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Infrared and Raman Investigation of Supported Phosphotungstic Wells-Dawson Heteropolyacid

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Abstract: The combination of both infrared and Raman spectroscopy are powerful tools to obtain information of catalytic materials at a molecular level. The present investigation shows, a systematic study *"in situ"* about the effects of the temperature in the molecular structure of the supported phosphotungstic Wells-Dawson heteropolyacid (HPA).

The infrared and Raman analyses of the samples were performed under *in situ* conditions from RT to 500 ^{o}C range in flowing helium. The oxide supported heteropolyacid was synthesized through a conventional impregnation method (in aqueous) at theoretical monolayer coverage.

These studies provided evidences on the dehydration of the HPA upon *in situ* calcination. Moreover, the *in situ* investigation allows establishing the surface molecular structure or the thermal stability of the HPA. Additionally, the presence of crystals of HPA over TiO_2 suggests that the "theoretical" monolayer loading should be re-evaluated.

Keywords: HPA, IR *in situ,* "Theoretical" Monolayer, Thermal Stability, Raman *in situ,* Wells-Dawson.

1. INTRODUCTION

The HPAs possess primary, secondary and tertiary structures. The primary structure is constituted by the polyanions, the secondary one correspond to the polyanions, cations, water of crystallization, etc. The tertiary structure corresponds to the solid heteropoly compounds (HPCs). In this context, the properties of the HPAs are somehow related with the structural modifications of their secondary and tertiary structures [1-4].

Previous studies, demonstrated that crystalline Wells-Dawson heteropolyacids possess molecules of water that are key to understand and to tune their catalytic activity. In this context, Baronetti et al. studied the catalytic performance of phosphotungstic Wells-Dawson acid to produce methyl tert-butyl ether (MTBE) from methanol and isobutylene in the gas phase at 100 °C. The results indicated that the Dawson acid keeps its heteropolyoxoanion structure up to 600 °C. The catalytic activity depends on the pretreatment temperature of the acid. The activity was approximately constant up to 200 ºC; then the activity decreased steadily until becoming null when the temperature was 400 °C [5].

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Gambaro *et al.* studied the chemisorption of isopropanol followed by temperature programmed surface reaction to determine the nature, amount and acid strength of the active sites of the HPA. That study showed that the fully hydrated acid possesses a higher amount of accessible sites than the fully dehydrated acid therefore; the amount of propylene is almost double in the first condition. However, no modification of the temperature of reaction of the isopropoxy species was observed [6].

Ross-Medgaarden and Wachs, combined Raman spectroscopy and other techniques to examine the molecular and electronic structures of well-defined W(VI) bulk mixed oxide reference compounds consisting of: (i) isolated WO_4 or WO_6 monomers, (ii) dimeric O_3W-O-WO_3, (iii) polymeric chain of alternating WO_4/WO_6 units, and (iv) WO_6-coordinated W_9-W_{18} clusters (HPA Keggin and Wells-Dawson). Raman spectroscopy was employed to confirm the identity and phase purity of the different tungsten oxide structures. The information was applied to determine the local structures of the molecularly dispersed surface W(VI) species present in supported WO_3/Al_2O_3, WO_3/ZrO_2, and WO_3/SiO_2 catalysts under ambient and dehydrated conditions [7].

More recently, some of us reported a systematic investigation about the effect of the temperature on the molecular structure of the bulk Wells-Dawson heteropolyacid through *in situ* Raman spectroscopy. The spectroscopic investigation of the Wells-Dawson HPA demonstrated that the bulk phos-

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photungstic heteropolyanion is stable at temperatures as high as 600 °C [8].

The present investigation extends that investigation towards phosphotungstic Wells-Dawson acid supported on TiO_2 at various loadings. The influence of hydration/dehydration on the molecular structure is investigated combining Raman and infrared spectroscopies under *in situ* conditions.

