Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 434 (2005) 81–87

thermochimica acta

www.elsevier.com/locate/tca

Influence of cations on active sites of the alkaline earth salts of 12-tungstophosphoric acid: microcalorimetric study

Lj. Damjanović[a,*], V. Rakić[b], U.B. Mioč[a], A. Auroux[c]

[a] *Faculty of Physical Chemistry, Studentski trg 12-16, P.O. Box 137, 11000 Belgrade, Serbia and Montenegro*
[b] *Faculty of Agriculture, Nemanjina 6, 11080 Zemun, Serbia and Montenegro*
[c] *Institut de Recherches sur la Catalyse, 2 Av. A. Einstein, 69626 Villeurbanne, France*

Received 7 November 2004; received in revised form 31 December 2004; accepted 5 January 2005
Available online 1 February 2005

Abstract

The acidic properties of the alkaline earth salts of 12-tungstophosphoric acid were investigated using ammonia absorption microcalorimetry. The number and the strength of acid sites of these catalysts as well as differential heats of ammonia absorption were determined. As a result of substitution of two protons with one alkaline earth cation, the decrease of both the total number of acid sites and the number of the strongest acid sites characterized by differential heats higher then 150 kJ/mol, compared to the values found in the case of initial 12-tungstophosphoric acid, were noticed. While all protons seem accessible for ammonia in Mg, Ca and Ba salts, in the case of Sr salt less then stoichiometric ammonia sorption was detected which can be explained by steric effect of these divalent cations.

Keywords: Microcalorimetry; Ammonia absorption; Keggin anion; 12-Tungstophosphoric acid; Alkaline earth salts

1. Introduction

Keggin-type heteropoly compounds (HPC) have attractive and important characteristics in terms of catalysis: the versatility of these materials and their compatibility with environmentally and economically attractive conditions led to their utilization in a variety of reactions, e.g. they are known to be effective catalysts for various kinds of acid-catalyzed reactions [1–3]. Importantly, solid HPC have been used for synthetic processes in both homogeneous and heterogeneous phases [3–5]. These compounds exhibit high tunability to experimental conditions: HPC have been used in both gas phase [2–5] and liquid phase reactions [6–8]. They consist of heteropoly anions and counter cations such as H^+, Cs^+, $NH_4{}^+$, etc. When the counter cations are protons, they are called heteropoly acids (HPA), also known as “super-acids”. An important characteristic of HPA, like 12-tungstophosphoric acid $H_3PW_{12}O_{40}$ (WPA), is the presence of acid sites corresponding to those classified as strong acids [9]. Heteropoly acids exhibit Brønsted acidity, significantly higher compared with the acidity of traditional mineral acid catalysts [10], which together with special structural properties has rendered this class of compounds as promising catalysts. HPA may potentially replace corrosive liquids in acid-catalyzed reactions thus leading to more environmentally friendly processes [11]. Furthermore, HPA and its derivatives have been shown to be valuable and significantly superior to HPC containing molybdenum in the removal and conversion of nitrogen oxides [12]. Ammonium salt of WPA has been shown to be effective for the reduction process of NO_x to N_2 [12]. Recently, it has been shown that heteropoly acids can act as photocatalysts in the processes of a decomposition of environmentally persistent pollutants [13]. But, characteristics of HPA strongly depend on temperature and relative humidity and it is necessary for industrial processes to have catalysts less sensitive to the surroundings [14–16].

The charge balancing protons of HPA can be substituted by cation exchange via salt formation. Substituted cations determine the crystallographic, secondary structure of the HPC

---

[*] Corresponding author. Tel.: +381 113282394; fax: +381 11187133.
E-mail address: ljiljana@ffh.bg.ac.yu (Lj. Damjanović).

0040-6031/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2005.01.004

and have large effects on the acidity, stability and the microstructure, thus may strongly affect catalytic properties of the HPC. Such salts are more stable systems and less sensitive to humidity and temperature than acids themselves. As an example, Cs salt of tungstophosphoric acid ($Cs_{2.5}H_{0.5}$WPA) exhibit importantly different physico-chemical characteristics in comparison with a parent acid [14]. Quite contrary to the parent acid, $Cs_{2.5}H_{0.5}$WPA and Pt–$Cs_{2.5}H_{0.5}$WPA are known as "water tolerant catalysts" and have been employed in different important industrial reactions [15,16]. While the acid forms and salts of monovalent cations have received the most attention [15], there are only few reports of studies describing the catalytic properties of WPA and 12-molybdophosporic salts with divalent cations and characterization of the surface and bulk properties of these materials [17–20].

