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Surface Acid Sites of $H_3PW_{12}O_{40}$ As Studied by the Adsorption of Stable Nitroxyl Radicals

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Abstract—The surface acidity of $H_3PW_{12}O_{40}$ and $Na_xH_{3-x}PW_{12}O_{40}$ (x = 1–3) was studied using the adsorption of 2,2',6,6'-tetramethyl-4-oxopiperidine-1-oxyl (TEMPON) and 2,2',6,6'-tetramethyl-4-hydroxypiperidine-1-oxyl (TEMPOL) radicals. It was found that the amount of surface proton sites determined from the adsorption of TEMPON decreased with the degree of substitution of Na^+ cations for protons. A correlation between amount of strong surface proton sites and catalytic activity of $Na_xH_{3-x}PW_{12}O_{40}$ (x = 0–3) in the dealkylation reaction of 2,6-di-*tert*-butyl-4-methylphenol was found.

INTRODUCTION

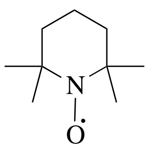
Tungstophosphoric heteropoly acid ($H_3PW_{12}O_{40}$) and its salts ($M_xH_{3-x}PW_{12}O_{40}$) are actively used as homogeneous and heterogeneous acid catalysts for a wide variety of organic reactions [1, 2]. Great interest in these compounds is due to their high Brønsted acidity, which is much higher than the acidity of commonly used solid acid catalysts, such as SiO_2–Al_2O_3, H_3PO_4/SiO_2, zeolites HX and HY, etc. [1, 2].

The surface acid properties of heteropoly acids (HPAs) have been intensively studied with the use of various physicochemical techniques, such as adsorption calorimetry [3], ^1H and ^{31}P(MAS) NMR spectroscopy [4], and indicator titration [5]. Early in the 1990s, IR spectroscopy was used for analyzing the state of adsorbed indicator molecules (pyridine, ammonia, *n*-butylamine, etc.) [6]. On this basis, the number and strength of acid sites in HPAs were quantitatively evaluated in terms of proton affinity (PA) scale. It was found that the PA of proton sites in $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ is 1120–1130 kJ/mol. The successive replacement of protons by sodium ions ($Na_xH_{3-x}PW_{12}O_{40}$) resulted in an increase in PA to 1160 kJ/mol and, correspondingly, in a decrease in the strength of sites. However, these acid sites are stronger than the acid sites of zeolites; for example, for zeolite HZSM-5, PA is 1170 kJ/mol. The amount of adsorbed pyridine per HPA molecule is equal to the basicity of the heteropoly anion. It was found that the adsorption capacity of $H_3PW_{12}O_{40}$ for pyridine is ~340 mmol/g, which is much higher than 4–15 μmol/g, the expected amount for surface acid sites (HPA landing surface area of ~130 Å^2 [1, 2]; S_{BET} = 3–5 m^2/g). The most plausible explanation for this fact consists in the penetration of pyridine into an HPA crystal (according to X-ray diffraction data, acid sites occur both within a crystal and on the surface) and the formation of a “pseudoliquid” phase [1, 2].

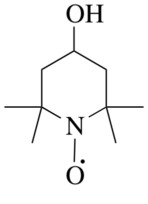
With the use of adsorption calorimetry [3], a nonuniformity of proton sites was found in the bulk HPA $H_3PW_{12}O_{40}$: a small amount of proton sites (0.03 mmol/g, i.e., 3%) with the heat of ammonia adsorption higher than 170 kJ/mol and sites with heats of adsorption of 165–140 kJ/mol.

The acid site strength distribution of HPA and its salts $M_3PW_{12}O_{40}$ (M = Ca^{2+}, Mg^{2+}, Zn^{2+}, Al^{3+}, and Na^+) was studied using nonaqueous indicator titration (*n*-butylamine) [5]. It was found that the strength and amount of sites essentially depend on HPA dehydration conditions: gas atmosphere (nitrogen, air, or hydrogen) and temperature. The greatest amount of strong sites ($-5.6 < H_0 < -3.3$) was observed after heating HPA in a nitrogen atmosphere at 200–300°C. The total amount of sites (with an indicator with $H_0 = 6.8$) in $H_3PW_{12}O_{40}$ and salts was equal to ~3.1 and 1.4–1.8 mmol/g, respectively.

