Solid-state NMR and FT-IR investigation of 12-tungstophosphoric acid on TiO_2

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The chemical and dynamic nature of the tungstophosphoric acid (TPA) species adsorbed on pressed, extruded, and powdered TiO_2 support was studied by ^{31}P and ^{1}H solid-state NMR spectroscopy and diffuse reflectance FT-IR. From ^{31}P NMR and FT-IR results the TPA appeared to be present in at least five forms on the titania surface: a bulk salt phase, two weakly bound intact Keggin species, a range of partially fragmented clusters such as the 11-“defect” Keggin ion, and a range of species formed by high or complete fragmentation of the Keggin ion. The relative amount of these species varied depending on the form of the support. Adsorption was incomplete on extruded titania resulting in bulk salt formation. There was almost complete adsorption on pressed titania pellets, yielding predominantly fragmented Keggin units, along with a small amount of bulk salt. However, complete adsorption (and fragmentation) without bulk salt formation was attained by impregnation of powdered TiO_2. The acidic nature of the catalysts and the degree of TPA dispersion were investigated by solid-state ^{1}H high-speed MAS-NMR. Pure TPA salt yielded resonances at about 6.5 ppm. The catalysts yielded acidic proton resonances at about 7–8 and 10–11.5 ppm. The broad resonance observed at 7–8 ppm is due to a dispersion of acidic sites on the surface. The intensity of the acidic resonance at around 11 ppm increased with adsorption effectiveness and could, therefore, be related to the formation of hydroxonium ions upon fragmentation of adsorbed Keggin ions.

Keywords: 12-tungstophosphoric acid, titania, ^{31}P and ^{1}H MAS-NMR

1. Introduction

Tungstophosphoric acid (TPA) has been the center of a great deal of attention recently, due to the interesting catalytic properties that its particular structure imparts. These highly acidic polyanions consist of 12 WO_6 octahedra surrounding a PO_4 tetrahedron (Keggin primary structure, see figure 1). The Keggin units can form relatively stable secondary structures with water molecules spanning the space between the individual Keggin units. This secondary structure is variable and will readily change depending on the availability of water or other guest molecules. 12-tungstophosphoric acid on titania is an excellent catalyst for the cogeneration of phenol/acetone [1] and for glycol ethers production [2]. ^{31}P NMR data have been obtained in an investigation of the effects of hydration level on the Keggin structure [3]. It has also been shown that TPA supported on SiO_2 or carbon exhibits high catalytic activity [4,5]. TPA/SiO_2 and TPA/Al_2O_3–SiO_2 have been the subject of ^{31}P and ^{1}H MAS-NMR and FT-IR investigation [6,7].

In this study, we have performed ^{31}P and ^{1}H magic angle spinning (MAS) NMR and diffuse reflectance FT-IR experiments to investigate the surface structure of TPA supported on extruded, pressed, and powdered TiO_2. In previous investigations, the ^{1}H MAS-NMR spectra were obscured by the presence of high surface concentrations of Si–OH groups [6,7].

In this study, the TiO_2 used gave very little ^{1}H NMR background signal which facilitated the easy observation of acidic protons associated with TPA. The chemical shift data obtained in the ^{1}H NMR experiments is valuable as it can be readily correlated with proton Brønsted acidity [8–13], and thus yields important catalytic information. We also examined the effect of the method of preparation (impregnation time, calcination temperature, and the physical form

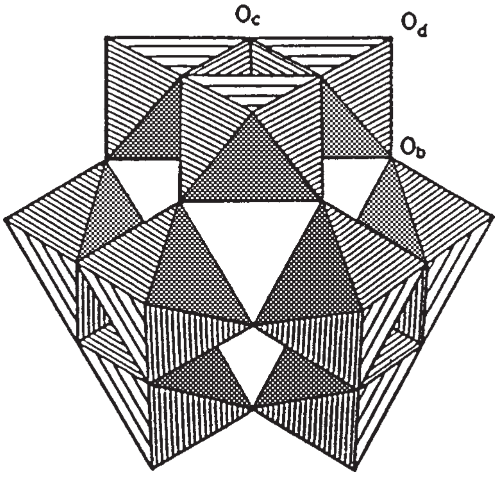

Figure 1. Keggin ion structure showing positions of W–O_d, W–O_b–O, and W–O_c–W.

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of the support during impregnation – extrudate, pellet, or powder) on the final TPA structure distribution on the catalyst surface. Another important objective was to determine if the Keggin unit remained intact during adsorption and calcining at 350 °C. ^{31}P NMR was utilized to observe the formation of different phosphorus species on the titania surface formed by intact adsorption and fragmentation of the TPA Keggin unit. Diffuse reflectance FT-IR was used to confirm the presence of intact and fragmented Keggin unit species.

