

Activation of Small Alkanes by Heteropolyacids, a H/D Exchange Study: The Key Role of Hydration Water

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The regiospecificity observed for the solid acid-catalyzed H/D exchange at 473 K between isobutane and the D₂O-exchanged H₃PW₁₂O₄₀ heteropolyacid of the Keggin type and its Cs_{1.9}H_{1.1}PW₁₂O₄₀ salt corresponds to an exchange solely with the hydrons present in the α position to the branched carbon. This is comparable to that observed with D₂O-exchanged strong acids such as sulfated zirconia, acid zeolites, and liquid 100% D₂SO₄. However, in exchanges with liquid superacids all the hydrons of the isobutane molecule are exchanged. This indicates that the heteropolyacid and its Cs salt are not superacids. The number of exchangeable protons of the isobutane at 473 K, after outgassing the two deuterated solid samples under dry nitrogen flow at 573 and 523 K, respectively, was very close to the proton content of the anhydrous forms of the heteropolyacids (HPAs): H₃PW₁₂O₄₀ and Cs_{1.9}H_{1.1}PW₁₂O₄₀. Moreover, if some D₂O molecules were still present after incomplete outgassing, then all of the deuterons [both from the anhydrous HPA (D⁺ counterions) and from crystallization D₂O] would undergo exchange with the hydrons of isobutane at 473 K. This shows that such a H/D exchange reaction is fast at this temperature and does not require strong acid sites. Infrared data confirm the presence of H(H₂O)_{*n*}⁺ clusters such as H₃O⁺ and/or H₅O₂⁺ in these catalysts, their concentration dependent on the hydration level. Heteropolyacids were shown to recover their protonic acidity by rehydration of the anhydride form in flowing N₂ + D₂O at 473 K, yielding completely deuterated HPA. The anhydrous forms of both samples were very active for the isomerization of *n*-butane to isobutane at 473 K, but their catalytic activity decreased when small amounts of water were added. This indicates that *n*-butane isomerization requires strong acid sites, while H/D exchange of isobutane depends on much weaker acid sites. © 1999 Academic Press

Key Words: heteropolyacid; H/D exchange; strong acids; superacids; acid sites; alkane activation.

1. INTRODUCTION

Heteropolyoxometalate compounds are ionic solids that may be prepared in a large variety of compositions and structures. The most extensively studied members of this family are those having the Keggin-type structure due to their higher stability and ease of preparation. The ability of these compounds to catalyze both acidic and redox processes has prompted intensive research in recent years; several review papers on this subject have been published recently (1–4).

The strength and number of acid sites in the solid state depend on the structure and composition of the heteropolyanion (HPA) and on its hydration state. It was claimed that, in the solid state, H₃PW₁₂O₄₀, one of the most stable and strongest acids in the Keggin series, has acid sites stronger than those of H-ZSM5 zeolite (5) and even has superacidic centers [based on adsorption calorimetry experiments (6)]. It has also been shown that its acid strength depends strongly on the presence of crystallization water: *H*₀ varies from –5.6 for H₃PW₁₂O₄₀ · 10H₂O, to –8.2 for H₃PW₁₂O₄₀ · 6H₂O (7), to –12.8 for H₃PW₁₂O₄₀ · 1–2H₂O (8).

The corresponding salts of large cations such as Cs⁺, K⁺, Rb⁺, and NH₄⁺, when obtained by precipitation from aqueous solution of the parent acid H₃PW₁₂O₄₀, are micro/mesoporous materials with much larger surface areas than the parent acid [60–200 m² g^{–1} against a few m² g^{–1} for H₃PW₁₂O₄₀ (9)]. The number of protons accessible to nonpolar reactant molecules is very much enhanced with respect to the starting H₃PW₁₂O₄₀ acid, and the specific catalytic activity of the porous salts is higher (1, 10, 11). Concerning the acid strength of porous HPAs compared with that of bulk HPA, NH₃ temperature-programmed desorption (TPD) revealed similar TPD profiles. This probably originates from the reaction of protonic species with gaseous NH₃, resulting in the formation of the neutral ammonium salt (NH₄)₃PW₁₂O₄₀ in the case of H₃PW₁₂O₄₀ and of mixed salts M_{*x*}(NH₄)_{3–*x*}PW₁₂O₄₀ starting from M_{*x*}H_{3–*x*}PW₁₂O₄₀ (12, 13).

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In aqueous solution or in other polar solvents, bulk heteropolyacids such as $\text{H}_3\text{PW}_{12}\text{O}_{40}$ are completely dissociated, while their porous salts are highly insoluble. Their aqueous solutions are described as being “much stronger acids” than equimolar solutions of mineral acids such as H_2SO_4 and HClO_4 (14, 15). Furthermore in a work based on calorimetric titration with bases in acetonitrile solution, it was concluded that $\text{H}_3\text{PW}_{12}\text{O}_{40}$ can exhibit a superacid character (16).

Determining the acidity of solid acids is a very difficult task, despite the large number of available methods. In particular, the use of Hammett’s indicators, often considered to be a reference method, has been highly criticized when used for solids (17).

