^{1}H, ^{31}P NMR MAS, infrared and catalytic studies of heteropolyacid $H_3PW_{12}O_{40}$ supported on MgF_2

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Abstract

^{1}H and ^{31}P NMR MAS spectra of heteropolyacid $H_3PW_{12}O_{40}$ (HPA) supported on high dispersed MgF_2 suggest the change of the structure of HPA compared with crystal HPA due to interaction with the support. ^{1}H NMR spectra at HPA content below 3 wt% do not reveal the ^{1}H NMR line from protons attached to HPA. In the samples with HPA content larger than 3 wt% the ^{1}H NMR line with $\delta \approx 5$ ppm was attributed to protons in isolated heteropolyanions bonded with support surface. At HPA contents larger than 20 wt% the crystals of HPA on MgF_2 surface are formed; this follows from appearance in ^{1}H NMR spectra of a line at $\delta = 9.3$ ppm typical for crystalline HPA. ^{31}P NMR and IR spectra suggest the destruction of HPA structure at low (less than 3 wt%) loading, and its preservation at larger HPA contents. The ^{19}F NMR signals were found in methanol after dissolving of HPA supported on MgF_2. Catalytic measurements show the drastic increase of activity of HPA/MgF_2 catalysts in reaction of isobutylene oligomerization on increase of HPA content.

Keywords: Heteropolyacids; High-resolution NMR; ^{1}H NMR; Magnesium fluoride; ^{31}P NMR; Solid-state NMR; Supported catalysts

1. Introduction

The catalysts based on heteropolyacids (HPA, the polyoxocompounds $H_mXY_{12}O_{40}$, where X = P, Si and Y = Mo, W; m = 3, 4) have found an application in many interesting catalytic reactions due to their high proton acidity [1]. They are used both as homogeneous and heterogeneous catalysts; in the latter case they are supported on porous materials, usually SiO_2. For supported HPA catalysts the dependence of catalytic properties on HPA content has been reported [2,3]. This indicates the change of the HPA structure due to interaction with support active sites. For $H_3PW_{12}O_{40}$ supported on SiO_2 this follows also

from ^{1}H and ^{31}P NMR MAS studies [4], where the types of supported species were found to be dependent on HPA content. For $H_3PW_{12}O_{40}/SiO_2$ the interaction with surface Si–OH groups was responsible for binding of HPA with SiO_2 surface. For these catalysts the observation of ^{1}H NMR signals from supported HPA species at small concentration was obscured by strong signal from Si–OH protons. This prevented the study of the proton structure of supported HPA at concentrations smaller than 5 wt%.

In this work we have used ^{1}H, ^{31}P MAS NMR and IR spectroscopy to elucidate the state of $H_3PW_{12}O_{40}$ supported on high-dispersed MgF_2 which a priori does not contain protons on its surface. ^{19}F NMR spectra of solution obtained after dissolving of supported HPA in methanol

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were used to obtain further insight into the interaction of HPA with the support. These data are discussed in relation to catalytic activity of these catalysts in reaction of isobutylene oligomerization which proceeds with the transfer of acidic proton to isobutylene molecule [3].

2. Experimental

The HPA used in this study ($H_3PW_{12}O_{40} \cdot 26H_2O$) was a commercial product. Before supporting procedure, HPA has been recrystallized from water and treated at 473 K in vacuum for 1 h. High-dispersion MgF_2 with BET specific surface area 31 m^2 g^{-1} was used as the support. MeOH was dried under $CaCl_2$. The samples of HPA supported on MgF_2 were prepared by impregnation of the support (1 g) with a methanol solution of HPA (10–150 g l^{-1}) with subsequent drying at 373 K and calcination at 473 K in air for 4 h. The content of supported HPA was determined from the difference of HPA concentrations in solutions before and after impregnation procedure (at equilibrium condition, achievable after ~2 h) as measured with Specord M-40 spectrophotometer in the range 4200–3200 cm^{-1}.