2. Experimental

All catalysts were made by the incipient wetness impregnation method using an aqueous solution of TPA, with the impregnation time varying from 2 to 24 h. The catalysts were dried at 150 °C for 2 h, and then calcined between 300 and 350 °C for 2–4 h. In a typical synthesis [14], to 125 cm^3 of titania extrudates ($1/8$ inch diameter, 51 m^2/g surface area, provided by the Norton Company) was added a solution of 10 g of 12-tungstophosphoric acid in 50 ml of distilled water. The mixture was stirred to adsorb the liquid into the pores of the solid and excess removed by slow rotary evaporation. A typical loading was approximately 15–16 wt% tungsten [14]. The titania used was purchased in the extruded (E-TiO_2) and pelletized forms (P-TiO_2) from the Norton Company and from Mallinckrodt Specialty Chemicals Company, to assess the effect of the form of the support on the impregnation process.

FT-IR spectroscopy was performed on a Biorad FTS-40 equipped with a Harrick Scientific diffuse reflectance accessory. Samples were prepared to 10 wt% in KBr, and spectra acquired from 4000 to 400 cm^{-1}.

The solid-state MAS-NMR was performed on a Varian VXR-300 NMR spectrometer equipped with a Chemagnetics solids accessory and a Varian Unity 300 spectrometer. The probes used were a Chemagnetics 7 mm CP/MAS probe, and a Doty Scientific high-speed 7 mm CP/MAS probe. The resonance frequencies of ^{31}P and ^{1}H were 121.7 and 299.99 MHz, respectively. The ^{1}H spectra were referenced to an external reference sample of TMS (0 ppm), while the ^{31}P NMR spectra were referenced to a 85% H_3PO_4 solution (0 ppm). Magic angle spinning rates of between 6 and 7 kHz were employed, along with $\pi/2$ pulse widths of 10 μs for ^{31}P, and 6 μs for ^{1}H. For the single pulse (SP) ^{1}H spectra 256 transients were collected with a 2 μs pulsewidth (30°), a 160 ms acquisition time, a 100 kHz sweep width, and a relaxation delay of 1 s. For the ^{31}P SP/MAS spectra between 256 and 2048 transients were obtained with a $\pi/2$ pulse, a 10 ms acquisition time, a 100 kHz spectral width, and a relaxation delay of 20–30 s. In the case of ^{31}P, cross polarization [15] spectra were obtained using a relaxation delay of 3 s, and a contact time of 1 ms. Spin-lattice (T_1) relaxation data was obtained by the inversion–recovery method [16]. Deconvolution of spectra was performed with the Unity spectrometer software and was done in an unconstrained manner assuming Lorentzian lineshapes.

3. Results and discussion

3.1. FT-IR data

The first samples to be discussed are two catalysts prepared on pressed titania (P-TiO_2) and extruded titania (E-TiO_2) supports. Figure 2 compares the diffuse reflectance FT-IR spectra of these two catalysts with that of the pure TPA salt. Absolute quantitative analysis of spectra acquired by reflectance methods are somewhat limited by the scattering effects associated with the technique. Specifically, the observed band intensities are dependent on particle size, particle distribution, and packing density of the (TPA/TiO_2)/KBr matrices. The spectrum of pure TPA shows fundamentals at 1080, 983, 889, 798, 596, 526, 484, 427 cm^{-1}. Combinations and overtones of these bands appear from 2200 to 1110 cm^{-1}. The broad feature extending from 3800 to 2700 cm^{-1} is indicative of the water present in the KBr-diluted matrices and/or complexed to the TPA. Tentative vibrational assignments are cataloged in table 1.