An important step towards better understanding of catalytic properties of the alkaline earth salts of WPA is the characterization of their acidic features, including the nature, strength and number of acid sites. Microcalorimetry of sorbed ammonia is known to be a powerful tool in elucidation of these important characteristics. It has been employed for the investigation of the acidity of heteropolyacids containing tungsten and molybdenum [9,21]. The aim of this work was to measure the acidity of the alkaline earth salts of WPA using ammonia absorption microcalorimetry, and to determine, to the best of our knowledge, for the first time the number and the strength of acid sites of these solid materials as well as differential heats of ammonia absorption. In order to investigate whether the presence of alkaline earth cations in the WPA structure caused the appearance of basic active sites or not, microcalorimetric measurements of SO_2 absorption were also performed. Additionally, TPD of ammonia which may be the most widely used method for the characterization of site distribution in solid acids, was also performed in this work.

2. Experimental

The magnesium, calcium, strontium and barium salts of WPA were prepared by adding equimolar amounts of the appropriate alkaline earth chloride to aqueous solution of the $H_3PW_{12}O_{40}\cdot 6H_2O$ (WPA-6), at 298 K, in order to prepare acid salts where two protons, i.e. oxonium ions are exchanged with divalent cation, analogous to the synthesis of acid salts of monovalent cations [22]. Recrystallization was performed three times. The overexchanged sample of beryllium WPA salt was obtained by addition of excess of $BeCl_2$ solution to aqueous solution of WPA-6, at 298 K. The obtained samples were kept in a desiccator above $CaCl_2\cdot 2H_2O$ at the constant humidity (RH = 35%).

Resulting materials were characterized by atomic absorption spectroscopy, IR spectroscopy, powder X-ray diffraction, MAS NMR and DTA measurements.

The cations content was determined by AAS using a Varian AA-775 spectrophotometer. The IR spectra were recorded on a Perkin-Elmer 983G spectrophotometer using KBr pellets technique, in the wavenumber range from 4000 to 250 cm^{-1}. Powder X-ray diffraction patterns were recorded on a Bruker (Simens) D5005 diffractometer at room temperature using Cu Kα radiation from $2\theta = 3°$ to 80° in a 0.02° steps with 1 s per step. ^{31}P MAS NMR spectra were obtained on Bruker DSX 400 spectrometer at 161 MHz with a spinning rate of 10 kHz and repetition time of 60 s. Phosphoric acid (85% solution) was used as external reference.

A Stanton Redcroft STA 1000 thermal analyzer in the temperature interval from 20 to 800 °C and at a heating rate of 10 °C/min in nitrogen atmosphere was used for determination of hydration degrees of obtained salts. The beryllium, magnesium, calcium, strontium and barium salts of WPA, kept at 35% RH, had 12, 11, 10, 6 and 7 water molecules, respectively.

The microcalorimetric study has been performed using a heat-flow microcalorimeter C80 from Setaram. The samples were outgassed under vacuum at 573 K prior to absorption of ammonia or sulfur dioxide in the calorimetric cell maintained at 423 and 353 K, respectively. Successive small doses of NH_3 or SO_2 were introduced onto the samples until a final equilibrium pressure of 66 Pa was achieved. The equilibrium pressure corresponding to each absorbed amount was measured by means of a differential pressure gauge from Datametrics. Subsequently, the sample was pumped, desorption peak was recorded and a re-absorption was performed at the temperature of absorption. The irreversibly absorbed amount of a chemisorbed gas was calculated from difference between primary and secondary isotherms.

Ammonia desorption experiments were performed using the TPD technique, performed on a Setaram TG-DSC 111 equipment coupled with a mass spectrometer (Thermostar from Pfeifer) as a detector. Capillary-coupling system was used. The TPD experiments were carried out in a flow, with helium as the carrier gas (10 ml/min). For each experiment, ca. 40 mg of a sample with ammonia absorbed in previously done microcalorimetric experiment was used. Initially, the samples were purged with helium at room temperature for 15 min and then heated at 5 K min^{-1} in helium up to 823 K. During this temperature increase, the mass spectrometer was set at $m/e = 15$ in order to avoid the interference of water fragmentation masses.

