

Location, Acid Strength, and Mobility of the Acidic Protons in Keggin 12-H₃PW₁₂O₄₀: A Combined Solid-State NMR Spectroscopy and DFT Quantum Chemical Calculation Study

Jun Yang,^{*,†} Michael J. Janik,[‡] Ding Ma,[§] Anmin Zheng,[†] Mingjin Zhang,[†]
Matthew Neurock,^{*,‡} Robert J. Davis,[‡] Chaohui Ye,[†] and Feng Deng^{*,†}

Contribution from the State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, P. R. China, Department of Chemical Engineering, University of Virginia, Charlottesville, Virginia 22904-4741, and State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China

Received August 28, 2005; E-mail: yangjun@wipm.ac.cn; mn4n@virginia.edu; dengf@wipm.ac.cn

Abstract: Solid-state ¹³C NMR experiments and quantum chemical Density Functional Theory (DFT) calculations of acetone adsorption were used to study the location of protons in anhydrous 12-tungstophosphoric acid (HPW), the mobility of the isolated and hydrated acidic protons, and the acid strength heterogeneity of the anhydrous hydroxyl groups. This study presents the first direct NMR experimental evidence that there are two types of isolated protons with different acid strengths in the anhydrous Keggin HPW. Rotational Echo DOuble Resonance (REDOR) NMR experiments combined with quantum chemical DFT calculations demonstrated that acidic protons in anhydrous HPW are localized on both bridging (O_c) and terminal (O_d) atoms of the Keggin unit. The CP/MAS NMR experiments revealed that the isolated acidic protons are immobile, but hydrated acidic protons are highly mobile at room temperature. The isotropic chemical shift of the adsorbed acetone suggested that the acid strength of the H(H₂O)_n⁺ species in partially hydrated HPW is comparable to that of a zeolite, while the acidity of an isolated proton is much stronger than that of a zeolite. Isolated protons on the bridging oxygen atoms of anhydrous HPW are nearly superacidic.

Introduction

Heteropolyoxometalates have attracted great attention for many years due to their strong acidity and redox properties, which have lead to broad application in industry as homogeneous catalysts and extensive investigations as promising heterogeneous catalysts.^{1–4} Due to their high catalytic activity in acid-catalyzed reactions^{5–13} such as isobutane alkylation by

n-butenes,^{5,6} solid tungstophosphoric acid is a potential replacement for corrosive and environmentally toxic liquid acid catalysts currently used industrially. The proton positions and acid strength of phosphotungstic acid, which are potential indicators of solid acid activity, are still actively debated in the literature. In this work, complementary solid-state NMR experiments and ab initio quantum mechanical calculations were used to identify two distinct positions of the protons. Moreover, these protons were determined to be nearly superacidic.

Tungstophosphoric acid (H₃PW₁₂O₄₀, abbreviated as HPW) has the strongest acidity among the Keggin-type heteropolyacids.^{1,2,14} The primary structure of HPW is the well-established Keggin unit (KU), in which a central P atom in tetrahedral coordination (PO₄) is surrounded by 12 metal–oxygen octahedra (WO₆).¹⁵ The HPW Keggin unit contains a negative three charge which is neutralized in the acid form by three protons in the form of acidic hydroxyl groups at the exterior of the structure. There are four types of oxygen atoms in a KU (Figure 1): 4 central oxygen atom (O_a), 12 oxygen atoms that bridge two tungsten atoms sharing a central oxygen atom (edge-sharing O_c), 12 oxygen atoms that bridge tungsten atoms not sharing a central

[†] Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences.

[‡] University of Virginia.

[§] Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

- (1) Kozhevnikov, I. V. *Russ. Chem. Rev.* **1987**, *56*, 811–825.
- (2) Okuhara, T.; Mizuno, N.; Misono, M. *Adv. Catal.* **1996**, *41*, 113–252.
- (3) Misono, M. *C. R. Acad. Sci. Paris, Serie IIc, Chimie/Chem.* **2000**, *3*, 471–475.
- (4) Misono, M. *Chem. Commun.* **2001**, 1141–1152.
- (5) Blasco, T.; Corma, A.; Martinez, A.; Martinez-Escolano, P. *J. Catal.* **1998**, *177*, 306–313.
- (6) Gayraud, P. Y.; Stewart, I. H.; Hamid, S. B. D.-A.; Essayem, N.; Derouane, E. G.; Vedrine, J. C. *Catal. Today* **2000**, *63*, 223–228.
- (7) Meuzelaar, G. J.; Maat, L.; Sheldon, R. A.; Kozhevnikov, I. V. *Catal. Lett.* **1997**, *45*, 249–251.
- (8) Corma, A.; Martinez, A.; Martinez, C. J. *Catal.* **1996**, *164*, 422–432.
- (9) Essayem, N.; Kieger, S.; Coudurier, G.; Vedrine, J. C. *Stud. Surf. Sci. Catal.* **1996**, *101*, 591–600.
- (10) Bardin, B. B.; Davis, R. J. *Topics Catal.* **1998**, *6*, 77–86.
- (11) Na, K.; Okuhara, T.; Misono, M. *J. Catal.* **1997**, *170*, 96–107.
- (12) Izumi, Y.; Hosano, K.; Hida, T. *Appl. Catal. A* **1999**, *181*, 277–282.
- (13) Verhoef, M. J.; Kooyman, P. J.; Peters, J. A.; Bekkum, H. v. *Microporous Mesoporous Mater.* **1999**, *27*, 365–371.

(14) Bardin, B. B.; Bordawekar, S. V.; Neurock, M.; Davis, R. J. *J. Phys. Chem. B* **1998**, *102*, 10817–10825.

(15) Pope, M. T.; Muler, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34–48.