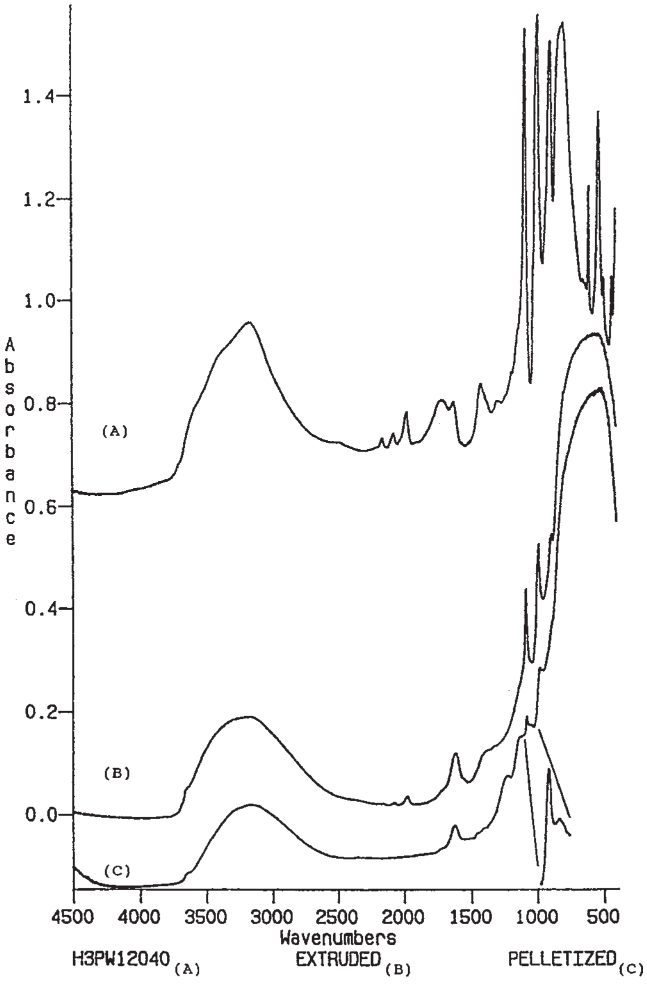

Figure 2. Diffuse reflectance FT-IR spectra of (a) TPA/KBr, (b) (TPA/E-TiO_2)/KBr, and (c) (TPA/P-TiO_2)/KBr.

Table 1
Infrared spectral assignments.

Frequency			Tentative assignments
Pure TPA	TPA/ E-TiO_2	TPA/ P-TiO_2	
3707			
	3659	3643	
3574			
3385			
3172	3179		
2489			
		2349	
2162	2161		2 (1080)
2091			
2075	2076		1080 + 983
2025			
1982			1080 + 889
1974	1973		2 (983)
1898			1080 + 798, 983 + 889
1710	1715	1715	
1625	1617	1626	OH mode – water in matrix or complexed
1416			1080 + 338, 889 + 526, 983 + 427
1395			798 + 596
1295			983 + 338, 889 + 427, 798 + 484
1235	1232		889 + 338, 798 + 427
1191			2 (596)
1136	1132		798 + 338
1080	1081	1080	P–O stretch
		1053	
983	982	981	W–O_d
889	886	885	W–O_b–W
798	795	796	W–O_c–W
641			
596			O–P–O bend
526			
484			
427			
382[a]			
338[a]			

[a] See [16].

The four intense bands observed from 1110 to 725 cm^{-1} serve as a signature of the Keggin anion. These are a particularly helpful marker for observing the degree of fragmentation of the Keggin unit upon adsorption. The P–O symmetric stretch is assigned to the vibrational transition 1080 cm^{-1}. According to studies by Rocchiccioli-Deltcheff et al. [17], the vibrational motion of the phosphate group is independent of the remaining "cage" of the anion. This theory is supported by the fact that the equivalent mode in free PO_4^{3-} is also observed at 1080 cm^{-1} [18]. The bands at 983, 889 and 798 cm^{-1} are associated with the stretching motion of the W–O–W bridges. The normal mode associated with the band at 983 cm^{-1} is defined predominantly by the W–O_d stretch coordinate (see figure 1). The band at 889 cm^{-1} may be described as a W–O_b–W stretch mode (inter-bridges between corner sharing octahedra). The band at 798 cm^{-1} is attributed to W–O_c–W stretch mode (intra-bridges between edge sharing octahedra). Some bend character is included in the normal coordinate description of the last two vibrations [17].

The structural integrity of the Keggin unit has been examined spectroscopically as a function of pH by McGarvey et al. [19]. A decrease in the intensity of the peak at 980 cm^{-1} and the appearance of a band at 950 cm^{-1} accompanies a decrease in acidity. Furthermore, the band at 1080 cm^{-1} "splits" into two features at 1105 and 1050 cm^{-1}. This is believed to be consistent with a transition from $PW_{12}O_{40}^{3-}$ (Keggin) to $PW_{11}O_{39}^{3-}$ (11-"defect" Keggin).

The spectrum obtained for TPA/E-TiO_2 shows an intense, broad, indistinct region extending from 1100 to 400 cm^{-1} attributable to TiO_2 [20]. The well-defined peaks in the spectrum clearly represent both the fundamentals and the stronger overtones and combinations of the intact Keggin unit structure. For this sample, one only observes the intact adsorption of TPA in its original form.

In the spectrum obtained for TPA/P-TiO_2, the vibrational features of the adsorbed TPA overlap the background spectrum of TiO_2. The intensities of the Keggin unit bands are far weaker than those observed for the TPA/E-TiO_2, implying that far less of the TPA has been adsorbed in the form of bulk salt or intact Keggin unit. An additional band is observed at 1053 cm^{-1} indicating the presence of 11-"defect" Keggin units and possibly other fragmentation products.