2. EXPERIMENTAL

2.1. Materials

The HPA was synthesized through ion exchange of the phosphotungstic salt $(NH_4)_6P_2W_{18}O_{62}.13H_2O$ with an ion exchange resin as reported previously [9-10]. This acid was dispersed at 3.4 %, 3.8 %, 4.5 %, 7.6 %, 10.5 %, 15.0 %, 19.4 %, 22.0 % and 31.9 % w/w loadings over TiO_2 (Aeroxide® P-18 Evonik Ind., 46.8 ± 0.1 m^2/g). The material called 19.4% HPA/TiO_2 would correspond to theoretical monolayer coverage based on geometric considerations [11]. The heteropolyanion possesses $1.57x10^{-18}$ m^2 per molecule if an elliptical projection over the oxide support is considered. Therefore one mol of molecules of the HPA (considering that the molecular weight of the $H_6P_2W_{18}O_{62}.24H_2O$ equals to 4804 g mol^{-1}) would occupy an area equals to 196.8 m^2/g. In this context, a monolayer of HPA on TiO_2 (having 46.8 m^2/g of surface area) would have a 19.2 % w/w of loading.

The samples were synthesized through conventional incipient wetness impregnation at 25 °C overnight. All the samples were dried at 100 °C for 1 h and calcined at 300 ºC for 4 h.

2.2. In Situ Temperature Programmed Raman Spectroscopy Analysis

Raman spectra were obtained with single monochromator Renishaw System 1000 equipped with a thermoelectrically cooled CCD detector (−73 ºC) and an edge filter. The characteristics of this equipment were reported previously [8].

The in situ studies were performed with an environmental cell (Linkam TS-1500) in a controlled temperature range going from 100 ºC to 500 ºC. In this context, a 10 ºC/min heating rate in steps of 50 ºC was used. The sample was maintained at 100 ºC for 1500 sec and then heated to 500 ºC at 10 ºC/min under an atmosphere of He.

2.3. In Situ Temperature Programmed Infrared Investigation

The supported materials were investigated through *in situ* transmission infrared spectroscopy on self-supported wafers (30 mg) pressed at 5 t cm^{-2} (diameter = 13 mm). The wafers were placed into a Pyrex IR cell fitted with water-cooled NaCl windows, which was attached to a conventional high vacuum system (base pressure = 1.33×10^{-4} Pa), equipped with a manifold for gas flow operation. The gas used in this study was of high purity grade He (AGA UHP 99.999%) and was further purified through a molecular sieve (3Å) and MnO/Al_2O_3 traps to remove water and oxygen impurities, respectively.

The evolution of the materials was followed by heating the IR cell from RT to 450 ºC at 10 ºC min^{-1} under flowing He (60 sccm). Along the temperature ramp, transmission infrared spectra were recorded at RT, 80, 100 and every 50 °C from 100 °C to 500 °C.

A Nicolet Magna 550 FTIR spectrometer with a DLATGS detector was used to acquire the spectra (4 cm^{-1} resolution, 100 scans). The overlapping bands, along with the measurement of peak areas, were solved using sum of lorentzian curves.

The high content of water of the bulk phosphotungstic Wells-Dawson heteropolyacid made impossible to prepare a self supported wafer for the IR study therefore, we were unable to perform this particular investigation.

3. RESULTS AND DISCUSSION

3.1. Molecular Structure of Wells-Dawson HPA/TiO_2 Supported at Theoretical Monolayer Coverage

In this section the molecular structure upon calcination of 19.4 % w/w HPA/TiO_2 is studied. Particularly, the molecular structure of the hydrated and dehydrated HPA is investigated through *in situ* TP-Raman and TP-FTIR spectroscopies upon heating from ambient towards 500 ºC.

The Fig. (**1**) shows the *in situ* TP-Raman spectra of the supported HPA over TiO_2. The strong Raman features due to TiO_2 limits the collection of the data bellow 800 cm^{-1}. The Raman spectra of 19.4 % w/w HPA/TiO_2 shows a signal at 994 cm^{-1} at room temperature that is attributed to the symmetric stretching vibration of the W=O species for a fully hydrated structure. This signal shifts towards 1021 cm^{-1} when the temperature increases. The presence of both signals at 994 cm^{-1} and 1021 cm^{-1} in the 100-400 °C range suggests a progressive dehydration of the HPA structure. The hydrated structure disappears and the vibration corresponding to the dehydrated material grows when the temperature increases above 400 °C.