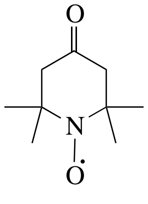
The use of each of the above techniques presents severe difficulties in the interpretation of quantitative results. Therefore, a search for new techniques and procedures for producing quantitative data on the acid properties of both bulk and supported HPAs has received increasing attention in the past few years. These quantitative data are required for the development of selection rules for effective acid catalysts based on HPAs.



TEMPO



TEMPOL



TEMPON

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It was found previously [7–10] that unique information on the structure and mutual arrangement of adsorption sites on the surface of oxide catalysts (Al_2O_3, SiO_2, zeolites, etc.) can be obtained by a spin probe method: the EPR spectroscopy of probe molecules such as 2,2',6,6'-tetramethylpiperidine-1-oxyl (TEMPO), nitrogen(II) oxide, and anthraquinone. The interaction of these molecules with surface adsorption sites can be judged from an analysis of the EPR spectra of adsorbed nitroxyl radicals, and the adsorption site can be directly observed in a number of cases. The TEMPO and di-*tert*-butylnitroxide radicals are selective indicators for acceptor sites like Al^{3+} [9, 11, 12]. The interaction of various adsorbates with a surface can be simulated by varying nitroxyl radical structure. Thus, with the use of the specific adsorption of these radicals, the distance between three-coordinated aluminum ions on the surface of Al_2O_3 was evaluated [13], and two forms of surface acid sites in $MgCl_2$ were detected [14].

Determination procedures for the concentrations of Lewis acid sites on the surface of oxide catalysts (primarily, alumina), aluminosilicates, dealuminated zeolites, and $MgCl_2$ were developed [9, 12, 15, 16]. Published data show that nitroxyl radicals are promising for use as spin probes in studies of the active centers of acid catalysts. However, the procedures for studying surface Brønsted acid sites with the use of these radicals were inadequately developed.

HPAs are typical solid acids, which exhibit only Brønsted acidity. The aim of this work was to develop a procedure for determining the concentration of proton sites on HPA surfaces with the use of stable nitroxyl radicals and to compare the results with data on the catalytic activity of the same samples.

EXPERIMENTAL

Chemicals. Reagent-grade $H_3PW_{12}O_{40} \cdot 19H_2O$ HPA was used in this study after additional purification by ether extraction. The $Na_xH_{3-x}PW_{12}O_{40}$ ($x = 1$–3) salts were prepared by the titration of $H_3PW_{12}O_{40}$ with corresponding Na_2CO_3 solutions in ethanol [17]. The amount of hydration water in the HPA was determined by weight loss after calcination at 500°C. The purity of the HPA was checked by ^{31}P NMR spectroscopy.

Hexane of reagent grade was purified by distillation. 2,6-Di-*tert*-butyl-4-methylphenol (BHT) was twice recrystallized from hexane.

The following stable nitroxyl radicals were used for studying active sites on catalyst surfaces: 2,2',6,6'-tetramethyl-4-oxopiperidine-1-oxyl (TEMPON) and 2,2',6,6'-tetramethyl-4-hydroxypiperidine-1-oxyl (TEMPOL).

Physicochemical measurements. The specific surface areas (S_{BET}) of samples were measured by thermal desorption of argon.