3. Results and discussion

Well-resolved XRD patterns of alkaline earth WPA salts, kept at the RH of 35%, showed that all investigated samples were crystalline, Fig. 1. The highest crystallinity was observed for overexchanged Be salt and crystallinity decreases in order Mg, Ba, Ca and Sr. In the case of Ca and Sr salts lower crystallinity and/or the presence of an amorphous phase is more pronounced compared to other investigated samples. The details about crystal structure are known only for MgH-

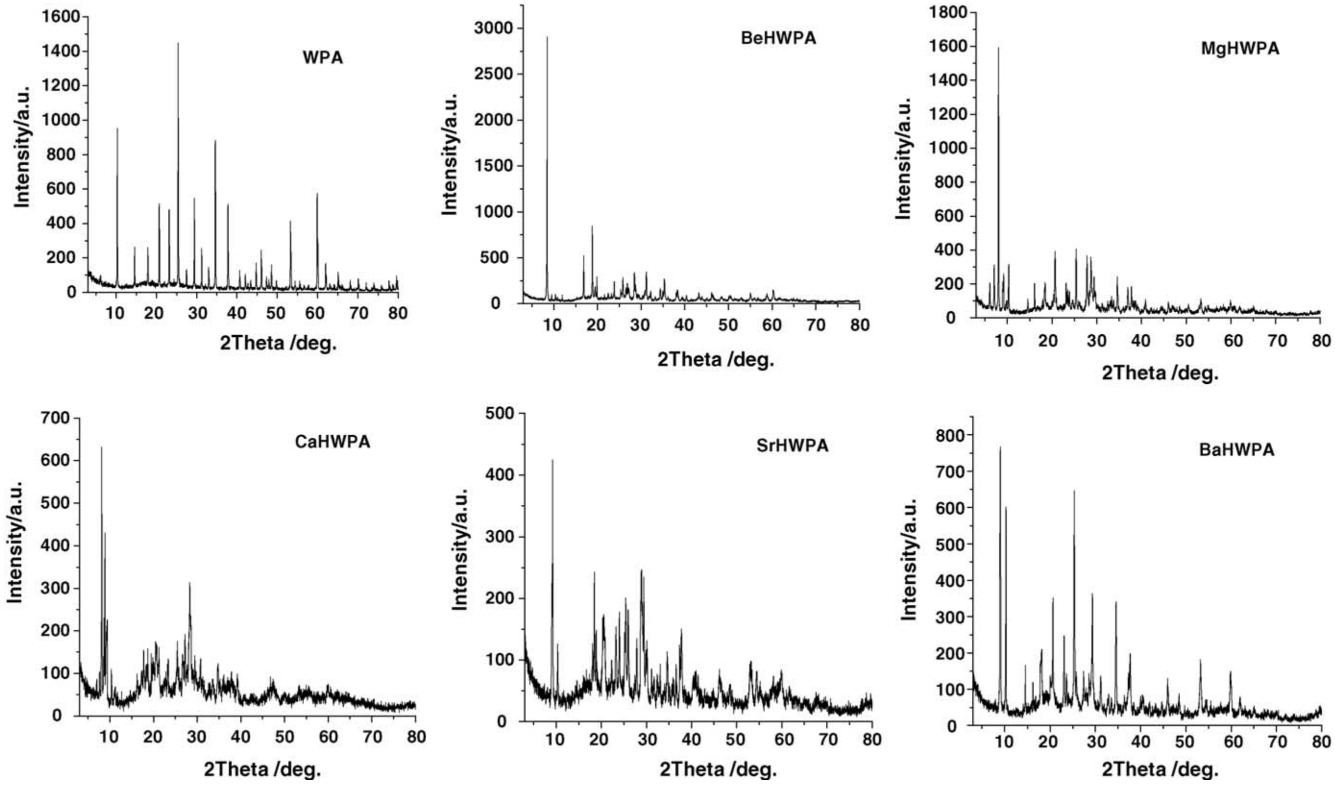

Fig. 1. XRD patterns of the alkaline earth salts of WPA kept at the RH of 35%.

WPA [23], while crystallographic studies of other alkaline earth WPA salts are in progress.

Results of infrared spectroscopy measurements, as a convenient and powerful tool for investigation of the primary (anion) structure of HPC, showed four peaks characteristic of the Keggin structure in the region 1200–600 cm^{-1} [24] confirming that Keggin polyanion is formed in all investigated samples (Fig. 2).