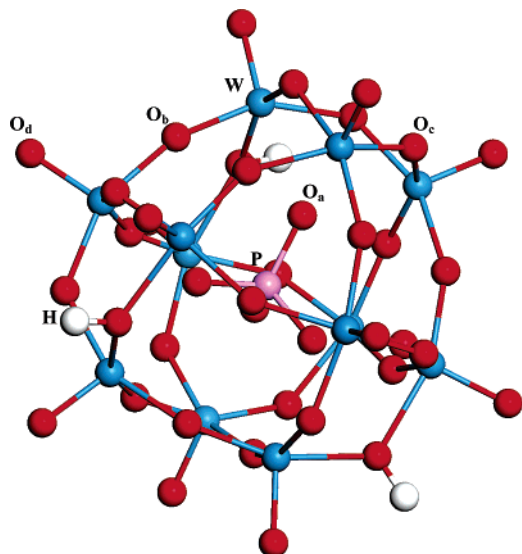


Figure 1. Keggin structure of $\text{H}_3\text{PW}_{12}\text{O}_{40}$. There are three types of exterior oxygen atoms: O_b , O_c , and O_d in the Keggin unit. O_a is the central oxygen atom.

oxygen atom (O_b), and 12 terminal oxygen atoms (O_d) bound to a single tungsten atom.

The molecular HPW Keggin units may crystallize along with water molecules into a secondary structure. The most stable secondary structure under ambient conditions contains six water molecules per KU,^{16,17} in which the polyanions at the lattice points of a body-centered cubic (bcc) structure are connected by H_5O_2^+ along the cubic faces.¹⁸ Crystallization water molecules desorb upon heating; however the Keggin structure is retained at temperatures less than 573 K. At intermediate stages of hydration, acidic protons are present in hydrated or anhydrous form.

The location of the H_5O_2^+ species in the hexahydrate form of HPW is confidently identified by neutron diffraction experiments.¹⁸ However, the location of the isolated protons in anhydrous HPW is difficult to determine by neutron diffraction techniques. The precise proton positions of phosphotungstic acid, which are essential to understanding of the nature of the catalytic site and the molecular mechanism of acid-catalyzed reactions, are still actively debated in the literature.^{1,19–24} Kozhevnikov et al.^{1,19} concluded from ^{17}O NMR spectroscopy that the protons are located on the terminal oxygen atoms. Ganapathy et al.²⁰ arrived at the same conclusion based on results from $^1\text{H}/^{31}\text{P}$ and $^{31}\text{P}/^1\text{H}$ REDOR NMR experiments and density functional theory (DFT) quantum chemical calculations of the proton affinity for a single proton. In contrast, infrared spectroscopy,²¹ extended Hückel molecular orbital calculations,²² and solid-state NMR

techniques²³ were used to argue that the anhydrous protons reside on the bridging oxygen atoms. Recently, DFT calculations, which considered the position of all three protons, indicated that the energy preference for either oxygen type is small and that protons are likely distributed among the oxygen types.²⁴

Though many experimental methods have been applied, the relative acid strength of HPW remains undetermined. It is well accepted that HPW is a pure Brønsted acid,²⁵ and Hammett indicator tests revealed that the anhydrous HPW is a superacid, with a Hammett acidity (H_0) value exceeding that of 100% sulfuric acid.²⁶ Other experimental methods, such as microcalorimetry²⁷ and thermal desorption^{26,28} of probe base molecules, suggested that solid HPW is a stronger acid than HZSM-5 and HY zeolites. In contrast, experimental results from Fourier transform infrared spectroscopy²⁹ and H/D exchange between isobutane and anhydrous HPW³⁰ are consistent with the acid strength of anhydrous HPW being comparable to that of a zeolite, which is not superacidic. Herein we report on the use of solid-state NMR spectroscopy of 2- ^{13}C -acetone adsorption and density functional theory quantum-chemical calculations to determine the location, acid strength, and mobility of the acidic protons in anhydrous and hydrated HPW.

Experimental and Computational Methods

1. Preparation of Acetone-Adsorbed Dehydrated HPW Samples.

The hydrate of HPW, $\text{HPW}\cdot x\text{H}_2\text{O}$, was purified twice by diethyl ether extraction. Sample purity was checked by ^{31}P NMR spectroscopy in aqueous solution and the solid state. A sample was first placed in a glass tube connected to a vacuum. The temperature was slowly (1.5 °C/min) increased to a specified value and held in a vacuum for 2 or 4 h to dehydrate the material. After the sample cooled to room temperature, a controlled amount of 2- ^{13}C -acetone (99% ^{13}C enriched, Cambridge Isotope Laboratories, Inc.) or trimethylphosphine (TMP, 99%) was introduced from a vacuum line and was frozen at liquid N_2 temperature. In some cases, TMP was added at a pressure of 40 Torr, and adsorption was equilibrated before the sample was degassed at room temperature for 1 h. The sealed sample was transferred into a ZrO_2 NMR rotor (sealed by Kel-F cap) under a dry nitrogen atmosphere in a glovebox.

2. Solid-State NMR Experiments.

All NMR experiments were performed with a 7.5 mm double-resonance probe on a Varian Infinityplus-300 spectrometer and a triple-resonance 5 mm probe on a Varian Infinityplus-400. ^{13}C MAS NMR spectra were acquired using one pulse with ^1H proton decoupling with a ^{13}C pulse width ($\pi/2$) of 4.3 μs , a ^1H decoupling field strength of 50 kHz, and a 80 s pulse delay. ^1H - ^{13}C CP MAS experiments were performed with a contact time of 2 ms, a repetition time of 2 s, and 600 scans. The $^{13}\text{C}/^{31}\text{P}$ REDOR NMR spectra were acquired using a standard REDOR pulse sequence.^{31,32} The ^{13}C NMR signal intensities were measured separately for the REDOR spectra with and without applying a series of rotor-synchronized π pulses to the ^{31}P channel, and their differences were used to determine ΔS . The π -pulse widths of ^{13}C and ^{31}P were 6.8 and 7.6 μs , respectively. The MAS spinning speed in REDOR experiments