The amount of HPA acid sites was determined by adsorption of nitroxyl radicals. EPR spectroscopy was used for measuring the adsorption of radicals on the surfaces of the HPA and its salts. The X-band EPR spectra were measured on an ERS-221 spectrometer. The microwave power in the resonator was 3 mW. The sensitivity of the spectrometer was 3×10^{10} spin/G at a time constant of 1 s. The microwave radiation frequency and magnetic field were measured with a ChZ-64 frequency meter and an MJ-100R magnetometer, respectively. The samples (10–20 mg) of the HPA and its salts were precalcined either in a vacuum or in an oxygen atmosphere directly in glass ampules ($d = 4$–6 mm). HPA samples PW-1 and PW-2 were prepared by calcination at 120 and 200°C, respectively, in a vacuum for a day, whereas HPA samples PW-3 and PW-4 were calcined at 200°C in an oxygen atmosphere for 2 and 8 h, respectively. Salt samples NaPW ($NaH_2PW_{12}O_{40}$), Na_2PW ($Na_2HPW_{12}O_{40}$), and Na_3PW ($Na_3PW_{12}O_{40}$) were calcined at 200°C in an oxygen atmosphere for 2 h. After cooling to room temperature, 1 ml of a nitroxyl radical solution in hexane (0–4 μmol/ml) was poured into the ampule. To prevent spectral line broadening, oxygen was removed by successively freezing and thawing the solutions in a vacuum. Sealed samples were allowed to stand for one or two weeks for equilibration. The amount of adsorbed radicals was determined by the decrease in their concentration in the liquid phase over the sample, as measured by EPR spectroscopy. The adsorption a of radicals was calculated from the equation $a = \frac{(C_0 - C_i)V}{m}$, where C_0 and C_i are the initial and final concentrations of a radical (μmol/ml), m is the sample weight (g), and V is the solution volume (ml). To evaluate the amounts of acid sites, we determined ultimate adsorption values, which correspond to plateaus in adsorption isotherms.

Kinetic measurements [18]. BHT dealkylation was performed in a thermostated glass reactor equipped with a magnetic stirrer and reflux condenser. BHT (9.8 g, 0.044 mol) was placed in the reactor and heated to 118°C. The moment at which a catalyst (2 wt %) was added was taken as the beginning of reaction. The reaction mixture was sampled at regular intervals; the catalyst was removed by shaking with a chloroform–water mixture (1 : 5, by volume), and the organic layer was analyzed by GLC. GLC analysis was performed on a Tsvet-500 chromatograph with a glass column (1 m × 3 mm) packed with 25% SE-30 on Chromosorb W and a flame-ionization detector under conditions of temperature programming from 90 to 270°C (20 K/min). Calibration coefficients for reactants and reaction products were determined with the use of model mixtures of corresponding alkylphenols. The conversion of BHT was lower than 50% with 100% selectivity for the formation of 2-*tert*-butyl-4-methylphenol. Isobutylene oligomers, which were formed in small amounts, were not taken into account in these calculations. First-order reaction

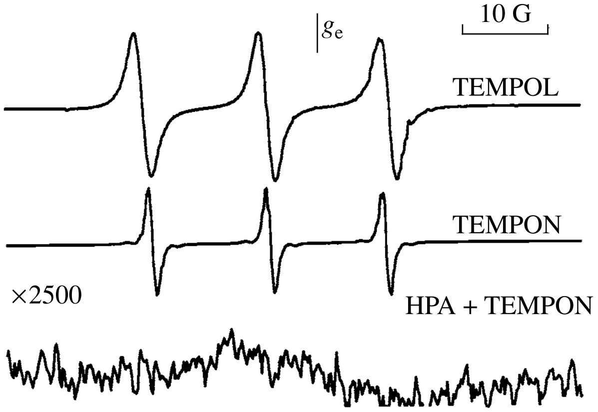


Fig. 1. EPR spectra (25°C) of nitroxyl radicals in hexane and on the surface of $H_3PW_{12}O_{40}$ (the amount of adsorbed radicals is $\sim 2.6 \times 10^{15}$ spin).