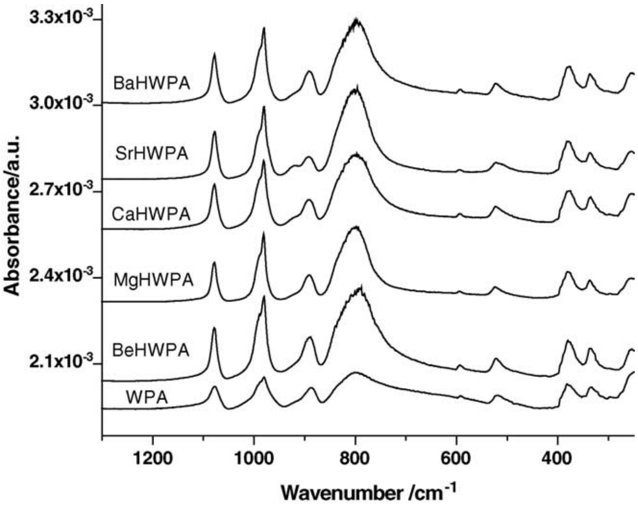

Fig. 2. IR spectra of the alkaline earth salts of WPA kept at the RH of 35%.

^{31}P MAS NMR spectrum of the WPA-6 exhibited only one narrow line with maximum at a chemical shift of −15.6 ppm indicating the uniformity and high symmetry of the structure, in accordance with previously reported results [5]. ^{31}P MAS NMR spectra of all alkaline earth WPA salts, kept at RH of 35%, also showed only one narrow line at the chemical shifts of: −15.1; −15.4; −15.6; −15.5 and −15.5 ppm for Be, Mg, Ca, Sr and Ba salts of WPA, respectively. Hence the observed chemical shifts confirm that the Keggin anions have been preserved following the preparative procedures, in accordance with the IR results, even though some local distortions had occurred.

DSC curves of investigated samples showed an exothermic peak at 598 °C for WPA and at 582, 583, 582, 582, 597 °C for Be, Mg, Ca, Sr and Ba salts of WPA, respectively (to be published). These peaks are assigned to the Keggin anion decomposition, since it is known that Keggin anions transform at about 600 °C in a new monophosphate bronze type compound PW_8O_{26} [25].

The experimental results of microcalorimetric measurements are shown in Figs. 3 and 4.

The differential heats of ammonia absorption versus gas uptake obtained for a parent WPA and all investigated salts are shown in Fig. 3. At low coverage (ammonia volume < 300 μmol/g) all investigated samples, except the beryllium salt, display a plateau of NH_3 absorption heats, indicating the existence of homogeneous acid sites active in the