On the other hand, the Raman signals of both the bulk and supported materials are similar even though the loading of HPA over TiO_2 (19.4 %) is considered the theoretical dispersion limit loading (i.e., "monolayer" coverage) as will be discussed in the following sections. Previous investigations reported by some of us showed that bulk phosphotungstic Wells-Dawson HPA possess an intense Raman signal at 998 cm^{-1} that belongs to the stretching vibrations of the doubled bonded W=O species [8, 12, 13]. Moreover, this signal shifts towards higher wavenumbers (from 998 cm^{-1} to 1014 cm^{-1}) upon calcination/dehydration similarly to the behavior observed in the spectra of the TiO_2 supported HPA.

This observation would indicate that either the theoretical monolayer content is really higher than a monolayer, or that the HPA do not dispersed adequately at *monolayer* coverage over the TiO_2 support.

The Fig. (**2**) presents the *in situ* infrared spectra of 19.4 % w/w HPA/TiO_2 at various temperatures. The spectra show the characteristic signal at 1080 cm^{-1} assigned to the vibration of P-O bond of the Wells-Dawson structure that remains unaltered with the increasing temperature in contrast with the

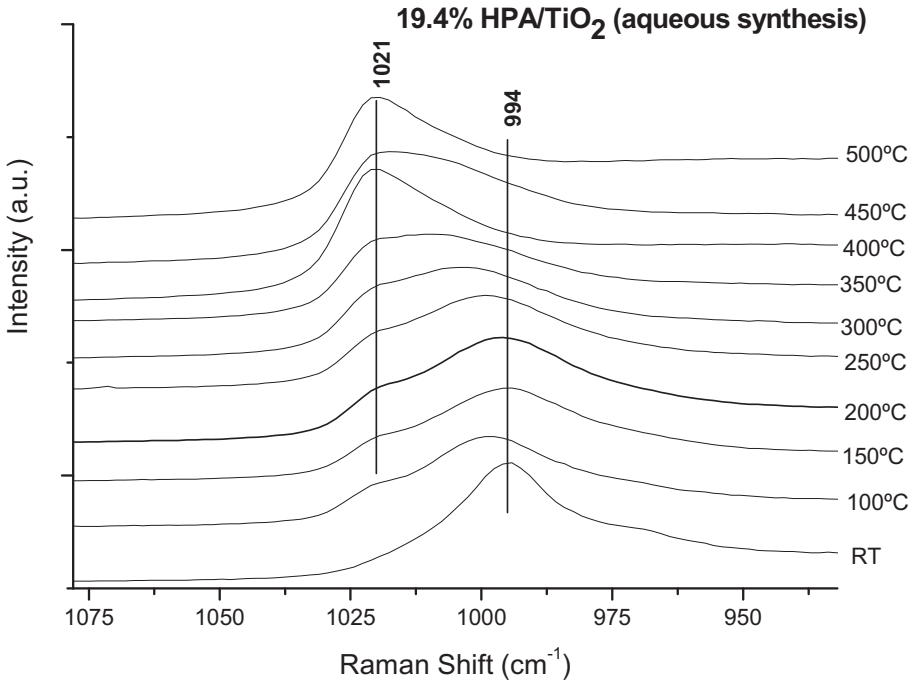

Fig. (1). *In situ* Raman spectra of 19.4 % w/w HPA/TiO_2 synthesized in aqueous media.

