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Investigation of the thermal stability of phosphotungstic Wells-Dawson heteropoly-acid through in situ Raman spectroscopy

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ABSTRACT

The present investigation applies laser Raman spectroscopy under in situ conditions to obtain insights on the effect of the temperature on the molecular structure of the bulk phosphotungstic Wells–Dawson heteropoly-acid $H_6P_2W_{18}O_{62} \cdot xH_2O$ (HPA). The in situ temperature-programmed studies followed the evolution of phosphotungstic Wells–Dawson and Keggin heteropoly-acids along with tungsten trioxide under controlled atmosphere and temperature. The spectroscopic investigation of the Wells–Dawson HPA demonstrated that in situ Raman spectroscopy is a suitable technique to follow the effect of a gradual dehydration on the secondary structure of such a complex structure. Moreover, the absence of the signals belonging either to the Keggin or WO_3 phases provides further evidence that the phosphotungstic heteropolyanion does not decompose towards those materials at temperatures below 600 °C.

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1. Introduction

Raman spectroscopy is a particularly versatile characterization technique to provide fundamental information about the structure and surface properties of materials at a molecular level [1]. In particular, Raman spectroscopy is suited to provide knowledge about the molecular structure of heterogeneous and homogeneous catalysts under in situ conditions. In this context, the in situ temperature programmed studies follow the evolution of a sample under controlled atmosphere and temperature. This methodology has been used to examine essentially all types of catalytic materials: bulk and supported metals, bulk mixed metal oxides, supported metal oxides, bulk and supported metal sulfides, zeolites and molecular sieves, clays and phosphomolybdic heteropolyoxo anions of the Keggin structure [2–5]. In this context, it has been shown that temperature-programmed Raman analyses can follow structural changes upon dehydration and decomposition of bulk and supported HPA's like 12-molybdophosphoric acid [5].

In general, the heteropoly-acids (HPAs) are composed of large polyanions, counter-cations and crystallization water. An important issue regarding HPAs is to distinguish among the several levels of primary, secondary and tertiary structure. The primary structure is constituted by the polyanions, meanwhile the secondary one

corresponds to the arrangement of polyanions, cations and water of crystallization. On the other hand, the tertiary structure is the structure of solid HPAs as assembled. The catalytic behavior of these materials is strongly influenced by the structural modifications that may occur in their secondary and tertiary structures upon heating [6–9]. Previous investigation by some of us, demonstrated that the degree of hydration directly influences the secondary structure and the accessibility of the active acid sites of the phosphotungstic Wells–Dawson heteropoly-acid $H_6P_2W_{18}O_{62} \cdot xH_2O$ [10,11].

In this context, the present investigation applies temperature-programmed laser Raman spectroscopy under in situ conditions to obtain further knowledge of the effect of the temperature on the molecular structure of the bulk phosphotungstic Wells–Dawson heteropoly-acid.

2. Experimental

2.1. Materials

Bulk Wells Dawson heteropoly-acid $H_6P_2W_{18}O_{62} \cdot 24H_2O$ was prepared according to the method described elsewhere [12]. Commercial phosphotungstic acid of the Keggin type $H_3PW_{12}O_{40} \cdot xH_2O$ (Aldrich Chemicals 99.995%) and tungsten oxide were also investigated. Tungsten trioxide was obtained via the in situ thermal decomposition of $(NH_4)_6H_2W_{12}O_{40}$ (J.T. Baker 81.4%). The sample was maintained at 100 °C for 1500sec and then heated to 500 °C at 10 °C/min under a stream of pure Helium at 30 sccm.

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The sample was maintained at constant temperature for 30 min every 50 °C (150 °C, 200 °C, 250 °C, 300 °C, 350 °C, 400 °C, 450 °C, 500 °C) and the spectra were obtained afterwards.

2.2. Temperature-programmed Raman spectroscopy in situ analyses (TP-Raman)

Raman spectra were collected using a single monochromator Renishaw System 1000 equipped with a thermoelectrically cooled CCD detector (−73 °C) and an Edge filter. The Edge filter removes the elastic scattering, and the Raman signal remains higher than when triple monochromator spectrometers are used. The samples were excited with the 514 nm Ar line and the spectral resolution was 3 cm^{−1}. The Raman spectrometer was equipped with an in situ environmental cell (Linkam TS-1500) where both the temperature and the gaseous composition are controllable. The samples were maintained at 100 °C for 1500 s and then heated to 500 °C at 10 °C/min under a stream of pure Helium at 30 sccm. The samples were maintained at constant temperature for 30 min every 50 °C (150 °C, 200 °C, 250 °C, 300 °C, 350 °C, 400 °C, 450 °C, 500 °C) and the spectra were obtained afterwards.