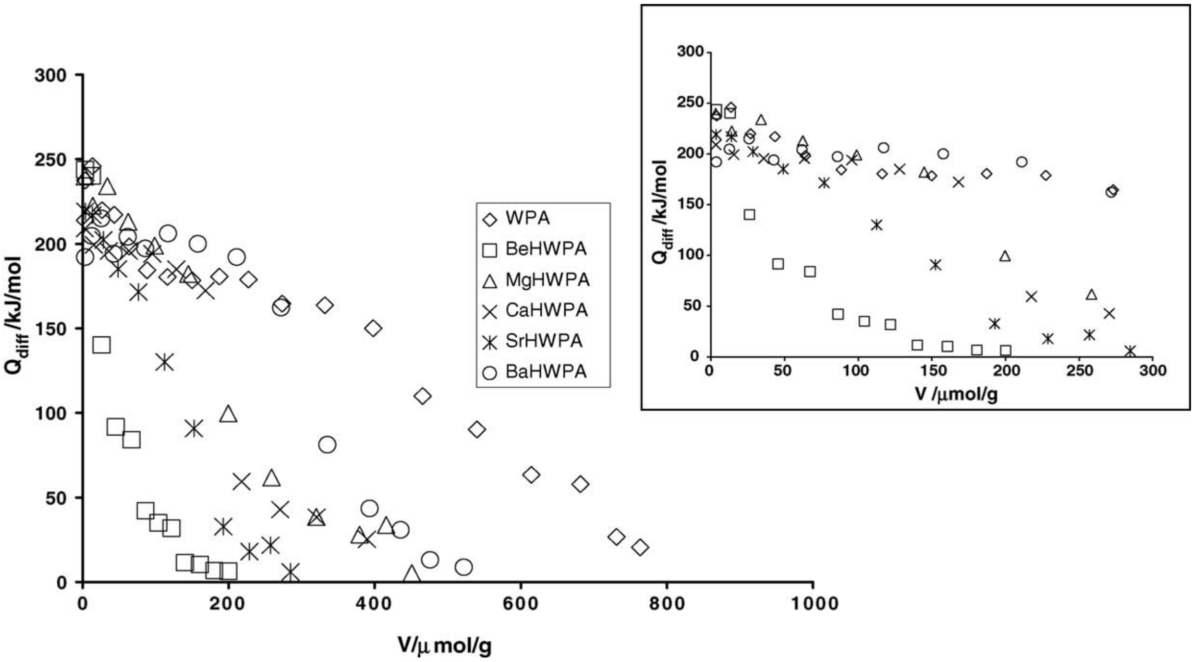

Fig. 3. Differential heats of ammonia as a function of coverage for the different alkaline earth salts and parent acid. Inset shows expanded differential heat curves.

absorption of base molecules. The acid strengths of the active sites of WPA appear to be rather homogeneous with the presence of a plateau at around 200 kJ/mol, in accordance with previously reported result [21]. The length of plateau, proportional to the number of the strongest acid sites, decreases in order Mg, Ca, Sr salt. At higher coverages (300 μmol/g < NH_3 volume < 800 μmol/g), all differential heat profiles exhibit a continuous decrease, indicating the heterogeneity of acid sites strength. Contrary to all other investigated samples, the absorption profile obtained in the case of Be salt shows a continuous decrease, in the whole range of surface coverage.

Table 1 compiles the total volumes of absorbed ammonia, and the amounts of NH_3 absorbed evolving the heats higher than 150 kJ/mol. Evidently, both the total amounts of absorbed ammonia and the amounts of ammonia absorbed at the strongest acid sites are lower for the alkaline earth salts than found for WPA itself. These results are confirmed by corresponding volumetric isotherms, presented in Fig. 4, and suggest that the acidity of investigated salts is lower compared to that of the parent WPA. It is well known that a so-called anhydrous protons act as Brønsted acid sites and each unit cell of WPA possesses three anhydrous protons [25–27]. Quanti-

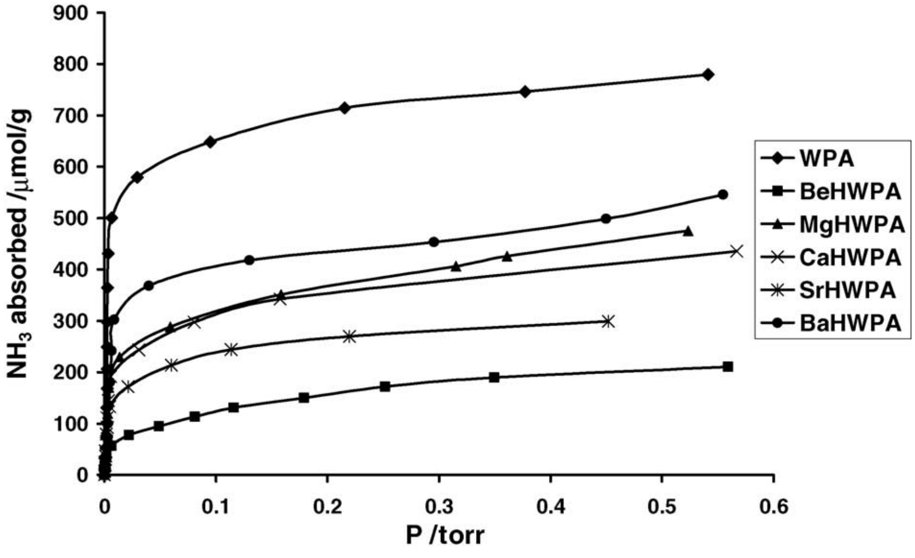

Fig. 4. Absorption isotherms of ammonia for the different alkaline earth salts and parent acid.

