

Polyaniline Supported Heteropolyacid ($\text{H}_4\text{SiW}_{12}\text{O}_{40}$) as the Catalyst for MTBE Synthesis

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A polyaniline-supported dodecatungstosilicic acid $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ catalyst was tested in the electrophilic addition of methanol to isobutene resulting in methyl-*tert*-butyl ether. The activity of the catalyst is poor after pretreatment in helium gas, but increases one order of magnitude after activation in air at 473 K. FTIR and XPS investigations indicated that the latter treatment is accompanied by the migration of protons from the bulk of the polymer matrix to the surface, thus increasing the concentration of the Brønsted acid centers considered to be catalytically active sites. © 1999 Academic Press

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INTRODUCTION

In a series of earlier publications the present authors studied the physicochemical and catalytic properties of catalysts containing heteropolyacids supported on conjugated polymers: polyacetylene (1), polypyrrole (2), and polyaniline (3). In all cases and independently of the method applied, doping of the polymer resulted in the formation of a catalytic system in which positive charge acquired by the polymer fibers was neutralized by heteropolyacid (HPA) anions. Such systems exhibit acidity high enough to enable the catalytic dehydration of ethanol to ethylene and/or diethyl ether. This activity is connected with the fact that HPA anions are present at the surface mostly or exclusively in the form of hydrogen anions such as $\text{H}_2\text{PW}_{12}\text{O}_{40}^-$ or $\text{HPW}_{12}\text{O}_{40}^{2-}$ (4, 5).

In the case of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ doped polypyrrole (2), it was observed that activation of the catalyst by heating at 593 K for 1 h in a current of air distinctly increased its activity in ethanol conversion. The activity was twice as high as that of the catalyst standardized in pure helium gas. This effect was assigned to the partial oxidative, or hydrolytic, or joint oxidative–hydrolytic degradation of the polymer

leading to heavy crosslinking of the polymer chains and re-generation of free heteropolyacid. The transformation of $\text{H}_2\text{PW}_{12}\text{O}_{40}^-$ or $\text{HPW}_{12}\text{O}_{40}^{2-}$ into neutral acid molecules was considered to result in an increase in the acid–base activity due to the higher acid strength of more strongly protonated acid species. It was also suggested that HPA molecules released by the polymer matrix may migrate to the polymer surface, thus increasing the concentration of acid sites accessible for ethanol molecules supplied from the gas phase.

From the three conjugated polymers studied by us as support for HPA, polyaniline (PANI) was thermally and chemically most stable and therefore it has been chosen for the further studies described in the present paper. The primary aim of this research was the search for HPA-based catalysts for the electrophilic addition of alcohols and water to olefins producing ethers and alcohols. Because of thermodynamic reasons, these reactions must be carried out at low temperature and hence need very active catalysts exhibiting strong Brønsted acidity. Heteropolyacids fulfill this condition very well and have found already industrial application in the liquid phase hydration of olefins. In the present research we studied the vapor phase reaction of methanol with isobutene resulting in the formation of methyl-*tert*-butyl ether (MTBE), an important additive for automotive fuel. Polyaniline-supported tungstosilicic acid $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (SiW/PANI) was used as the catalyst. The same reaction was previously studied by us at 313–353 K, using unsupported $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ as the catalyst (6).

Doping of the polyaniline with heteropolyacids leads to the protonation of the nitrogen atoms in the polymer chains. The resulting positive charge is neutralized by the HPA anions migrating into the bulk of the polymer matrix (3).

Heteropolyacids as the catalysts for MTBE gas phase synthesis were studied by several authors. Shikata *et al.* investigated unsupported (7) and silica-supported (8) Keggin- and Dawson-type heteropolyacids. The effect of pseudo-liquid-phase behavior in $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ was investigated by Shikata and Misono (9).

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Catalytic and physico-chemical properties of unsupported $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ were described by Baronetti *et al.* (10). Preliminary experiments have shown that polyaniline-supported $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ standardized in helium before catalytic experiments was a rather poor catalyst for MTBE synthesis and conversion of the order of 2% at 333 K was obtained. However, subsequent catalyst regeneration by heating of the catalyst at 473 K in a current of air rendered it 10 times more active. Hence the elucidation of the nature of this activation process became the second aim of the present study.

EXPERIMENTAL

The catalyst contained 38.5 wt% $\text{H}_4\text{SiW}_{12}\text{O}_{40}$. Its synthesis involved the preparation of polyemeraldine base by condensation-polymerization of aniline in aqueous HCl using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as the oxidant, followed by deprotonation with aqueous ammonia. Polyemeraldine base was then protonated with heteropolyacid by stirring it for 24 h in a 0.1 M solution of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ in acetonitrile. Excess heteropolyacid was removed by washing the product with acetonitrile. Full details of this procedure are given in (5). The BET surface area of the catalyst was $14.6 \text{ m}^2/\text{g}$. FTIR spectra of the catalyst were registered with a Bruker IFS 48 spectrometer using KBr pellets.

