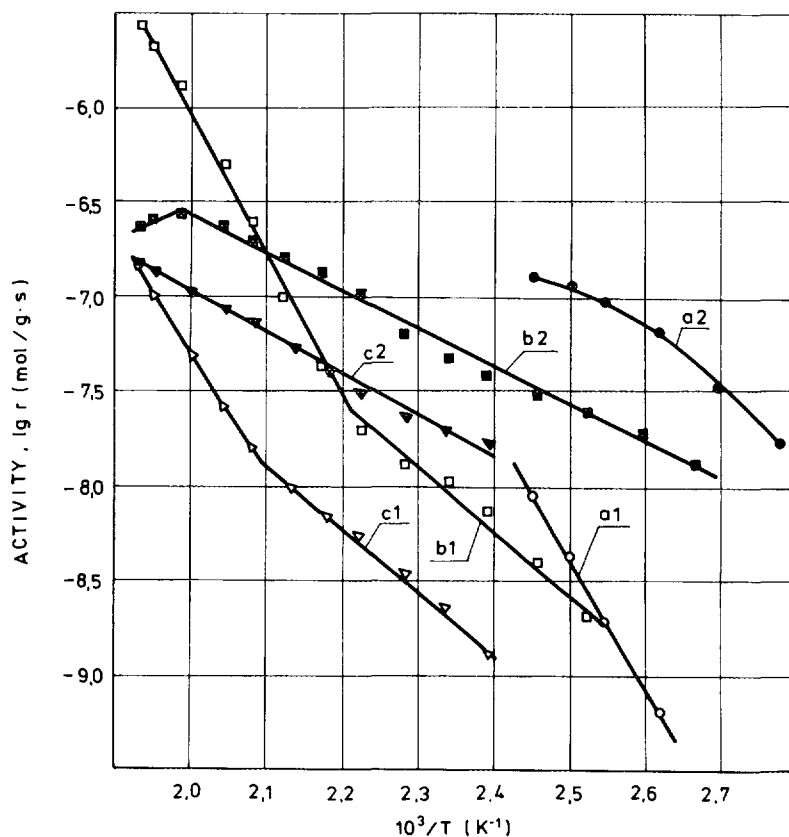


FIG. 8. Arrhenius plots of isopropanol decomposition over (a) S-II-1 catalytic sample, (b) S-II-2 catalytic sample, and (c) S-II-3 catalytic sample. (1) Propylene; (2) acetone.

concentration of heteropolyanions. This increase of the activation energy results in much stronger temperature dependence of the reaction rate. This behaviour can be taken to be an indirect manifestation of the degradation

of heteropolyanion-doped conjugated polymers. The degradation proceeds usually via deprotonation-assisted cross linking which results in the re-creation of acid molecules (21). As a result the behaviour of the catalyst should resemble more closely the behaviour of unsupported HPA in the reaction of dehydration.

In the S-II-2 sample the increase in the dehydration reaction rate observed for higher temperatures causes a deficit in alcohol supply for the slower, at these temperatures, dehydrogenation reaction which in turn leads to a decrease in its rate, as is clearly seen in Fig. 8b. The identical phenomenon has been observed previously (22).

The most intriguing observation from the catalytic point of view is a significant drop in the activation energy of dehydrogenation reaction observed for the most diluted samples of S-II series. Several phenomena can contribute to this effect and their precise identification requires further studies. Simultaneously with the activation energy drop, a decrease in normalized (per 1 g HPA) redox activity is observed for the samples with decreasing surface concentration of HPA despite the fact that, in the same time, the specific surface area of the samples increases.

For the same temperature, the redox activity of the most HPA concentrated sample from the S-II series

TABLE 5

Activation Energies of the Catalytic Isopropanol Decomposition Reaction

Catalyst	Temperature range (K)	Activation energy (kJ/mole)	
		Dehydration reaction	Dehydrogenation reaction
H ₃ PW ₁₂ O ₄₀	347–354	104.4	72.1
	374–382	21.6 ^a	72.1
S-I	356–382	146.0	64.3
	391–406	146.0	38.6
S-II-1	360–382	136.2	69.4
	393–408	136.2	27.3
S-II-2	375–449	66.1	39.1
	460–502	141.8	39.1
S-II-3	418–469	64.1	41.7
	480–518	118.8	41.7

^aDiffusion range.

(S-II-1) is comparable with that of unsupported crystalline HPA. This leads us to the conclusion that the redox properties of HPA are preserved upon its molecular dispersion via the polyaniline protonation reaction. However, the catalytic activity probably does not involve only one Keggin unit, since it is strongly affected by the decrease of HPA surface concentration, which implies greater distances between individual Keggin units. This may be particularly true for those redox reactions which involve more than one electron as in the case of the conversion of isopropanol to acetone. The reduction of HPA is a multielectron process (23) but the addition of one electron is easier than the addition of each consecutive electron in the same Keggin unit. It is therefore reasonable to assume that simultaneous reduction of two closely located Keggin units with one electron each will be favoured in the catalytic process over the reduction of one Keggin unit with two electrons. In this case a decrease in catalytic activity with the increase of the average distance between the unit is expected as experimentally observed for more surface diluted samples.

CONCLUSIONS

To summarize, we have demonstrated that polyaniline can serve as a new type of catalytic support on which heteropolyanions originating from 12-tungstophosphoric acid can be molecularly dispersed via a protonation reaction. This protonation-assisted dispersion results in an efficient blocking of acid-base functions. As a result in catalytic conversion of isopropanol, contrary to unsupported $H_3PW_{12}O_{40}$, the catalyst exhibits predominantly redox activity and very high selectivity towards acetone. The catalytic behaviour of these new catalysts depends on the concentration of HPA on the polymer surface. In particular, for lower concentrations the activation energy of the dehydrogenation reaction decreases.

The redox activity of the samples with higher concentration of HPA is comparable to that measured for unsupported heteropolyacid and then decreases with the decrease of HPA concentration.

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