Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Catalysis 241 (2006) 221–224

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Research Note

Relationship between infrared spectra and stoichiometry of pyridine-$H_3PW_{12}O_{40}$ salts using a new TGA-infrared coupling

Alexandre Vimont [a,*], Arnaud Travert [a], Claude Binet [a], Céline Pichon [b], Pierre Mialane [b], Francis Sécheresse [b], Jean-Claude Lavalley [a]

[a] *Laboratoire Catalyse et Spectrochimie, UMR CNRS-ENSICAEN, Université de Caen, 6 bd Maréchal Juin, F-14050 Caen cedex, France*
[b] *Institut Lavoisier, UMR 8180, Université de Versailles Saint-Quentin, 45 Avenue des Etats-Unis, 78035 Versailles cedex, France*

Received 4 January 2006; revised 27 March 2006; accepted 7 April 2006

Abstract

A new thermogravimetric–infrared coupled apparatus was used to determine the stoichiometry of the pyridinium salts resulting from absorption of pyridine on $H_3PW_{12}O_{40}$ (HPW). Gravimetric measurements showed that two pyridinium salts with definite stoichiometry—$(Py_2H^+)_3PW_{12}O_{40}$ (bis-pyridinium salt) and $(PyH^+)_3PW_{12}O_{40}$ (mono-pyridinium salt)—are formed. Their infrared spectra closely correspond to those reported for pyridinium salts in strong acid solutions. The splitting of the ν8b and ν19b bands of absorbed pyridine (1610–1603 cm^{-1} and 1540–1532 cm^{-1}, respectively) is characteristic of mono-pyridinium formation in the HPW structure.

Keywords: Infrared; TGA; Pyridinium; Pyridine; Acidity; 12-Tungstophosphoric acid; Heteropolyacid

1. Introduction

$H_3PW_{12}O_{40}$ (12-tungstophosphoric acid; HPW), one of the strongest Brønsted solid acids, has high activity in demanding reactions, such as alkylation and alkane isomerization. In the case of acid–base reactions involving polar molecules (e.g., alcohol dehydration), all protons in bulk HPW can take part in the reaction [1,2]. Pyridine absorption followed by infrared (IR) spectroscopy has demonstrated the absence of Lewis acidity [3], because only pyridinium species are observed. The pyridinium IR spectra present a remarkable peculiarity; splitting of the ν8b and ν19b bands is clearly observed for a definite pyridine-HPW stoichiometry [3,4]. To the best of our knowledge, such a splitting has never been reported for any other material, including other heteropolyacids, such as $H_3PMo_{12}O_{40}$ (HPMo). However, previous studies disagree on the nature of the pyridinium species that give rise to such splitting. From volumetric measurements and photoacoustic Fourier transform IR spectroscopy (PAS), Highfield and Moffat [3] have reported that the splitting becomes just discernible at a loading of 1 pyridine molecule per Keggin unit (KU). On further addition of pyridine, the ν8b and ν19b doublets develop progressively until the spectrum ultimately closely resembles that of the pyridinium salt, $(PyH^+)_3PW_{12}O_{40}$. This corresponds to the formation of mono-pyridinium (PyH^+) species. At higher pyridine uptakes (6 Py/KU), the typical ν19b pyridinium band at 1545 cm^{-1} does not occur, which is explained by invoking the formation of bis-pyridinium ($PyH^+\cdots Py$) species [3,5]. In contrast, Essayem et al. [4] have proposed that the splitting is related to the formation of bis-pyridinium species. This proposal has been recently supported by ^1H nuclear magnetic resonance studies of Py-HPW and Py-HPMo salts, comparing the relative integral intensities of CH and NH protons [6].

To determine the actual Py-HPW stoichiometry at which the splitting occurs, it is necessary to obtain IR spectra and quantative data under the same conditions. Coupling of an IR spectrometer to a Mac-Bain microbalance should allow such determinations [7]. However, bulk HPW is weakly transparent in the middle IR range, precluding the use of self-supported pellets for transmission studies. Highfield and Moffat used PAS,

---

[*] Corresponding author. Fax: +33 231452822.
E-mail address: alexandre.vimont@ensicaen.fr (A. Vimont).