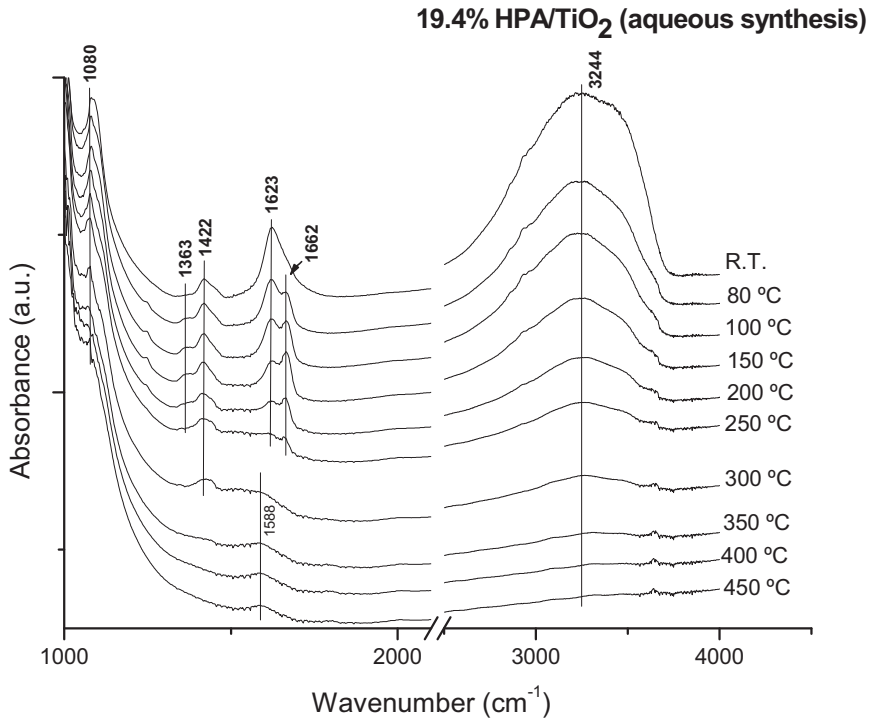

Fig. (2). *In situ* IR spectra of 19.4 % w/w HPA/TiO_2 synthesized in aqueous media.

signals at 1620 cm^{-1} and 3244 cm^{-1}. These vibrations correspond to adsorbed H_2O molecules and O-H vibrations, respectively. Additionally, another signal at 1623 cm^{-1} that corresponds to the vibration of water molecules adsorbed on the material is observed [5, 14, 15].

From 80 °C there is a splitting of the signal envelope centered at 1623 cm^{-1}, which shows a second vibration centered at 1662 cm^{-1}. Both signals are present from 80 °C to 250 °C. However an increase in the intensity of the signal at 1662 cm^{-1} and a decrease of the one at 1623 cm^{-1} is observed when raising the temperature. The signal at 1662 cm^{-1} could be attributed to the crystallization water molecules that are involved in the structure of the HPA and are not perturbed at least up to 250 °C. In fact the gradual removal of physisorbed water (desorption begins at 80 °C) allows revealing the signal at 1662 cm^{-1}.

Table 1. Surface coverage, specific surface Area and HPA Loading on TiO_2 at contents above and below the theoretical monolayer coverage.

Theoretical Surface Coverage *[1]	Weight HPA/ Surface Area of the Support (mg/m^2) *[2]	S_{BET} (m^2/g)	HPA Loading w/w % *[3]
15 %	0.7	46.5 +/- 0.7	3.4
17 %	0.8	50.3 +/- 0.4	3.8
20 %	1.0	45.8 +/- 0.1	4.5
35 %	1.8	50.0 +/- 0.3	7.6
50 %	2.5	50.2 +/- 0.2	10.5
75 %	3.8	49.8 +/- 0.2	15.0
100 %	5.0	49.9 +/- 0.1	19.4
120 %	6.0	49.9 +/- 0.2	22.0
200 %	10.0	45.5 +/- 0.1	31.9

(*[1]) The surface coverage is the percentage of support that was covered with the HPA.
(*[2]) HPA weight per unit area of the support
(*[3]) HPA weight / (weight of HPA and TiO_2 support).

On the other hand, the signal at 3244 cm^{-1}, corresponding to the vibration of the O-H bonds, decreases in the interval ranging from room temperature to 350 °C.

Previous studies established that the HPA loses 22 water molecules from 66 °C to 114 °C and the last two molecules of crystallization water are released at temperatures above 300 °C which is consistent with the in situ TP-FTIR spectra in Fig. (**2**) [4, 5].

Fig. (**2**) shows that a significant modification in the spectra in the temperature range from 300 °C to 450 °C occurs. In this context, the signals at 1623 cm^{-1} and 1662 cm^{-1} disappear and a new signal centered at 1588 cm^{-1} is observed. This observation is consistent with the fact that the HPA has dried completely, leaving only protons in the structure. In this context, the signal in 1588 cm^{-1} could be assigned to the H^+ that are part of the primary structure of the phosphotungstic acid $H_6P_2W_{18}O_{62}$.