Within the scope of preparing heteropolyacids for alkane activation, and their performance as catalysts, this paper addresses the acidity of solid HPAs (strength and number of sites) through H/D exchange and the *n*- to isobutane activities, as well as the key role of the hydration state of such materials for these reactions.

2. EXPERIMENTAL

2.1. Catalyst Preparation

Pure heteropolyacid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was prepared according to a classic method including synthesis of the sodium form, extraction of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ by diethyl ether, and recrystallization. The acid crystals were dried on a Buchner filter to obtain the more stable lower hydrates such as $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 21\text{H}_2\text{O}$ and $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 13\text{H}_2\text{O}$. The preparation of the cesium salt was achieved by adding an aqueous solution of CsCl (5 M) to an aqueous solution of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (0.1 M), with a molar Cs/P ratio of 2. The suspension was then stirred for 24 h. The precipitate was washed twice with distilled water, separated from the liquid phase by centrifugation, and dried at room temperature.

2.2. Thermogravimetric Experiments

Thermogravimetric and differential thermal analyses were carried out under dry N_2 ($1.2 \text{ dm}^3 \text{ h}^{-1}$) using a Setaram 92-12 microbalance and about 30 mg of sample. Two heating procedures were used. In the first procedure, there was a continuous rise in the temperature, at a constant heating rate equal to 5 K min^{-1} . In the second procedure, the rise in temperature was interrupted by a plateau, at a given temperature chosen between 473 and 673 K, to depict the activation conditions used for the catalytic reactions.

2.3. Procedure for H/D Exchange Reactions

H/D exchange reactions were carried out in two steps:

First, the solid samples were deuterated under flowing gas at 473 K. About 500 mg of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ or of its Cs

salt was pretreated under nitrogen flow ($2.4 \text{ dm}^3 \text{ h}^{-1}$) at a given temperature (from 473 to 673 K) for 2 h in an all-glass grease-free flow system (18). Deuteration was then carried out under a gas flow of 3 vol% D_2O in N_2 ($2.4 \text{ dm}^3 \text{ h}^{-1}$) at 473 K (corresponds to $3 \text{ mmol D}_2\text{O/h}$). The deuteration was checked to determine whether it was as complete as possible by verifying that no hydrogen atoms were present in the outlet flowing D_2O (by liquid ^2H and ^1H NMR performed on D_2O condensed at the outlet of the apparatus) at the end of the experiment. The samples were then dried by a dry N_2 flow ($2.4 \text{ dm}^3 \text{ h}^{-1}$).

Second, for the H/D exchange reaction, diluted isobutane (5% in N_2) was passed at 473 K at a rate of $1.2 \text{ dm}^3 \text{ h}^{-1}$ over 500 mg of the deuterated solid for 50 min and condensed in a cold trap at the outlet of the reactor for quantitative and qualitative liquid NMR analysis of the deuterium content of isobutane. The amount of isobutane treated was equal to 2 mmol.

2.4. Liquid and Solid NMR Measurements

^1H and ^2H liquid NMR measurements of condensed isobutane were recorded with a Bruker AM 400 spectrometer (400 MHz) at low temperature. For quantitative analysis, a standard mixture of $\text{CDCl}_3/\text{CHCl}_3$ was added to the condensed alkane. The sample volume was adjusted by adding Freon 113.

MAS-NMR study of solid HPA samples were carried out with a Bruker DSX 400 spectrometer at ambient temperature with a spinning rate equal to 12 kHz and H_3PO_4 as an external reference for ^{31}P . The solid HPA samples were treated in the same way as for the H/D exchange test. The spectra were recorded without care against moisture.

2.5. In Situ FTIR Spectroscopy Study

IR spectra were recorded with a Bruker Vector 22 FTIR spectrometer using an *in situ* IR cell equipped with ZnSe windows. The HPA samples (about 2 mg) were dispersed on a thin Ge plate. IR spectra were recorded at room temperature after treating the catalyst at the desired temperature under nitrogen flow ($1.2 \text{ dm}^3 \text{ h}^{-1}$).

2.6. Gas-Phase *n*-Butane Isomerization Reaction

The *n*-butane isomerization reaction was carried out in a differential flow microreactor under the following conditions: catalyst weight = 200 mg, $T_{\text{reaction}} = 473 \text{ K}$, 4.24% *n*- C_4 in nitrogen, total flow rate $1.32 \text{ dm}^3 \text{ h}^{-1}$. To add small amounts of water, an additional nitrogen flow was first saturated with water, by means of a saturator kept at 273 K, and the partial pressure of water was later reduced using a cold trap placed in a cryostat kept below 273 K. The catalysts were pretreated for 2 h at 473 K with a dry or wet N_2 flow ($1.2 \text{ dm}^3 \text{ h}^{-1}$).

3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization

The HPA compounds were characterized by X-ray diffraction, thermogravimetric analysis (TGA), and infrared spectroscopy. The Cs salt, prepared as described under Experimental, has a cubic structure and its chemical composition, calculated from chemical analysis of Cs and W contents, corresponded to the formula $\text{Cs}_{1.9}\text{H}_{1.1}\text{PW}_{12}\text{O}_{40} \cdot 10\text{H}_2\text{O}$ (its hydration level was obtained by TGA). The surface areas of the two samples determined by the BET method were equal to $7 \text{ m}^2 \text{ g}^{-1}$ for H_3P and $71 \text{ m}^2 \text{ g}^{-1}$ for the Cs salt.