The X-ray photoelectron spectra were taken on protonated polyaniline powders pressed onto a copper mesh using an VSW ESCA 100 spectrometer. Mg K_α radiation of 1253.6 eV and a pressure lower than 5×10^{-3} Pa were applied. This low pressure was achieved after 24 h evacuation at 300 K. As internal standard the C $1s = 284.6$ eV line was used. In the course of recording, the samples were cooled to 150 K to improve the quality of the spectra.

A constant flow quartz microreactor was used for the catalytic experiments. Helium carrier gas was at first saturated with methanol vapor and subsequently mixed with a current of isobutene ($i\text{-C}_4$) supplied from a steel cylinder (p.a. Aldrich). Two series of experiments were carried out at a fixed methanol partial pressure of 12.2 kPa and an isobutene partial pressure of 7.0 or 14.2 kPa, thus giving an isobutene/methanol molar ratio R close to 0.5 or 1.2. The catalytic reactor was connected on line with a Hewlett-Packard 6980 II A gas chromatograph; a Porapak QS filled column was used for chromatographic analyses. The experiments were carried out with a 0.5-g sample (containing 0.193 g $\text{H}_4\text{SiW}_{12}\text{O}_{40}$) at 313, 333, and 353 K. At a gas flow of 0.030 L/min, the contact time of the feed was 4 s. Before catalytic experiments the catalyst was kept for 30 min in a current of helium at 373 K and then the first run (lasting usually 6 h) was carried out. Subsequently, the catalyst was treated for 1 h with a current of air at 473 K and the catalytic test was carried out again for 6 h. In some cases the "regeneration in air-catalytic test" cycles were repeated several times.

RESULTS

In most of the experiments the only product detected by gas chromatography was methyl-*tert*-butyl ether. Only at an isobutene/methanol molar ratio of $R = 1.2$ did traces of isobutene dimer occasionally appear.

Figure 1 shows the results of a typical catalytic run carried out at 333 K and an isobutene/methanol molar ratio $R = 1.2$. Curves I and II in Fig. 1a show the conversion of isobutene ($\alpha = \frac{p_{i\text{-C}_4}^0 - p_{i\text{-C}_4}^t}{p_{i\text{-C}_4}^0} \cdot 100\%$, where $p_{i\text{-C}_4}^0$ and $p_{i\text{-C}_4}^t$ are isobutene partial pressures in the feed and at the reactor outlet,

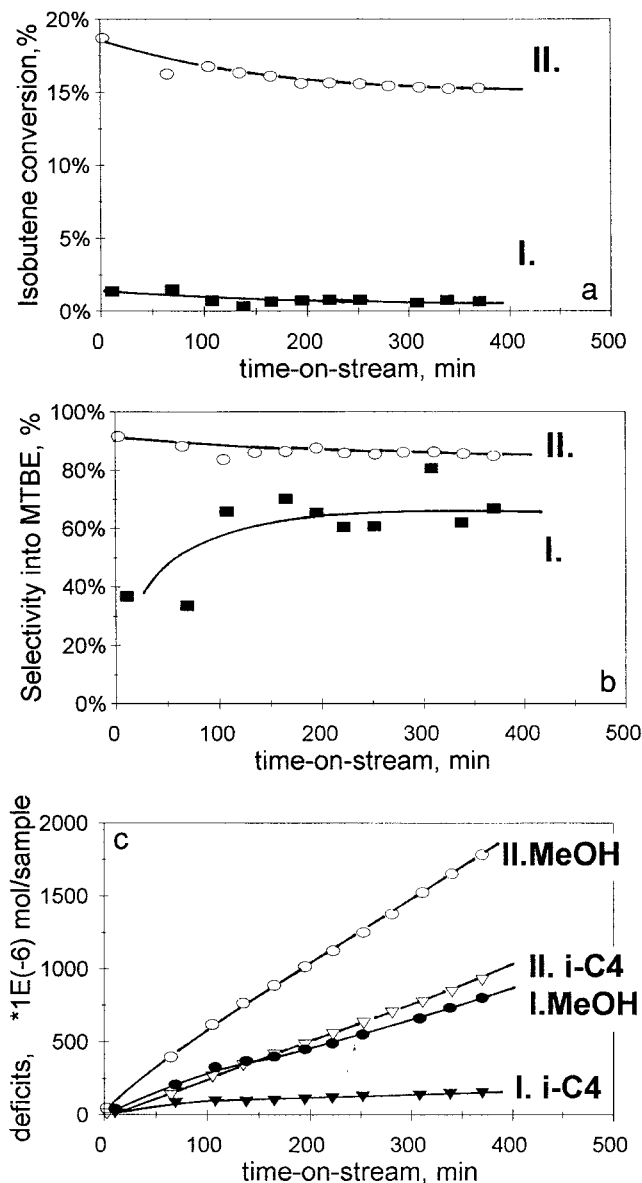


FIG. 1. Typical catalytic run on the catalyst standardized in helium at 373 K (I) and regenerated in air at 473 K (II). (a) Isobutene conversion, (b) selectivity into MTBE, (c) deficits of isobutene and MeOH cumulated on the catalyst during the run, versus time-on-stream. Temperature 333 K; isobutene/methanol molar ratio $R = 1.2$.