0021-9517/$ – see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2006.04.007

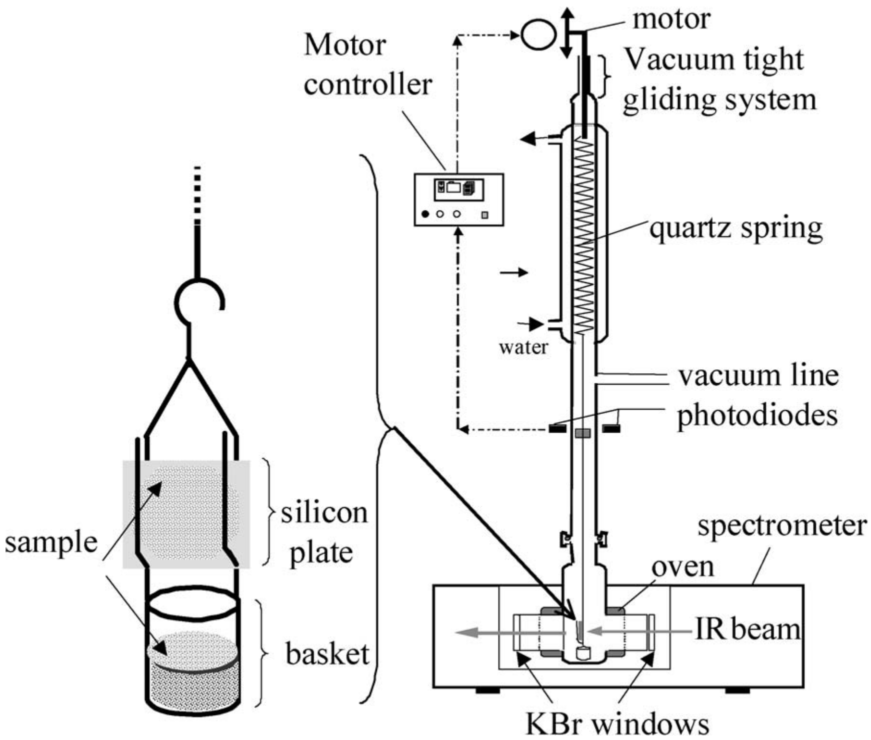

Fig. 1. Setup for coupled TGA-infrared measurement. The device for the sample holder is magnified (left).

whereas Essayem et al. used HPW either diluted in KBr or supported on silicon plates.

In this paper, we report the simultaneous determination of the stoichiometry and IR spectra of pyridine-HPW salts. We have modified a thermogravimetric (TGA)-IR device [7] to increase the sample mass, so as to obtain accurate mass variations while still allowing the recording of transmission IR data.

2. Experimental

TGA measurements were obtained using a Mac-Bain-type balance, modified to fix the position of the sample. The bottom of the balance was designed for use as an IR cell; two KBr windows allow the IR beam to pass through the sample, and an oven allows the sample to be heated up to 873 K. A vacuum line is connected for the activation process of the sample and the introduction of an equilibrium pressure of probe molecule [7]. Because HPW is hardly transparent in the mid-IR range, a small amount of sample (2 mg) was dispersed in deionized water and spread on a silicon wafer for IR measurements. Simultaneously, to improve the accuracy of gravimetric measurements, additional HPW material (104 mg) was placed in a basket just below the IR beam (Fig. 1). With this setup, applied pressure and temperature were the same for both samples (HPW deposited on the silicon wafer and HPW in the basket). The total mass of material used was 106 mg.

$H_3[PW_{12}O_{40}]$ was purchased from Merck (analysis grade). Pyridine (Aldrich, 99+% grade) was dried on molecular sieves before use. The IR spectra (4 cm^{-1} resolution) were recorded with an Avatar Nicolet spectrometer equipped with a TGS detector and a KBr beam splitter.

The compound $[C_5H_6N]_3[PW_{12}O_{40}]\cdot 2CH_3CN$ was synthesized as follows: C_5H_5N (76 μL, 0.926 mmol) was added to $H_3PW_{12}O_{40}\cdot 6H_2O$ (500 mg, 0.167 mmol) dissolved in acetonitrile (20 mL). The solution was stirred for 1 h at room temperature and allowed to slowly evaporate overnight. Colorless crystals were then collected by filtration and washed with diethyl ether. Yield: 280 mg (56% based on $H_3PW_{12}O_{40}$). Elemental analysis exp. (calcd.): W 66.27 (68.95), P 1.03 (0.97), C 7.12 (7.13), H 0.69 (0.76), N 2.21 (2.24). The compound $[C_5H_6N]_3[PW_{12}O_{40}]$ can be obtained after heating the $[C_5H_6N]_3[PW_{12}O_{40}]\cdot 2CH_3CN$ species at 348 K overnight. Its elemental analysis, reported in the next section, confirms its composition.