3.1.1. Quantitative Determination of Crystallization

Water and Concentration of Brønsted Acid Sites by Thermogravimetric Analyses

The determinations were carried out as follows:

Under dynamic conditions. It is well known that by TGA (or TPD), two types of water loss can be distinguished: the water of crystallization ($n\text{H}_2\text{O}$) and the constitutional water (i.e., $1.5\text{H}_2\text{O}$ for $\text{H}_3\text{PW}_{12}\text{O}_{40}$) (13, 19, 20). The number of Brønsted sites is estimated from the weight loss occurring between 523 and 800 K (loss of constitutional water). These results are very close to the values calculated from the chemical analysis of the Cs salt and from the Keggin structure formula ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) for the 12-tungstophosphoric acid (Table 1). The state of the solid between the end of the loss of the protonic sites (800 K) and the crystallization of the constitutive oxides (873 K) is often ascribed to the anhydride phase (19, 21–27). In the literature, this anhydride phase, existing within a narrow temperature range, is described as still having the Keggin structure but with oxygen vacancies and no protonic sites ($\text{PW}_{12}\text{O}_{38.5}$ for the present

TABLE 1

Number of Brønsted Sites (H^+ in Position of Counteraction) in HPA Samples from Dynamic Thermogravimetric Analysis under Nitrogen Flow (Water Loss from 523 to 800 K) and Deduced from Chemical Analysis for the Cs Salt

Catalyst	Number of Brønsted acid sites from TGA		Theoretical number of Brønsted sites	
	meq g^{-1}	H^+/KU^a	meq g^{-1}	H^+/KU^a
$\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 21\text{H}_2\text{O}$	0.97	3.16 ^b	0.92	3 ^c
$\text{Cs}_{1.9}\text{H}_{1.1}\text{PW}_{12}\text{O}_{40} \cdot 10\text{H}_2\text{O}$	0.30	1.0	0.33	1.1 ^d

^a KU = Keggin unit.

^b After studying many $\text{H}_3\text{P} \cdot n\text{H}_2\text{O}$ samples, we estimate the accuracy of the method to be around 10%.

^c $3\text{H}^+/\text{KU}$ (assuming pure Keggin structure formula).

^d Drawn from the chemical analysis (wt% Cs and wt% W: W/Cs = 6.3, 1.1 H^+ per KU).

TABLE 2

Remaining Proton Contents of Solid HPA Compounds after Isothermal Step Treatments: 2 h at 473, 573, or 673 under Flowing Dry Nitrogen (Rate = $1.2 \text{ dm}^3 \text{ h}^{-1}$) as Measured by Thermogravimetric Analysis (Loss from the Step Temperature up to 1023 K, Heating Rate of 5 K min^{-1})

Catalyst	Step T (K)	Number of remaining protonic sites after isothermal step		
		$\text{H}_2\text{O}/\text{KU}$	H^+/KU	meq $\text{H}^+ \text{ g}^{-1}$
$\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 21\text{H}_2\text{O}$	473	1.59	3.18	0.97
	573	1.33	2.7	0.83
	673	0.6	1.2	0.37
$\text{Cs}_{1.9}\text{H}_{1.1}\text{PW}_{12}\text{O}_{40} \cdot 10\text{H}_2\text{O}$	473	0.5	1	0.32
	573	0.28	0.56	0.18

case). Rehydration of the latter cluster was claimed to restore the initial hydrated 12-tungstophosphoric acid (13, 25). The existence of the anhydrous phase is well accepted but that of the anhydride phase is still debatable (19). As already mentioned (15), thermal treatment conditions (vacuum, gas flow, increasing temperature rates, duration of an isothermal plateau if any) may significantly affect the phase transformations. That is why it is essential to characterize HPA compounds under conditions as close as possible to those under which the catalysts are activated.

Under near-stationary conditions. Such an experimental procedure has been previously used to determine the hydration state of bulk HPA after an isotherm treatment (15, 28). This procedure was applied to both samples at three temperatures for the isothermal plateau. The quantitative experimental proton contents after the isothermal steps are given in Table 2. These data indicate that a thermal plateau of $\text{H}_3\text{PW}_{12}\text{O}_{40}$, performed at 573 K, gives an H content close to the stoichiometry within 10% accuracy. It appears that the deprotonation of the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ sample after the isothermal step of 2 h at 673 K resulted in a cluster with $1.2\text{H}^+/\text{KU}$ (Keggin unit). After this treatment, part of the HPA should correspond to an intermediate deprotonated phase as $\text{H}_{3-x}\text{PW}_{12}\text{O}_{40-x/2}$, with $0 \leq x \leq 3$, or a mixture of anhydrous acid and anhydride.

Moreover, these data prove that the acidic Cs salt was much more sensitive to deprotonation than was the bulk acid. The isothermal treatment at 473 K gave a proton content close to stoichiometry, while after the isothermal plateau at 573 K it was reduced by half. The lower stability of the acidic Cs salt toward deprotonation does not contradict the high thermal stability of the neutral salt $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ if we consider that the acidic Cs salt corresponds to a $\text{H}_3\text{PW}_{12}\text{O}_{40}$ phase entrapped in the porous $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ (10, 11). Thus it is more easily deprotonated than the bulk acid.

