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THERMAL STABILITY OF HETEROPOLY ACIDS AND CHARACTERIZATION OF THE WATER CONTENT IN THE KEGGIN STRUCTURE

M. Varga[1], *B. Török*[2] *and Á. Molnár*[1*]

[1]Department of Organic Chemistry,
[2]Organic Catalysis Research Group of the Hungarian Academy of Sciences (József Attila University), H-6720 Szeged, Dóm tér 8, Hungary

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Abstract

The thermal stability of heteropoly acids of the Keggin type ($H_4[SiMo_{12}O_{40}]$, $H_3[PMo_{12}O_{40}]$, $H_4[SiW_{12}O_{40}]$ and $H_3[PW_{12}O_{40}]$), being important new catalytic materials, was studied by DSC. Two groups of signals were observed: the low temperature endothermic peak group belongs to the water content, while the high temperature one is exothermic and indicates the thermal decomposition of the acids. The effect of microwave irradiation on the target compounds was also studied. The emphasis, however, was placed on the characterization of the water content of the acids. Several types of water can be classified and DSC curves provide additional information to explain the differences in the catalytic behavior. The study of the effect of heat treatment and the subsequent water absorption of the acids provided additional unique information concerning the *pseudoliquid phase* in the secondary structure of heteropoly acids.

Keywords: differential scanning calorimetry, heteropoly acids, microwave irradiation, thermal stability, water content

Introduction

According to the recent environmental considerations and safety demands there is a strong driving force to find alternatives to very hazardous and corrosive catalysts such as HF and sulfuric acid [1]. A class of inorganic materials, namely heteropoly acids (HPAs), good candidates for this purpose, has recently been introduced to the chemical industry as catalysts [1–7]. According to their unique structural properties they exhibit bifunctional catalytic behaviour [2].They can

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* Author for correspondence: fax: 36-62-322-668, e-mail: amolnar@chem.u-szeged.hu

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be applied in electrophilic catalysis and also promote oxidations [3–10]. Due to their multifunctional character, applicability in heterogeneous, pseudo-liquid, homogeneous and phase-transfer catalytic reactions, and favorable technological properties there has been a growing interest in the chemistry of heteropoly acids.

However, these aims obviously require the knowledge of their thermal stability and their transformations occurring during thermal treatments considering that most catalytic reactions require energy donation to reach the activation energy barrier. The thermal stability of heteropoly acids has hardly been studied [2, 11–13]. More observations are available from the catalytic literature. In these cases, although a thermal treatment was applied, the effect was not studied with thermoanalytical methods [14, 15]. Additionally, heteropoly acids contain more or less water in different forms [4, 10]. Two types of protons have been found in crystalline HPAs, (i) non-localized hydrated protons, (ii) non-hydrated protons localized at the pheripheral oxygen atoms of the polyanion. When the water content decreases the protons become localized to a large extent. Thus, the water plays a crucial role in the formation of proton distribution and catalytic features of HPAs [16].

In the present paper we describe the thermal stability, dehydration and decomposition characteristics of several heteropoly acids of the Keggin type [17, 18], studied by DSC. The emphasis has been placed on the characterization of the water content considering its essential role in electrophilic applications.

Experimental

Materials

$H_4[SiMo_{12}O_{40}]\cdot\sim14H_2O$ (denoted as $SiMo_{12}$) and $H_3[PMo_{12}O_{40}]\cdot\sim26H_2O$ (PMo_{12}) were purchased from Aldrich, $H_4[SiW_{12}O_{40}]\cdot\sim26H_2O$ (SiW_{12}) from Riedel-de-Haen while $H_3[PW_{12}O_{40}]\cdot\sim19H_2O$ (PW_{12}) was a Serva product.

Pretreatments

Two different pretreatments were applied, one is a simple microwave irradiation in a conventional microwave oven (Samsung M6148) at 400 W power for 2 min. The second is a conventional heat treatment at 573 K for 2 h in flowing argon atmosphere.

Calorimetry

A Perkin Elmer DSC-2 differential scanning calorimeter with a computer controlled temperature scan system was used. Measurements were carried out with 5.0±0.5 mg samples with a heating rate of 20 K min^{-1}. The temperature range studied was between 270–980 K. Samples were measured in a closed graphite sample holder covered with graphite cap purchased from Perkin Elmer. The calorimeter was calibrated with indium (*m.p.* 429 K) and zinc (*m.p.* 692 K) reference samples. Before each run a blank scan was recorded for the baseline correction to eliminate the asymmetry of the calorimeter.