3.2. NMR data

Figure 3 shows the ^{31}P SP/MAS-NMR spectra obtained on the TPA/P-TiO_2 and TPA/E-TiO_2 catalysts and pure TPA salt. From the similarity of spectra (a) and (b), we conclude that the TPA/E-TiO_2 catalyst contains large deposits of bulk TPA salt, while the TPA/P-TiO_2 catalyst has the majority of the TPA present in some other form (possibly dispersed, intact/fragmented Keggin units on the titania surface).

Deconvolution of the TPA/E-TiO_2 catalyst lineshape, assuming Lorentzian lines, reveals the presence of five component resonances (figure 4). The chemical shifts and deconvoluted signal intensities of the component lineshapes are given in table 2. The chemical shift positions of the singularities observed in the ^{31}P and ^{1}H spectra are given in table 3 for fresh and used [21] catalyst samples. Precipitated TPA salt on the surface (resonance at -16 ppm) accounts for 40% of the adsorbed phosphorus. Varying amounts of four other species are observed at ca. -4 (3%), -8 (3%), -11 (38%), and -13 ppm (16%). The resonance at -4 ppm is due to adsorbed phosphorus species deriving from a highly fragmented Keggin unit. The resonance at -8 ppm may indicate the presence of phosphate character due to the partial fragmentation of the Keggin unit to produce 11-"defect" Keggin species and species of the type W_nO_y–O_3P–OH, in which a phosphate is coordinated to a tungsten–oxygen cluster fragment. The resonances at -13 and -11 ppm could be due to intact Keggin units interacting with surface hydroxyl groups to form species such as (Ti–OH_2^+)($H_2PW_{12}O_{40}^-$) and (Ti–OH_2^+)$_2$($HPW_{12}O_{40}^{2-}$).

Figure 5 shows the deconvolution of the TPA/P-TiO_2 catalyst spectrum. The four component resonances appear-

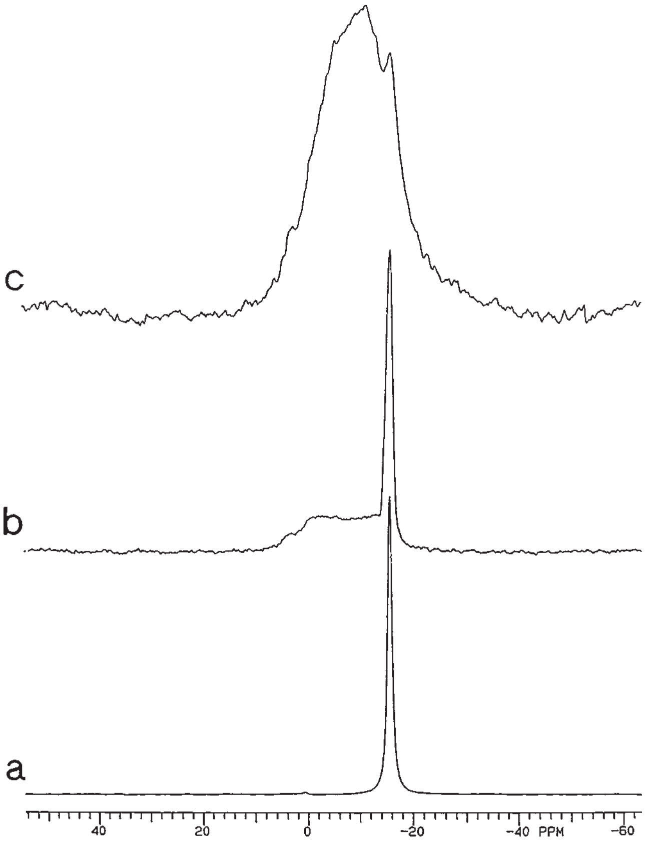

Figure 3. ^{31}P NMR spectra of (a) pure TPA salt, 32 transients, 10 s recycle delay; (b) fresh TPA/E-TiO_2, 720 transients, 30 s recycle delay; (c) fresh TPA/P-TiO_2, 472 transients, 25 s recycle delay.