respectively) on the catalyst standardized in helium at 373 K and on the catalyst regenerated in air at 473 K, respectively, both as a function of time on stream. The curves in Fig. 1b represent the selectivity ($s = \frac{p_{MTBE}}{p_{i-C_4}^o - p_{i-C_4}^r} \cdot 100\%$, where p_{MTBE} is partial pressure of MTBE at the reactor outlet) of the isobutene transformation into MTBE also as a function of time on stream. It should be observed that the mass balance of the products in the gas phase always exhibited a deficit of isobutene as well as methanol. By integration of the deficits obtained from the chromatographic analyses, the cumulated deficit could be calculated as described in a previous publication (6). The deficits cumulated in the course of experiments carried out with the samples standardized in helium and regenerated in air are shown in Fig. 1c. Repetition of the activation in air and catalytic test showed that the shapes of all curves were practically identical with those obtained after the first activation in air.

The dependence of the isobutene conversion on temperature for the first runs on the catalysts standardized in helium and the catalyst regenerated in air is shown in Fig. 2 and the effect of temperature on the selectivity is illustrated in Fig. 3.

Figure 4 shows FTIR spectra of the pristine catalyst standardized in helium for 0.5 h at 373 K, the catalyst

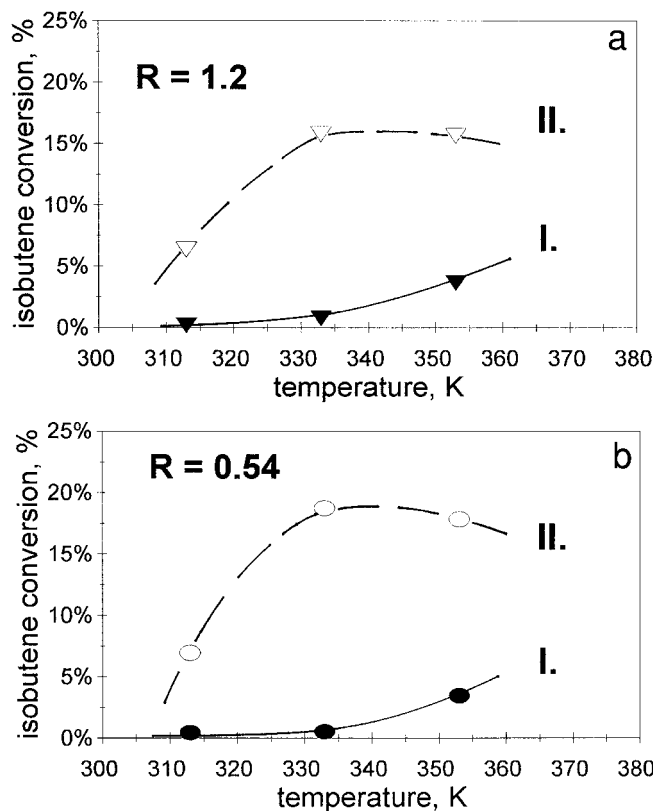


FIG. 2. Temperature dependence of the isobutene conversion for isobutene/MeOH molar ratio $R = 1.2$ (a) and $R = 0.54$ (b) of samples standardized in helium at 373 K (I) and regenerated in air at 473 K (II).

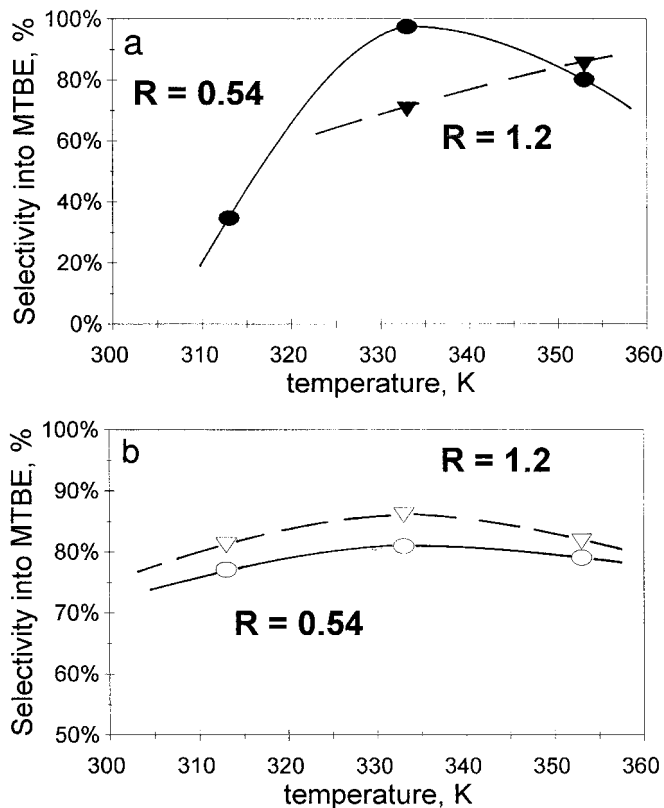


FIG. 3. Selectivity of isobutene transformation into MTBE versus reaction temperature. (a) Sample standardized in helium at 373 K and (b) regenerated in air at 473 K.

