A theoretical–experimental study of Wells–Dawson acid
An explanation of their catalytic activity

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Abstract

A theoretical–experimental study about the behaviour of the protons and their interactions with water molecules on the Wells–Dawson acid and their influence on the catalytic activity was done. The Wells–Dawson acid ($H_6P_2W_{18}O_{62} \cdot nH_2O$) was characterised by TGA analysis. Besides, DRIFTS and ^{1}H MAS-NMR measurements as a function of acid treatment temperature were done. These experimental results, consistent with prior studies, suggest that the protonic acidity is related to the presence of water molecules in the heteropolyoxoanion (HPA) structure. In particular, the $H_5O_2^+$ species associated with the last two H_2O molecules determined by TGA analysis and the ^{1}H MAS-NMR measurements show that the presence of $H_5O_2^+$ species plays an important role in the acidity–catalytic activity relationship.

The Wells–Dawson acid structure formation was studied by calculating the relative energy of the system. The possible acid molecular structure ($P_2W_{18}O_{62}H_6 \cdot nH_2O$) was analysed considering different steps by associating to the Wells–Dawson anion $(P_2W_{18}O_{62})^{-6}$, the protons, water molecules and secondary structures. The theoretical calculus by extended Hückel method (EHMO) was done analysing the most energetically favourable positions for the protons. The theoretical results indicate that three different water species associated to the Wells–Dawson acid structure can exist. Besides, these results show that the $H_5O_2^+$ species are the most energetically stable ones in the acid structure. These species bonds two secondary structures of Wells–Dawson acid leading to minimum system energy. It can be expected that these species are the last water molecules lost in the acid structure at the end of acid dehydration process. This assumption is in agreement with the results obtained with the three experimental techniques previously mentioned.
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1. Introduction

Solid heteropolyoxoanions (HPAs) are ionic crystals, composed of large polyanions, counter-cations and crystallisation water, and other molecules, which have been shown to be effective in heterogeneous catalysis. An important point with respect to HPAs is to distinguish among the several levels of primary, secondary and more recently tertiary structure [1]. The primary structure is constituted by the polyanions, meanwhile the secondary one correspond to the arrangement of polyanions, cations, water of crystallisation, etc. On the other hand, the tertiary structure is the structure of solid HPAs as assembled. The different properties of the solids such as size of the

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particles, pore structure, etc. are determined by the tertiary structure.

The catalytic behaviour of these materials is strongly influenced by the structural modifications that may occur in their secondary and tertiary structures. [1–3]. Solid acid HPAs posses pure Bronsted acidity and the protons play the role of catalytic active sites. Particularly, for acid-type HPAs several authors [4–8] reported that their catalytic activity depends on: (i) the hydration state, (ii) the strength of acid sites and (iii) the accessibility of the protons.

The best known of the above mentioned acid-type HPAs are the Keggin-type structures. There are a few studies of the Wells–Dawson structures [6,9,10].

In a previous work [6], we have been shown that the catalytic activity of Dawson acid for methyl *tetra*-butyl ether (MTBE) synthesis and methanol dehydration to diethyl ether in gas phase at $100\,^\circ$C was directly related to the presence of water molecules in its secondary structure. In fact, the isobutene conversion was approximately constant with calcination temperature up to $200\,^\circ$C, but the activity decreased at higher temperatures until no activity at a pre-treatment temperature of $400\,^\circ$C. The same effect was found for the second reaction. The decrease of activity is due to the loss of the crystallisation water molecules leading to a new phase, the anhydrous $H_6P_2W_{18}O_{62}$. In this dehydrated Dawson–Wells type framework, protons remain trapped between primary units but inaccessible to the reagents, thus in this way the catalytic activity drop to zero.

The aim of the present work is to analyse theoretically and experimentally the behaviour of protons and their interactions with water molecules on the Wells–Dawson acid ($H_6P_2W_{18}O_{62} \cdot n H_2O$) and their influence on the catalytic activity.