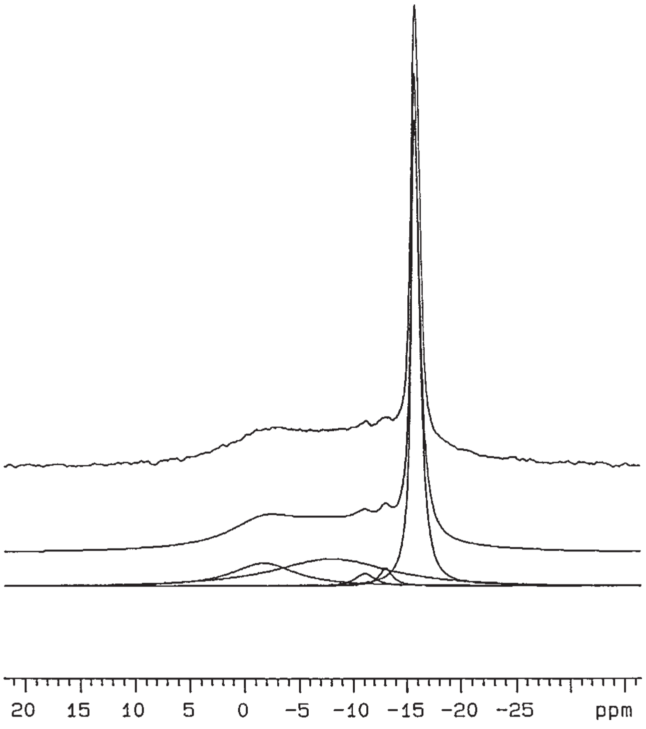

Figure 4. Deconvolution of ^{31}P NMR spectrum of fresh TPA/E-TiO_2.

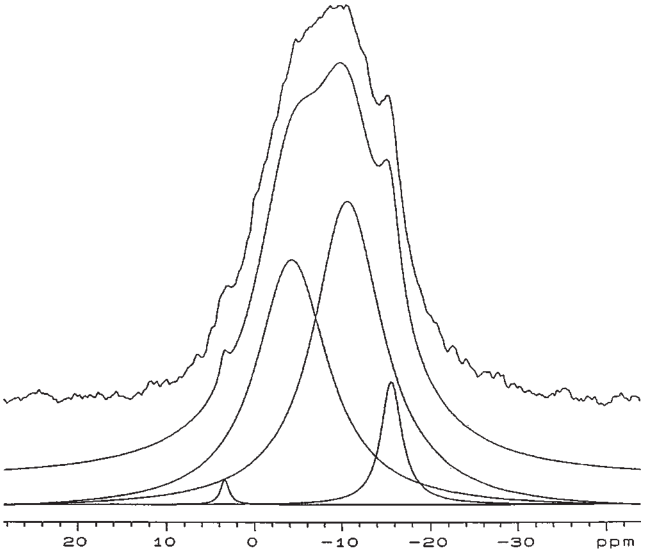

Figure 5. Deconvolution of ^{31}P NMR spectrum of fresh TPA/P-TiO_2.

Table 2
Peak position and intensity data from lineshape deconvolutions.

Sample	Peak position (ppm)	Normalized integral intensity
Fresh TPA/E-TiO_2	−2	16
	−8	38
	−11	3
	−13	3
	−16	40
Fresh TPA/P-TiO_2	4	1
	−4	40
	−11	55
	−15	4

Table 3
12-tungstophosphoric acid-on-titania – new and used peak positions ^{31}P and ^{1}H NMR spectra.

Sample	^{1}H (ppm)	^{31}P (ppm)
12-tungstophosphoric acid	6.2, 6.5	−15.6
Fresh TPA/P-TiO_2	8.2, 11.4	−4.9, −10.6, −15.6
Fresh TPA/E-TiO_2	7.5	1.2, −3.1, −12.9, −15.6
TPA/P-TiO_2 powder	7.6, 11.4	−11.1
Used TPA/P-TiO_2	7.6	4.0 −12.5, −15.5

ing at +4, −4, −11 and −16 are evidence of the increased adsorption of TPA onto the support surface. The deconvolution reveals the presence of both a strongly adsorbed highly fragmented Keggin unit (−4 ppm, 40% of the phosphorus) and an adsorbed, partially fragmented Keggin unit (−11 ppm, 55% of the phosphorus). Also, in the TPA/P-TiO_2 catalyst there is signal intensity at around 4 ppm which may correspond to the presence of pure mono-phosphate. A pure mono-phosphate could be formed upon complete fragmentation of the Keggin unit to tungstate and phosphate.