- (16) Nakamura, O.; Ogino, I.; Kodama, T. *Mater. Res. Bull.* **1980**, *15*, 1049–1054.
 (17) Nakamura, O.; Ogino, I.; Kodama, T. *Solid State Ionics* **1981**, *3–4*, 347–351.
 (18) Brown, G. M.; Noe-Spirlet, M. R.; Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1977**, *B33*, 1038–1046.
 (19) Kozhevnikov, I. V.; Sinnema, A.; Bekkum, H. v. *Catal. Lett.* **1995**, *34*, 213–221.
 (20) Ganapathy, S.; Fournier, M.; Paul, J. F.; Delevoeye, L.; Guelton, M.; Amoureux, J. P. *J. Am. Chem. Soc.* **2002**, *124*, 7821–7828.
 (21) Lee, K. Y.; Mizuno, N.; Okuhara, T.; Misono, M. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1731–1739.
 (22) Moffat, J. B. *J. Mol. Catal.* **1984**, *26*, 385–396.
 (23) Ueda, T.; Tatsumi, T.; Eguchi, T.; Nakamura, N. *J. Phys. Chem. B* **2001**, *105*, 5391–5396.
 (24) Janik, M. J.; Campbell, K. A.; Bardin, B. B.; Davis, R. J.; Neurock, M. *Appl. Catal. A* **2003**, *256*, 51–68.

- (25) Mizuno, N.; Misono, M. *Chem. Rev.* **1998**, *98*, 199–217.
 (26) Okuhara, T.; Nishimura, T.; Watanabe, H.; Misono, M. *J. Mol. Catal.* **1992**, *74*, 247–256.
 (27) Drago, R. S.; Dias, J. A.; Maier, T. O. *J. Am. Chem. Soc.* **1997**, *119*, 7702–7710.
 (28) Misono, M.; Mizuno, N.; Katamura, K.; Kasai, A.; Konishi, Y.; Sakata, K.; Okuhara, T.; Yoneda, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 400.
 (29) Paze, C.; Bordiga, S.; Zecchina, A. *Langmuir* **2000**, *16*, 8139–8144.
 (30) Essayem, N.; Coudurier, G.; Vadrine, J. C.; Habermacher, D.; Sommer, J. *J. Catal.* **1999**, *183*, 292–299.
 (31) Gullion, T.; Schaefer, J. *J. Magn. Reson.* **1989**, *81*, 196–200.
 (32) Gullion, T.; Schaefer, J. *Adv. Magn. Reson.* **1989**, *13*, 57.

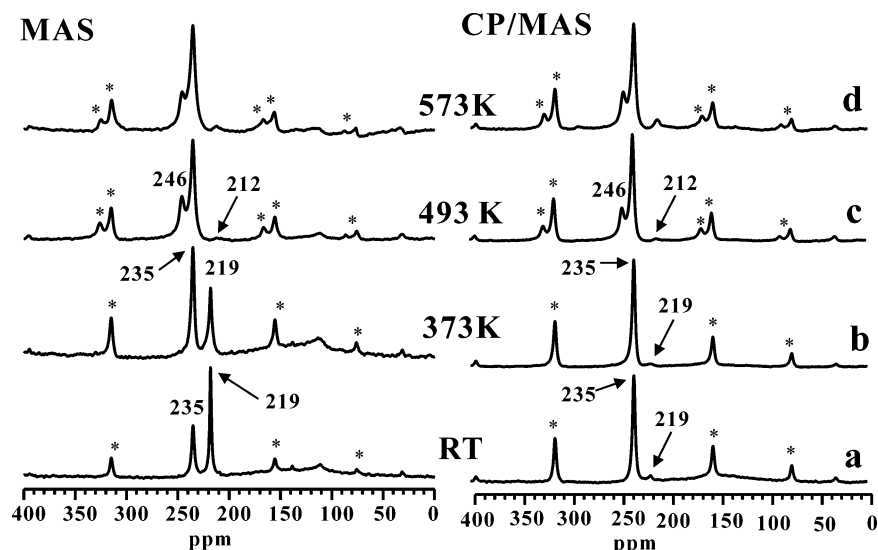


Figure 2. ^{13}C MAS (left) and CP/MAS (right) NMR spectra of 2- ^{13}C -acetone (0.3 molecule/KU) adsorbed on HPW after dehydration at (a) room temperature for 4 h, (b) 373 K for 2 h, (c) 493 K for 2 h, and (d) 573 K for 2 h. All spectra were acquired with a spinning rate of 6 kHz at room temperature. The ^{13}C MAS NMR spectra were recorded with a recycle delay of 80 and 104 scans. The CP/MAS spectra were recorded with a contact time of 2 ms, a recycle delay of 2 s, and 600 scans. The signal at 212 ppm in (c) and (d) is due to the product of the bimolecular reaction of acetone.⁴⁰ The signal at ca. 110 ppm in the ^{13}C MAS spectra is due to the background of the NMR rotor. Asterisks denote spinning sidebands.

was 4000 ± 2 Hz. First, second, and third spinning sidebands of the ^{13}C signals were included in the determination of $\Delta S/S_0$. The simulation program used for fitting the REDOR data was kindly provided by Prof. Gullion.

3. Computational Methods. Density functional theory quantum chemical calculations were carried out to determine the relative energies of acetone adsorbed at different locations on the phosphotungstic acid surface. Calculations were performed with the Vienna ab Initio Simulation Package (VASP).^{33–35} The Perdew–Wang (PW91) form of the generalized gradient approximation was used to calculate the exchange and correlation energies.³⁶ Ultrasoft pseudopotentials described the electron–ion interactions.³⁷ A $1 \times 1 \times 1 \text{ \AA}^3$ Monkhorst–Pack mesh was used to sample the first Brillouin zone.³⁸ A cutoff energy of 396.0 eV was used for the plane-wave basis set. A $20 \times 20 \times 20 \text{ \AA}^3$ unit cell was used in which 8 \AA of vacuum space separates the molecular HPW/acetone complexes in adjacent cells. All structures were relaxed using a quasi-Newton algorithm and converged such that the forces on each atom were less than 0.05 eV \AA^{-1} . This method has been previously shown to predict an equilibrium Keggin unit structure in agreement with experiment.²⁴ Adsorption energies are reported as the difference in energy between the equilibrium structure with acetone adsorbed to the Keggin unit and the energies of the separated Keggin unit and acetone species.