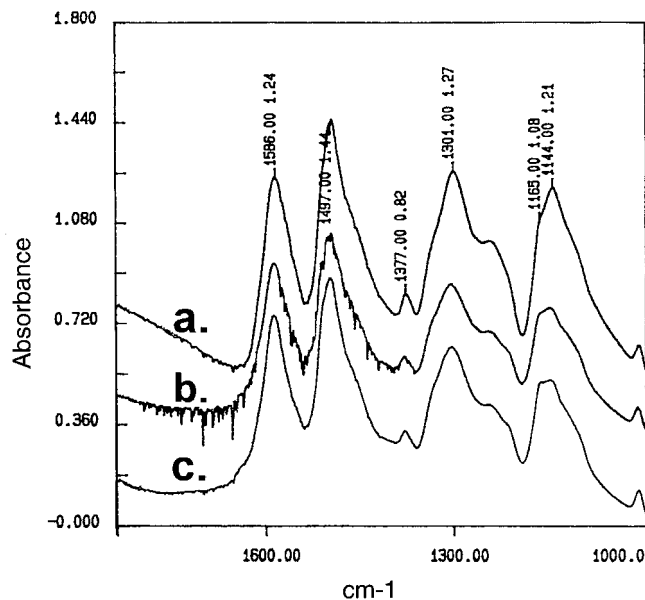


FIG. 4. FTIR spectra of polyaniline-supported $H_4SiW_{12}O_{40}$ samples. (a) Standardized in helium for 0.5 h at 373 K, (b) standardized in air for 1 h at 473 K without contact with reagents, (c) after two cycles: test-regeneration in air at 473 K—test.

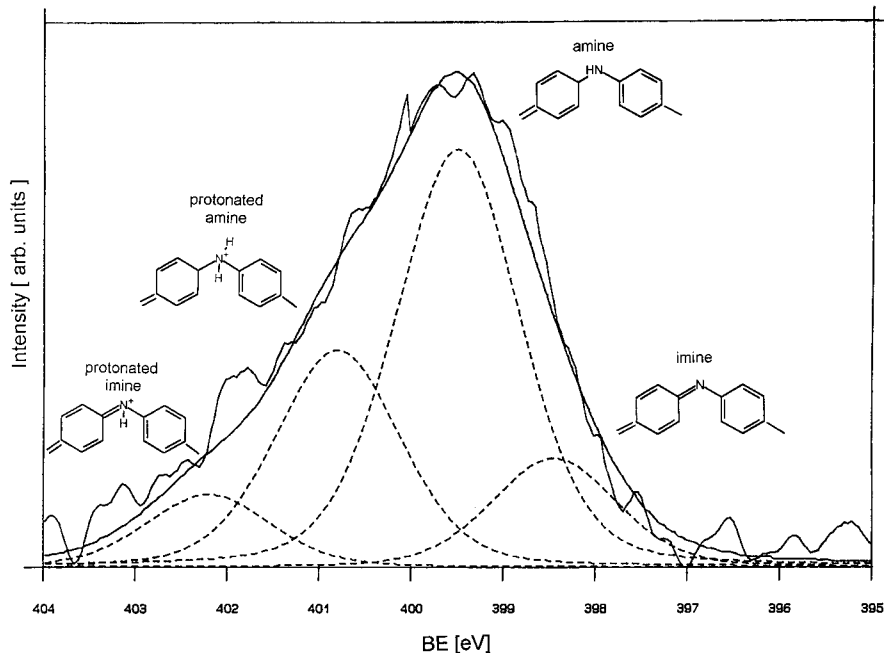


FIG. 5. N 1s XPS spectrum of polyaniline-supported $H_4SiW_{12}O_{40}$ standardized in helium for 0.5 h at 373 K.

standardized in air for 1 h at 473 K without contact with reagents, and the catalyst after two cycles: catalytic test—regeneration in air at 473 K—catalytic test.

Figure 5 presents the XPS spectrum N 1s of the pristine catalyst standardized in helium at 373 K. Spectra of catalyst sample standardized in air at 473 K, and the same

catalyst which after the catalytic runs has been regenerated in air at 473 K had the same shape as the spectrum of pristine sample. XPS spectrum O 1s for the pristine sample is given in Fig. 6. The binding energies and peak contributions of XPS spectra of oxygen and nitrogen are listed in Table 1.