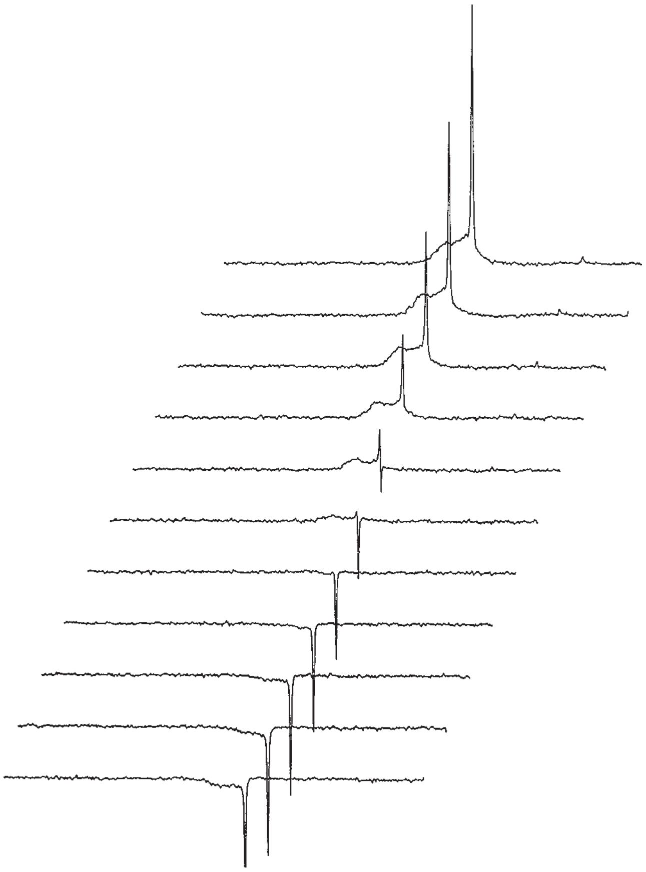

Figure 6. T_1 array experiment on fresh TPA/E-TiO_2, 32 transients, 30 s recycle delay.

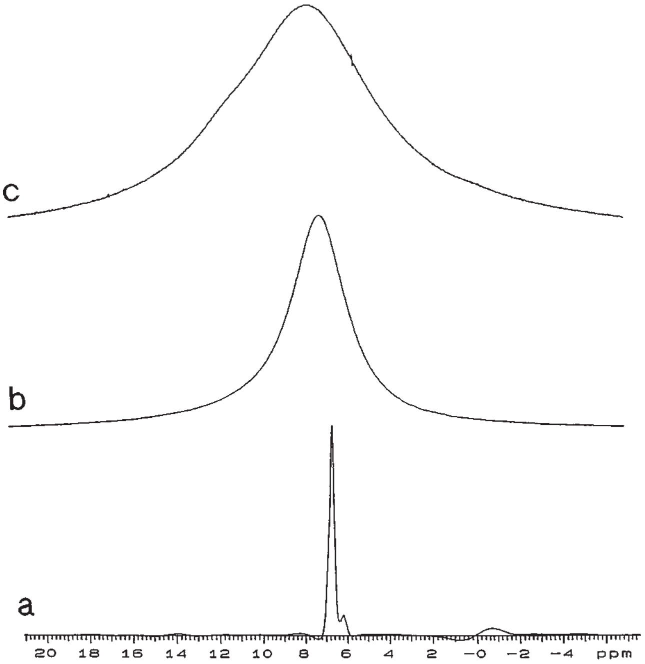

Figure 7. ^1H NMR spectra of (a) TPA with MAS, 33 transients; (b) fresh TPA/E-TiO_2, 256 transients; (c) fresh TPA/P-TiO_2, 256 transients. 1 s recycle times were used.

An inversion–recovery experiment was run to ascertain the ^{31}P longitudinal relaxation times (T_1) of the different adsorbed species, and the result is shown in figure 6. The T_1 times of the two strongly adsorbed species were about 1.6 s, the T_1 of the adsorbed partially fragmented species was about 3 s, and for the TPA salt phase, 5.6 s. These values support the differing degrees of interaction of the ^{31}P nucleus with the TiO_2 surface; it was observed in previous work on P/Al_2O_3 [22] catalysts that strongly adsorbed phosphate species have much shorter T_1 values than the pure salts. This reduction in T_1 relaxation times upon adsorption was echoed in the inversion–recovery experiments performed to obtain the complementary ^1H T_1 information. Pure TPA salt was found to have a ^1H T_1 value of 28 ± 2 ms, while the protons in the adsorbed TPA phase exhibited a T_1 of 5.7 ± 0.2 ms.

The acidic nature of these fresh catalysts was investigated further by performing ^1H MAS-NMR experiments in order to observe the acidic protons directly. Figure 7 shows the ^1H SP/MAS spectra obtained for TPA salt (figure 7(a)), TPA/E-TiO_2 (figure 7(b)), and TPA/P-TiO_2 (figure 7(c)). Probe background signals were subtracted from the spectra. Also, it was found that a blank P-TiO_2 support sample yielded no proton signal under our experimental conditions. Hydroxyls are known to be present on the TiO_2 surface. Therefore, the lack of signal indicates that the protons motion on the surface is such as to render them undetectable on the NMR timescale under our experimental conditions.