Results and Discussion

^{13}C MAS NMR Experiments. Adsorption of 2- ^{13}C -acetone can be used in conjunction with ^{13}C MAS NMR chemical shift as a measure of relative acid strength of various solid acids.^{39–47} The formation of a hydrogen bond between the acidic proton and the carbonyl oxygen of adsorbed acetone will cause a downfield shift of the carbonyl carbon. Bigalow et al.³⁹ proposed an acidity scale based on their measurements of the ^{13}C NMR

chemical shift of the carbonyl carbon of acetone molecules adsorbed on different solid acid catalysts relative to the resonance of the carbonyl carbon in pure acetone. Haw et al.^{42,43} demonstrated that this scale reasonably reflects the acid strength of solid acids, whereas the application of the Hammett acidity scale is not rigorous. According to Haw et al.,^{42,43} the threshold acid strength of a solid superacid, which corresponds to a 100% H_2SO_4 solution, gives rise to an isotropic ^{13}C NMR chemical shift of 245 ppm of adsorbed 2- ^{13}C -acetone.

Figure 2 shows the ^{13}C MAS NMR spectra of 2- ^{13}C -acetone (ca. 0.3 molecules/KU) adsorbed on HPW samples dehydrated at different temperatures. Following degassing at room temperature for 4 h, two signals at 219 and 235 ppm were observed in the ^{13}C MAS spectrum. After dehydration at 373 K for 2 h, the 219 ppm signal in the ^{13}C MAS spectrum decreased in intensity slightly while the 235 ppm signal increased in intensity. In the corresponding ^1H – ^{13}C CP/MAS spectrum, the 235 ppm signal was enhanced while the 219 ppm signal decreased significantly, despite the use of a broad range (0.1 to 15 ms) of contact times. After dehydrating at 493 K for 2 h, the 219 ppm signal in the ^{13}C MAS NMR spectrum disappeared completely (the signal at 212 ppm in spectra c and d is due to the product of the bimolecular reaction of acetone⁴⁰), and a new signal at 246 ppm appeared. The signals of 235 and 246 ppm were still present in the HPW samples dehydrated at 573 K.

(33) Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *47*, 558–561.
 (34) Kresse, G.; Furthmüller, J. *Comput. Mater. Sci.* **1996**, *6*, 15–50.
 (35) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169–11186.
 (36) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671–7895.
 (37) Vanderbilt, D. *Phys. Rev. B* **1990**, *41*, 7892–7895.
 (38) Monkhorst, H. J.; Pack, J. D. *Phys. Rev. B* **1976**, *13*, 5188–5192.

(39) Bigalow, A. I.; Gorte, R. J.; White, D. J. *Catal.* **1994**, *148*, 779–786.
 (40) Bigalow, A. I.; Gorte, R. J.; White, D. J. *Catal.* **1994**, *150*, 221–224.
 (41) Bigalow, A. I.; Sepa, J.; Gorte, R. J.; White, D. J. *Catal.* **1995**, *151*, 373–384.
 (42) Xu, T.; Munson, E. J.; Haw, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 1962–1972.
 (43) Haw, J. F.; Nicholas, J. B.; Xu, T.; Beck, L. W.; Ferguson, D. B. *Acc. Chem. Res.* **1996**, *29*, 259–267.
 (44) Xu, M.; Arnold, A.; Buchholz, A.; Wang, W.; Hunger, M. *J. Phys. Chem. B* **2002**, *106*, 12140–12143.
 (45) Song, W.; Nicholas, J.; Haw, J. F. *J. Phys. Chem. B* **2001**, *105*, 4317–4323.
 (46) Xu, T.; Kob, N.; Drago, R.; Nicholas, J. B.; Haw, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 12231–12239.
 (47) Xu, T.; Torres, P. D.; Beck, L. W.; Haw, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 8027–8028.

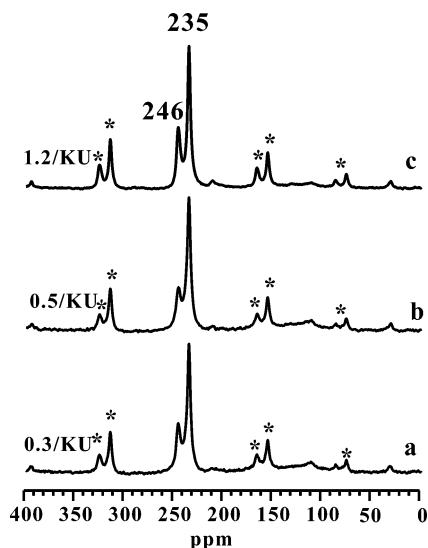


Figure 3. ^{13}C MAS NMR spectra of different amounts of 2- ^{13}C -acetone adsorbed on HPW after dehydration at 493 K for 2 h. The ^{13}C MAS NMR spectra were recorded at room temperature with a recycle delay of 80 and 104 scans. The signal at ca. 110 ppm is due to the background of the NMR rotor. Asterisks denote spinning sidebands.

Figure 3 shows the ^{13}C MAS spectra of different amounts of acetone adsorbed on dehydrated HPW (dehydrated at 493 K for 2 h prior to acetone exposure). With increasing adsorption from 0.3 to 1.2 acetone molecules per KU, neither new peaks nor changes of the chemical shifts of the 235 and 246 ppm signals in the ^{13}C MAS spectra were observed. In addition, the ratio of the integral intensities of the 246 and 235 ppm peaks (including the intensity of the spinning sidebands) was almost independent of the amount adsorbed and was reproducible. Generally, the low amount of adsorbed acetone (ca. 0.1 molecule/acid site) was chosen to avoid chemical exchange among acetone molecules adsorbed on different Brønsted acid sites.^{42,43} The ^{13}C NMR experimental results with varying amounts of adsorbed acetone demonstrate the homogeneous distribution of acetone molecules into the solid bulk of HPW.