Results and discussion

In this study four heteropoly acids of Keggin type were used namely $H_4[SiMo_{12}O_{40}]$, $H_3[PMo_{12}O_{40}]$, $H_4[SiW_{12}O_{40}]$ and $H_3[PW_{12}O_{40}]$. Although, a wide variety of heteropoly acids is described, these four acids are commercially available and, therefore, commonly used in organic transformations as acid catalysts.

One of the most important questions in catalytic reactions is what happens to the catalyst since this can affect the lifetime, the reproducibility or the regeneration of the catalytic material. Therefore, a test of the catalyst before and after the reactions, can provide important information about the actual changes taking place during the transformations. The thermal stability, one of the most important factors, was studied by DSC. The DSC method has a distinct advantage over conventional calorimetry and other thermal methods, namely that it is performed with a very small amount of sample (less than 10 mg). The DSC patterns of the commercially available four heteropoly acids are shown in Figs 1 and 2. Since these acids were used in microwave assisted reactions as well [19], the microwave irradiated samples were also studied and plotted in Figs 1 and 2, while the characteristic temperatures of the heat effect are collected in Table 1.

Table 1 Peak temperature data in the DSC curves of the untreated samples of the $H_n[XM_{12}O_{40}]$ heteropoly acids of the Keggin type (all values are given in K)

Sample	Endothermic effects				Exothermic effects
	T_1	T_2	T_3	T_4	T_5
$SiMo_{12}$	352.8	381.9	401.9	–	658.4
PMo_{12}	318.9	363.9	393.0	406.9	717.3
SiW_{12}	352.7	476.4	–	–	818.2
PW_{12}	346.6	462.7	–	–	885.1

As the curves show both the molybdenum- and tungsten-containing acids exhibit specific patterns. Basically, two separate group of peaks can be observed: endothermic peaks are detected in the 300–480 K region, while at higher temperature (640–920 K) a single exothermic peak is always recorded. The endothermic region belongs to the loss of water from the original heteropoly acid structure, while the exothermic peak shows the thermal decomposition of the acids to different kinds of simple oxoacids [2]. The microwave irradiation (2 min, 400 W) does not substantially influence the DSC patterns characteristic of the untreated samples: only slight changes in the ratio of the endo- and exothermic peaks occurred. It is clearly seen that dehydration of the samples during microwave pretreatment is almost negligible.

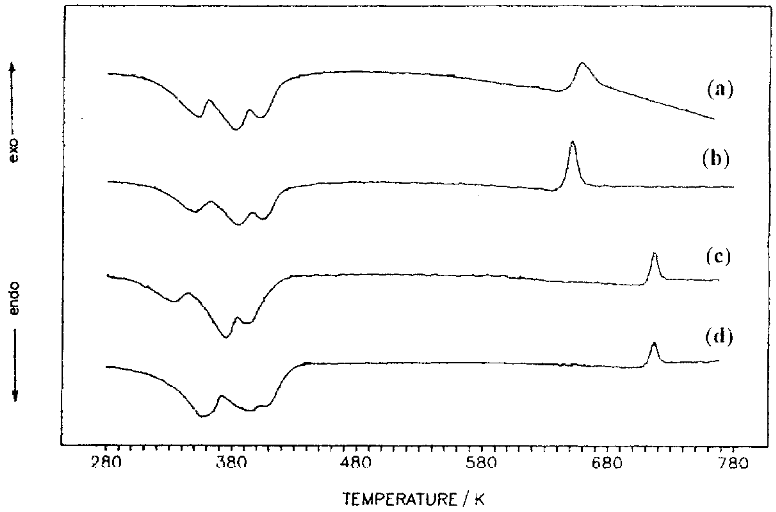

Fig. 1 DSC patterns of $H_4[SiMo_{12}O_{40}]$ (a) before and (b) after and $H_3[PMo_{12}O_{40}]$ (c) before and (d) after microwave irradiation