Table 1
Chemical analysis and the amounts of ammonia absorbed on the investigated samples

Sample	Mass[a] (mg/g)	The exact formula	Irreversibly absorbed NH_3		V_{NH_3} ($Q_{dif} > 150$ kJ/mol)	
			μmol/g	Molecules/unit cell	μmol/g	Molecules/unit cell
WPA		$H_3PW_{12}O_{40}$	660	3.0	393	1.8
BeHWPA	3.00	Overexchanged Be salt of WPA	84	0.4	25	0.1
MgHWPA	8.08	$Mg_{0.87}H_{1.13}PW_{12}O_{40}$	307	1.1	165	0.6
CaHWPA	13.22	$Ca_{0.98}H_{1.02}PW_{12}O_{40}$	308	1.0	178	0.6
SrHWPA	28.50	$Sr_{0.92}H_{1.08}PW_{12}O_{40}$	209	0.8	95	0.4
BaHWPA	43.96	$Ba_{0.85}H_{1.15}PW_{12}O_{40}$	367	1.1	285	0.8

[a] Mass of alkaline earth cation (mg) per gram of sample.

tative results obtained in this work and expressed as number of absorbed NH_3 molecules per unit cell of investigated solid (see Table 1), clearly show that one molecule of NH_3 reacted with Brønsted acid site in the case of parent WPA and its Mg, Ca and Ba salts. In other words, all protons seem accessible for ammonia in the mentioned materials, while in the case of Sr salt less then stoichiometric ammonia sorption was detected which can be explained by steric effect of this divalent cation. Result obtained for overexchanged Be salt shows absorption of 0.4 molecules of NH_3 per unit cell (see Table 1). It is known for WPA salts of monovalent cations that even when they are prepared to be stoichiometric residual quantities of protons remain [9]. Result of microcalorimetric measurements obtained in this work shows that residual acidity is present even in the overexchanged Be salt of WPA.

The alkaline earth cations act as counter ions to Keggin anion in materials investigated in this work. In order to check whether the obtained salts of WPA have the alkaline character or not, the absorption of SO_2 was performed. However, the absorption of SO_2 was not found in any of the samples investigated in this work.

As it can be expected, the results presented so far indicate that a substitution of two protons with the alkaline earth cation results in decrease of the total number of sites active in ammonia absorption. Additionally, the number of strong acid sites important in possible catalytic reactions, characterized by differential heats higher then 150 kJ/mol, becomes also lower, as a result of H^+ substitution with alkaline earth cation. A plateau at ∼200 kJ/mol, similar to that one obtained for WPA is obtained only for Ba salt. In addition, it could be concluded that, except for the parent WPA, energetic heterogeneity is noticed for the investigated salts.

Fig. 5 presents the distributions of acid site strengths found by ammonia absorption for all investigated samples. It is known that there are four types of oxygen atoms (internal, edge-sharing, corner-sharing, and terminal) in the Keggin structure characteristic for WPA [26]. The anhydrous protons can exist as “free protons” [28] and/or can interact with bridging or terminal oxygen atoms where the energy difference between these sites is small and depends on the relative location of other protons. Besides these positions, computational results indicate that protons in the anhydrous structure also prefer to bridge between Keggin units where they are shared between two terminal O_d atoms or between a terminal O_d and a bridging O_c atom of the Keggin anion. These protons are located in the area between Keggin units where it will be more difficult for reactant molecules to access them [29]. One proton from the alkaline earth WPA salts can occupy any of these positions, depending on particular crystalline structure of each salt and it will be influenced by the cation position. Evidently, the energetic heterogeneity of the investigated systems originates from these different positions where anhydrous proton can be located.

Results of TPD experiments performed in this work additionally explain the heterogeneity of the investigated salts. Fig. 6 shows the TPD spectra of ammonia preabsorbed on the investigated samples. As it can be seen from the figure, the absorption of ammonia on parent WPA results in the formation of strongly bonded species on the surface. The TPD profile is sharp; the desorption takes place in the high temperature region (around 600 °C), indicating energetic homogeneity. This is in accordance with our previously published results [27] but also with the other found in the literature [8,9,30] and it is a clear indication of very strong interaction between ammonia and Brønsted acid sites of WPA. In fact, from the results obtained in this work, it could be inferred that a true chemical reaction (forming of a salt) took place instantaneously after the chemisorption step. These results are compatible with those obtained employing photoacoustic FT-IR spectroscopy to study the absorption of ammonia, which have shown that after the absorption of 3 ammonia