^{1}H, ^{31}P and ^{19}F NMR spectra were recorded on a Bruker CXP-300 spectrometer operating at a magnetic field of 7.04 T under the following experimental conditions.

^{1}H NMR MAS spectra were obtained at 300.066 MHz, using frequency range 50 kHz, pulse duration 5 μs, time delay between pulses 10 s, number of scans 500. Chemical shifts were measured with respect to external TMS. Prior to NMR measurements, the samples were placed in 7 mm o.d. and 12 mm length glass sample tubes and then evacuated at 473 K at 10^{-3} Pa for 10 h. The ^{1}H NMR MAS spectra were measured with the use of quartz rotors (rotation frequency about 3 kHz) and a special probe-head with a minimal ^{1}H NMR background signal. The concentrations of protons in the samples were measured by comparison with the standard sample SiO_2 (evacuated at 573 K) which contained 5×10^{19} OH groups.

^{31}P NMR MAS spectra were recorded at 121.46 MHz in the frequency range 50 kHz, pulse duration 10 μs and pulse repetition time 10 s. The number of scans was from 500 to 5000. The chemical shifts were measured with respect to 85% H_3PO_4 as the external reference. The ^{31}P NMR MAS spectra were recorded in polymethylmethacrylate Andrew–Beams rotors (rotation frequency ~4 kHz).

^{19}F NMR spectra of solutions obtained after washing of supported HPA with methanol were measured in 5 mm o.d. standard NMR sample tubes with respect to the external C_6F_6 at frequency 282.23 MHz in the range 40 kHz, pulse length 5 μs and pulse repetition time 5 s. The number of scans was 1000.

Infrared spectra were recorded on Specord IR-75 spectrometer in the range 400–2000 cm^{-1} with compressed pellets of 5 mg catalysts plus 500 mg KBr as samples.

The reaction of isobutylene oligomerization was carried out at 70°C (± 0.1°C) in a closed thermostatted glass reactor equipped with a sampling and stirrer apparatus. Pentadecane was used as a solvent. The amount of catalyst in the reaction mixture was 6.2 wt%. To exclude diffusion effects, the catalyst particles with the size as small as 0.1–0.2 mm were used, and the mixture was vigorously stirred (1000 rpm). The gas mixture with volume composition $C_4H_8:CH_4 = 10:1$ was blown down over reactor mixture. At appropriate time intervals, the probes of gas mixture were taken and analyzed with GLC equipped with 2 m column packed with 5% SE-30 on Chromosorb W (0.16–0.25), 30°C; methane was used as the internal standard.

Second-order rate constants, k, were calculated in a way similar to that reported in [5].

3. Results and discussion

^{1}H NMR MAS spectra of MgF_2 support and of the samples HPA supported on MgF_2 for different amounts of the supported active material are presented in Fig. 1. The spectrum of MgF_2 manifests
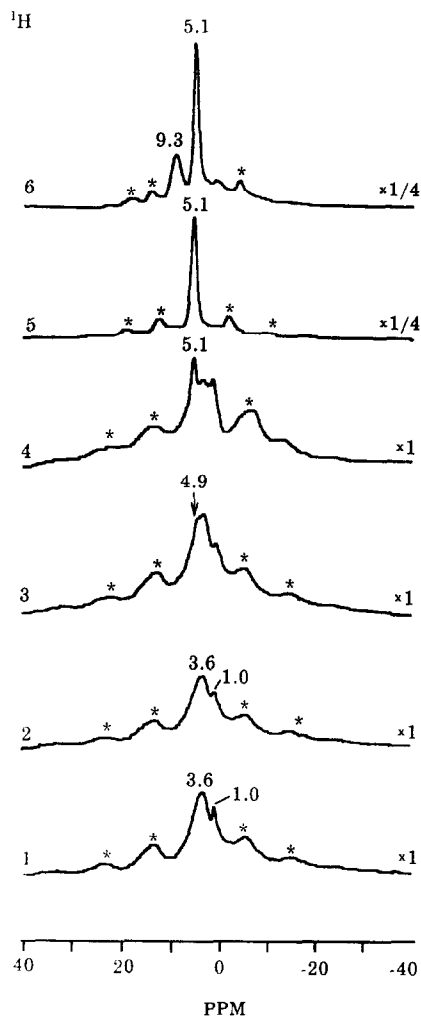
Fig. 1. ¹H NMR MAS spectra of (1) MgF₂ and of HPA/MgF₂ catalysts with various amount of supported H₃PW₁₂O₄₀: (2) 1 wt%; (3) 3 wt%; (4) 5 wt%; (5) 20 wt%; (6) 40 wt%.