The spectrum of TPA salt reveals two narrow resonances the most intense of which is at 6.6 ppm and the less intense resonance at 6.2 ppm. These data may be compared with those reported by Jozefowicz et al. [23] at 423–523 K. The catalyst spectra reveal much broader resonances than the salt and slightly different chemical shifts. A resonance is observed at 7.5 ppm for the TPA/E-TiO_2, and 8.2 ppm for the TPA/P-TiO_2. These shifts are indicative of fairly acidic protons roughly equivalent to the acidity of isolated hydroxonium ions [24,25]. Prior studies of 12-tungstophosphoric acid supported on silica by Gao and Moffat, likewise show an increase in acid strength of the TPA protons [26], particularly at high heteropoly acid loadings. Their ^1H MAS-NMR chemical shifts, ranging from 5.3 to 8.2 ppm, are in good agreement with our primary data.

In figure 7(c), a second resonance is observed as a shoulder in the TPA/P-TiO_2 sample at around 11 ppm. This is a shift that may be associated with hydrogen-bonded hydroxonium ion [24,25]. The deconvolution of the ^1H resonance of the TPA/P-TiO_2 sample is shown in figure 8. The deconvolution shows the 11.4 ppm band corresponding to about 3% of the ^1H signal. This resonance is due to an extremely acidic proton.

Another observation to note is the increase in the ^1H linewidth of the TPA/E-TiO_2 and TPA/P-TiO_2 catalysts compared to the pure TPA salt. The broadening of the surface proton resonances may be due to several factors, such as fragmentation of the Keggin units to form a wide dispersion of W–OH, Ti–OH and P–OH types, and other types of surface acid sites such as (Ti–OH_2^+)($H_2PW_{12}O_{40}^-$)

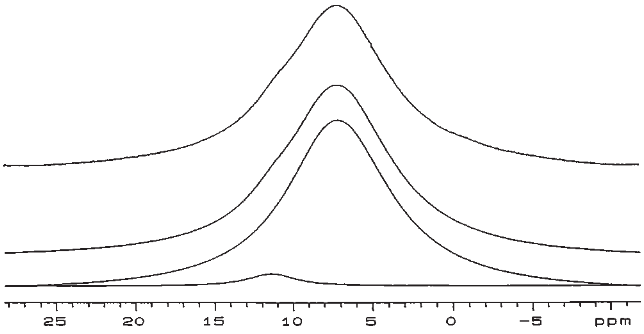

Figure 8. Deconvolution of the ^{1}H BD/MAS spectrum of TPA/P-TiO_2.

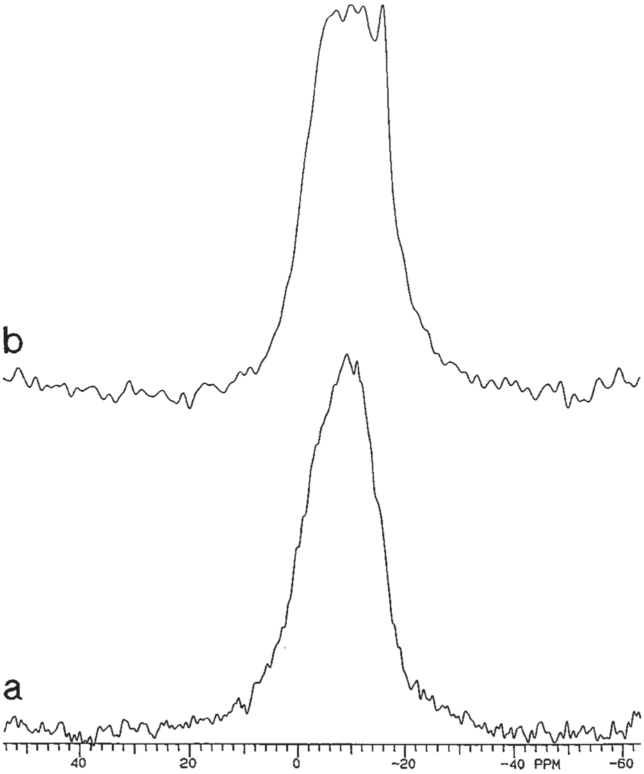

Figure 9. ^{31}P MAS-NMR spectra of 24 h impregnated TPA/TiO_2. (a) Powder impregnated, (b) pellet impregnated. 25 s recycle delay and 160 transients.

and $(Ti–OH_2^+)_2(HPW_{12}O_{40}^{2-})$. Also, this broadening may be due to a higher dipole–dipole interaction, i.e., the ^{1}H–^{1}H dipolar interaction may be much stronger on the catalyst surface. Surface proton exchange and motions may be restricted once adsorption of large TPA clusters and fragments has occurred and the TPA acid protons may become localized on the bridging W–O–W oxygens.