3.1.2. Characterization of HPA Samples in Different Hydrated States by *in Situ* Infrared Spectroscopy and ^{31}P MAS-NMR Techniques

The characterization of the protonic sites of heteropolyacids is not an easy task, since a broad band from 2700 to 3600 cm^{-1} , typical of hydrogen-bonded hydroxyl species, is usually observed. Since the existence of an anhydride phase of the HPA and of its rehydration to the initial phosphotungstic acid does not seem well established in the literature, we have used *in situ* infrared spectroscopy and ^{31}P MAS-NMR techniques to check it. IR spectroscopy is known to give absorption bands characteristic of lattice vibrations of the Keggin structure, while ^{31}P MAS-NMR spectra are very sensitive to the Keggin structure symmetry and thus to its hydration state.

The IR spectra of the HPA sample, as a function of its hydration state, are shown later in Fig. 3. On flushing the sample for 1 h at 301 K, in addition to the fingerprint of the HPA in the region 1250–500 cm^{-1} , the spectra are characterized by a broad and intense band in the νOH stretching domain 3600–2700 cm^{-1} and by the band at 1710 cm^{-1} ascribed to the deformation vibration of protonated water (Fig. 1).

After flushing the samples at 473 K for 2 h, the intensity of the band at 1710 cm^{-1} decreased together with the absorption band in the νOH region (Fig. 1b). After treatment at 673 K, the νOH stretching vibration and the deformation band of protonated water disappeared almost completely (Fig. 1c). After 3 h of rehydration at 473 K with 3% H_2O in a N_2 flow, the IR spectrum indicated that the absorption bands characteristic of the protonic species (broad νOH band in the region 3600–2700 cm^{-1} and the band near 1710 cm^{-1}) were restored at more than 70% of the initial

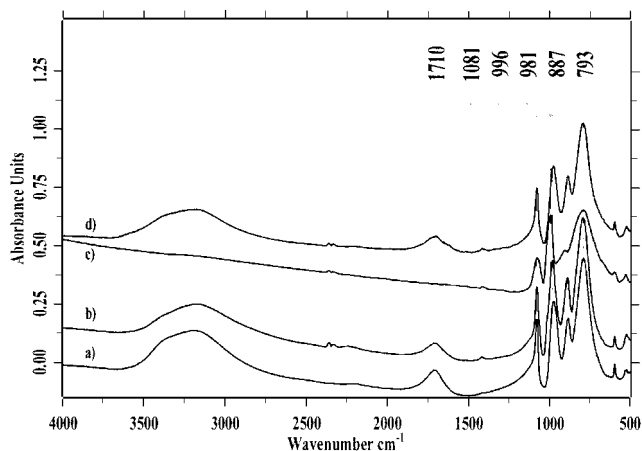


FIG. 1. Infrared spectra of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in the wavenumber range 4000–500 cm^{-1} . (a) $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ treated for 1 h under a dry N_2 flow of 1.2 $\text{dm}^3 \text{h}^{-1}$ at 301 K. (b) Treatment under the same N_2 flow for 2 h at 473 K. (c) Further treatment for 2 h at 673 K under the same N_2 flow. (d) Further rehydration step for 3 h at 473 K with 3% H_2O in N_2 followed by flushing for 1 h at 473 K under the same N_2 flow.

intensity for the band at 1710 cm^{-1} and almost completely for the broad νOH band, according to the accuracy of the method, which is very poor for such broad bands. In the vibration mode region of the HPA compound, it was observed that, on rehydration, the fingerprint of the Keggin structure was restored. Such a Keggin structure is characterized by the νPO vibration peak at 1081 cm^{-1} , the $\text{W}=\text{O}_t$ vibration band at 981 cm^{-1} , and the $\nu\text{W}-\text{O}-\text{W}$ vibration bands at 887 and 793 cm^{-1} . After dehydration at 673 K with flowing N_2 , the $\text{W}=\text{O}_t$ vibration band shifted from 981 to 996 cm^{-1} , and the νPO and $\nu\text{W}-\text{O}-\text{W}$ vibration bands became broader. On rehydration at 473 K, the intensity of the νPO vibration was recovered at 85%, and the $\nu\text{W}=\text{O}_t$ band shifted back to its initial position at 981 cm^{-1} .

An important feature of the protonic species of HPA was the presence of the vibration at 1710 cm^{-1} which shows the presence of protonated water clusters. The intensity of these absorption bands depends on the hydration state of the HPA sample (Fig. 1). It is striking that the infrared spectra are quite similar to those of concentrated solutions of strong mineral acids as well as of solid Nafion resin in equilibrium with the partial pressure of water (29, 30). These absorption bands were assigned to the protonated water species $\text{H}(\text{H}_2\text{O})^+$, $\text{H}(\text{H}_2\text{O})_2^+$, or larger clusters $\text{H}(\text{H}_2\text{O})_n^+$. Such a band has been already observed by IR for heteropolyacids (26, 28, 31) which contain well-defined $\text{H}(\text{H}_2\text{O})_2^+$ species (32, 33). Our IR data clearly show that these HPA compounds contain protonated water clusters.