3. Results and discussion

Fig. 2 shows the mass variation (Fig. 2A) and the IR spectra (Fig. 2B) of HPW recorded before (spectrum 1) and after (spectrum 2) the activation stage. After activation, the absence of the band near 1710 cm^{-1} (δHOH), clearly observed before activation, indicates complete dehydration of the sample. The corresponding mass of the sample, m_0, was used to determine the number of KU. The mass loss resulting from heating under vacuum corresponds to the loss of 6 H_2O molecules per KU. This is in agreement with literature data [5,8] and validates our experimental setup. The spectrum after activation presents a broad ν(OH) band centered at 3110 cm^{-1}, characteristic of the dehydrated HPW [9]. The weaker band at 2100–2200 cm^{-1} corresponds to combination or overtone modes [10].

Fig. 3 shows the mass variation (Fig. 3A) and the IR spectra (Fig. 3B) during a pyridine absorption experiment. Un-

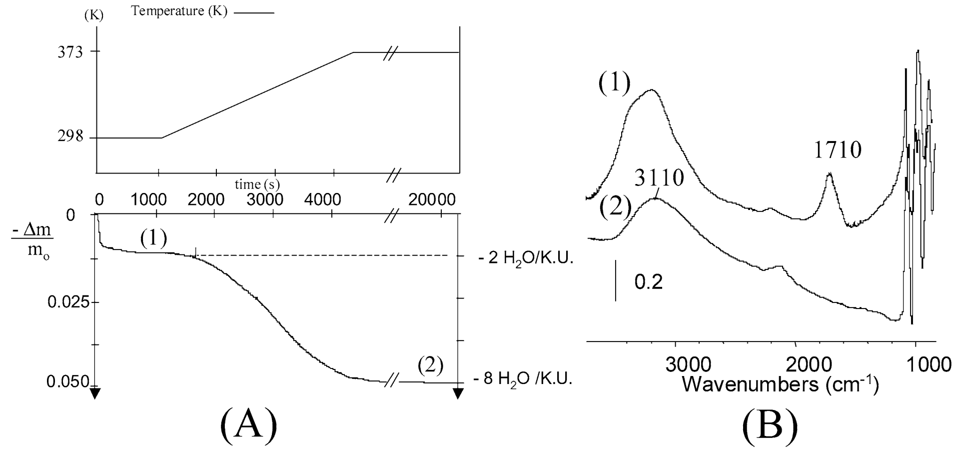

Fig. 2. Relative mass loss (A) and IR spectra (B) of HPW recorded during the activation stage. (1) Before activation (spectrum 1); (2) after outgassing 4 h at 373 K (spectrum 2).

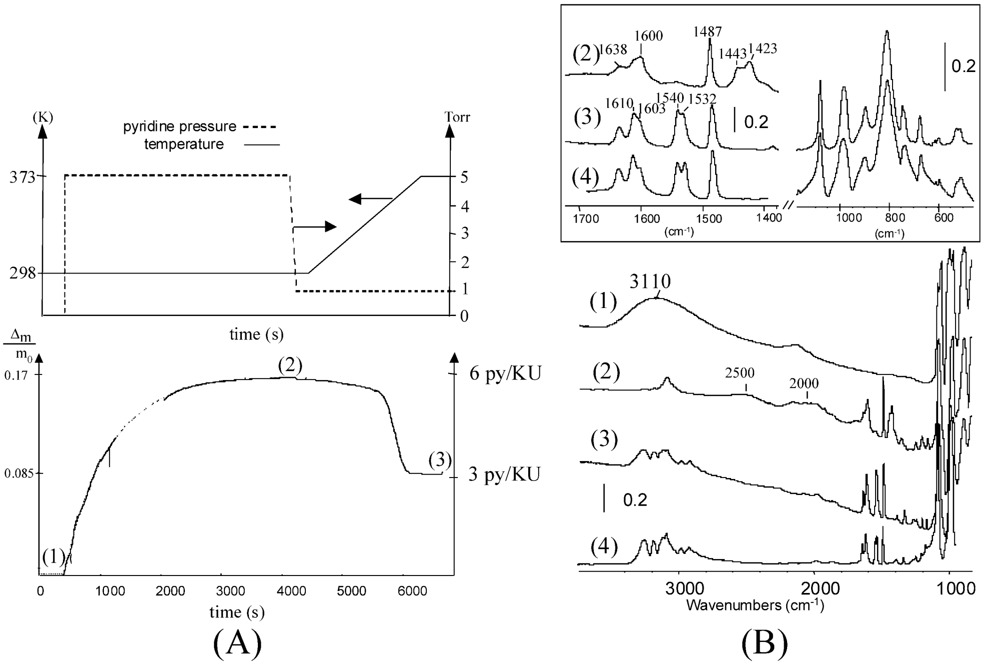

Fig. 3. Relative mass variation (A) and IR spectra (B) of the sample during pyridine absorption experiment. HPW activated at 373 K (spectrum 1); after 1 h under a large excess of pyridine at room temperature (5 Torr at the equilibrium pressure) (spectrum 2); and then a progressive heating from room temperature to 373 K under an equilibrium pressure of 1 Torr of pyridine (spectrum 3). For comparison, spectrum of the $(PyH^+)_3PW_{12}O_{40}$ salt synthetized ex situ is reported (spectrum 4).