2. Experimental

2.1. Wells–Dawson acid synthesis

The Wells–Dawson acid ($H_6P_2W_{18}O_{62}$ aq.) were synthesised according to the Dreschel method from a α/β $K_6P_2W_{18}O_{62} \cdot 10H_2O$ isomer mixture [6]. This potassium salt was prepared as described in detail in a previous work [6]. The Wells–Dawson acid was obtained from an aqueous solution of α/β

$K_6P_2W_{18}O_{62} \cdot 10H_2O$ salt, which was treated with ether and concentrated HCl (37%) solution. The acid so released formed an addition compound with the ether, which allowed it to be separated from the solution. The remaining solution was placed in a vacuum-desiccator until crystallisation.

2.2. Wells–Dawson acid characterisation

2.2.1. TGA analysis

TGA analysis was carried out in Shimadzu TGA-50H and DTA-50 equipment, respectively. Acid sample was heated in a He stream from room temperature (RT) to $500\,^\circ$C at a rate of $2\,^\circ$C min^{-1}.

2.2.2. DRIFTS spectroscopy measurements

The DRIFTS spectra were obtained using Nicolet 510P equipment with KBr optics and a DTGS detector. The DRIFTS chamber equipped with ZnSe window (Spectra Tech 0030-101), allows "in situ" measurements up to $500\,^\circ$C at an atmospheric pressure to be carried out [11]. The solid acid was placed inside the chamber, without packing or dilution in KBr, with a N_2 stream of $50\,$ml min^{-1}. For each spectrum two hundred scans were obtained with a $4\,$cm^{-1} resolution. The spectrum of an Al mirror was used as background in N_2 atmosphere. The DRIFTS spectroscopy was analysed between room temperature and $300\,^\circ$C at a rate of $5\,^\circ$C min^{-1}.

2.2.3. ^1H MAS-NMR spectroscopy

^{1}H MAS-NMR spectra were performed at $400\,$MHz using a Varian Unity-400 NMR spectrometer. The external magnetic field used was $9.4\,$T. The measurements were carried out at room temperature, and the sample was spun at $3000\,$Hz in a $7\,$mm zirconia rotor at the magic angle ($54^\circ\ 44'$ with respect to the magnetic field). The ^{1}H spectrum was obtained with a single-pulse with $20\,\mu$s, corresponding to the 90° flip angle. From 1 to 32 scans were acquired. Prior to these measurements, the acid was dehydrated under flowing dry N_2 at 25, 100, 200 and $330\,^\circ$C for $2\,$h. After that, the acid sample was transferred into the zirconia rotor, this manipulation was carried out in a dual manifold providing dry N_2 to avoid the moisture contamination. Chemical shifts were referenced to an external standard TMS solution.

Table 1
Parameters employed in the EHMO

Atom	s		p		d				
	H_{ii}	Exp	H_{ii}	Exp	H_{ii}	Exp1	Coef1	Exp2	Coef2
H	−13.6	1.3							
O	−32.3	2.275	−14.8	2.275					
P	−18.6	1.75	−14.0	1.30					
W	−8.26	2.341	−5.17	2.309	−10.37	4.982	0.694	2.068	0.5631

2.3. Theoretical method and cluster model description

To represent the Dawson acid primary structure the MOLMOD program was used. The acid clusters were built by taking specific angles and average distances reported by D'Amour [12]. The semi-empirical extended Hückel method (EHMO) is an acceptable approach to the electronic structure of a molecule when transition metals are involved. Although the method does not give representative absolute results, it predicts well the relative variations, so allowing trends to be defined with a simple calculation procedure [13]. The relative energy of the system (E_r) includes terms for both repulsion and binding energies and the H_{ii} parameters and coefficients (ξ_{ii}) used for the calculations are indicated in Table 1. The Wolfsberg–Helhmotz constant employed was 1.70.

3. Results and discussion

3.1. Dawson acid characterisation

The Wells–Dawson acid was synthesised in a hydrated form, $H_6P_2W_{18}O_{62} \cdot nH_2O$. Several authors have shown that water play an important role in the catalytic activity of the HPAs [3–5,8]. In this way, Bardin et al. [5,8] have reported that pre-treatment temperature of HPAs has a clear influence on the catalytic activity. They indicated that an increase of temperature leads to a diminution of Keggin acid activity in butene isomerisation and this fact is due to a lost of structure water molecules. We found similar results for Dawson acid activity in MTBE synthesis [6]. In this previous work, TGA analysis of Dawson acid in standard conditions (samples were heated from room temperature to 800 °C with a heating rate

of 10 °C min^{-1}) were done. In these experiments, two steps for the water loss were observed [6]. Whereas, in the present work, more careful TGA measurements (heating rate of 2 °C min^{-1}) were performed. These measurements indicated that the loss of crystal water occurs in three temperature intervals. In the last one, the acid loses two water molecules, as is shown in Table 2. These dehydration steps indicated that three different types of interaction can exist between H_2O molecules, hydrated protons or protons and primary acid anion units.