The observations described above indicates that the molecules of water associated with the HPA structure possess characteristic infrared signals which is in agreement with previous findings in salt hydrates [16].

3.2. Investigation of the Molecular Structure of TiO_2 Supported HPA Above and Below the Theoretical Dispersion Limit Loading (Monolayer Coverage)

The results presented in the previous sections show that both the bulk HPA and the 19.4 % w/w HPA/TiO_2 possess similar Raman signals suggesting that either the loading is above the monolayer coverage or that the HPA forms crystals on the oxide support instead of dispersing uniformly. Along these ideas, a series of TiO_2-supported HPA with a wide range of loadings were investigated (below and above the theoretical monolayer) in order to assess evidences on the real monolayer coverage.

Table **1** shows the theoretical percentage of covered area, the weight of HPA per surface area unit of the support, the specific surface area and weight percentage of the material at contents above and below the theoretical monolayer. It can be seen that the content by weight of HPA corresponding to a theoretical coverage of 100 % is 19.4 % w/w.

Figs. (**3** and **4**) show the Raman spectra of the materials presented in Table **1**. In all cases, the materials were pretreated *in situ* at 300 °C for 30 minutes and then Raman spectra were obtained. The pretreatment of the samples assures that the spectra corresponding to dehydrated samples are compared for both the bulk and supported HPA.

The series of HPA/TiO_2 ranging from 75 % to 200 % of surface coverage possess Raman signals that are similar to the ones of the bulk HPA. The Fig. (**3**) clearly shows two signals at 1015 cm^{-1} and 991 cm^{-1} associated with the symmetric and anti-symmetric stretching of the W=O bond of dehydrated HPA as was discussed above (see Table **1**). The spectra of the materials with 35 % and 50 % of surface coverage (correspond to 7.6 % and 10.5 % w/w, respectively) is dominated by two Raman signals at 1018 cm^{-1} and 1008 cm^{-1} of similar intensity (see Fig. **4**). The signal that corresponds to the bulk HPA (1018 cm^{-1}) greatly diminishes giving rise to the new one at 1008 cm^{-1}. Finally the signal belonging to the crystals disappears when the HPA loadings are 4.3 % w/w or less (15 % to 20 % coverage). In this particular case the spectra are dominated by a single signal located at 1002 cm^{-1}. These new signals at 1002 cm^{-1} and 1008 cm^{-1} can not be attributed to the decomposition of the Wells-Dawson HPA in the Keggin heteropolyacid and/or tungsten trioxide. In this context, the Keggin type HPA possess a strong signal at 1014 cm^{-1} at 300 °C (see Table **2**) while WO_3 would present an intense signal at 805 cm^{-1}.

The investigations of the structures of WO_x species molecularly dispersed on transition metal oxides supports at various loadings in the dehydrated condition should be considered as a tool in order to provide insights in the new signals observed in a more complex structure such as the HPA. Wachs *et al.* demonstrated that the WOx species shows a

Table 2. Raman signals and assignments of bulk phosphotungstic Wells-Dawson and Keggin heteropolyacids at various temperatures.

	Temperature (°C)					
Materials	**R.T.**	**≥ 80**	**≥ 200**	**≥ 350**	**500**	**Assignments**
	998 (s)	1014 (s)	1014(m)	1014(m)	1014(m)	ν_s (W=O_t)
$H_6P_2W_{18}O_{62}.xH_2O$	972 (m)	972 (m)	992 (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(m)	762(m)	unknown
	1007 (s)	1011 (s)	1022 (s)	1022 (s)	1022(m)	ν_s (W=O_t)
$H_3PW_{12}O_{40}.xH_2O$	992 (m)	992 (m)				ν_{as} (W=O_t)
	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