$\delta = 5.1$ ppm from supported HPA (Fig. 1-4). This line increases its intensity with the increase of HPA content and dominates in the spectrum of
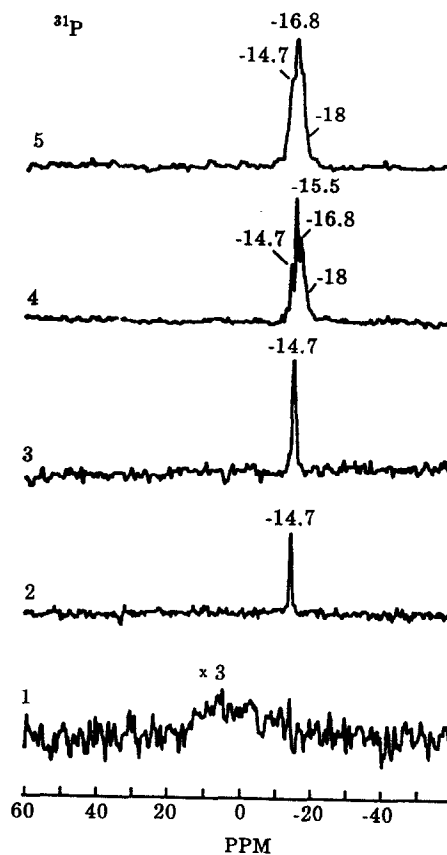

Fig. 2. ³¹P NMR MAS spectra of H₃PW₁₂O₄₀ supported on MgF₂, for various HPA loading: (1) 1 wt%; (2) 3 wt%; (3) 5 wt%; (4) 20 wt%; (5) 40 wt%.
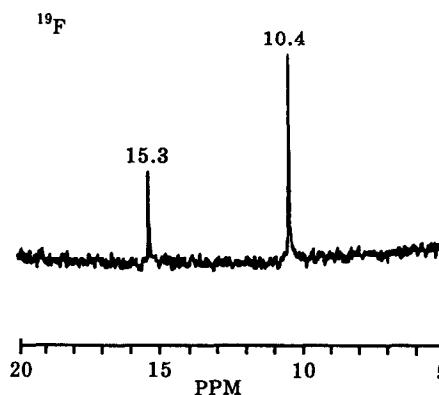
Fig. 3. ¹⁹F NMR spectrum of the solution obtained after washing with methanol of the catalyst 5 wt% H₃PW₁₂O₄₀ supported on MgF₂.