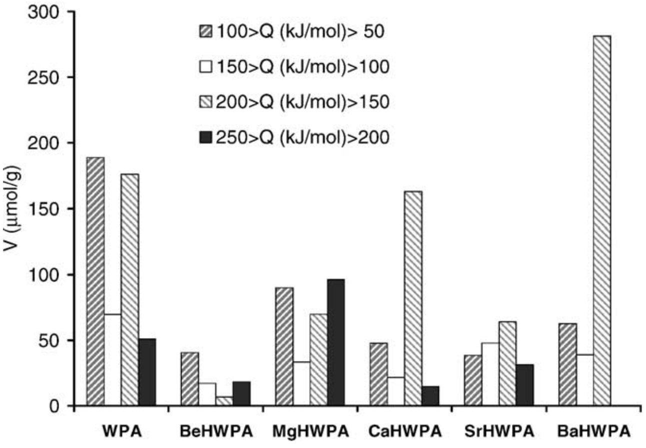

Fig. 5. Acid site energy distribution for the alkaline earth salts of WPA.

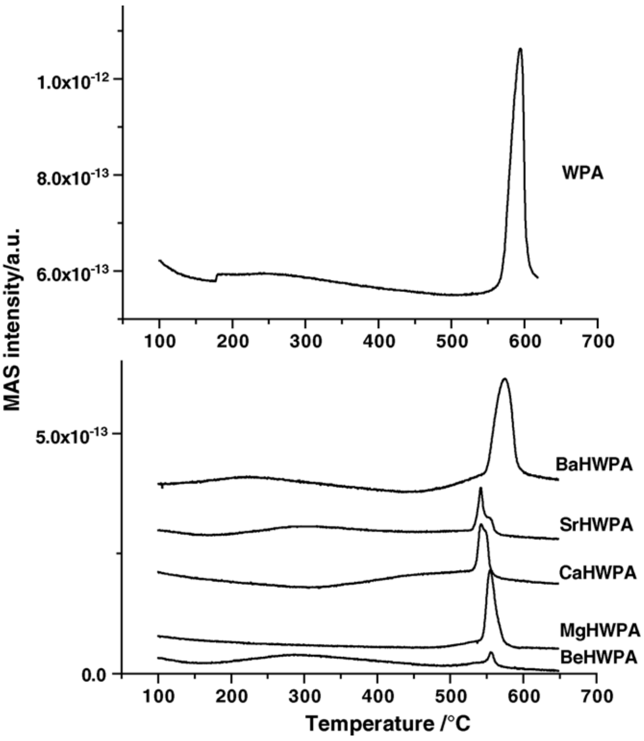

Fig. 6. TPD spectra of 12-tungstophosphoric acid and its alkaline earth salts.

molecules per Keggin unit the PAS FT-IR spectrum was virtually identical to that of the ammonium salt prepared from aqueous solution [31]. It should also be pointed out that what is measured is not the acidity of the salts but the heat of formation of the ammonium salt of the polyoxometalate, which corresponds to the neutralization of the acid proton and to the energy of formation of the crystal.

Contrary to the result obtained for the parent WPA, TPD profiles recorded during ammonia desorption from the investigated salts indicate their energetic heterogeneity, in accordance with microcalorimetric results presented in this work. Complex desorption profiles found in a broad temperature region (150–650 °C), composed of at least three overlapped peaks indicate energetic heterogeneity of investigated systems. It is worth noticing that the TPD profile obtained for a Ba salt of tungstophosphoric acid with 0.5 residual protons in a unit cell, already published in the literature [8], lies in the same temperature region as a TPD spectrum obtained in this work. In accordance with different number of protons per one unit cell, the relative intensities of the overlapped peaks in the reference [8] and those found in this work are different.

4. Conclusion

In this work, the acidity of 12-tungstophosphoric heteropoly acid and its overexchanged beryllium and stoichiometric magnesium, calcium, strontium and barium salts was investigated using ammonia absorption microcalorimetry and temperature programmed desorption of preabsorbed ammonia. Performed absorption of SO_2 has proved that the examined salts show no alkaline character.

The acidity of investigated systems originates form the so-called anhydrous protons, which act as Brønsted acid sites, their number being determined by the stochiometry of a Keggin anion and the presence of other counter cations. The results obtained in this work show that in the case of a parent acid and its Mg, Ca and Ba salts all protons seem accessible for ammonia molecules. Quite contrary, less then a stoichiometric ammonia sorption was found for Sr.

Very strong Brønsted acid sites are detected in the investigated systems, characterized with the heat of ammonia absorption higher then 150 kJ/mol. The number of these strong Brønsted acid sites depends on the cation present in the structure.