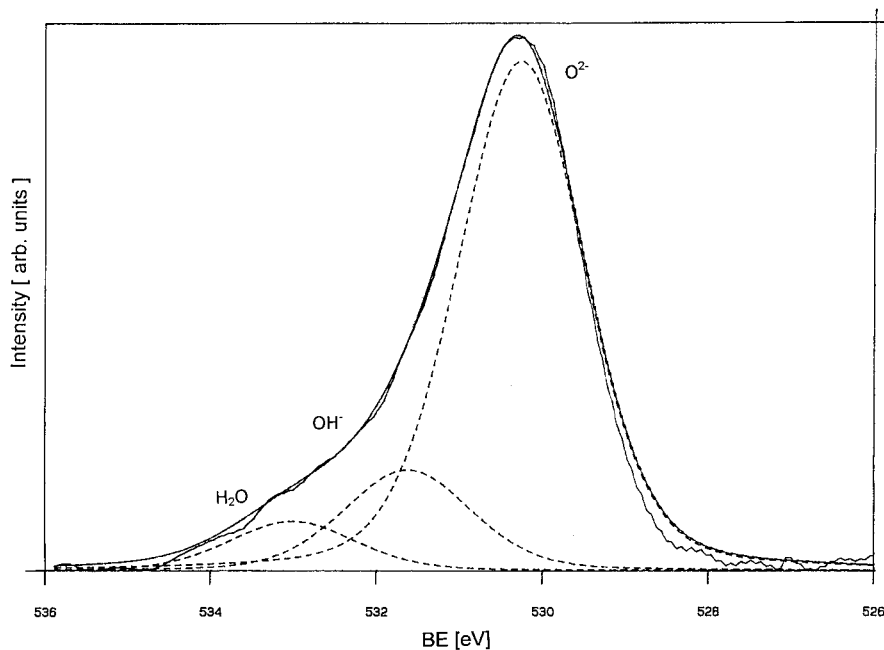


FIG. 6. O 1s XPS spectrum of polyaniline-supported $H_4SiW_{12}O_{40}$ standardized in helium for 0.5 h at 373 K.

TABLE 1

The Binding Energies and Peak Contributions of XPS Spectra of Oxygen and Nitrogen

Sample	-N=	-NH-	-NH ₂ ⁺ -	-NH ⁺ =
Nitrogen N 1s (binding energies, eV)				
a	398.5	399.5	400.8	402.2
b	398.6	399.5	400.7	402.0
c	398.5	399.6	400.7	402.1
Nitrogen N 1s (peaks contribution, %)				
a	13	51	27	9
b	13	40	32	15
c	11	35	38	16
Oxygen O 1s (binding energy, eV)				
a	530.3	531.6		533.0
b	530.25	531.8		533.15
c	530.4	531.7		533.2
Oxygen O 1s (peaks contribution, %)				
a	77	15		8
b	73	15		12
c	61	24		15

Note. a, sample standardized in helium for 0.5 h at 373 K; b, sample standardized in air for 1 h at 473 K without contact with reagents; c, sample after two cycles: test-regeneration in air at 473 K-test.

DISCUSSION

Figure 1a shows that the activity of polyaniline-supported dodecatungstosilicic acid is poor after standardization in helium gas and that it increases one order of magnitude after the additional treatment in air at 473 K for 1 h. In some cases after the run on such activated catalyst the activation in air was repeated but no essential further increase in activity was observed. The activation improves also the selectivity. As Fig. 1b shows in the first run (at 333 K and $R=1.2$) after standardization in helium it was initially about 40% and gradually increased to about 60%. After the subsequent standardization in air it was 91% initially and only slightly decreased when reaching the steady state. Generally after activation in air, the selectivity was almost constant at all temperatures and reached values of 77–86 mol%.

Selectivity observed in the present research was similar to that obtained in (8) where at $R=1.0$ silica-supported H₄SiW₁₂O₄₀ catalyst pretreated in N₂ at 423 K was used. At 323 K selectivity in (8) was 82.5% and at 383 K it was 29.7%. The same authors, when investigating Amberlyst-15 resin as the catalyst, obtained selectivities of 84.1 and 28.9% at 323 and 383 K, respectively.

Figure 1a shows also that the activity of the catalyst was fairly stable during 6 h at 333 K and an isobutene/methanol molar ratio $R=1.2$. The same was observed at 313 and 353 K and $R=0.54$.