a signal with the peaks at $\delta = 3.6$ and 1.0 ppm (Fig. 1-1) due to proton impurities that originate from the material used for MgF₂ preparation and that localized mainly in the bulk of the sample. Their total content was estimated to be $\sim 5 \times 10^{19}$ g^{-1}. Supporting of 1 wt% of HPA on catalyst surface does not bring new lines in the ¹H NMR spectrum (Fig. 1-2). For the sample, containing 3 wt% HPA, the line at $\delta \approx 4.9$ ppm of small intensity (corresponding to the proton concentration about 5×10^{18} g^{-1}) overlaps with the spectrum of the support (Fig. 1-3). The further increase of HPA content results in appearance of the line at
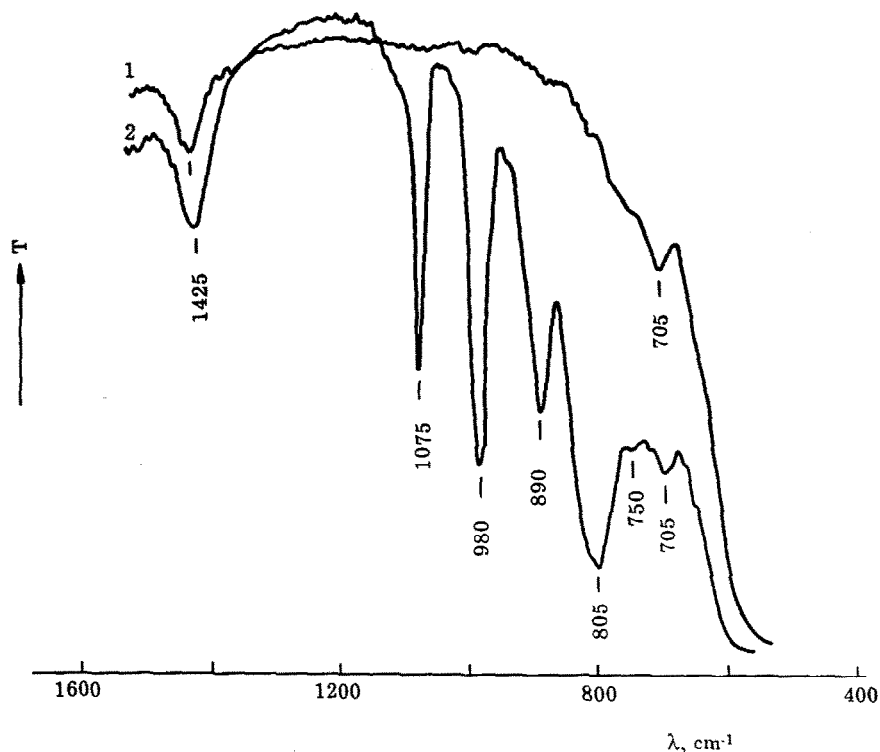
Fig. 4. IR spectra of (1) MgF$_2$ and (2) 3 wt% H$_3$PW$_{12}$O$_{40}$ supported on MgF$_2$. The bands at 1075, 980, 890 and 805 cm^{-1} belong to HPA; the bands at 1425 and 705 cm^{-1} are due to MgF$_2$ support.

Fig. 1-5. Along with this line, a new line at $\delta = 9.3$ ppm appears in the spectrum at HPA content 40 wt% (Fig. 1-6). No considerable changes of the signal from support has been detected.

Thus, ^{1}H NMR spectra show the presence of at least two types of acidic protons in the supported HPA. The first one has a chemical shift near 5 ppm and is observed at concentrations of HPA larger than 3 wt%. This type of signals has been found previously for H$_3$PW$_{12}$O$_{40}$ supported on SiO$_2$ [3]. It has been attributed to isolated HPA species loosely bonded with SiO$_2$ surface. At increased HPA contents, the crystals of HPA on the catalyst surface are formed as evidenced from the appearance of the line with $\delta = 9.3$ ppm, a value which is characteristic of the bulk H$_3$PW$_{12}$O$_{40}$ [3].

The spectra presented in Figs. 1-3 and 1-2 show that at HPA content below 5 wt% there is a significant change in the state of protons in supported HPA. This change reflects itself in the absence of the signal near 5 ppm that is typical for regular

supported H$_3$PW$_{12}$O$_{40}$. This conclusion is supported also by the ^{31}P NMR MAS spectra (Fig. 2).