3. Results and discussion

Fig. 1 shows the spectra of the phosphotungstic heteropoly-acid H₆P₂W₁₈O₆₂·xH₂O (HPA from now on) at various temperatures and Table 1 summarizes the assignments of the Raman bands.

The phosphotungstic heteropolyanion with the Wells Dawson structure P₂W₁₈O₆₂^{6−} is composed by a framework of distorted octahedral units WO₆ [6,9,10]. Those species possess an intense Raman signal centered at 998 cm^{−1} along with another signal of lower intensity at 972 cm^{−1} that corresponds to the stretching vibrations of the tungsten atoms double bonded to terminal oxygen atoms (W=O) within the WO₆ units [13,14].

Additionally, the signals at 853 cm^{−1} and 920 cm^{−1} belong to the stretching vibrations of the bridging W–O–W species of the extended polytungstate framework surrounding the central phosphorous atom [13,14] (see Table 1). The increase of the temperature from 80 °C to 250 °C progressively shifts the bands at 998 cm^{−1} and 972 cm^{−1} towards 1014 cm^{−1} and 992 cm^{−1}, respectively. Moreover, an additional signal of low intensity is observed at 762 cm^{−1} upon calcination from 250 °C to 500 °C.

Previous investigations reported by Sambeth and col. demonstrated that the Wells-Dawson HPA possesses 24 molecules of water per formula unit (H₆P₂W₁₈O₆₂·24H₂O). These water molecules are associated with protons forming large protonated water clusters H⁺(H₂O)_n which degrade to H₃O⁺ and H₅O₂⁺ at 200 °C and finally to isolated protonic sites when the acid is completely dehydrated. In this context, the HPA loses 22 moles of water upon heating from 80 °C to 250 °C. Moreover, the acid loses

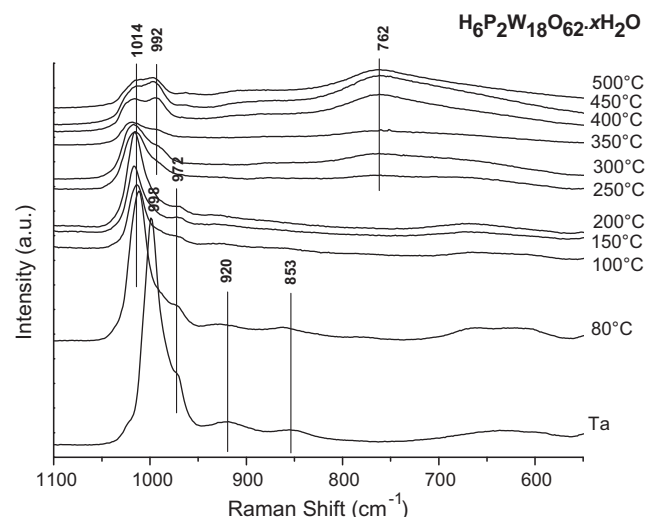


Fig. 1. In situ Raman spectra of the bulk phosphotungstic Wells Dawson acid at various temperatures.

the last 2 moles of water when the temperature increases from 250 °C to 300 °C [9]. Therefore, the water molecules are removed upon calcination at 300 °C leaving dehydrated proton H⁺ species and keeping intact the primary structure (the P₂W₁₈O₆₂^{6−} heteropoly-anion) of the acid [11]. Online with these findings it is possible to correlate the shifts of the Raman vibrations with a gradual dehydration of the HPA which in turn, modifies the secondary structure of the HPA. Previous investigations demonstrated that further thermal treatment of the dehydrated Wells-Dawson HPA produces instability of the P₂W₁₈O₆₂^{6−} heteropoly-anion. In this context, the early investigations reported by Lunk and col. suggested that the HPA decomposes into tungsten trioxide [15]. More recently, some of us investigated the thermal stability of the Wells-Dawson potassium salt K₆P₂W₁₈O₆₂·10H₂O [16]. A detailed TGA-DTA analysis revealed a weight loss step between room temperature to 280 °C which corresponds to the number of water molecules involved in the K₆P₂W₁₈O₆₂·10H₂O structure. Although, no additional weight loss was observed at higher temperatures, the DTA analysis revealed a small exothermic peak around 600 °C attributed to a structural rearrangement without weight loss that results in the generation of new phases composed of a mixture of W₁₈P₂O₅₉, the phosphotungstic Keggin structure PW₁₂O₄₀^{−3} and a surface amorphous phase of unknown composition generated by decomposition of the Keggin phase. Based on these results, the phosphotungstic Keggin HPA along with WO₃ were further studied in order to obtain more insights on the structure modification that might occur when the fully dehydrated Wells-Dawson HPA is further calcined from 300 °C upwards.

