JOURNAL OF CATALYSIS **132**, 311–318 (1991)

$H_3PMo_{12}O_{40}$-Doped Polyacetylene as a Catalyst for Ethyl Alcohol Conversion

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Received September 5, 1990

A new and highly efficient catalyst was obtained by exploiting the unique ability of polyacetylene to incorporate heteropolyanions (HPA) of the Keggin type via oxidative doping. 12-Molybdophosphoric acid, 20.8 wt%, was introduced into the polymer. A uniform distribution of HPA over the cross section of the polymer film was found. However, the concentration of HPA seemed to be higher at the surface of the polymer fibers than in their bulk. The conversion of ethyl alcohol was used as a catalytic test reaction. The catalyst exhibited both acid–base activity (formation of ethylene and diethyl ether) as well as redox activity (formation of acetaldehyde). The acid–base activity was 10 times higher than that of unsupported $H_3PMo_{12}O_{40}$, and the redox activity was about 40 times higher.

INTRODUCTION

Conjugated polymers have recently attracted increasing attention due to their unique electronic and electrochemical properties (*1*). Although insulating in their neutral form they can be rendered conductive through appropriate oxidation (sometimes called *p*-type doping) or reduction (*n*-type doping). In these reactions neutral polymer chains are transformed into polycations (or polyanions) and an appropriate number of counterions are inserted into the polymer matrix in order to compensate the positive charge imposed on the chain. The oxidative (*p*-type) doping results in charge withdrawal from the spatially extended π-bonding system of the polymer with simultaneous creation of solitons, polarons, or bipolarons as major charge storage configurations depending on the symmetry of the polymer chains (*2, 3*). It should be stressed that during the oxidative doping only the π system of the polymer is involved in the electron transfer, the σ-bonding system remaining intact; thus the structural identity of an individual chain is preserved to a large extent. Conjugated polymers are therefore almost ideal matrices in which anionic species with interesting properties can be dispersed on a molecular scale.

In some respects polyacetylene $(CH)_x$ is quite unique among all the conjugated polymers. It is the simplest conjugated polymer and can be prepared in a form exhibiting a high degree of crystallinity. In addition, upon appropriate doping it gives a highly conductive organic conductor, whose conductivity at room temperature approaches that of copper (*4*). Main group (*5*) and transition-metal halides (*6*), halogens (*7*), as well as protonic acids (*8*) have been used as dopants capable of converting polyacetylene into such highly conducting material.

Recently some of the present authors demonstrated that polyacetylene can be doped with anions as large as the anions originating from 12-molybdophosphoric

0021-9517/91 $3.00

acid (*9*), the diameter of which is of the order of 15 Å. The doping results in a significant increase of the polymer conductivity and induces the same IR active modes of the polymer as those typically observed with "classical" dopants such as metal halides. In addition several rather sharp bands characteristic of the complex anion of 12-molybdophosphoric acid, the so-called Keggin unit, are superimposed on the broad doping-induced modes of polyacetylene.

Our belief was that the insertion of large molybdophosphoric anions into the polyacetylene crystallites must create (sub)microvoids in the fibrillar lattice of the polymer, the voids accessible for small molecules thus penetrating to the vicinity of the dispersed heteropolyanions (or partly neutralized acid molecules). Considering the fact that dodecaheteropolyacids and their salts exhibit distinct catalytic properties, it can be supposed that dodecaheteropolyacid-doped polyacetylene will represent an interesting catalytic system. The aim of the present investigation was to examine this hypothesis. The catalytic conversion of ethyl alcohol, whose polar molecules are much smaller than the Keggin unit diameter, was taken as the test reaction. The results were compared with the results of a study of the same reaction with a nonsupported $H_3PMo_{12}O_{40}$ catalyst (*10*).

EXPERIMENTAL

Polyacetylene was obtained by the polymerization of C_2H_2 carried out at 195 K using the $Ti(OBu)_4/AlEt_3$ catalyst dissolved in toluene as first proposed by Ito *et al.* (*11*). A polymer film formed on the surface of the catalytic solution. It was then separated and repeatedly washed with pentane in order to remove the contamination with the catalyst. Finally the samples were vacuum dried.

The doping of polyacetylene with heteropolyacid was performed via chemical oxidation in acetonitrile containing 12-molybdophosphoric acid and minute amounts of a suitable complexing agent (*9*) or by anodic oxidation in $H_3PMo_{12}O_{40}$–acetonitrile electrolyte using polyacetylene film as the anode. After doping, the films, exhibiting metallic lustre, were washed with dry acetonitrile and again vacuum dried. The samples were stored in vacuum-sealed glass tubes. The sample used for the present investigation contained 20.8 wt% of $H_3PMo_{12}O_{40}$.