A difference in ^{1}H linewidth is observed upon comparison of the TPA/E-TiO_2 and TPA/P-TiO_2 spectra, with the lineshape for TPA/P-TiO_2 being considerably broader. An explanation may lie in the fact that the TPA/E-TiO_2 catalyst contains predominantly bulk TPA. The inefficient surface adsorption and lack of fragmentation would be expected to yield a narrower ^{1}H NMR resonance than a complete adsorption/fragmentation on the basis of both a lower dipole–dipole interaction (due to continued rapid exchange of surface protons) and a lower chemical type dispersion.

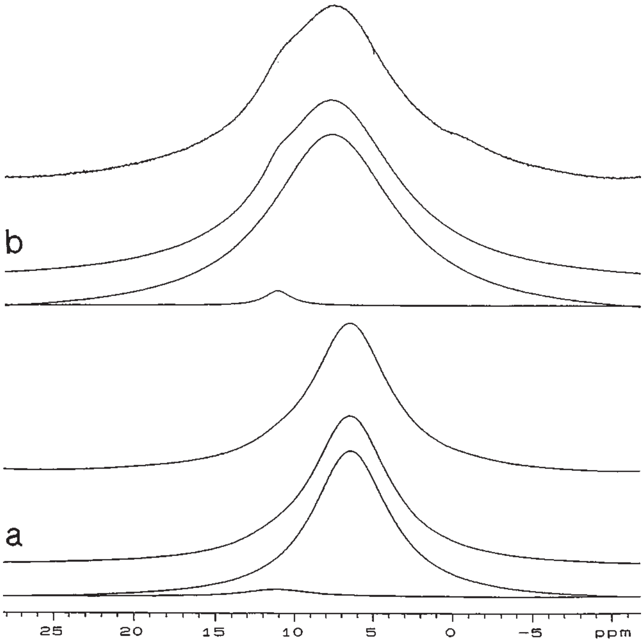

Figure 10. Spectra and deconvolutions of the ^{1}H BD/MAS experiments performed on (a) TPA on pelletized P-TiO_2, and (b) TPA on powdered P-TiO_2.

The differences between the catalysts produced by 24 h impregnation of both ground titania powder and commercial titania pellets were investigated by ^{31}P NMR (figure 9 (a) and (b), respectively). The results clearly show that incomplete adsorption occurs when one impregnates the pellets indicated by the bulk TPA resonance at -16 ppm. Total adsorption of TPA occurs upon impregnation of the ground powder (no bulk TPA resonance is observed). A supporting observation is made on the difference in the ^{1}H SP/MAS spectra obtained on the impregnated pellets and powder (figure 10 (a) and (b), respectively). The deconvolutions show the increased linewidth of the impregnated powder and the increased intensity of the acidic proton resonance at 11.4 ppm, which corresponds to 1.6% of the observed proton signal intensity.

4. Conclusions

It has been shown that important information on the surface structure of adsorbed heteropoly acids can be obtained by solid-state ^{31}P and ^{1}H MAS-NMR. Analysis of the ^{31}P data indicates that there are at least five types of phosphorus on the fresh catalyst surface – a bulk salt phase, two weakly bound intact Keggin unit species, a strongly bound partially fragmented Keggin unit, a strongly bound highly fragmented Keggin unit, and a pure phosphate phase formed by complete fragmentation of the Keggin unit to tungstate and phosphate. Thus, it appears that there is a shift to lower shielding of the ^{31}P as the degree of adsorption, and the degree of fragmentation, increases. It was observed that the method of preparation profoundly effects the final distribution of catalyst surface species. It was found that impregnation of powdered TiO_2, rather than pellets, resulted in a better distribution of the phosphorus types on the titania surface, with the final distribution being heavily weighted toward Keggin units in varying degrees of fragmentation.

^{1}H NMR allows the investigation of the acidic protons involved in the catalytic process. Adsorption of Keggin ion onto the TiO_2 surface leads to an increase in the acidity of the Keggin unit acid protons. With increasingly effective adsorption of the Keggin ions, it was found that there is an accompanying dispersion in the types of acid sites present on the surface, along with perhaps a decrease in the mobility of the acidic protons on the surface. A second acidic proton resonance was observed at 11.4 ppm in catalysts containing well-dispersed TPA. This shift corresponds to hydrogen-bonded hydroxonium ions that represent about 1–3% of the protons present on the surface.

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