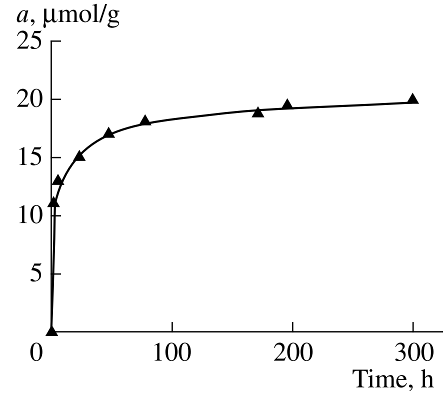


Fig. 2. Kinetics of TEMPOL adsorption on $H_3PW_{12}O_{40}$ (calcined at 120°C in a vacuum for 24 h) from a hexane solution.

rate constants were calculated by the equation $k = \frac{1}{t}\ln\frac{[\mathrm{BHT}]_0}{[\mathrm{BHT}]}$.

RESULTS AND DISCUSSION

Figure 1 shows the experimental EPR spectra of TEMPON and TEMPOL nitroxyl radicals in hexane solutions. The isotropic spectra of radicals dissolved in hexane are consistent with published data [7]. We failed to detect the anisotropic signal of a nitroxyl radical adsorbed on the surface of HPA. This is most likely due to the disproportionation of radicals on the surface, which exhibits strong proton acidity.

Adsorption of TEMPOL on HPA. Figure 2 demonstrates the kinetics of adsorption of the TEMPOL radical on the surface of HPA. It can be seen that the equilibration time in the system is ~200 h at 25°C. Because of this, all subsequent experiments were performed at contact times of 200–240 h. For all test systems, adsorption isotherms are of the L2 type (Fig. 3) [19]. The table summarizes maximum adsorption values.

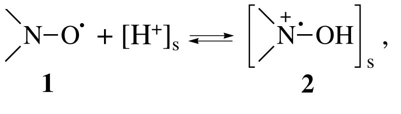
The presence of crystallization water significantly affects the adsorption of radicals. According to adsorption measurements (Fig. 3), adsorption increases with the amount of water in the system. Thus, $C_{\mathrm{TEMPOL}} = 28 \pm 8$ µmol/g for HPA calcined at 120°C in a vacuum for a day (Fig. 3, curve *3*), whereas $C_{\mathrm{TEMPOL}} = 4$ µmol/g for HPA calcined at 200°C in oxygen for 2 h (Fig. 3, curve *1*). This is inconsistent with the order of increasing strength and amount of acid sites on the surface of HPA [5] and, most likely, can be explained by an increase in the solubility of the radical in crystallization water (5–7 water molecules are the constituents of $H_3PW_{12}O_{40}$ calcined at 120°C). On this basis, samples free of crystallization water (which was completely removed by calcination at 200°C) were used in subsequent experiments.

Figure 3 shows the adsorption isotherms of the TEMPOL radical on HPA dehydrated under various conditions. It can be seen that adsorption depends on several parameters: calcination temperature, calcination time, and gas-phase composition. The influence of each particular parameter remains unclear. Published data indicate that the removal of water at 200°C resulted not only in a disordered crystal lattice of HPA [1] but also in partial degradation of HPA molecules on the surface [19]. A likely consequence of these processes is an increase in the amount of surface acid sites, which was observed upon sample calcination in a vacuum.

The degree of substitution of sodium cations for HPA protons affects only slightly the adsorption of the TEMPOL radical (table). The adsorption values normalized to specific surface area (N_{TEMPOL}) are similar in all of the $Na_xH_{3-x}PW_{12}O_{40}$ ($x = 0$–3) samples treated in oxygen at 200°C.

Adsorption of TEMPON on HPA. The adsorption isotherms of the TEMPON radical on HPA and its sodium salts belong to the L2 type (Fig. 4), as in the case of the adsorption of the TEMPOL radical. The adsorption values (C_{TEMPON}, table) decrease in the order $H_3PW_{12}O_{40} > Na_2HPW_{12}O_{40} > Na_3PW_{12}O_{40}$. A comparison between the adsorption values of the two radicals on HPA demonstrates that C_{TEMPON} is higher than C_{TEMPOL} by a factor of ~2. This difference in adsorption values can be explained by different interactions of adsorbed radicals with each other on the surface of HPA.