The distribution of HPA in the bulk of the polyacetylene sample was checked on a cross section of the film using a Kevex X-ray microspectrometer working in connection with a Jeol 50 electron scanning microscope.

EPR spectra were measured by means of a computer-controlled spectrometer operating in X-band with 100 kHz modulation. DPPH was used as a g factor standard (g = 2.0036).

ESCA measurements were made on a Vacuum Science Workshops (VSW, UK) ESCA-100 System spectrometer at 10^{-9} Torr. The binding energy (BE) of molybdenum was determined with respect to the C 1*s* peak of the polymer.

Thermogravimetric studies were performed using a Mettler thermoanalyser TA-2.

Catalytic experiments were carried out at 503 K using a pulse microreactor in which 0.200 g of polyacetylene film cut into small pieces (2 × 2 mm) was placed. Pulses of 0.5 μl of C_2H_5OH were introduced at 20 min intervals. Helium was used as the carrier gas and the reaction products were analyzed by a gas chromatograph connected on-line and fitted with a column filled with Porapak QS. Katharometric detection of the products has been applied. Before the catalytic runs the catalyst was heated for 30 min at 373 K and 1 h at 503 K in a current of He.

RESULTS AND DISCUSSION

The presence of heteropolyanions in the polymer matrix was verified by elemental analysis, which gave Mo : P : O ratios consistent with the stoichiometry of the Keggin unit. Additional information concerning the identification of the anion and the determination of its oxidation state was provided by EPR and ESCA measurements.

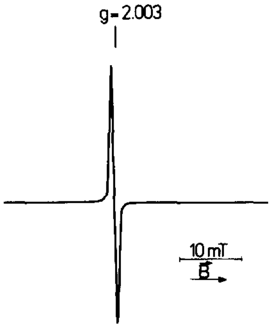

FIG. 1. EPR signal of polymer radical in HPA-doped polyacetylene (registered at 77 K).

EPR spectra of $H_3PMo_{12}O_{40}$-doped polyacetylene reveal a single narrow line ($\Delta B = 0.3$ mT) with g value of 2.003 (Fig. 1) characteristic of unpaired spin originating from a defect in the π-bonding system. This observation is not unexpected since doping-induced *cis–trans* isomerization of polyacetylene chains always results in the creation of ca. 1 unpaired spin per 3000 carbon atoms (*12*). No lines attributable to partially reduced Keggin units could be detected in a fresh sample (before catalytic reaction). It can therefore be concluded that in heteropolyanions inserted into the polymer matrix all molybdenum atoms are in the Mo(VI) oxidation state. This conclusion is further corroborated by magnetic susceptibility studies that show that the inserted anions are diamagnetic (*13*).

The presence of only one type of molybdenum in the Mo(VI) oxidation state is clearly evidenced by ESCA measurements (Fig. 2). The spectrum can be fitted with only one doublet due to Mo $3d_{5/2}$ and Mo $3d_{3/2}$ transitions. The observed chemical shifts are typical of Mo(VI) (*14*). The concentration of heteropolyanions calculated from the relative integrated intensity of the C $1s$ and Mo_{3d} peaks are ca. 6 to 8 times higher than the overall concentration determined on the basis of elemental analysis. Since XPS is a surface probe it is evident that heteropolyanions are not homogeneously distributed within the polymer fibers and remain preferentially in the vicinity of their surface. On the other hand microprobe analysis shows uniform distribution of molybdenum along its cross section (Fig. 3). This apparent discrepancy can be rationalized by taking into account the peculiar morphology of polyacetylene film. Polyacetylene has a complex morphology of entangled fibers whose diameter may vary between 100 and 300 Å depending on the preparation conditions. Only ca. one-third of the volume is filled with fibers, which facilitates the penetration of the dopant into the microporous bulk of the film. Since the resolution of the microprobe is lower than the average fiber diameter the distribution of the dopant will always be uniform in the microprobe studies. Further penetration from the fiber surface to its bulk requires solid state diffusion. Taking into account the large dimension of the Keggin units this diffusion may be mainly limited to the subsurface layer. The inner part of the fibers may therefore remain undoped or only weakly doped. The simplest way to verify this hypothesis is to perform X-ray diffraction studies. Undoped polyacetylene gives rise to three Bragg reflections in the vicinity of 3.7, 2.8, and 2.1 Å, the exact position of which depends on the *cis* to *trans* ratio in the polymer chains. The introduction of small dopant species, such as $FeCl_4^-$, results in a gradual decrease of the intensity of these reflections. Simultaneously, new reflections