As already said in the previous section, the only gaseous product observed in chromatographic analysis was methyl-*tert*-butyl ether and only occasionally traces of isobutene dimer appeared. However, the mass balance indicated always a certain deficit of both isobutene and methanol, which was the reason why no 100% selectivity was observed (Fig. 1c). A deficit of isobutene and methanol was observed in our previous study (6) in which the formation of MTBE on unsupported H₄SiW₁₂O₄₀ was studied. Deficit of isobutene was also observed by Shikata *et al.* (8) in the case of silica-supported heteropolyacids. Additional sorption and FTIR study (11) led to the conclusion that deficit of methanol was due to the penetration of its polar molecules into the bulk of HPA crystallites. On the other hand, no such volume sorption of nonpolar isobutene was observed and in this case formation of isobutene oligomer at the external surface took place accompanied by visually observed darkening of the white pure H₄SiW₁₂O₄₀ catalyst. In the present investigation independent sorption experiments have shown appreciable sorption capacity of the polyaniline supported catalyst. At room temperature and 8.70 kPa 8.6 wt% of butene was taken up and 8.3 wt% of methanol was taken up in another experiment. Considering the BET surface area 14.6 m²/g of the our catalyst this corresponds to about 18 monolayers of isobutene or 17 monolayers of methanol. The similarity of both figures seems to suggest that there exists spatial limitation of sorption typical of sorbents in which micropores dominate. However, it should be observed that at room temperature the behavior of adsorbed molecules was different. While sorption of methanol was fully reversible, the sorption of isobutene was irreversible, indicating the oligomerization under these conditions (room temperature). It seems logical to assume that deficit of isobutene in the present research on supported catalyst (when no crystalline HPA was present) was due to the formation of oligomers in the pores and/or at the external surface and deficit of methanol (possibly also in the form of MTBE) due to its adsorption mainly in the micropores. In the experiment, the results of which are shown in Fig. 1, the final deficit of methanol in run I corresponded to 34% of catalyst sorption capacity and that in run II corresponded to 46%. Analogous figures for isobutene are 17 and 92%, respectively. Due to the fact that the catalyst was black, no visual observation of its expected darkening was possible. At 333 K and $R=1.2$, the deficit observed during steady state was distinctly lower in the first run with the sample standardized in helium than it was in the second run after regeneration in air. Simultaneously the above-mentioned increase of selectivity was observed, which indicates that the increase of the rate of MTBE formation was higher than the simultaneous increase of the rate of deficit growth. In fact in the case of catalyst standardized in helium (Fig. 1c) for 1 mol of isobutene transformed into MTBE 0.71 mol of i-C₄ remained at the catalyst forming

deposit. On the other hand, after catalyst had been activated in air this figure decreased to 0.16 only. It should be here observed that from the data given by Shikata *et al.* (8) this value could be calculated as 1.2 for unsupported $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ and 1.4 for Amberlyst-15, both at 383 K. For silica-supported $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ it was 0.20 at 323 K and 2.11 at 383.

Figure 2 shows that the effect of temperature on isobutene conversion is different depending on the catalyst pretreatment. After standardization in helium, conversion is generally very low but increases with temperature. On the other hand, after additional treatment in air catalysts are much more active and conversion passes through a flat maximum at about 333 K. In the former case the yield of MTBE ($\beta = \frac{p_{\text{MTBE}}}{p_{\text{i-C}_4}^0} \cdot 100\%$) is much lower than that calculated for the equilibrium state. For example at 313 K and $R = 0.54$ the observed yield of MTBE corresponded only to 0.5% of the equilibrium yield and even at 353 K it was 12% of the equilibrium yield, thus indicating that the reverse reaction, the decomposition of MTBE, can be neglected.

On the other hand, the yield observed at 333 K in the case of samples activated in air was 30% of the theoretical yield and even 63–68% at 353 K, indicating an increasing participation of the reverse reaction and explaining the leveling off of the observed isobutene conversion at 353 K. The equilibrium yield β (%) has been calculated from the equation

$$K_p = \frac{p_{\text{MTBE}}}{p_{\text{i-C}_4} p_{\text{CH}_3\text{OH}}} = \frac{100 \beta}{(100 - \beta)(100 p_{\text{CH}_3\text{OH}}^0 - \beta p_{\text{i-C}_4}^0)}, \quad [1]$$

where $p_{\text{i-C}_4}^0$ and $p_{\text{CH}_3\text{OH}}^0$ denote partial pressures of isobutene and methanol in the feed, respectively, and $p_{\text{i-C}_4} = p_{\text{i-C}_4}^0 \frac{100 - \beta}{100}$, $p_{\text{MTBE}} = p_{\text{i-C}_4}^0 \frac{\beta}{100}$, and $p_{\text{CH}_3\text{OH}} = p_{\text{CH}_3\text{OH}}^0 - \frac{\beta}{100} p_{\text{i-C}_4}^0$ are the partial pressures of isobutene, MTBE, and methanol at the equilibrium state, respectively. The equilibrium constant K_p was obtained from the equation

$$\ln K_p = \frac{7300}{T} - 4.75 \ln T + 0.0117 T - 4.8 \times 10^{-6} T^2 + 2.5 \times 10^{-5} T^3 + 4.80, \quad [2]$$

given in (12).

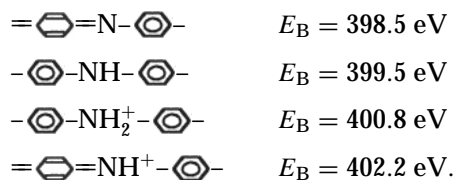
Figure 3 shows that in the first run at $R = 0.54$ selectivity passes through a maximum at 333 K. At $R = 1.2$ an analogous maximum seems to be shifted to 353 K or higher temperature. The selectivity in the run after regeneration in air exhibits a flat maximum (Fig. 3b) at 333 K. It is somewhat higher for $R = 1.2$ than for $R = 0.54$.