The present IR observations also support the formation of the anhydride phase ($\text{PW}_{12}\text{O}_{38.5}$) after isothermal plateau treatment at 673 K which, to a large extent, recovered its symmetrical Keggin structure through rehydration at 473 K together with its protonic species.

To check the extent to which the HPA Keggin structure is restored after the rehydration procedure, the ^{31}P MAS-NMR spectrum of the rehydrated sample was recorded. The spectrum reported in Fig. 2a shows two well-resolved peaks: an intense peak at –14.9 ppm and a smaller one at –11.8 ppm. It is well known that the highly symmetrical Keggin structure of the hydrated phosphotungstic acid is characterized by a narrow resonance line near –15 ppm (25, 34). The ^{31}P NMR chemical shift for highly dehydrated 12-tungstophosphoric acid has been observed near –11 ppm (10, 25, 34). The peak at –14.9 ppm, assigned to the hydrated Keggin structure, represents 86% of the total P atoms. The assignment of the peak at –11.8 ppm is more difficult even if such intermediate lines have been previously ascribed to an intermediate hydrated phase (25, 34). Figure 2b shows the spectra after the total decomposition of the Keggin structure at 1023 K. A broad peak centered at –11.5 ppm was observed, while the resonance line observed at –11.8 ppm on the HPA after rehydration at 473 K was much narrower. This result shows that the small peak at –11.8 ppm does not correspond to the decomposed Keggin structure. This peak, which has a position halfway

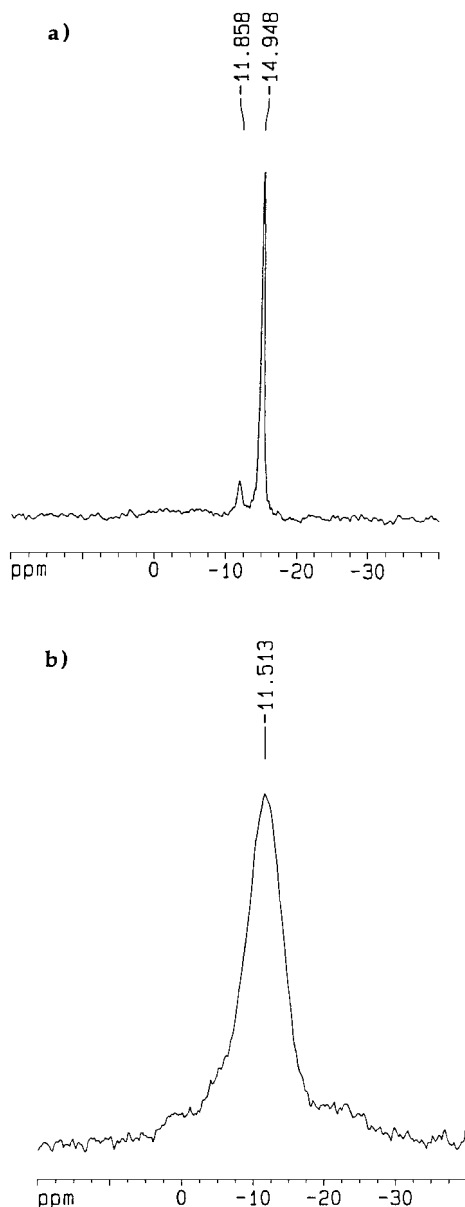


FIG. 2. ^{31}P MAS-NMR spectra of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (a) treated for 2 h at 673 K under a dry N_2 flow of $1.2 \text{ dm}^3 \text{ h}^{-1}$ and rehydrated at 473 K with 3% H_2O in N_2 for 3 h and (b) treated for 2 h at 1023 K under the same dry N_2 flow.

between the dehydrated 12-tungstophosphoric acid and the hydrated form, should rather be assigned to the incompletely rehydrated acid phase.

3.2. H/D Exchange between Isobutane and Deuterated Solid Heteropolyacids

3.2.1. Regiospecificity of the Exchange

The H/D exchange at 473 K between isobutane and the solid HPA acid and its Cs salt, deuterated as described un-

der Experimental, showed in all cases that, whatever the pretreatment temperature (from 473 to 673 K), before deuteration, only the primary hydrons were exchanged. This was shown by ^1H and ^2H liquid NMR analyses performed on the condensed $i\text{-C}_4$ after the exchange experiment (see Fig. 3).

We have recently shown that, in the presence of deuterated superacids, alkanes exchange their protons for deuterons with a regioselectivity in accordance with the relative σ basicity of the C-H bonds (35, 36). In addition to these results, we have also shown that the H/D exchange that occurs between D_2O -exchanged strong solid acids (sulfated zirconia, zeolites) and light alkanes exhibits a very different regioselectivity in the sense that, in isoalkanes, only the hydrons in the α position to the branching carbon were exchanged while those on the branching carbon were not (37). This exchange pattern is the same as that between isoalkanes and pure 100% D_2SO_4 (38–40). It can be concluded that, like other strong solid acids, solid HPA does not behave as a liquid superacid. The nature of the initial step is still unknown, but the equilibrium between the trimethyl carbenium ion and the isobutene is the cause of the regiospecific deuteration of the isobutane, as shown in the catalytic cycle in Scheme 1.