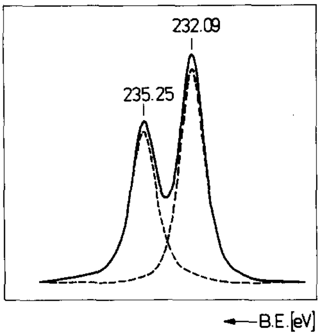

FIG. 2. ESCA spectrum of Mo $3d$ transitions in HPA-doped polyacetylene.

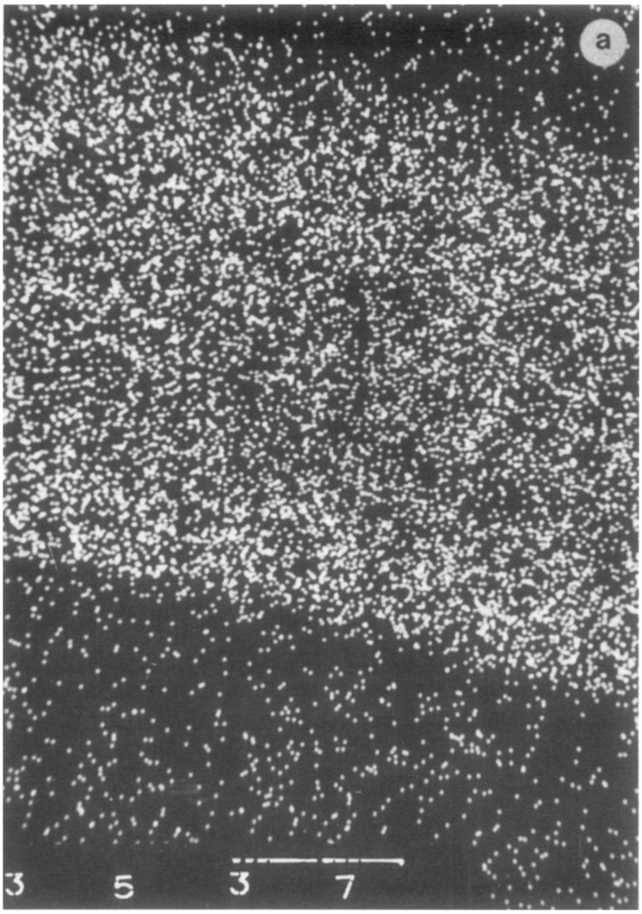

FIG. 3. Electron probe microanalysis of molybdenum on the surface of cross section of HPA-doped polyacetylene: (a) the distribution of molybdenum over the surface; (b) the intensity of Mo characteristic X-ray emission along a line on the surface of film cross section.

appear because the doped phase has crystallographic parameters different than those of pristine polyacetylene. At intermediate doping levels Bragg reflections of pristine polyacetylene and the new doped phase coexist. At the final doping level no Bragg reflections due to pristine polyacetylene can be detected (*15*).

In heteropolyanion-doped polyacetylene no reflections corresponding to any new phase were observed. However, with increasing concentration of dopant the intensity of the X-ray reflections characteristic of pristine polyacetylene become weaker. On the other hand they never vanished completely and could be registered even at the highest applied concentration of dopant corresponding to the formula $[\mathrm{CH}(\mathrm{PMo}_{12}\mathrm{O}_{40})_{0.0045}]_n$. It can therefore be concluded that doping decreases the crystallinity of the polymer but a certain amount of unchanged polyacetylene always remains forming the inner part of polymer fibers.

The IR spectra of the catalyst before and after the catalytic experiments exhibited bands characteristic of polyacetylene and bands characteristic of the Keggin unit (*16*), thus indicating that during the catalytic run no appreciable destruction of dodecamolybdophosphoric anions took place.