According to published data, nitroxyl radicals can be protonated in strong acid solutions [20, 21] in the following manner:



$$\rangle N{-}O^{\bullet} + [H^+]_s \rightleftarrows \left[\rangle \overset{+\bullet}{N}{-}OH\right]_s, \qquad \text{(I)}$$

1 2

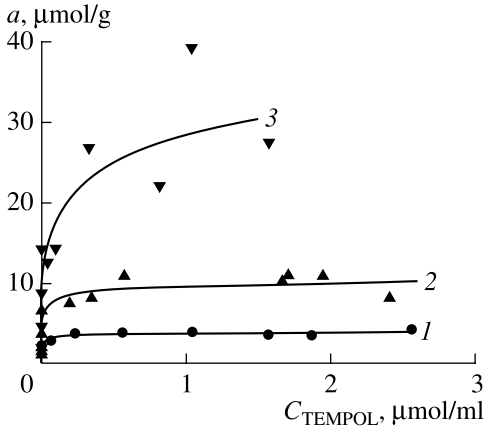


Fig. 3. Isotherms of TEMPOL adsorption on $H_3PW_{12}O_{40}$ from a hexane solution at 25°C. Sample preparation conditions: (*1*) O_2, 200°C, 2 h; (*2*) vacuum, 200°C, 24 h; and (*3*) vacuum, 120°C, 24 h.

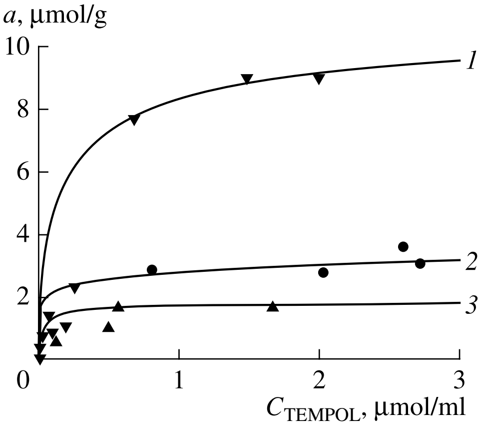
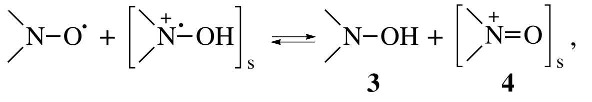
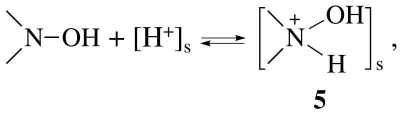


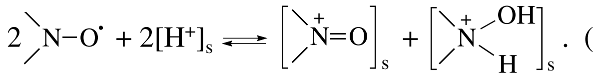
Fig. 4. Isotherms of TEMPON adsorption from (*1*) $H_3PW_{12}O_{40}$, (*2*) $Na_2HPW_{12}O_{40}$, and (*3*) $Na_3PW_{12}O_{40}$ from a hexane solution at 25°C. The samples were heated at 200°C in an oxygen atmosphere for 2 h.



(II)



(III)



(IV)

Therefore, the most probable reason for the disappearance of paramagnetism (the absence of an anisotropic EPR signal due to a radical on the surface of HPA) consists in the disproportionation of nitroxyl radicals to form oxoammonium salts and hydroxylamines by mechanisms (I)–(III) with overall reaction (IV) [20, 21].

Because HPA is a sufficiently strong acid, it is to be expected that reaction equilibrium (IV) is strongly shifted to the right. Hydroxylamines **3**, which are stronger bases than the nitroxyl radicals, formed at step (II) are not desorbed into the liquid phase [22]. As a result of this, the stoichiometry of adsorption is retained: two radicals from the liquid phase are adsorbed per two acid sites.

Evidently, the observed difference in the adsorption of radicals on HPA and its salts (table) is due to the presence of different functional groups in the radical structures (keto and hydroxyl groups in TEMPON and TEMPOL, respectively).