FTIR spectra of undoped and $\text{H}_3\text{PMO}_{12}\text{O}_{40}$ doped polyaniline were described by us in (5). In the spectral region above 1000 cm^{-1} they all were very much similar

with the exception of the region in the 1100–1200 cm^{-1} range in which undoped polyaniline exhibited a band at 1164 cm^{-1} ascribed to the $-\text{N}=\text{C}_6\text{H}_4=\text{N}-$ vibration. On increasing protonation this band gradually vanished and at 1140 cm^{-1} a band grew corresponding to the vibrations of $=\text{C}_6\text{H}_4=\text{NH}^+-\text{C}_6\text{H}_4-$ or $-\text{C}_6\text{H}_4-\text{NH}_2^+-\text{C}_6\text{H}_4-$ (C_6H_4 and C_6H_5 are quinone and benzene rings, respectively). Below 1000 cm^{-1} , where the vibrations of the Keggin unit were observed, no changes were observed except for some increase of the intensities, depending on the sample treatment.

In the present investigation both bands at 1144 and 1165 cm^{-1} were present in the spectra of all kinds of samples (Fig. 4). However, in the pristine sample standardized in helium the intensity of 1144 cm^{-1} band is high and 1165 cm^{-1} is present only in the form of the shoulder, thus indicating a high degree of protonation. On the other hand, in the case of samples standardized in air or heated in air after the first catalytic run the intensities of both bands are similar, or even the band at 1144 cm^{-1} predominates, thus indicating deprotonation of the polymer. All these effects are well reproducible.

N 1s XPS spectra of the same samples are given in Table 1 and also in Figs. 5 and 6. XPS spectra of polyaniline-supported $\text{H}_3\text{PMO}_{12}\text{O}_{40}$ were described in (5) and in (4, 13) spectra of polyaniline-supported $\text{H}_4\text{SiW}_{12}\text{O}_{40}$. Deconvolution of the N 1s XPS spectra in the case of various polyaniline materials was proposed previously (13). Using this method, the N 1s spectrum of our samples indicates the presence of four peaks:



Such an assignment of the N 1s peaks is strongly supported by the results of atomic potential model calculations published by Monkman *et al.* (14). They obtained the following results for N-containing moieties: 398.8 eV attributed to the imine state ($=\text{N}-$), 399.3 eV attributed to the amine ($-\text{NH}-$), and peaks at 401.5 eV ($-\text{C}_6\text{H}_4-\text{NH}_2^+-\text{C}_6\text{H}_4-$) and 402.5 eV ($=\text{C}_6\text{H}_4=\text{NH}^+-\text{C}_6\text{H}_4-$) were ascribed to the protonated nitrogen species (N^+).

No changes in their position are observed during the different treatments of the samples before XPS measurements. However, distinct changes are observed in their relative intensities (Table 1). It is clearly seen that activation of the sample in air increases the proportion of protonated nitrogen ($E_B = 401.5$ and 402.5 eV) and decreases that of amine nitrogen in the surface layer of polymer support. These effects are still stronger in the case of the sample which was taken for XPS analysis after the first run and subsequent prolonged regeneration in air.

Also the O 1s spectra indicate an increased protonation of oxygen in the surface layer. Three O 1s peaks were registered: at 530.3 eV attributed to O²⁻, 531.6 eV attributed to oxygen in the OH⁻ group, i.e., protonated oxygen atoms of the Keggin unit, and 533.0 eV attributed in (13) to oxygen in water. An interesting alternative of the previously assumed O 1s component with BE = 533.0–533.2 eV is the concept proposed by Monkman *et al.* (14). They calculated the chemical shift of the -N=O moiety using the Pauling model of atomic potential. The resulting BE equal

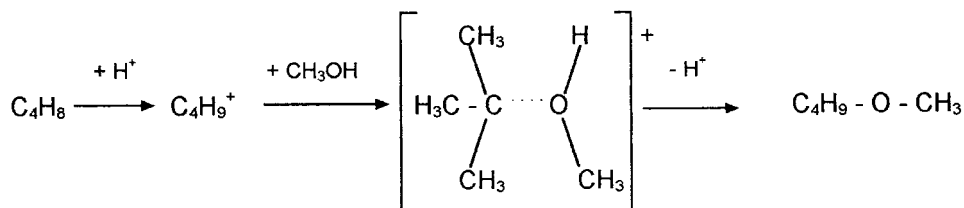
to 534.6 eV, as well as the standard values for -C(=O)-NH₂ (532.2 eV (15)), -C(=O)-O-C(=O)- (533.5 eV (16)), and hydroquinone (533.5 eV (17)), suggest that the peak at 533.3 eV may also be—at least partially—asccribed to oxygen inserted into the polyaniline matrix.