On the other hand, "in situ" DRIFTS spectra in the range of 4800–2800 cm^{-1} for the Wells–Dawson acid as a function of the temperature were obtained (Fig. 1). At room temperature (25 °C), it can be observed a vibration band at 887 cm^{-1} which can be assigned at W–O–W bond where the oxygen is shared by two octahedral WO_6 and the other band at 983 cm^{-1} correspond to W=O species [14].

This spectrum also shows two bands at 1011 and 1080 cm^{-1} attributed to PO species. The first one corresponds to νPO_2 and the last one corresponds to the stretching frequency of the tetrahedral PO_4 species [14].

Also, at room temperature it can be observed a vibration band at 1106 cm^{-1} associated to an another band close to 3440 cm^{-1}, shown in Fig. 2. According to several authors [7,15] these bands correspond to a $H_5O_2^+$ species. In fact, Bielanski et al. [7] reported that the band at 3440 cm^{-1} frequency can be attributed

Table 2
TGA results for Wells–Dawson acid

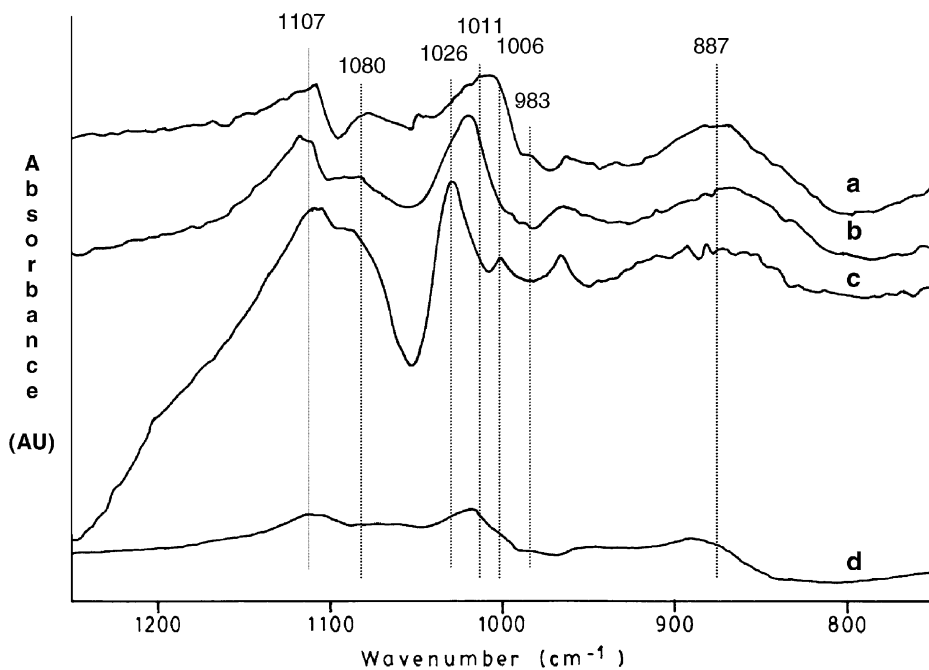| Water lost (mol H_2O/Wells–Dawson unit)	Temperature intervals (°C)
17	66–72
5	97–114
2	308–318