The crystalline H$_3$PW$_{12}$O$_{40}$ shows a single line with $\delta = -16.7$ ppm and the line width $\Delta \nu_{1/2}$ about 100 Hz [3]. At the lowest HPA content (1 wt%) a line at $\delta \approx 2$ ppm and $\Delta \nu_{1/2} \approx 2.5$ kHz was detected (Fig. 2-1). Increase of HPA loading to 3 wt% results in appearance of the narrow line ($\Delta \nu_{1/2} \approx 150$ Hz) at $\delta = -14.7$ ppm typical for P atoms in regular PO$_4$ tetrahedra. This line could be attributed to P atoms in the Keggin structure. Increase of loading up to 5 wt% results in the increase of the intensity of this line (Fig. 2-3). For the samples containing 20 and 40 wt%, along with the line at -14.7 ppm also the lines at -15.5; -16.8 and -18 ppm were found (Figs. 2-4,5). A line at -16.8 ppm corresponds to crystalline H$_3$PW$_{12}$O$_{40}$ with the regular Keggin structure. Presence of other lines indicates distortions of the crystal structure, probably, due to the pres-
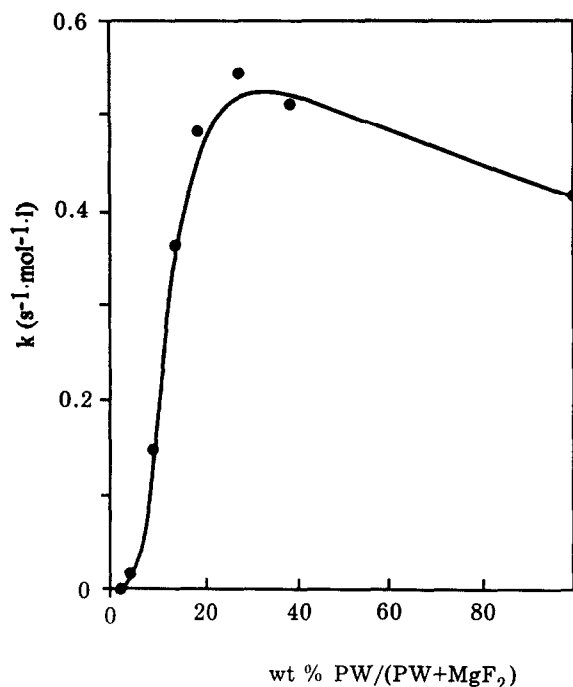
Fig. 5. The dependence of the second-order rate constant k of isobutylene oligomerization on the $H_3PW_{12}O_{40}$ content on the MgF_2 surface.

ence of defects in $H_3PW_{12}O_{40}$ crystals, deposited in the pores of the support.

Thus, ^{31}P NMR data show two different types of species formed on the support surface. Indeed, at 1 wt% loading, a highly distorted environment of P atoms (which is quite different from that in highly symmetric Keggin structure) is evidenced by a large NMR line width and a chemical shift which is different from that for crystalline HPA. This indicates a strong interaction between HPA and the support surface sites which results in the destruction of HPA structure. The amount of sites which are responsible for such interaction (their nature is still not identified) is estimated to be 5×10^{18} g^{-1}, i.e., they occupy only small part ($\sim$ 1-2%) of the support surface.

At contents greater than 3 wt% the new surface states which have the HPA structure, are formed. This type of surface species is characterized by the line at $\delta \approx 5$ ppm in the ^{1}H NMR spectra and the line at ca. -15 ppm in the ^{31}P NMR spectra. The spectra with such parameters have been observed earlier for $H_3PW_{12}O_{40}/SiO_2$ catalysts

[3] and have been attributed there to isolated HPA anions loosely bonded with the support surface. At last, the crystals of HPA are deposited over MgF_2 surface at contents more than 20 wt%.

^{19}F NMR spectra of the solution obtained after dissolving of the catalyst with 5 wt% HPA in methanol, revealed two lines with the chemical shifts 10.4 and 15.3 ppm with respect to C_6F_6 and concentration of F about 10^{-3} mol $\times l^{-1}$ (Fig. 3). No signals have been detected after washing of MgF_2 support itself with methanol. This suggests that at small loading HPA interacts with specific surface sites of MgF_2 which occupy only a small part of the total surface. Upon this interaction the products are formed which can be then dissolved in methanol. Further studies are needed to elucidate the composition and structure of these surface products. The ^{31}P NMR spectra clearly show that their structure is different from that typical for HPA.

The decomposition of HPA on MgF_2 is supported also by IR spectra (Fig. 4) which show that at 3 wt% HPA, along with the bands at 1075, 980, 890 and 805 cm^{-1} from the regular Keggin structure [7], also a band at 750 cm^{-1} from a destroyed HPA is present.