Table 1

Raman signals and assignments of phosphotungstic Wells-Dawson and Keggin heteropoly-acids at various temperatures.

Materials	Temperature (°C)				Assignments
	R.T.	≥80 °C	≥200 °C	≥350 °C	
H ₆ P ₂ W ₁₈ O ₆₂ ·xH ₂ O	998 (s)	1014 (s)	1014 (m)	1014 (m)	ν _s (W=O _t)
	972 (m)	972 (m)	992 (m)	992 (m)	ν _{as} (W=O _t)
	920 (w)				ν _{as} (W–O _b –W)
	853 (w)				ν _s (–O–W–O–)
				762	Unknown
H ₃ PW ₁₂ O ₄₀ ·xH ₂ O	1007 (s)	1011 (s)	1022 (s)	1022 (s)	ν _s (W=O _t)
	992 (m)	992 (m)			ν _{as} (W=O _t) asymmetric stretch
	982 (m)	982 (m)	982 (w)		
	904 (w)	904 (w)	904 (w)	939 (w)	ν _{as} (W–O _b –W)

s, strong; m, medium; w, weak; O_t, terminal oxygen atom; O_b, corner-shearing oxygen atom.

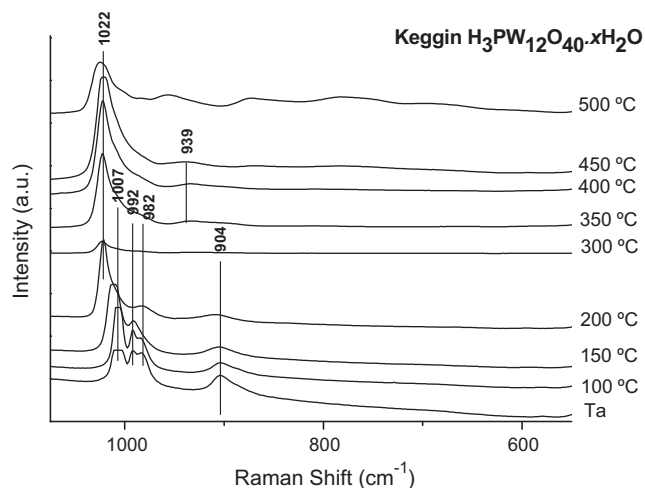


Fig. 2. In situ Raman spectra of the Keggin phosphotungstic heteropoly-acid.

The Keggin anion's $[XW_{12}O_{40}]^{-3}$ structure is composed of a globe-like cluster of corner and edge-sharing WO_6 unit that enclose a central XO_4 unit (where X represents P, Si, among others) [6,7].

The Raman spectra of the Keggin heteropoly-acid at room temperature exhibits bands between 904 and 1007 cm^{-1} (see Fig. 2 and Table 1). The Raman band at 1007 cm^{-1} , attributed to symmetric stretching of the tungsten-terminal oxygen ($W=O$) within WO_6 octahedra, is observed from room temperature to 200 °C . Similarly to the Wells-Dawson HPA, the vibration of the $W=O_t$ species strongly depends on water molecules coordinated to the Keggin heteropoly-anion. This observation explains the shifts of such signal from 1007 cm^{-1} towards 1022 cm^{-1} upon dehydration [17].

Tungsten trioxide, WO_3 , possesses a crystalline structure and exhibits characteristic intense bands at 715 and 805 cm^{-1} , attributed to the symmetric stretching vibration of the double bonded tungsten-terminal oxygen species $W=O_t$ (spectra not shown). The absence of the signals characteristic of Keggin or WO_3 phases provides evidences that the phosphotungstic Wells-

Dawson heteropolyanion does not decomposes into these materials upon calcination from 300 °C to 500 °C .

4. Conclusions

The spectroscopic investigation of the phosphotungstic Wells-Dawson heteropoly-acid at various temperatures demonstrated that in situ Raman spectroscopy is a suitable technique to follow the gradual dehydration of such a complex structure. Moreover, the absence of the signals belonging either to the Keggin or WO_3 phases provides further evidence that the phosphotungstic heteropolyanion does not decompose towards those materials at temperatures below 600 °C .

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