Generally, dehydration in a vacuum at temperatures higher than 493 K for 2 h can completely remove the crystallization water molecules of HPW.⁴⁸ Therefore, the 246 and 235 ppm signals in the ^{13}C spectra of samples dehydrated at 493 and 573 K should be assigned to acetone adsorbed on isolated acidic protons rather than hydrated protons. After dehydration at room temperature (RT) for 4 h, some crystallization water molecules still remain in HPW.⁴⁸ The 219 ppm signal, which was present in the ^{13}C spectra of samples dehydrated at RT and 373 K and disappeared completely in the spectra of samples dehydrated 493 and 573 K, can be assigned to acetone adsorbed on the hydrated proton species. The ^{13}C chemical shift of this signal (219 ppm) indicates that the acidity of the hydrated proton is comparable to zeolites (having a ^{13}C chemical shift of adsorbed 2- ^{13}C -acetone around 220 ppm^{42,43}). The greater chemical shift of acetone adsorbed on samples dehydrated at higher temperatures indicates that the acid strength of an isolated proton is much stronger than that of zeolites. The large ^{13}C chemical shift of the 246 ppm signal is similar to that of 100% H_2SO_4 , which is the threshold of superacidity.^{42,43}

(48) Uchida, S.; Inumaru, K.; Misono, M. *J. Phys. Chem. B* **2000**, *104*, 8108–8115.

In previous studies, most authors have assumed that all anhydrous protons are localized at the same type of oxygen atoms. For example, Ganapathy et al.²⁰ fit their $^1\text{H}/^{31}\text{P}$ REDOR $\Delta S/S_0$ data of anhydrous HPW with the assumption that the three protons lie in the same plane as the phosphorus atom and the three corresponding P–H distances are identical. However, this assumption is not supported by our probe molecule adsorption experiments. Our ^{13}C NMR spectra provide the first direct experimental evidence that there are two types of isolated acidic protons with different acid strengths in anhydrous HPW. The different interaction of the isolated acidic protons (Brønsted acid sites) with adsorbed acetone leads to the appearance of the two downfield signals at 235 and 246 ppm. By measuring the integrated areas of the 235 and 246 ppm signals (including their spinning sidebands), the concentrations of the corresponding isolated acidic protons under the controlled adsorption condition (0.3 acetone molecule/KU) are determined to be 0.19 and 0.11 H^+/KU for the HPW sample dehydrated at 493 K, respectively. The concentrations remain unchanged for the HPW sample dehydrated at 573 K. Since relatively low acetone loadings were used to avoid chemical exchange among acetone molecules adsorbed on different acidic protons, it is impossible either to cover 100% acid sites of the anhydrous HPW or to determine the concentration of total acid sites by using acetone as a probe. The concentration of the total acid sites can be measured by ^1H MAS NMR (see Supporting Information), and the corresponding values are 2.9 and 2.1 H^+/KU for HPW samples dehydrated at 493 and 573 K, respectively.

To rule out the possibility that the downfield ^{13}C NMR signals (at 235 and 246 ppm) result from interaction of acetone with Lewis sites that are likely generated during the sample dehydration, we recorded ^{31}P MAS NMR spectra of TMP adsorbed on HPW samples dehydrated at different temperatures. TMP is an extensively used probe molecule for discriminating Brønsted and Lewis acid sites and measure their relative concentrations in various solid acids.^{49,50} It is well accepted that the formation of the TMPH^+ ion due to the interaction of TMP with Brønsted acid sites of zeolite will give rise to a ^{31}P resonance at about 0 ppm, while TMP molecules bound to Lewis acid sites will result in a resonance in the shift range from -32 to -58 ppm, and physisorbed TMP molecules will give rise to a ^{31}P NMR signal at about -60 ppm. In the ^{31}P MAS NMR spectra (see Supporting Information) of TMP adsorbed on HPW samples dehydrated at temperatures from 343 to 593 K, besides signals at -10 to -16 ppm (due to the P atoms in the Keggin unit), only the signal at -3 ppm (due to TMP adsorbed on Brønsted acid sites) was observed over the wide dehydration temperature range, indicating that no Lewis acid sites are present on the dehydrated HPW samples.

At temperatures of interest for acid-catalyzed reactions, some degree of hydration of the acidic protons is expected, and therefore the effect of water on the acid properties of the catalyst must be understood. It has been reported that the H_0 acid strength of HPW depends strongly on its hydration state: H_0 varies from -5.6 for $\text{HPW}\cdot 10\text{H}_2\text{O}$ to -8.2 for $\text{HPW}\cdot 6\text{H}_2\text{O}$ ⁵¹ to -12.8 for $\text{HPW}\cdot 1-2\text{H}_2\text{O}$.⁵² Our probe molecule adsorption experiments

(49) Lunsford, J. H.; Rothwell, W. P.; Shen, W. J. *J. Am. Chem. Soc.* **1985**, *107*, 1540–1547.

(50) Kao, H. K.; Grey, C. P. *Chem. Phys. Lett.* **1996**, *259*, 459–464.

(51) Hayashi, H.; Moffat, J. B. *J. Catal.* **1982**, *77*, 473–484.

(52) He, Y.; Li, F.; Wang, P.; Du, Z. *Prepr. Symp. Solid Superacids Div. Petrol. Chem. 214th Nat. Meet. Am. Chem. Soc.* **1987**, *42*, 722.

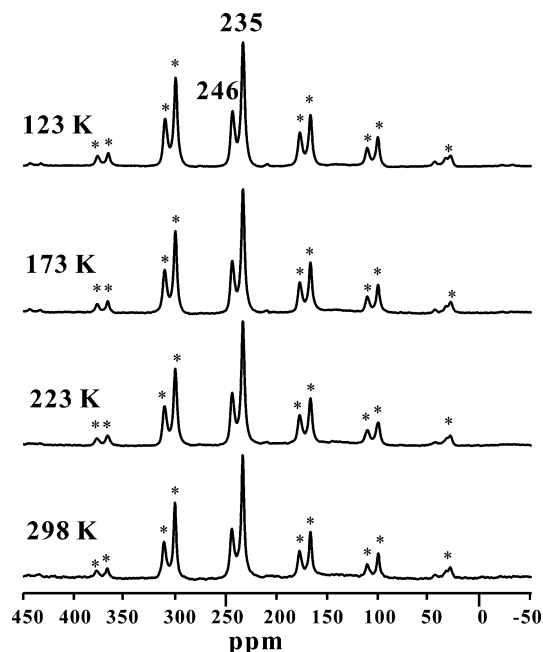


Figure 4. Variable-temperature ^{13}C CP/MAS NMR spectra of 2- ^{13}C -acetone (ca. 0.3/KU) adsorbed on the HPW dehydrated in a vacuum at 493 K for 2 h. Asterisks denote spinning sidebands.

indicate that this trend is due to an increase in the number of isolated acidic protons with a decrease in the number of crystallization water molecules, as isolated protons possess a much stronger acid strength than the hydrated protons. As shown in the ^{13}C MAS spectra (Figure 2a and 2b), the intensity of the 235 ppm signal increased and the 219 ppm signal decreased with an increase in dehydration temperature from RT to 373 K.