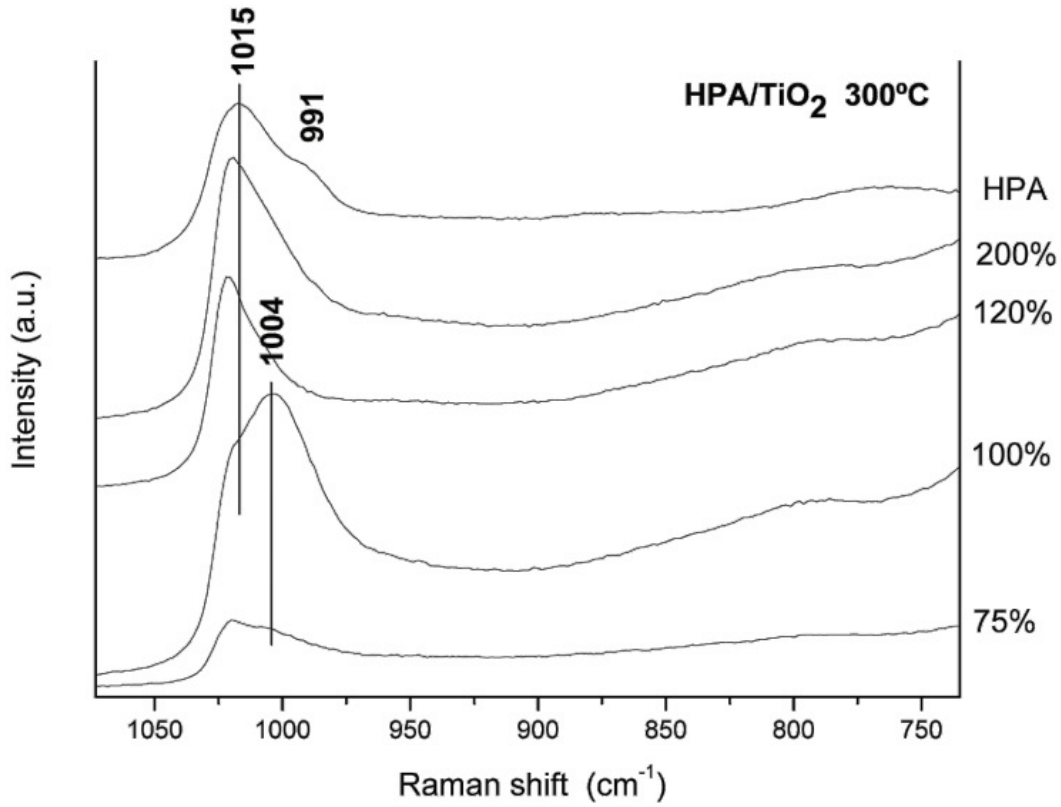

Fig. (3). Raman spectra at 300 °C of bulk HPA and supported on TiO_2 at high coverage (high HPA loadings).

Raman band that shifts from 1007 cm^{-1} to 1016 cm^{-1} with increasing tungsten oxide surface coverage [17]. They attributed the vibrational shift to the continuous polymerization of the surface monotungstate species to surface polytungstate species that is produced with the increase of the tungsten oxide surface coverage [17, 18]. These investigations provide evidences that the signals at 1008 cm^{-1} and 1002 cm^{-1} could be assigned to the symmetric stretching vibration of tungsten-oxygen double bond ν_s(W=O) when this species is isolated in the dried material [7, 17-19].

4. CONCLUSION

A controversial topic in the catalysis area based on heteropolyacids is the role of water in the stability of the material. The series of Wells-Dawson heteropolyacid supported