der a large excess of pyridine at room temperature (5 Torr at the equilibrium), the mass increases continuously and stabilizes after 1 h of contact time. Then the mass increase, $\Delta m/m_0$, corresponds to the absorption of ~6 pyridine molecules per KU. Considering that 3 protons are associated with each KU, such a value corresponds to the absorption of 2 pyridine molecules per proton. This stoichiometry is the same than that reported by Highfield and Moffat [3] using volumetric measurements in similar conditions (exposure of HPW to an excess pyridine at room temperature). The decrease in pyridine pressure down to 1 Torr does not significantly modify the amount of absorbed pyridine. The corresponding spectrum, corrected from the contribution of gas-phase pyridine, is shown in Fig. 3B (spectrum 2). It no longer presents the broad ν(OH) band, indicating that all OH groups of HPW are interacting with pyridine. The lack of any ν8a band below 1600 cm^{-1} indicates that no physisorption occurs in such conditions. The bands at about 3000 cm^{-1} are assigned to the ν(CH) modes of absorbed pyridine [11]. Besides, two broad bands centered at around 2500 and 2000 cm^{-1} are observed. In the 1400–1700 cm^{-1} range, the characteristic ν19b band of classical pyridinium species expected at 1545 cm^{-1} is not observed. In contrast, the pyridinium ν8a band at 1638 cm^{-1} is clearly observed. Moreover, supplementary bands at 1443 and 1423 cm^{-1} (ν19b region) are observed. Similar spectra have been reported on various solid acids [3,12] and are assigned to bis-pyridinium $(PyH^+\cdots Py)$ ring vibrations. The broad doublet at 2500–2000 cm^{-1} also closely matches that characterizing the bis-pyridinium ion $(PyH^+\cdots Py)BF_4^-$ in pyridine solution [13] and $(PyH^+\cdots Py)ClO_4^-$ in acetonitrile [14]. Thus, both TGA data and IR spectra recorded simultaneously provide evidence under a large excess of pyridine, HPW absorbs 2 pyridine molecules per proton, leading to the formation of bis-pyridinium species.

A progressive heating of the sample from room temperature to 373 K under an equilibrium pressure of 1 Torr of pyridine provokes a rapid loss of mass at 350–365 K. A plateau is then reached (Fig. 3A). When the sample is further heated up to 473 K under vacuum, no additional mass loss is observed (experiment not shown). Thus, the plateau reached above 365 K results from the formation of thermally stable species. Considering the initial mass of the activated sample m_0, the relative mass gain $\Delta m/m_0$ corresponded to the absorption of three pyridine molecules per Keggin unit, i.e. one pyridine molecule per proton. This result is in agreement with the studies of Misono [15] who has shown on HPW and HPMo heteropolyacids that introduction of an excess of pyridine followed by thermodesorption at 373 K or higher also leads to a pyridine to proton ratio of 1.

The spectrum recorded at 373 K (Fig. 3, spectrum 3) is clearly different from the previous one (spectrum 2). Broad, intense bands are observed between 3300 and 2800 cm^{-1}. Their complicated structure very looks like that observed for $\text{PyH}^+\cdots\text{ClO}_4{}^-$ in CD_3CN solution [16]. It results from Fermi resonances between the ν(NH) mode and overtones and combination modes of PyH^+ ring vibrations [12,16]. The pyridine ring vibrations range, shows a typical spectrum of pyridinium species (ν8a and ν19a bands at 1638 and 1487 cm^{-1}) with a splitting of the ν8b (1610–1603 cm^{-1}) and ν19b (1540–1532 cm^{-1}) bands, as already reported by different authors [3,4]. Taking into account the pyridine to proton ratio close to 1, we conclude that the corresponding spectrum is that of mono-pyridinium species.