3.2.2. Quantitative Aspect of the H/D Exchange

H/D exchange reaction between the anhydrous forms of both samples and isobutane at 473 K. The deuteration of the HPA compounds was performed on the nearly anhydride phase as described above, obtained after a thermal treatment under flowing N_2 for 2 h at 673 K for $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and for the Cs salt at 573 K. The deuteration was performed at 473 K in both cases with 3% D_2O in N_2 for 3 h. The deuterated bulk heteropolyacid and its acidic Cs salt were then carefully swept for 1 h with dry nitrogen flow at 573 and 523 K, respectively, to obtain the nearly anhydrous

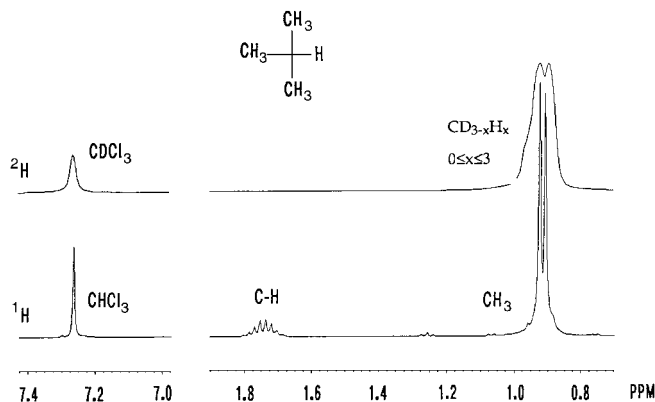
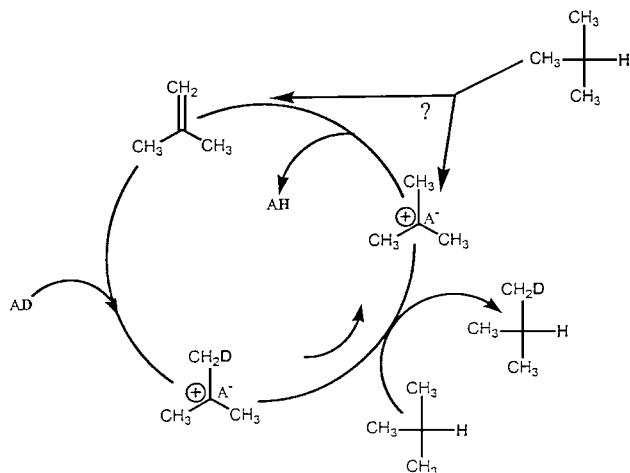
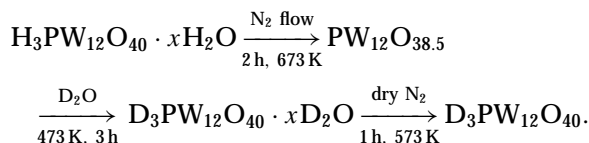


FIG. 3. ^1H and ^2H NMR spectra of condensed isobutane after the H/D exchange reaction between isobutane and deuterated HPA.



SCHEME 1. Catalytic cycle of H atom exchange between isobutane and deuterated HPAs.

deuterated forms without crystallized D_2O molecules. The following scheme describes the procedure:



The number of exchangeable protonic sites at 473 K, on contact with the deuterated samples and isobutane for 50 min and determined quantitatively by the liquid NMR technique, is given in Table 3. It is striking that the experimental values are close to the number of protonic sites as measured by TGA (Table 1 or 2). This also shows that exchange occurred even between bulk deuterons of the solids (in the case of the H_3P sample) and isobutane which is a nonpolar compound, indicating that such deuterons were mobile enough at 473 K to give rise to the exchange reaction. This obviously holds true when deuteration of the samples is complete.

TABLE 3

Number of Exchangeable Protonic Sites at 473 K in Anhydrous HPA Compounds Calculated from ^1H and ^2H NMR Analyses of Exchanged Liquid Isobutane^a

Catalyst	Amount of D found in i-C ₄ (meq g ⁻¹ cat)
D ₃ PW ₁₂ O ₄₀	0.89
Cs _{1.9} D _{1.1} PW ₁₂ O ₄₀	0.30

^a Conditions: sample pretreated at 673 K for 2 h (at 573 K for 2 h for the Cs salt), deuterated with D_2O for 3 h at 473 K, heated at 573 K for 1 h (at 523 K for 1 h for the Cs salt), and exchanged with i-C₄ at 473 K for 50 min (N_2 and i-C₄ dried before use).

TABLE 4

Number of Exchangeable Protonic Sites at 473 K in Hydrated HPA Compounds Calculated from ^1H and ^2H NMR Analyses of Exchanged Liquid Isobutane^a

Catalyst	Amount of D found in i-C ₄ (meq g ⁻¹ cat)
D ₃ PW ₁₂ O ₄₀ · nD ₂ O	2.36
Cs _{1.9} D _{1.1} PW ₁₂ O ₄₀ · nD ₂ O	3.28

^a Conditions: samples pretreated at 473 K for 2 h, deuterated with D_2O for 1 h, flushed with dry N_2 for 15 min, and exchanged with i-C₄ (N_2 and i-C₄ dried before use) at 473 K for 50 min.