Fig. 1. In situ DRIFTS spectra of the Wells–Dawson acid as a function of temperature in the range 1300–800 cm^{-1}; (a) 25 °C, (b) 100 °C, (c) 200 °C, (d) after rehydration.
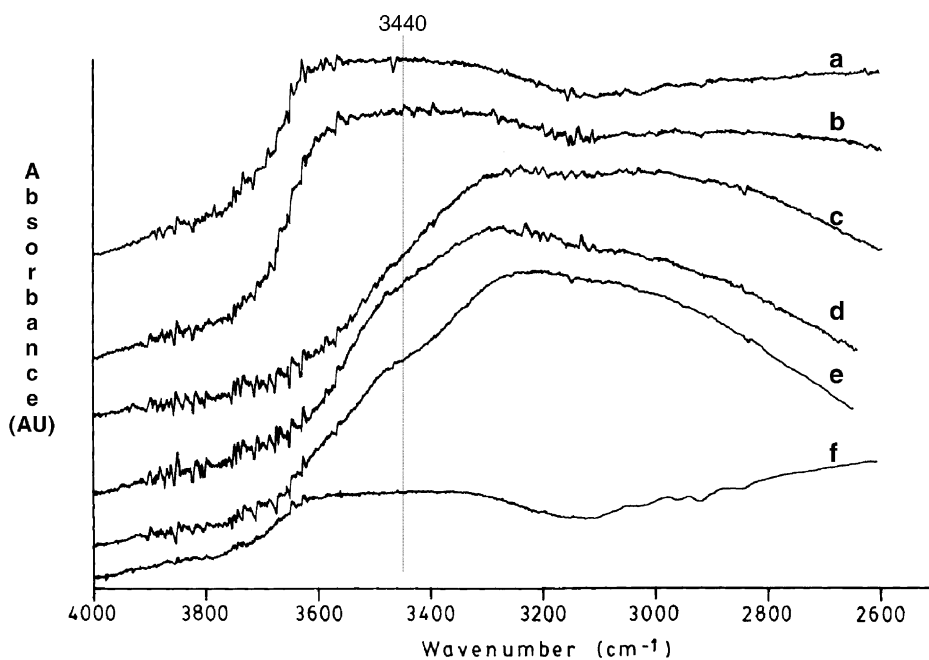

Fig. 2. In situ DRIFTS spectra of the Wells–Dawson acid as a function of temperature in the range 2800–4000 cm^{-1}; (a) 25 °C, (b) 100 °C, (c) 200 °C, (d) 300 °C, (e) 400 °C, (f) after rehydration.

to a bond between a hydrogen bonded to terminal oxygen atoms (W=O) and this unit joined to an oxygen of water molecule, forming the dioxonium structure ($H_5O_2^+$).

When the temperature increases, a shift is observed in the bands localised between 800 and 1200 cm^{-1} (Fig. 1) and a diminution in the 4000–3000 cm^{-1} region (Fig. 2), which is attributed to the acid dehydration. Both the shifts and the acid dehydration suggest that during the loss of water, changes can occur in the secondary structure of Dawson acid. In fact, these phenomena are in agreement with the results reported by Mioc et al. [16] and our own previous results [6]. Both studies indicated that the Keggin and Dawson secondary structures, respectively, suffer morphological changes when the treatment temperature increases.

It can be observed in Fig. 1 when the temperature is incremented that the band at 983 cm^{-1} is shifted to 1006 cm^{-1}. According to Kozhevnikow [2] the above-mentioned shift in the W=O band clearly shows a water loss in the HPA structure.

A shift to higher wavenumbers for the bands at 1011 and 1080 cm^{-1} is also observed. Both bands have a shift of 15 and 10 cm^{-1}, respectively. This fact allows us to suggest that the bond length of P–O is modified with the dehydration of the Dawson acid. On the other hand, at 200 °C it can be observed a broadening in the 1190 cm^{-1} zone, which could be associated to a change in the P–O co-ordination, such as Cabello and Baran reported in their IR and Raman studies about the structures of transition metal and rare earth phosphates [17].