Generally, the acidity of the investigated systems can be described as strong. However, it is uniform only in the case of parent tungstophosphoric acid. Quite contrary, energetic heterogeneity of other investigated solids is evidenced, both from differential heats versus ammonia uptake profiles and from the results of temperature programmed desorption of ammonia.

References

[1] M.T. Pope, A. Muller (Eds.), Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications, Kluwer, Dordrecht, The Netherlands, 2001.
[2] A. Corma, Chem. Rev. 95 (1995) 559.
[3] N. Mizuno, M. Misono, Chem. Rev. 98 (1998) 199.
[4] C.L. Hill, C.M. Prosser-McCartha, Coord. Chem. Rev. 143 (1995) 407.
[5] M. Misono, Chem. Commun. (2001) 1141.
[6] I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171.
[7] I.V. Kozhevnikov, Appl. Catal. A: Gen. 256 (2002) 3.
[8] G. Koyano, K. Ueno, M. Misono, Appl. Catal. A: Gen. 181 (1999) 267.
[9] L.C. Jozefowicz, H.G. Karge, E. Vasilyeva, J.B. Moffat, Micropor. Mater. 1 (1993) 313.
[10] M.N. Timofeeva, Appl. Catal. A 256 (2003) 19.
[11] M. Misono, Top. Catal. 21 (2002) 89.
[12] J.B. Moffat, in: C.A.C. Sequeira, J.B. Moffat (Eds.), Chemistry, Energy and the Environment, Royal Society, London, 1998, p. 167.
[13] H. Hori, E. Hayakawa, H. Einaga, S. Kutsuna, K. Koike, T. Ibusuki, H. Kiatagawa, R. Arakawa, Environ. Sci. Technol. 38 (2004) 6118.
[14] S. Choi, Y. Wang, Z. Nie, J. Liu, C.H.F. Peden, Catal. Today 55 (2000) 117.
[15] T. Okuhara, N. Mizuno, M. Misono, Appl. Catal. A: Gen. 222 (2001) 63.
[16] E.F. Kozhevnikova, E. Rafiee, I.V. Kozhevnikov, Appl. Catal. A: Gen. 260 (2004) 25.
[17] G.B. McGarvey, N.J. Taylor, J.B. Moffat, J. Mol. Catal. 80 (1993) 59.
[18] Y. Saito, H. Niiyama, J. Catal. 106 (1987) 329.
[19] H. Hayashi, J.B. Moffat, J. Catal. 81 (1983) 61.
[20] R. Voyatzis, J.B. Moffat, J. Catal. 142 (1993) 45.
[21] F. Lefebvre, F.X. Liu-Cai, A. Auroux, J. Mater. Chem. 4 (1994) 125.
[22] U.B. Mioč, M. Davidović, B.R. Stanisavljev, M.R. Todorović, Z.P. Nedić, S.M. Uskoković-Marković, J. Serb. Chem. Soc. 61 (1996) 759.

[23] U.B. Mioč, M.R. Todorović, S. Uskoković-Marković, M. Davidović, A. Kremenović, A. Spasojević-de Bire, T. Čajkovski, V. Likar-Smiljanić, R. Biljić, Solid State Ionics 162 (2003) 217.
[24] C. Rocchiccioli-Deltcheff, R. Thouvenot, R. Franck, Spectrochim. Acta A 32 (1976) 587.
[25] U.B. Mioč, R.Z. Dimitrijević, M. Davidović, Z.P. Nedić, M.M. Mitrović, Ph. Colomban, J. Mater. Sci. 29 (1994) 3705.
[26] G.M. Brown, M.R. Noe-Spirlet, W.R. Busing, H.A. Levy, Acta Crystallogr. B 33 (1977) 1038.
[27] V. Rakić, V. Dondur, U. Mioč, D. Jovanović, Top. Catal. 19 (2002) 241.
[28] U.B. Mioč, Ph. Colomban, M. Davidović, J. Tomkinson, J. Mol. Struct. 326 (1994) 99.
[29] M.J. Janik, R.J. Davis, M. Neurock, J. Phys. Chem. B 108 (2004) 12292.
[30] N. Essayem, R. Frety, G. Coudurier, J. Vedrine, J. Chem. Soc., Faraday Trans. 93 (1997) 3243.
[31] J.G. Highfield, J.B. Moffat, J. Catal. 88 (1984) 177.