The formation of heteropolyacids containing F atoms in their structure has been reported in [4]. However, for our samples this possibility can be ruled out since in the ^{19}F NMR spectra no splitting due to F–W spin–spin interaction with the typical for such compounds J in the range from 9 to 58 Hz [6], has been observed.

Testing of the catalysts with various HPA contents in the reaction of isobutylene oligomerization has showed that reaction rate depends on HPA loading (Fig. 5). The sample with the smallest HPA content (3 wt%) did not show any activity. Increase of HPA content up to about 20 wt% leads to a continuous increase of the activity. A further increase of HPA content resulted in a decrease of the activity, most probably, due to a decrease of the specific surface area of the active component.

The following facts prove that under our experimental conditions the reaction of isobutylene oligomerization is a heterogeneous process: (i)

HPA is insoluble in pentadecane used as the solvent; (ii) reaction stops when the catalyst is filtered off; (iii) reaction rate depends on the stirring speed; (iv) reaction rate increases with the increase of the support surface area.

This reaction is assumed to proceed via fast reversible adsorption of isobutylene accompanied by proton transfer with the formation of carbonium ions [8]

$$(CH_3)_2C=CH_2 + H^+ \rightleftharpoons (CH_3)_3C^+$$
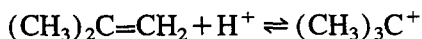
The change of the reaction rate constant with HPA loading suggests different acidities of the surface proton sites which are present on MgF_2 at small and large HPA contents.

4. Conclusion

The results presented above show that several different surface species are formed upon supporting of $H_3PW_{12}O_{40}$ on MgF_2 surface. At small HPA content (~ 1–3 wt%) HPA interacts strongly with specific surface sites which results in destruction of HPA anions. This interaction includes a chemical bonding with surface F atoms, the so formed fluorine containing species can be dissolved in methanol. At intermediate HPA contents (5–20 wt%) the isolated monomeric HPA molecules loosely bonded with the support surface are also present in the catalyst. At still greater HPA

contents, the crystals of HPA are formed. As follows from catalytic experiments, different types of surface species exhibit different catalytic properties. At the smallest HPA content no activity was found, since according to the ^1H NMR spectra the surface species formed in these conditions do not contain protons in their structure. The isolated HPA anions that demonstrate the line at $\delta \approx 5$ ppm in ^1H NMR spectra from the acidic protons, show high activity in isobutylene oligomerization, which is comparable with that for crystal HPA.

Thus, the combined ^1H, ^{31}P MAS NMR, IR and catalytic studies of $H_3PW_{12}O_{40}$ supported on MgF_2 have revealed several different support species which have different catalytic properties.

References

[1] K.I. Matveev, Kinet. Katal., 18 (1977) 862.
[2] S.M. Kulikov, M.N. Timofeeva, I.V. Kozhevnikov, V.I. Zaikovsky, L.M. Plyasova and I.A. Ovsyannikova, Isv. AN SSSR Ser. Khim., 4 (1989) 763.
[3] I.V. Kozhevnikov and M.N. Timofeeva, J. Mol. Catal., 75 (1992) 179.
[4] V.M. Mastikhin, S.M. Kulikov, A.V. Nosov, I.V. Kozhevnikov, I.L. Mudrakovsky and M.N. Timofeeva, J. Mol. Catal., 60 (1990) 65.
[5] I.V. Kozhevnikov, S.Z. Khankhasaeva and S.M. Kulikov, Kinet. Katal., 30 (1989) 50.
[6] F. Chaveau, P. Doppelt and L. Lefebre, Bull. Soc. Chim. France, 1 (1983) 197.
[7] C. Rocchiccioli-Deltcheff, R. Thouvenot and R. Franck, Spectrochim. Acta, A32 3 (1976) 587.
[8] Ya.T. Eidus and B.K. Nefyodov, Usp. Khim., 29 (1969) 833.