On raising the temperature above 300 °C, in the wavenumber zone upper to 2800 cm^{-1}, the band at 3440 cm^{-1} disappears or does not detected. After a rehydration of the system, this band is recovered and in consequence indicated the presence of $H_5O_2^+$ species (see Fig. 3). This phenomenon is coincident with the results previously obtained [6]. We reported that dehydrated Dawson acid does not show catalytic activity for methanol dehydration reaction. Nevertheless, the exposure to an air stream saturated with water, resulted in complete regeneration of its catalytic activity for the methanol dehydration reaction. This fact could indicate that the $H_5O_2^+$ species are related to catalytic activity of Dawson acid.
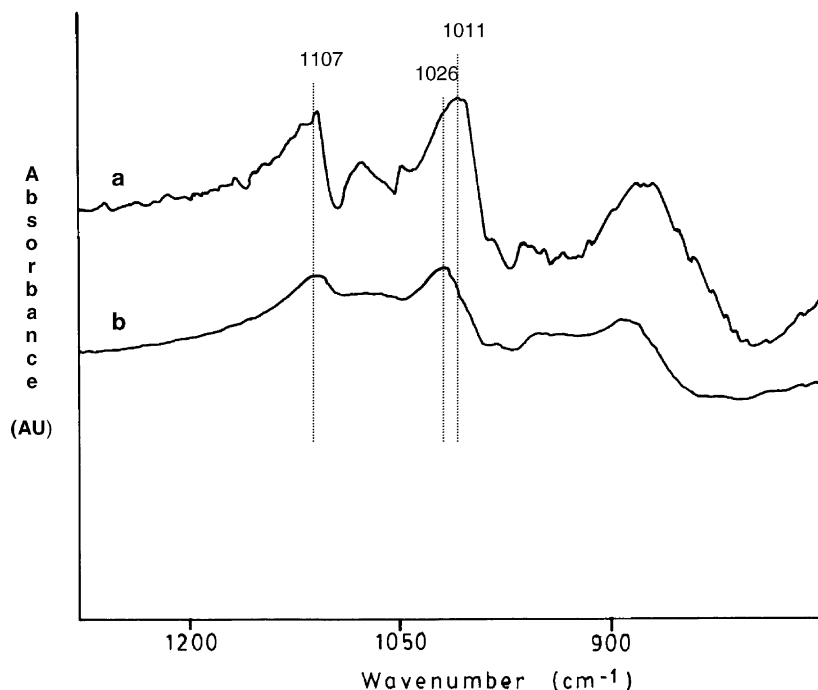

Fig. 3. In situ DRIFTS spectra of the Wells–Dawson acid in the range 1300–800 cm^{-1}; (a) 25 °C, (b) after rehydration.

Table 3
Chemical shift values of ^{1}H MAS-NMR for Wells–Dawson acid as a function of treatment temperature

Temperature (°C)	Chemical shifts, δ_H (ppm)
25	7.3
25	5.9
100	8.8
200	7.6

Bronsted acid sites in solid acids can be characterised using ^{1}H MAS-NMR measurements and the chemical shift value of ^{1}H can be related with the acidity of the proton. It has been shown that increasing the value of chemical shifts correspond to an increase of the acid strength [18]. The main idea is that more acidic proton has less electron in its vicinity, therefore, is less shielded, and subsequently, its NMR chemical shift value (δ_H) will be more positive (lower-field shift) [19].

The ^{1}H MAS-NMR measurements of Dawson acid as a function of dehydration degree between 25 and 330 °C were done. The results are indicated in Table 3 and it can be observed that a change in the environment of the protons or the presence of different type of protons as a function of temperature. At room temperature (25 °C) two peaks are detected: a main peak at 7.3 ppm and the other at 5.9 ppm. The peak at 7.3 ppm corresponds to a large protonated water clusters as $H^+(H_2O)_n$ due to the sample is fully hydrated and the peak at 5.9 ppm would correspond to a residual neutral water in the structure [19]. After dehydration at 100 °C, the Dawson acid shows only one peak but shifted to higher chemical shift. at 8.8 ppm. This peak can be attributed to a H_3O^+ species [19]. On the other hand, when the dehydration temperature increases from 100 to 330 °C, it can be observed a diminution of the chemical shift values (Table 3). In fact, δ_H values of 7.6 and 6.7 ppm were observed for the acid treated at 200 and 330 °C, respectively.

In order to explain these results, the TGA measurements must be considered. These indicate that at 200 °C, the Dawson acid retains two water molecules in their structure, $H_6P_2W_{18}O_{62} \cdot 2H_2O$. Consequently, the peak at 7.6 ppm obtained after dehydration at 200 °C (Table 3) could correspond to protonic sites like $H^+(H_2O)_2$ species.