H/D exchange reaction for partly hydrated samples. Both samples were incompletely flushed after the deuteration step to retain some of the D_2O molecules in addition to the Brønsted sites (H^+ or D^+). The deuteration was performed at 473 K on the anhydrous HPA, obtained after thermal treatments for 2 h at 473 K in both cases. In these experiments the deuterated samples were outgassed under nitrogen flow at 473 K for 15 min (instead of 573 and 523 K for 1 h for the acid and its Cs acid salt, respectively). The H/D exchange reaction between the deuterated samples and isobutane was carried out as above at 473 K for 50 min. The number of deuterium atoms exchanged by hydrogen atoms in both samples is given in Table 4. The number of exchangeable deuterons was found to exceed the number of deuterons of the “anhydrous” acid form (3/KU for the bulk acid and 1.1/KU for the Cs salt). Thus, it is assumed that, in the clusters $D(D_2O)_n^+$ present on solid HPAs, all the deuterons are active with respect to the H/D exchange reaction with isobutane at 473 K. For the bulk acid, the largest ratio between the number of deuterons of the anhydrous form and the number of exchangeable deuterons is near 2.5, a value that can be explained by the presence of both $D(D_2O)_2^+$ and $D(D_2O)^+$ species. For the Cs salt, the ratio between the number of deuterons of the anhydrous form and the number of exchangeable deuterons reached 10. This result could be explained by the participation of deuterons in species larger than $D(D_2O)_2^+$. However, a more realistic proposal is that only surface species, such as $D(D_2O)^+$ or at most $D(D_2O)_2^+$, participate in the exchange reaction and that at higher water contents, a very fast exchange occurs between H^+/D^+ and the neutral D_2O . D_2O retained in the microporosity of the Cs salt could participate to this exchange.

In addition, the number of exchangeable deuterons measured on nonporous HPAs (the “anhydrous” acid $D_3PW_{12}O_{40}$ or a hydrated form $D_3PW_{12}O_{40} \cdot nD_2O$) showed that all the deuterons participate in the exchange. This demonstrates the high mobility of the protons/deuterons in such materials. This result is in agreement with a recent study that demonstrates that by ^{31}P and ^1H MAS-NMR (41).

In a study of silica–alumina catalysts, Haldeman and Emmett (42) showed that small amounts of water on such catalysts greatly enhance (by a factor of 25) the isobutane H/D exchange reaction and play a role in the D distribution in the isobutane molecule. The authors correlated such properties to the acidity of the samples and to the transformation of Lewis to Brønsted sites in the presence of small amounts of water. In our case, only Brønsted sites were detected (12), which supports our conclusion that, for protonated water molecules, all H atoms give rise to isotopic exchange.

3.3. Catalytic Activity in the *n*-Butane Isomerization Reaction

Both samples, bulk acid and its Cs salt, had high activity for *n*-butane isomerization at 473 K after the samples had been pretreated in a flow of dry nitrogen at 473 K for 2 h. The initial rate of isobutane formation was equal to 4×10^{-8} and $32 \times 10^{-8} \text{ mol s}^{-1} \text{ g}^{-1}$, respectively (43).

In the present study, we investigated the role of water in the catalytic performance of both samples in the *n*-butane isomerization reaction at 473 K. Different water partial pressure was added to the carrier gas during both pretreatment of the catalyst and the catalytic reaction. Figures 4 and 5 show the catalytic activities with time on stream over $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{Cs}_{1.9}\text{H}_{1.1}\text{PW}_{12}\text{O}_{40}$, respectively. The initial activity decreased with increasing water content in the feed.

We showed previously (43) that the catalytic activity of W-based HPA was reduced when the sample was outgassed at 573 K instead of 473 K for 2 h in a dry nitrogen flow. This pretreatment induced a decrease in the proton content, particularly in the case of the Cs salt as shown by the TGAs reported in Table 1. Catalytic results, presented in Fig. 4, show that the anhydrous 12-tungstophosphoric acid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ exhibits the highest catalytic activity for *n*-butane isomerization, corresponding to the largest amount of strong acid sites, and that the decrease in catalytic ac-

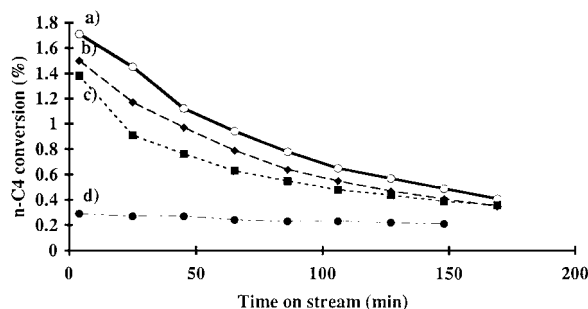


FIG. 4. Activity of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in *n*-C₄ isomerization at 473 K as a function of time on stream in the presence of different partial pressures of water: (a) 0 kPa, (b) 0.011 kPa, (c) 0.038 kPa, (d) 0.8 kPa.