According to IR-spectroscopic data, an intramolecular hydrogen bond can be formed in the TEMPOL molecule [23, 24]. Consequently, the formation of an intermolecular hydrogen bond may be expected in the

Main characteristics of the test samples

Sample	Sample treatment conditions	S_{BET}, m^2/g	Adsorption				$k \times 10^4$, s^{-1}**	$k_{H_s}^{***}$, g µmol^{-1} s^{-1}
			C_{TEMPOL}, µmol/g	N^*_{TEMPOL}	C_{TEMPON}, µmol/g	N^*_{TEMPON}		
PW-1	vacuum, 120°C, 24 h	–	28 ± 8	–	–	–	–	–
PW-2	vacuum, 200°C, 24 h	7	11	1.22	–	–	–	–
PW-3	oxygen atmosphere, 200°C, 2 h	4	4	0.44	9.1	1.76	14.4	160
PW-4	oxygen atmosphere, 200°C, 8 h	–	6	–	–	–	–	–
NaPW	oxygen atmosphere, 200°C, 2 h	12	12	0.78	–	–	–	–
Na_2PW	oxygen atmosphere, 200°C, 2 h	13	11	0.66	2.8	0.18	0.9	30
Na_3PW	oxygen atmosphere, 200°C, 2 h	13	12	0.72	1.5	0.06	0	0

* N_{TEMPOL} and N_{TEMPON} are the amounts of radicals adsorbed per HPA molecule (landing surface area of ~130 Å^2 [19]).

** BHT dealkylation reaction (melt, 118°C, 2 wt % catalyst) [18].

*** Rate constant calculated on a proton-site basis ($k_{H_s} = k/C_{TEMPON}$).

adsorption of this radical on the surface of HPA from hexane. This may be responsible for the enhanced affinity of TEMPOL molecules for the surface of HPA salts (whose acidity is lower than that of HPA), as compared with TEMPON molecules, which cannot form hydrogen bonds. In turn, this enhanced affinity has the result that, unlike TEMPON, TEMPOL can be sorbed at weaker acid sites.

It is highly probable that the occurrence of a hydrogen bond between the TEMPOL radicals adsorbed on a surface increases the effective surface area occupied by an adsorbed radical to create considerable steric hindrances for adsorption at the neighboring proton site of HPA. Therefore, on bulk HPA, where the surface density of proton sites is high, the maximum amount of adsorbed TEMPOL radicals is much smaller than that of TEMPON radicals.

BHT dealkylation reaction. The reaction of BHT dealkylation in a melt was used as a test reaction for studying the relationship between catalytic activity and the amount of HPA surface acid sites, which were determined by the spin probe method. The table summarizes data on the catalytic activity of the test samples. Previously, it was found that the catalytic activity (k) of HPA correlates with the degree of substitution of sodium ions for protons [18]. The results suggest a correlation between the catalytic activity of samples and the concentration of acid sites determined by the adsorption of TEMPON (C_{TEMPON}).

It can be seen in the table that not only the concentration (C_{TEMPON}) but also the catalytic activity of proton centers ($k_{H_s} = k/C_{\text{TEMPON}}$) decreased with the degree of substitution of Na^+ cations in HPA. The highest value of k_{H_s} was observed in $H_3PW_{12}O_{40}$, whereas the lowest value was observed in the completely substituted sodium salt. The activity of the disubstituted salt was somewhat higher than that of the completely substituted sodium salt and much lower than the activity of $H_3PW_{12}O_{40}$. As the Na^+ cation content of HPA is decreased, C_{TEMPON} increases in the same order.

Thus, the results obtained in this work indicate that the spin probe method can be used for determining the amounts of proton acid sites in HPA and its salts. It is reasonable to use the TEMPON radical for this purpose. This radical is selectively adsorbed on stronger acid sites, which are active in catalytic reactions. The procedure developed for the adsorption of nitroxyl radicals in combination with catalytic tests allowed us to evaluate changes in the strength of proton sites on the surfaces of HPA and its salts. Analogously, spin probes can be used for studying Brønsted acidity in other solid catalysts.

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