On the other hand, TGA results indicated that for a temperature of 330 °C the solid lost the last two water molecules, resulting in an environment protons with lower acidity ($\delta_H = 6.7$ ppm). As already mentioned, we found that the catalytic activity of Dawson acid for MTBE synthesis and methanol dehydration to diethyl ether in gas phase at 100 °C was directly related to the presence of water molecules in its secondary structure [6]. In fact, the isobutene conversion was approximately constant with calcination temperature up to 200 °C, but the activity sharply decreases after a pre-treatment of 300 °C and it was practically null when pre-treatment temperature was 400 °C. The same effect was found for the second reaction (methanol dehydration).

According to the TGA analysis and the ^{1}H MAS-NMR measurements after dehydration at 200 °C, the Dawson acid retains two water molecules and shows the presence of $H_5O_2^+$ species associated with them. Taking into account the above catalytic results, the presence of $H_5O_2^+$ species plays an important role in the acidity–catalytic activity relationship of solid Dawson acid.

3.2. Theoretical method and cluster models

The Wells–Dawson acid structure formation was studied by calculating the relative energy of the system (E_r). The E_r was calculated by using the equation:

$$E_r = Ej - E(j-1)$$

where E_r, with $r = 0$, 1 and 2, can be seen in Table 4.

The possible acid molecular structure—$P_2W_{18}O_{62} H_6 \cdot nH_2O$— was analysed, considering different steps by associating to the Wells–Dawson anion $(P_2W_{18}O_{62})^{-6}$: (a) the six protons (E_0), (b) 'n' water molecules (E_1) and (c) 'm' secondary structures (E_2).

Besides, Fig. 4 shows the E_r values calculated in each step. The theoretical calculus by EHMO method was done analysing the most energetically favourable positions for the six protons. Thus, more than 300 possibilities of O–H bonds, both terminal oxygen (W=O) and bridging in bi-coordinated oxygen to W atoms (W–O–W), were analysed. The results show that the protons with the highest stability ($E_0 = -211.3$ eV) were those localised in terminal oxygens (W=O). These results are in agreement with that reported by Kozhevnikov et al. [20,21], who determined using ^{17}O NMR measurements that the predominant protonation sites in solid HPA with Keggin structure are the terminal oxygens.

Table 4
Relative energy of the system to adding to the Wells–Dawson anion six protons, 'n' water molecules and 'm' secondary structure

| E_r	Observations
$E_0 = E_{(P_2W_{18}O_{62}H_6)} - E_{(P_2W_{18}O_{62}{}^{-6})}$	E_0 is the energy to adding to the Wells–Dawson anion $(P_2W_{18}O_{62})^{-6}$ each one of the six protons
	$E_{(P_6W_{18}O_{62})^{-6}}$ is the anion energy of the acid primary structure
$E_1 = E_{(P_2W_{18}O_{62}H_6 \cdot nH_2O)} - E_{(P_2W_{18}O_{62}H_6)}$	E_1 is the energy to adding to the structure $P_2W_{18}O_{62}H_6$ each one of the H_2O molecules and to form the secondary structure
$E_2 = E_{(P_2W_{18}O_{62}H_6 \cdot nH_2O)m} - E_{(P_2W_{18}O_{62}H_6 \cdot nH_2O)}$	E_2 is the energy to join each one of secondary structure and to form the tertiary structure
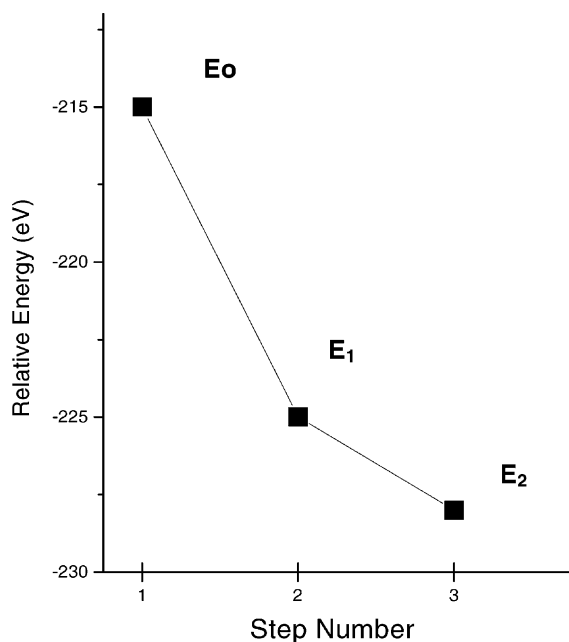
Fig. 4. Relative Energy of the system for the Wells–Dawson acid structure formation. (E_0, E_1 and E_2 see Table 2).