Although water adsorption reduces the acid strength of the HPW protons, a small amount of water can improve the catalytic performance for some acid-catalyzed reactions. The catalytic activity of HPW under dry conditions declined with time on stream for both butene double-bond isomerization and pentane skeletal isomerization, whereas treatment with water vapor substantially recovered the catalytic activity.⁵³ Upon increasing the hydration level of HPW, the activity for cyclopropane isomerization was shown to initially increase and then significantly decreases.⁵⁴ This initial enhancement was speculated to be caused by increased proton mobility. The decrease in activity at higher hydration levels may probably result from a decrease in acid strength. Our ^{13}C NMR experimental results of probe molecule adsorption demonstrate the difference in mobility between hydrated and isolated protons. In the ^{13}C NMR spectra of adsorbed acetone acquired at temperatures from 123 to 298 K (see Figure 4), the strong spinning sideband, high polarization transfer efficiency, and independence of the line width with respect to temperature of the 235 and 246 ppm signals indicate the tight binding and restricted mobility of both the isolated acidic protons and adsorbed acetone molecules even at room temperature. The experimental results are consistent with the previous ^1H variable temperature solid-state NMR studies. Baba et al.^{54,55} and Uchida et al.⁴⁸ demonstrated that the line width of the ^1H MAS signal in anhydrous HPW was independent of

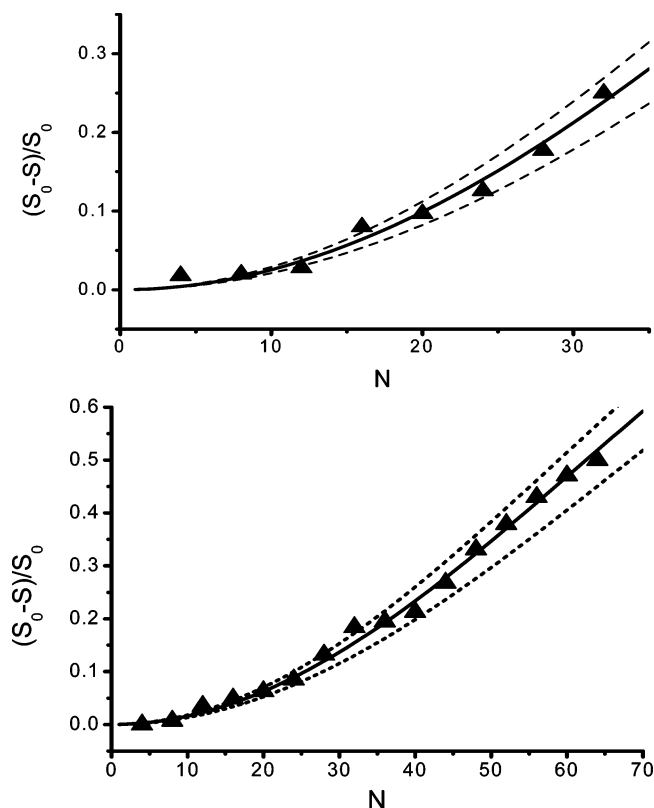


Figure 5. $^{13}\text{C}/^{31}\text{P}$ REDOR NMR results of 2- ^{13}C -acetone adsorbed on HPW after dehydration at 493 K for 2 h. “N” refers to the number of rotor cycles, and \blacktriangle denotes the experimental data points. The solid line was fitted with an internuclear distance of $R_{\text{C-P}} = 7.4$ Å for the 246 ppm signal (top) and 8.0 Å for the 235 ppm signal (bottom). The dotted lines were calculated by varying $R_{\text{C-P}}$ by ± 0.2 Å. The MAS spinning speed was 4000 ± 2 Hz.

temperatures from 173 to 298 K and 298 to 373 K, respectively, indicating the immobility of the anhydrous proton. In contrast, according to our ^{13}C CP/MAS NMR experimental results, the hydrated acidic proton is mobile. The absence of a spinning sideband and the low ^1H – ^{13}C polarization transfer efficiency of the 219 ppm signal in the CP spectra (Figure 2a and 2b) suggest the high mobility of the hydrated protons and the adsorbed acetone molecule at room temperature. The increase of proton mobility enhanced by small amounts of water has been explained by quantum chemical DFT calculations.⁵⁶

$^{13}\text{C}/^{31}\text{P}$ REDOR Experiments. The Rotational Echo DOuble Resonance (REDOR) technique was proposed by Gullion and Schaefer to recouple the heteronuclear dipolar coupling which is removed by MAS.^{31,32} Since the ^{13}C MAS NMR spectra of acetone adsorption indicates that the anhydrous protons of HPW may be positioned at different oxygen atoms at the exterior of the Keggin unit, and each phosphorus atom is coupled with three protons, multiple H–P distances may be expected. However, in the ^1H MAS NMR spectra (see the Supporting Information) of anhydrous HPW, signals from the different types of isolated protons cannot be resolved, and therefore $^1\text{H}/^{31}\text{P}$ REDOR experiments are not capable of differentiating the multiple locations of isolated protons. Furthermore, the fitting of the $\Delta S/S_0$ data of the $^{31}\text{P}/^1\text{H}$ REDOR of multispin with three different P–H vectors is very difficult. Ganapathy et al.²⁰ had to fit their

(53) Bardin, B. B.; Davis, R. J. *Appl. Catal. A* **2000**, *200*, 219–231.