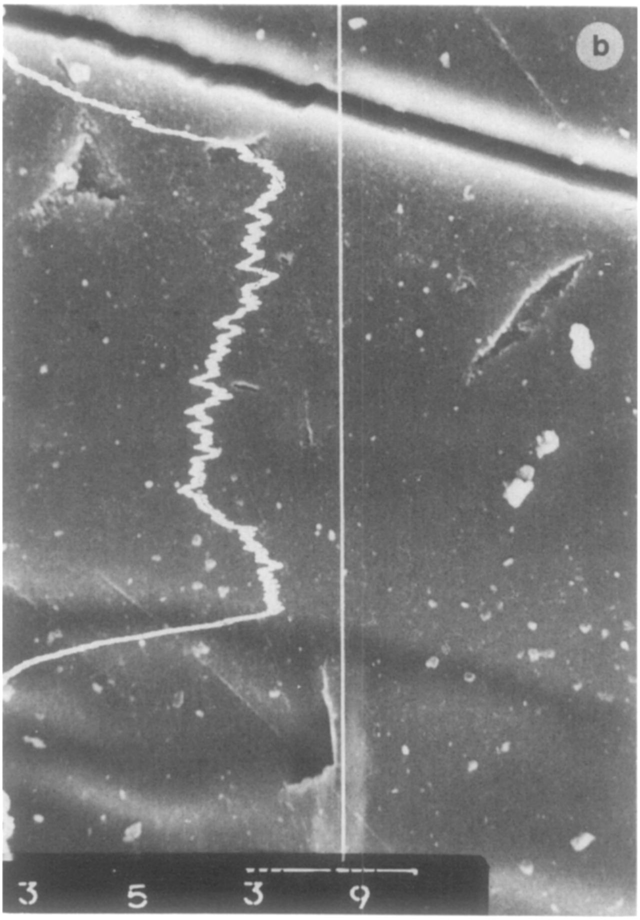

FIG. 3—*Continued*

This conclusion is further supported by the EPR spectrum of the catalyst registered after the catalytic reaction (Fig. 4). Besides the sharp signal of the polymer radical with $g \doteq 2.003$ a new anisotropic signal appears with $g_\perp = 1.944$ and $g_\parallel = 1.900$, which is similar to that observed by Fricke and Öhlmann (*17*) for Mo(V) in thermally treated 12-molybdophosphoric acid with reversibly released constituent water. Serwicka (*18*) has shown that this type of signal is characteristic of Mo(V) adjacent to an anion vacancy in the Keggin unit. The EPR spectrum thus indicates that in the course of the catalytic reaction only partial reduction and dehydration of the heteropolyanion occurs but its structure remains unchanged.

In view of the use of heteropolyanion-doped polyacetylene in catalysis its thermal stability was studied in greater detail. Ther-

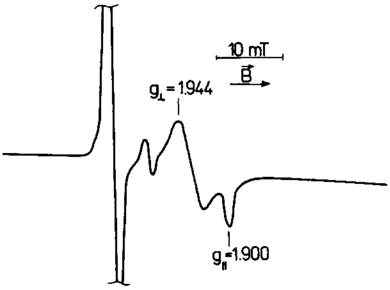

FIG. 4. EPR spectrum of HPA-doped polyacetylene after the catalytic reaction (registered at 77 K).

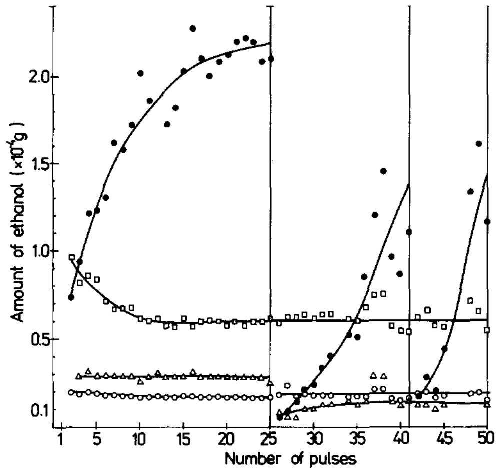

FIG. 5. Yield of diethyl ether (△), ethylene (○), acetaldehyde (□), and unreacted alcohol (●) as the function of the pulse number. Pulses of 3.6 × 10^{-4} g alcohol, amounts of the products expressed as equivalent amount of ethanol.

mogravimetric analysis showed that the sample loses about 1.5% of its weight on heating between 313 and 393 K but subsequently its mass remains practically constant up to about 523 K. A distinct endothermic DTA peak was observed at 743 K and a less distinct one at 683 K. Within this temperature region the rate of polymer degradation was highest. At 773 K the weight loss was equal to 28%. On the basis of the above results we have selected the temperature of 503 K as the most suitable for the catalytic tests.