Table 5
The H^+ position bonded to W=O (comments in text)

W(4)	O(−30)
W(7)	O(31)
W(8)	O(−31)
W(10)	O(−26)
W(13)	O(−34)
W(15)	O(−33)

In Table 5, the H^+ position bonded to W=O, where the number between brackets corresponding to the numbering of the atoms reported by D'Amour [12] are listed.

Once the protons were placed, the water molecules positions were studied. The co-ordinates assigned to the water molecules in the D'Amour's report [12] correspond to the oxygen atom to form it. In consequence, the protons must be localised and then look for the more favoured positions of them, not only in the H_2O interaction with primary Dawson acid units but also the H_2O interaction with protons of the acid (W=O–H).

The results indicate that three different water species can exist. In the Fig. 5 can be observed the different H_2O molecules associated to the Wells–Dawson acid structure.

In the following scheme we can see the different water species,

(i)	W=O$\cdots$HOH	H (of H_2O) interaction—O (of W=O) (E_{H_2O})
(ii)	W=OH$\cdots$OH$_2$	O (of H_2O) interaction—bonded H^+ to a O (W=O), hydration state associated with H_3O^+ species ($E_{H_3O^+}$)
(iii)	W=OH - - O $\overset{\diagup\text{H}}{\underset{\diagdown\text{H - - OH}_2}{}}$	Hydration state associated with $H_5O_2{}^+$ ($E_{H_5O_2^+}$)

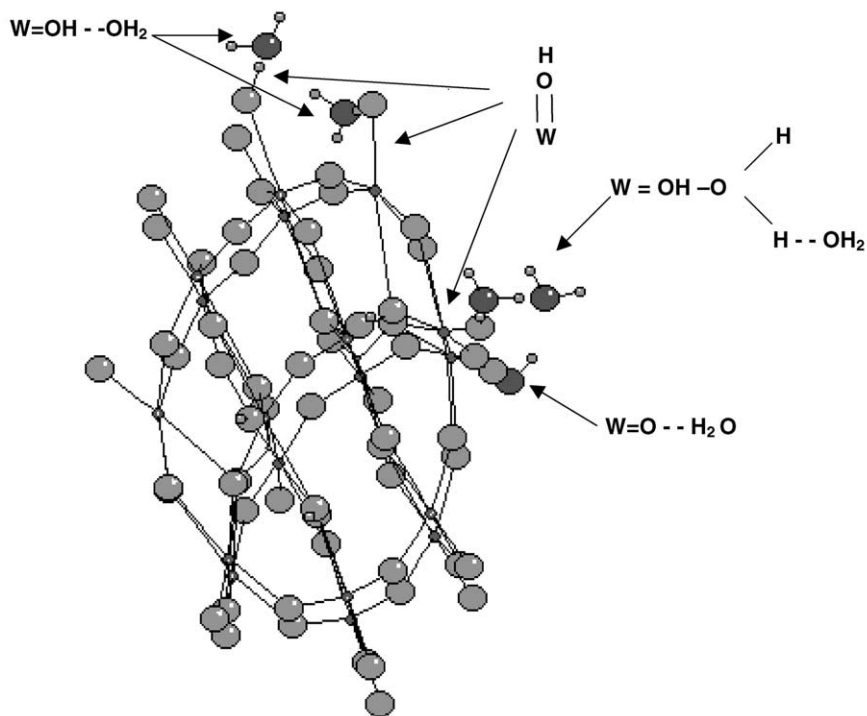Fig. 5. Representation of secondary structure of Wells–Dawson acid.

where the order of E_r is $E_{H_5O_2^+} < E_{H_3O^+} < E_{H_2O}$.

These theoretical results indicated that the $H_5O_2^+$ species are the most energetically stable ones in the structure and bonds two secondary structures of Wells–Dawson acid (Fig. 6a and b) leading to the minima system energy (E_2) (Fig. 4). In consequence, it can be expected that these species are the latter water molecules lost in the acid at the end of acid dehydration process. This assumption is in agreement with the results obtained with the three experimental techniques previously discussed.