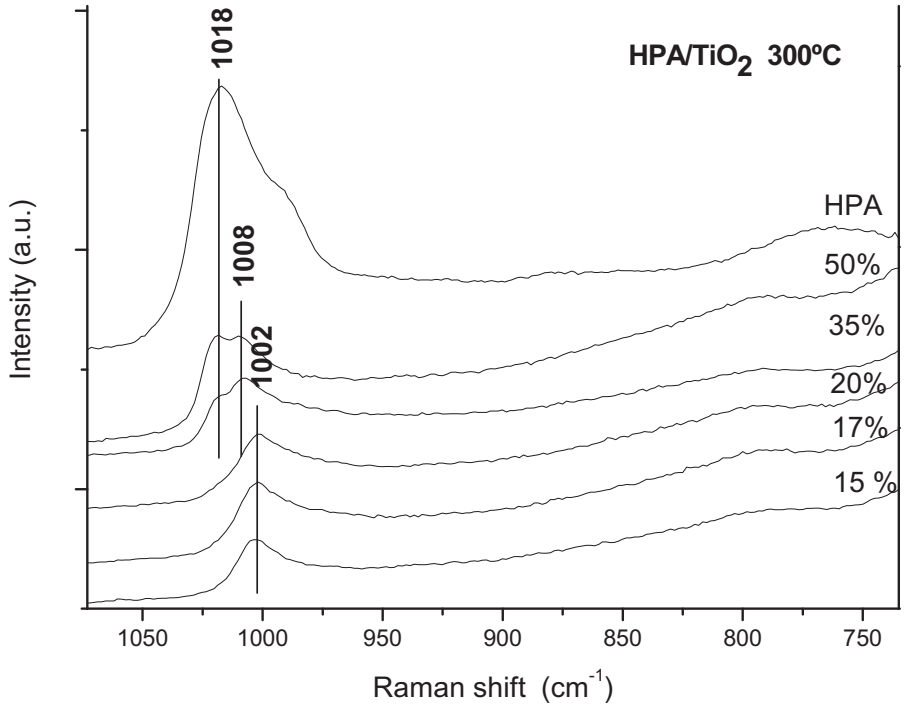

Fig. (4). Raman spectra at 300°C of bulk HPA and supported on TiO_2 at low coverage (low HPA loadings).

on TiO_2 screened in the present investigation clearly evidences that the HPA does not decompose (towards a Keggin based structure or WO_3) when dehydrated at 300 °C. Moreover, the molecules of water associated to the HPA structure shows two very distinctive infrared signals at 1623 cm^{-1} and 1662 cm^{-1}. The signal at 1623 cm^{-1} is attributed to the large water clusters $H^+(H_2O)_n$ that desorbs from 80 °C leaving $H_5O_2^+$ species. Desorption of the water clusters reveals the presence of an infrared signal at 1662 cm^{-1} (most probably associated with the $H_5O_2^+$ species) that remains unperturbed up to 300 °C. This signal vanishes at such temperature, in parallel with the dehydration of the HPA due to the desorption of the last molecules of water.

The manuscript works on the hypothesis that the 19.4 % HPA/TiO_2 catalyst is at its "theoretical monolayer coverage" of the phosphotungstic heteropolyacid on that particular oxide support. The amount of Wells-Dawson heteropolyanion $P_2W_{18}O_{62}^{-6}$ at "theoretical monolayer coverage" was calculated considering the dimensions of the anion reported in the literature as discussed in the section 2.1. The investigation of the molecular structure of a series of supported materials with various HPA loadings is the most reliable method to assess the real monolayer coverage on a particular oxide support. In this context, the present investigation suggests that the molecular structure of the HPA supported on TiO_2 from 0.7 mg/m^2 to 1.0 mg/m^2 exhibits the Raman signal of W=O species under dehydrated conditions up to their monolayer coverage.

On the other hand, the combined Raman and UV-Vis spectroscopic investigations of Wachs et al. demonstrated that dehydrated WOx species supported on oxide supports is composed of isolated surface $O_4W{=}O$ monotungstate at low coverage and surface WO_5/WO_6 polytungstate species as they approach monolayer coverage [18]. The similarity between these species and the WO_6 clusters of the dehydrated isolated HPA units is a key to understand that the HPA units forming a complete monolayer or not over the oxide support shows a different Raman signal than the dehydrated crystals (1008-1002 cm^{-1} versus 1018-1015 cm^{-1}).

The presence of Raman signals at 1018 cm^{-1} and 1008 cm^{-1} provides evidences of the coexistence of crystals and isolated heteropolyacid molecules in the systems containing 1.8 mg/m^2 and 2.5 mg/m^2. Above 2.5 mg/m^2 (> 10.5 wt. %) the HPA loading exceeds the monolayer coverage therefore, the HPA forms crystals over TiO_2. At this point, two signals at 1018-1015 cm^{-1} and 991 cm^{-1} are observed in the Raman spectra.

The real monolayer coverage of the Wells-Dawson heteropolyacid $H_6P_2W_{18}O_{62}.24H_2O$ on TiO_2 is around 1.0 mg/m^2 according to the experimental evidences.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

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