(54) Baba, T.; Ono, Y. *Appl. Catal. A* **1999**, *181*, 227–238.

(55) Baba, T.; Ono, Y. *J. Phys. Chem.* **1996**, *100*, 9064–9067.

(56) Janik, M. J.; Davis, R. J.; Neurock, M. *J. Am. Chem. Soc.* **2005**, *127*, 5238–5245.

(57) Gullion, T. *Concepts Magn. Reson.* **1998**, *10*, 277–289.

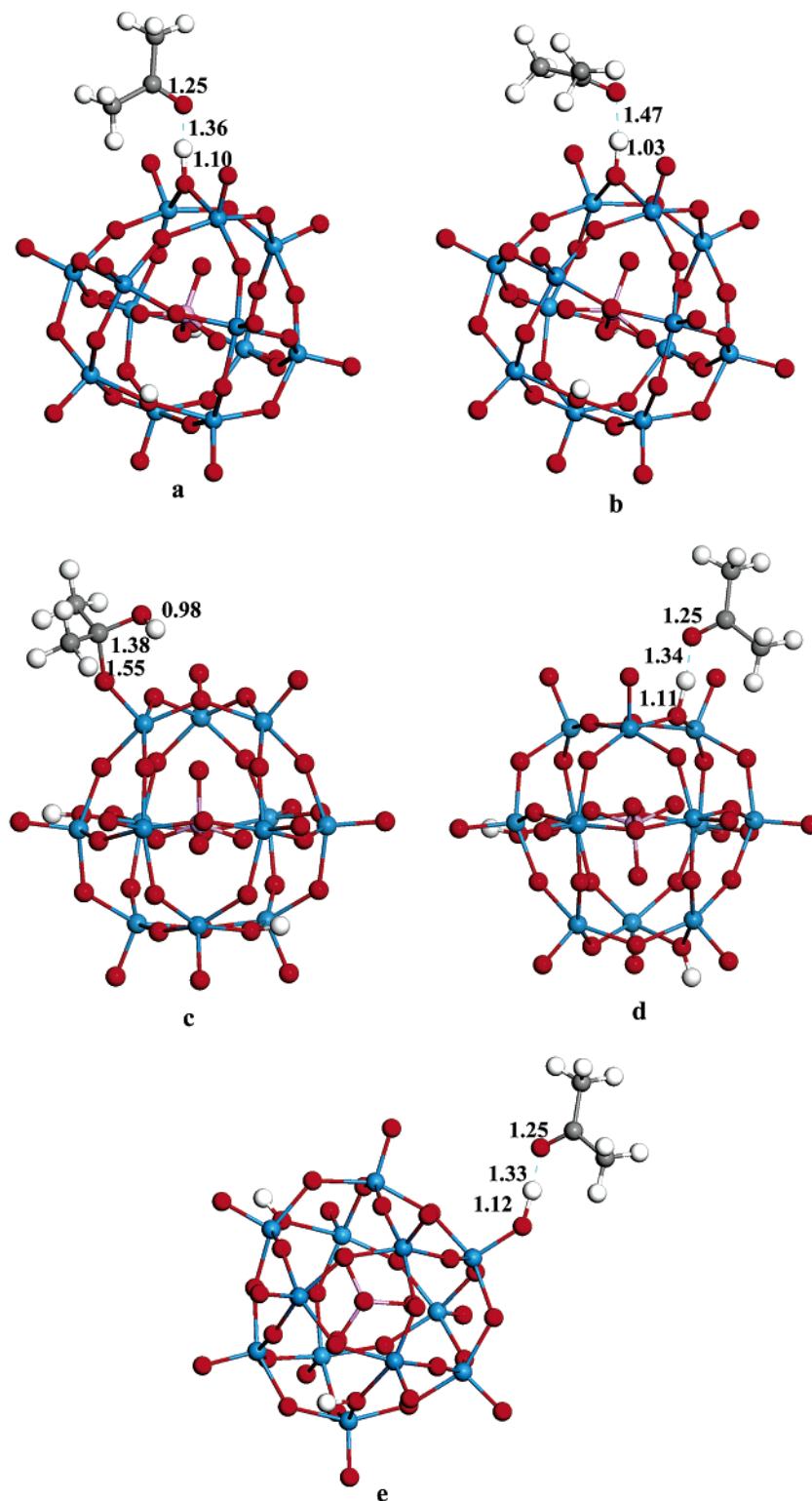


Figure 6. Equilibrium structures of acetone adsorbed to anhydrous phosphotungstic acid at different locations at the exterior of the Keggin unit. All distances are in Å. (a) A hydrogen bond is formed between the proton residing on an O_c atom and the oxygen atom of acetone. (b) The starting geometry placed the center of the $\text{C}=\text{O}$ π -bond of acetone over the proton; however during optimization the acetone molecule was shifted such that the binding mode appears more as a hydrogen bond with a lone pair of the acetone oxygen atom. (c) Acetone adsorbed to an O_d atom through the C_2 carbon with protonation of the oxygen atom of acetone. The proton is presumed to have started on an O_c atom. (d) A hydrogen bond is formed between the proton residing on an O_b atom and the oxygen atom of acetone. (e) A hydrogen bond is formed between the proton residing on an O_d atom and the oxygen atom of acetone.