The changes in the intensities of the oxygen XPS peaks (Table 1) clearly show that protons migrating to the surface layer are bonded not only by nitrogen atoms of polyaniline but also by oxygen (II) atoms of the heteropolyanions, thus forming OH⁻ ions or H₂O molecules and decreasing the protonation of O²⁻ ions.

The W 4f_{7/2} XPS spectrum was deconvoluted into a doublet, 35.2 and 37.4 eV. This doublet was not influenced by the different treatments of the sample, indicating stability of the tungsten atoms in the Keggin unit.

The apparent discrepancy of the results supplied by the IR and XPS spectroscopies can be understood if we remember that the information obtained by the first method concerns principally the bulk of the polymer grains while that given by the second one is limited to a surface layer as thin as about 20 Å. The IR investigation shows that on heating the catalyst in air deprotonation of polyaniline in the bulk occurs. On the other hand, XPS indicates protonation of HPA anions and also of polyaniline at the surface. The increased concentration of oxygen in form of H₂O molecules suggests the oxidation of the polymer support. Hence one may conclude that activation of the catalyst by heating in air is the result of migration of protons from the bulk to the surface, hence increasing the acidity of the surface.

Protons play an essential role in MTBE formation which is a typical electrophilic addition reaction in which the protonated isobutene reacting with methanol molecule is the most probable intermediate according to Scheme 1 (6).



SCHEME 1

TABLE 2

Ratios of Conversion and Selectivity of the Supported and Unsupported HPA

Temperature (K)	R = i-C ₄ /CH ₃ OH	Conversion ratio		Selectivity ratio	
		I run ^a	II run ^b	I run ^a	II run ^b
333	1.2	0.06	1.10	0.93	0.89
353	1.2	0.32	1.38	0.93	0.89
333	0.54	0.03	1.20	1.13	0.94
353	0.54	0.21	1.09	0.98	0.96

^a Supported catalyst standardized in helium at 373 K.

^b Supported catalyst regenerated in air at 473 K.

The increased concentration of protons forming catalytic active centers at the surface is an appropriate explanation of the increase of catalytic activity.

The migration of protons might result in the formation of an electrical double layer. However, considering the fact that protonated polyaniline is a good *p*-type conductor of electricity one can suppose that positive charge of the surface is compensated by an appropriate redistribution of electrical current carriers. The simultaneous migration of HPA anions to the surface, which is also another possibility, was not confirmed because the ratio of the intensity of the W 4f peak to the sum of the intensities of all N 1s peaks was constant within the limits of experimental accuracy. No detailed mechanism of the interaction of the catalyst surface with oxygen resulting in the catalyst activation can be given on the basis of the presented data. However, it should be observed that the surface becomes richer in oxygen as the ratio of intensities of all O 1s peaks to those of N 1s increases from 7.2 to 7.9.

The results of the catalytic experiments with polyaniline-supported H₄SiW₁₂O₄₀ were compared with those obtained on unsupported crystalline HPA.

In the latter case the amount of anhydrous heteropolyacid used (0.2 g) was equal to that contained in the polyaniline sample on which catalytic tests were carried out and the conditions of catalytic runs were the same. Table 2 shows the ratios of the isobutene conversion and the selectivity to MTBE of the supported and unsupported HPA reached after different treatments. It is clear that after treatment of the catalyst in helium only a weak activity of the

supported catalyst in comparison to the unsupported HPA is observed. On the other hand, the activity of the supported HPA per 1 g of HPA is higher if the sample is treated in air. The ratio of both activities was the highest at $R=1.2$ and 353 K, reaching the value 1.38.

Owing to the low protonation of the surface the supported catalyst standardized in helium was not active. Treatment in air increasing the protonation of Keggin units dispersed over a relatively large surface of the polymer (7.3 m² per sample 0.5 g containing 0.2 g HPA) made it possible to reach an activity larger than that in crystalline H₄SiW₁₂O₄₀ with a smaller surface area (1.6 m² per 0.2 g of HPA). One may say that the reactants see larger numbers of heteropolyacid molecules on the supported versus unsupported catalyst. On the other hand, the supported catalyst always shows a somewhat lower selectivity.

CONCLUSIONS

Polyaniline-supported dodecatungstosilicic acid H₄SiW₁₂O₄₀ is weakly active in the synthesis of methyl-*tert*-butyl ether after it has been standardized in helium at 373 K. However, its activity increases one order of magnitude if it is treated in air at 473 K. FTIR results indicated that the protonation of polyaniline (NH⁺ or NH²⁺ moieties) in the bulk of polymer decreased. On the other hand, XPS indicated an enrichment of the surface in protons which were localized both on nitrogen atoms of the polymer and on oxygen atoms of the heteropolyanion in the form of OH⁻ and H₂O. The strongly acidic OH⁻ groups of the heteropolyacid are considered to be the catalytically active centers. A surface carbenium ion C₄H₉⁺ is supposed to form a transition complex with methanol [C₄H₉⁺OH(CH₃)]⁺ in the catalytic reaction.

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