In conclusion, the experimental results obtained by TGA, DRIFTS and ^{1}H MAS-NMR suggested that the protonic acidity is related to the presence of water molecules in Dawson acid structure. In particular, the $H_5O_2^+$ species associated with the last two H_2O molecules determined by TGA analysis and the ^{1}H MAS-NMR measurements shown that the presence of $H_5O_2^+$ plays an important role in the acidity–catalytic

activity relationship. As already mentioned, we reported that the catalytic activity of Dawson acid for MTBE synthesis and methanol dehydration to diethyl ether in gas phase at $100\,^\circ$C was directly related to the presence of water molecules in its secondary structure [6]. Thus, according to this previous work [6] and our present results, we can conclude that the loss of catalytic activity of Dawson acid with the increase of pre-treatment temperature is due to the loss of the latter two water molecules. EHMO calculations show that $H_5O_2^+$ species bonds two secondary structures of Wells–Dawson acid, as mentioned (Fig. 4).

EHMO calculations allow us to conclude that the activity decreases due to the loss of water molecules, that lead to a new crystalline phase, $H_6P_2W_{18}O_{62}$ anhydrous [6]. This phase has energy similar to E_0, in contrast to E_2, which is associated with the catalytic activity and the accessibility of the protons.
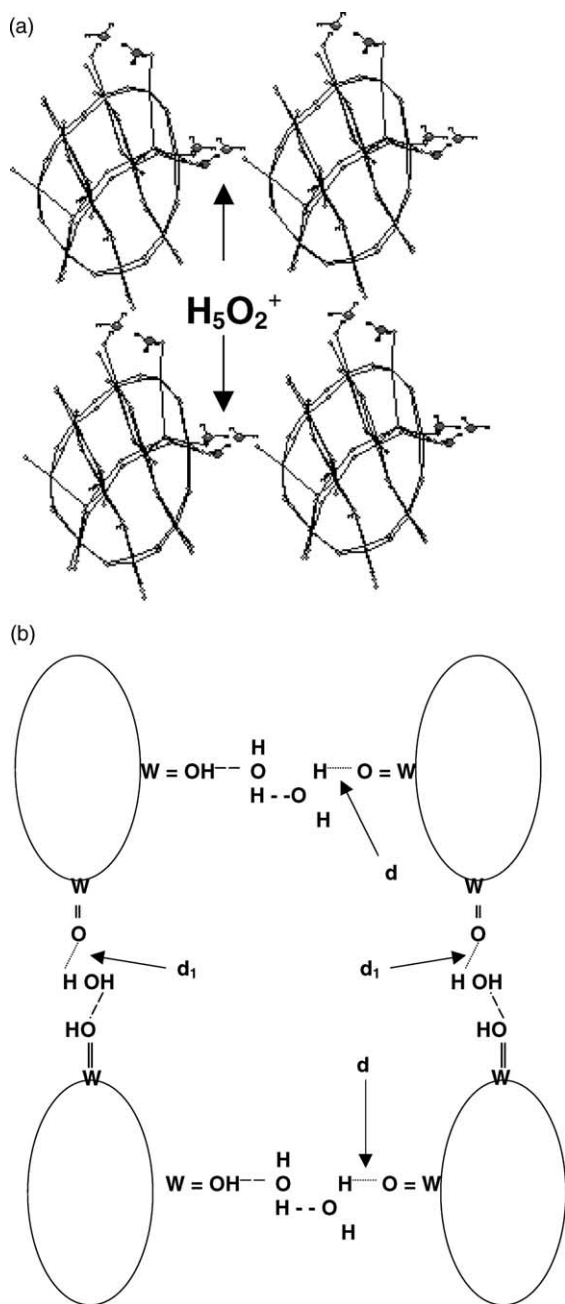
Fig. 6. (a) Representation of tertiary structure of Wells–Dawson acid. (b) Schematic representation of tertiary structure; d (distance between W=O–($H_5O_2^+$)$\cdots$O=W) = 1.05 Å; d_1 (distance between W=O–(H_3O)$^+$$\cdots$O=W) = 1.03 Å.

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