The results of the catalytic experiments are shown in Fig. 5. Only three products of alcohol transformation were present: acetaldehyde, diethyl ether, and ethylene. Acetaldehyde, which is the product of the reaction occurring on redox centers, was the main product, in contrast to the results obtained previously with unsupported $H_3PMo_{12}O_{40}$ under the same experimental conditions (*10*), where its yield was equal to that of ethylene and only half that of diethyl ether. In the course of 10 initial pulses the observed yield of acetaldehyde decreased (about 40%) but then remained fairly constant. The yield of ethylene and diethyl ether (the products forming on the Brønsted acid sites) was constant since the very beginning of the catalytic experiment. Hence, it is seen that the catalyst obtained by doping of polyacetylene with dodecamolybdophosphoric acid exhibits two functions: an acid–base function evidently connected with the insertion of strong acid and a redox function the enhancement of which probably associated with the electronic structure of the catalyst and in particular with its semiconducting properties. No catalytic activity was exhibited by the undoped polyacetylene under the same conditions.

It can be seen from Fig. 5 that the amount of ethyl alcohol detected in particular pulses leaving the catalyst bed was the lowest in the first pulse and rapidly increased up to about 2.2 × 10^{-4} g C_2H_5OH after 12 pulses. It has also been found that the sum of the

TABLE 1

Yield per Pulse Calculated per 1 g of $H_3PMo_{12}O_{40}$ and Expressed as the Amount of C_2H_5OH used for Formation of the Given Product

Catalyst	CH_3CHO	C_2H_4	$(C_2H_5)_2O$	Sum of products
Unsupported $H_3PMo_{12}O_{40}$	3.22×10^{-5}	3.66×10^{-5}	7.36×10^{-5}	14.25×10^{-5}
Doped polyacetylene	1.382×10^{-3}	0.406×10^{-3}	0.688×10^{-3}	2.476×10^{-3}
Ratio of yields on polyacetylene and unsupported $H_3PMo_{12}O_{40}$	42.9	11.1	9.4	17.4

amounts of ethylene, diethyl ether, and acetaldehyde (all three expressed as the amount of alcohol needed to produce them) as well as unreacted alcohol detected chromatographically was always lower than the amount of alcohol introduced in the pulse. Considering the fact that no other products were detected chromatographically it may be supposed that this deficit is mainly due to the relatively strong sorption of alcohol by the catalyst. At the beginning of the catalytic test, alcohol is most strongly sorbed and the amount of unreacted alcohol detected together with the products is the smallest. In subsequent pulses the solid becomes more and more saturated with the sorbed alcohol and the amount of unreacted alcohol detected chromatographically distinctly increases. It is striking that the yields of ethylene and diethyl ether and also acetaldehyde (after 10 initial pulses) remain practically constant, independent of the amount of sorbed alcohol. This may indicate that most of the sorbed C_2H_5OH molecules do not have contact with the catalytically active centers, e.g. they are mainly sorbed in the voids existing between pristine fibers of polyacetylene into which heteropolyanions have not penetrated.

After 25 pulses the experiment was stopped, the reactor was filled with helium gas, and the measurements were continued after only 3 days. There was no change in the yield of acetaldehyde and ethylene, but the yield of diethyl ether decreased to roughly one-third. The amount of alcohol detected was initially very small (its deficit was as high as 2.6×10^{-4} g C_2H_5OH/pulse), thus indicating strong sorption. This may be explained by the supposition that during the long interruption in the measurements, desorption of "irreversibly" sorbed alcohol took place, thus enabling increased sorption in the new series of pulses. As Fig. 5 shows, the amount of alcohol detected with the products increases rapidly with increasing number of pulses, thus indicating progressive saturation of the catalyst with alcohol. The same behavior was observed each time the measurements were resumed after a long pause.

It is interesting to compare the catalytic activity of the $H_3PMo_{12}O_{40}$-doped polyacetylene with that of the unsupported $H_3PMo_{12}O_{40}$ determined in the same catalytic reactor and practically the same experimental conditions as described in Ref. (*10*).

The data corresponding to the constant activities reached after about 20 pulses, collected in Table 1, clearly indicate that the dispersion of heteropolyacid on the polyacetylene strongly increased its catalytic activity. Supported heteropolyacid gave nearly 20 times more products than the unsupported one. In the case of acetaldehyde the activity increased roughly 43 times, thus indicating a very strong increase in the redox activity. Nevertheless, also in the case of acid–base processes, the activity of supported $H_3PMo_{12}O_{40}$ was about 10 times higher.

ACKNOWLEDGMENT

This research was partially financed by the Polish Ministry of Education under Grant CPBP 01.18.

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