To confirm this stoichiometry, pyridine-HPW salts were synthesized ex situ from HPW and pyridine and further analyzed by IR spectroscopy (KBr pellets), chemical analysis, and TGA. The IR spectrum of the prepared solid (Fig. 3B, spectrum 4) was identical to those obtained in situ. In particular the splitting of the ν8b and ν19b bands is clearly observed. At lower wavenumbers, the occurrence of strong bands at 1079, 982, 895, and 805 cm^{-1} characterize KUs as already reported for the pure $\text{PW}_{12}\text{O}_{40}$ anion [17] and its pyridinium salt [4]. Carbon and nitrogen contents of the salt are 5.91 and 1.32 wt%, respectively, values close to those expected for $(\text{PyH}^+)_3\text{PW}_{12}\text{O}_{40}$ salt (5.78 and 1.35 wt%, respectively). Finally, the TGA carried out from room temperature to 1023 K showed a weight loss of 8.71%, in good agreement with the expected value (8.85%) for the mono-pyridinium salt.

4. Conclusion

We have set up an apparatus allowing the simultaneous determination of mass variations and IR spectra of opaque materials. Most of the sample was placed in a basket, allowing us to record a significant mass variation of a solid. This basket is close to the IR beam, which analyzes only a very small amount of the solid deposited on a silicon plate. The method can be used to determine the amount of adsorbed species formed on catalysts not very transparent to the IR beam. In the present study, this method was used to determine the stoichiometry of the pyridinium salts resulting from absorption of pyridine on HPW. Gravimetric measurements show that two pyridinium salts with definite stoichiometry are formed: $(\text{Py}_2\text{H}^+)_3\text{PW}_{12}\text{O}_{40}$ (bis-pyridinium salt) and $(\text{PyH}^+)_3\text{PW}_{12}\text{O}_{40}$ (mono-pyridinium salt). The bis-pyridinium salt is formed at room temperature under an excess of pyridine, whereas the mono-pyridinium salt is formed after heating at 373 K. The IR spectra of both salts closely correspond to those reported for pyridinium salts in strong acid solutions. The splitting of the ν8b and ν19b bands of absorbed pyridine (at 1610–1603 cm^{-1} and 1540–1532 cm^{-1}, respectively) is related to the mono-pyridinium formation in the HPW structure.

Acknowledgments

The authors thank Sébastien Aiello for the design of the quartz basket, including a supported wafer.

References

[1] M. Misono, Chem. Commun. 13 (2001) 1141.

[2] T. Okuhara, N. Mizuno, M. Misono, Adv. Catal. 41 (1996) 113.

[3] J.G. Highfield, J.B. Moffat, J. Catal. 89 (1984) 185.

[4] N. Essayem, A. Holmqvist, G. Sapaly, J.C. Védrine, Y. Ben Tâarit, Stud. Surf. Sci. Catal. 135 (2001) 340.

[5] M. Misono, N. Mizuno, K. Katamura, A. Kasai, Y. Konishi, K. Sakata, T. Okuhara, Y. Yoneda, Bull. Chem. Soc. Jpn. 55 (1982) 400.

[6] N. Essayem, C. Lorentz, A. Tuel, Y. Ben Tâarit, Catal. Commun. 6 (2005) 539.

[7] F. Thibault-Starzyk, B. Gil, S. Aiello, T. Chevreau, J.-P. Gilson, Microporous Mesoporous Mater. 67 (2004) 107.

[8] Y. Kanda, K.Y. Lee, S. Nakata, S. Asaoka, M. Misono, Chem. Lett. (1988) 139.

[9] C. Paze, S. Bordiga, A. Zecchina, Langmuir 16 (2000) 8139.

[10] J.C. Edwards, C.Y. Thiel, B. Benac, J.F. Knifton, Catal. Lett. 51 (1998) 77.

[11] A. Travert, A. Vimont, A. Sahibed-Dine, M. Daturi, J.C. Lavalley, Appl. Catal. A, in press, doi:10.1016/j.apcata.2006.03.011.

[12] R. Buzzoni, S. Bordiga, G. Ricchiardi, C. Lamberti, A. Zecchina, Langmuir 12 (1996) 930.

[13] R. Clement, J.L. Wood, J. Mol. Struct. 17 (1973) 265.

[14] S.E. Odinokov, A.A. Mashkovsky, V.P. Glazunov, Spectrochim. Acta, Part A 32 (1976) 1355.

[15] M. Misono, Stud. Surf. Sci. Catal. 20 (1985) 147.

[16] V.P. Glazunov, S.E. Odinokov, Spectrochim. Acta, Part A 38 (1982) 409.

[17] C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck, R. Thouvenot, Inorg. Chem. 22 (2) (1983) 207.