$^1\text{H}/^{31}\text{P}$ REDOR $\Delta S/S_0$ data of anhydrous HPW with the assumption that the three corresponding P–H distances were identical. However, because the isolated acidic protons were differentiated by the ^{13}C NMR spectra of acetone adsorption,

the isolated C–P spin pair allows straightforward fitting of the $\Delta S/S_0$ data of the $^{13}\text{C}/^{31}\text{P}$ REDOR NMR experiments. Therefore, $^{13}\text{C}/^{31}\text{P}$ REDOR NMR experiments of acetone adsorption are suitable to study the precise location of the acidic protons in

Table 1. Adsorption Energies and Geometries for the Adsorption of Acetone to Phosphotungstic Acid Calculated Using DFT Methods^a

H ⁺ position	ads. mode	ΔE_{ads} kJ mol ⁻¹	E_{relative} kJ mol ⁻¹	C ₂ -P Å	structure in Figure 6
O _c	lone pair	-85.4	0.0	7.23	a
O _c	π -bond	-54.7	+30.7	7.04	b
O _c	alkoxy	-46.3	+39.1	6.70	c
O _b	lone pair	-58.3	+27.1	6.90	d
O _d	lone pair	-82.3	+3.1	8.17	e

^a The structures with acetone adsorbed are illustrated in Figure 6.

anhydrous HPW. For the isolated spin pair, the analytical expressions of the REDOR evolution of powder samples can be written:⁵⁷

$$\Delta S/S_0(N T_r) = 1 - \frac{1}{2\pi} \int_0^\pi \int_0^\pi \cos \left[\frac{N_c T_r d}{\pi} \sqrt{2} \sin 2\beta \sin \alpha \right] \sin \beta d\alpha d\beta \quad (1)$$

where S_0 and S describe the control signal and the dipolar dephasing signal, respectively, $\Delta S = S_0 - S$, T_r is the dephasing period, N_c is the number of rotor periods, $d = \gamma_P \gamma_C / R^3_{C-P}$ is the dipolar coupling, and α and β are polar angles that describe the orientation of the rotor axis with respect to the C-P vector.

We carried out ¹³C/³¹P REDOR NMR experiments on the dehydrated HPW samples with acetone adsorbed. An obvious REDOR effect was observed for the 235 and 246 ppm signals. The corresponding REDOR $\Delta S/S_0$ curves are shown in Figure 5. The best fit of the experimental data for the isolated spin pair gives internuclear distances between the P atom of HPW and the C₂ atom of adsorbed acetone, $R_{(P-C)}$, of **7.4 Å** for the 246 ppm signal and **8.0 Å** for the 235 ppm signal.

DFT Calculations. Quantum chemical calculations were performed to determine the P-C distances of acetone adsorbed to protons located at various exterior oxygen atoms of the Keggin unit. Five structures were examined with a single acetone molecule adsorbed to a proton of anhydrous HPW. The optimized equilibrium structures are illustrated in Figure 6. First, for adsorption involving a proton on an O_c atom, three adsorption modes were explored: formation of a hydrogen bond between the O_c-H group and a lone pair of the oxygen atom of acetone (Figure 6a), formation of a hydrogen bond between the O_c-H group and the C=O π -bond (Figure 6b), and protonation of the acetone oxygen atom with the C₂ atom of acetone binding to a terminal O_d atom (Figure 6c). The adsorption energies of each mode are included in Table 1. The first mode allows for substantially stronger adsorption, with an exothermic adsorption energy of -85.4 kJ mol⁻¹. Rotation of the adsorbed species by 180° about the O_c-H⁺ axis alters the adsorption energy by less than 1 kJ mol⁻¹ and the C₂-P distance by less than 0.05 Å.

The adsorption energy and structure were then calculated for the preferred mode (hydrogen bond formation with the lone pair of the acetone oxygen atom) at the other two oxygen atom types on the exterior of the KU. For the calculation of adsorption energy, a reference structure with two protons on O_c atoms and

one proton on an O_b atom is used for adsorption at the bridging oxygen atoms. This is the lowest energy molecular structure of H₃PW₁₂O₄₀.²⁴ For the adsorption at the O_d atom, a reference structure with one proton on each of the O_b, O_c, and O_d atoms is used. This structure, with a proton moved from an O_c atom to an O_d atom, is 3.4 kJ mol⁻¹ higher in energy. For direct comparison of the energy of the adsorbed structures, a relative energy is included in Table 1 in which the energy of each structure is referenced to the lowest energy adsorbed structure. Adsorption to a proton located on an O_b atom occurs with an energy release of -58.3 kJ mol⁻¹ (Figure 6d). The acetone adsorption energy is -82.3 kJ mol⁻¹ to a proton located on an O_d atom (Figure 6e).

The DFT results indicate that adsorption at the O_c bridging atom or at the O_d terminal atom is preferred and of similar energy. For adsorption to a proton on a bridging oxygen atom, the C₂-P distance is 7.23 Å. For adsorption to a proton on a terminal oxygen atom, the C₂-P distance is 8.17 Å. These distances can be compared with those determined from the REDOR NMR experiments to determine the adsorbed acetone position associated with each peak in the ¹³C NMR spectra. According to the REDOR and calculated results, we assign the 246 ppm signal to acetone adsorbed at the bridging oxygen atom (O_c) and the 235 ppm signal to adsorption at the terminal oxygen atom (O_d).

Conclusions

In summary, the location, acidic strength, and mobility of acidic protons in anhydrous and hydrated HPW were revealed using solid-state NMR techniques combined with DFT quantum chemical calculations. In the anhydrous state, REDOR experiments demonstrated that acidic protons are localized on both bridging (O_c) and terminal (O_d) oxygen atoms of the Keggin unit. Experimental results from acetone adsorption indicate that the acid strength of the H(H₂O)_n⁺ species in partially hydrated HPW is comparable to that of a zeolite, while the acidity of an isolated proton is much stronger than that of a zeolite. Isolated protons on the bridging oxygen atoms of anhydrous HPW are nearly superacidic. The present study shows the power of combining experimental evidence and quantum chemical theoretical calculations for understanding the structure and properties of complex systems.

Acknowledgment. We are grateful for the support of the National Natural Science Foundation (20573133, 20425311, 10234070, 20273082) and State Key Fundamental Research Program (2002CB713806) of China as well as the National Science Foundation (CTS-0124333) in the USA. M.J.J., M.N., and R.J.D. thank the Environmental Molecular Science Laboratory at Pacific Northwest Laboratories (Project 3568) for computational support.

Supporting Information Available: ¹H MAS NMR spectra of HPW and ³¹P MAS NMR spectra of trimethylphosphine adsorbed on HPW are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA055925Z