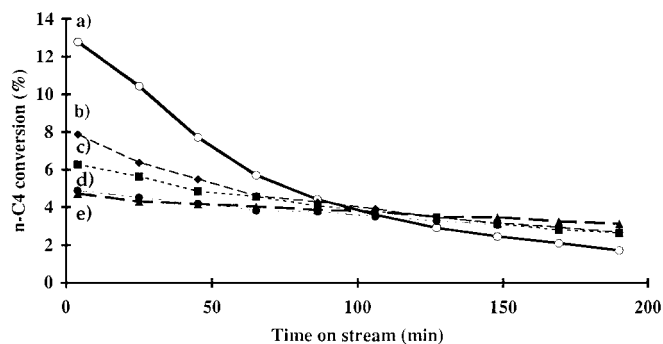


FIG. 5. Activity of $\text{Cs}_{1.9}\text{H}_{1.1}\text{PW}_{12}\text{O}_{40}$ sample in *n*-C₄ isomerization at 473 K as a function of time on stream in the presence of different partial pressures of water: (a) 0 kPa, (b) 0.009 kPa, (c) 0.047 kPa, (d) 0.32 kPa, (e) 0.67 kPa.

tivity in the presence of water presumably corresponds to the lower acid strength of the sites due to the solvation of the protons. $\text{Cs}_{1.9}\text{H}_{1.1}\text{PW}_{12}\text{O}_{40}$ exhibits the same behavior (Fig. 5): its catalytic activity in the *n*-butane isomerization was the highest after pretreatment in dry N_2 at 473 K, and in presence of low partial pressure of water its catalytic activity was also reduced. The selectivity changes (Table 5) in the presence of water may be due to the lower conversion.

In the two reactions performed at 473 K, *n*-C₄ isomerization and H/D exchange between deuterated HPA and isobutane, the presence of water generated opposite effects. It is clear that the two reactions studied in this work are not energetically comparable (40). That is the principal reason why the addition of small amounts of water, in the case of *n*-butane isomerization, leads to a decrease in the rate of the reaction. On the other hand, the extent of the H/D exchange reaction with isobutane, a less demanding reaction, improved in the presence of D_2O on the catalyst surface, although the strength of the sites decreased due to the solvation. In the latter case, the acidity of all the Brønsted sites in species such as D_3O^+ and $\text{D}(\text{D}_2\text{O})_2^+$ was probably strong enough for H/D exchange, but not for *n*-butane-to-isobutane isomerization reaction.

TABLE 5

Activity and Selectivity for the *n*-Butane Isomerization Reaction in the Presence of Water over $\text{Cs}_{1.9}\text{H}_{1.1}\text{PW}_{12}\text{O}_{40}$ (after 4 min on Stream)

$p_{\text{H}_2\text{O}}$ (kPa)	Conversion of <i>n</i> -C ₄ (%)	Selectivity (%)			
		C ₃	<i>i</i> -C ₄	<i>i</i> -C ₅	C ₅
0	12.8	8.0	84.0	5.4	2.6
0.009	7.9	4.3	90.0	3.6	2.1
0.047	6.3	3.5	91.3	3.2	2.0
0.32	4.9	3.0	92.5	2.6	1.9
0.67	4.7	3.3	92.5	2.8	1.4

4. CONCLUSION

In the present work we have shown that solid heteropolyacid $H_3PW_{12}O_{40}$ and the Cs salt $Cs_{1.9}H_{1.1}PW_{12}O_{40}$ are strong acid catalysts but not superacids, as demonstrated by the regioselectivity in H/D isotopic exchange between the deuterated samples and isobutane at 473 K. In fact, the regioselectivity of the exchange was different from that observed with liquid superacid, $HF-SbF_5$, but was similar to that observed with sulfated zirconia, zeolites, and 100% sulfuric acid: only the hydrons in the α position to the branching carbon atom were exchanged. Moreover, all deuterons, even bulk deuterons in the $D_3PW_{12}O_{40}$ sample, are acidic/mobile enough to give rise to total exchange at 473 K, although isobutane is a nonpolar compound.

Ionic $H(H_2O)_n^+$ clusters are shown by IR spectroscopy to be present on hydrated heteropolyacids. Moreover, anhydride heteropolyacid, close to the $PW_{12}O_{38.5}$ formula, was observed by *in situ* IR spectroscopy and ^{31}P MAS-NMR to rebuild (more than 85%) its initial, highly symmetrical Keggin structure and its active protonic species through contact with molecular water at 473 K. The ability of such species to exchange with isobutane in their deuterated form as $D(D_2O)_n^+$ is higher (by a factor of 2.5 to 10) than the number of structural protons for the bulk acid and its Cs salt. This shows that, in such clustered species, fast exchanges occurred between hydrogen atoms. It follows that the hydrated state of the samples is particularly important for their catalytic properties, depending on the strength of the acid required for the reaction. A similar effect of small amounts of water was also observed in the reaction of *n*-butane isomerization at 473 K and was shown to be detrimental, while the opposite was true for the H/D exchange reaction of isobutane with the deuterated HPA samples.

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