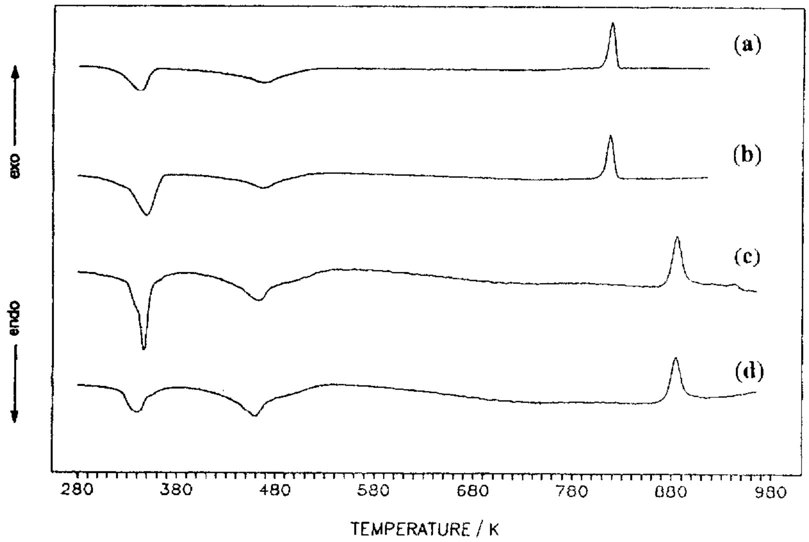

Fig. 2 DSC patterns of $H_4[SiW_{12}O_{40}]$ (a) before and (b) after and $H_3[PW_{12}O_{40}]$ (c) before and (d) after microwave irradiation

This is a crucial piece of information relevant to the application of heteropoly acid catalysts in organic transformations. The regular temperature region applied in the great majority of common organic reactions is well below 573 K. The above observations show that the thermal decomposition of the heteropoly acids is negligible in the usual temperature range of organic transformations. It is also demonstrated, that the acids tested can be considered as unaltered material during microwave irradiation except some changes in their water content *(vide infra)*. As a consequence, any disturbing transformations of the catalytic material in microwave assisted organic reactions can be excluded.

Further studies were focused on the endothermic transformations. A systematic investigation was performed with all four acids studying the effect of dehydration and the water absorption on the position and intensity of DSC signals. The DSC patterns recorded with all four acids are shown in Figs 3–6. These series of curves show the development of the DSC pattern immediately after heat treatment and after subsequent contact with air at room temperature (usually, 1, 3, 23 and 72 h).

As shown, in each case separate peaks are observed in this temperature range in contrast with the TG and DTA studies, where only one broad peak is found resulting from the samples of Keggin structure continuously reabsorbs water molecules. In the case of the molybdenum-containing acids the original DSC patterns are almost completely restored during three days. This shows that the removal and the absorption of water is completely reversible. In contrast, the tungsten-containing acids show different behaviour; moreover, the behaviour of PW_{12} and

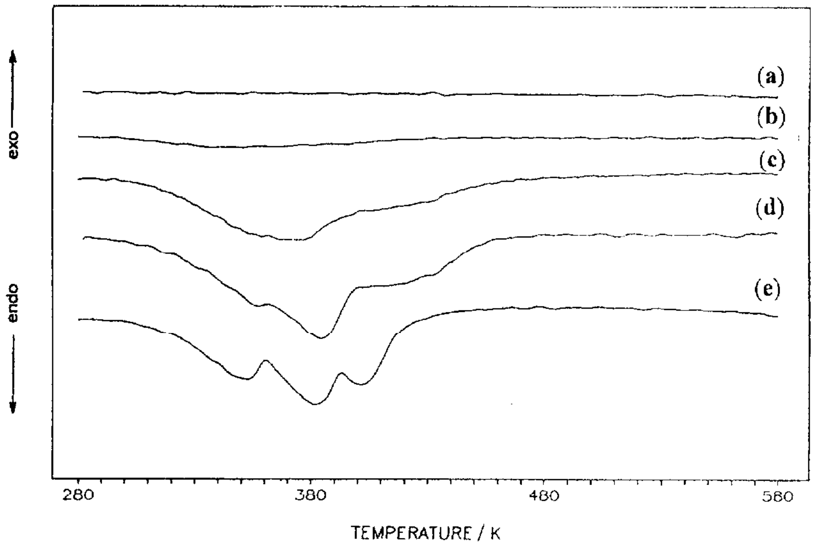

Fig. 3 DSC patterns of $H_4[SiMo_{12}O_{40}]$ after several pretreatments; (a) heat treatment at 573 K; the heat treated sample after contact with air at room temperature (b) for 1 h, (c) for 23 h, (d) 72 h, (e) as received

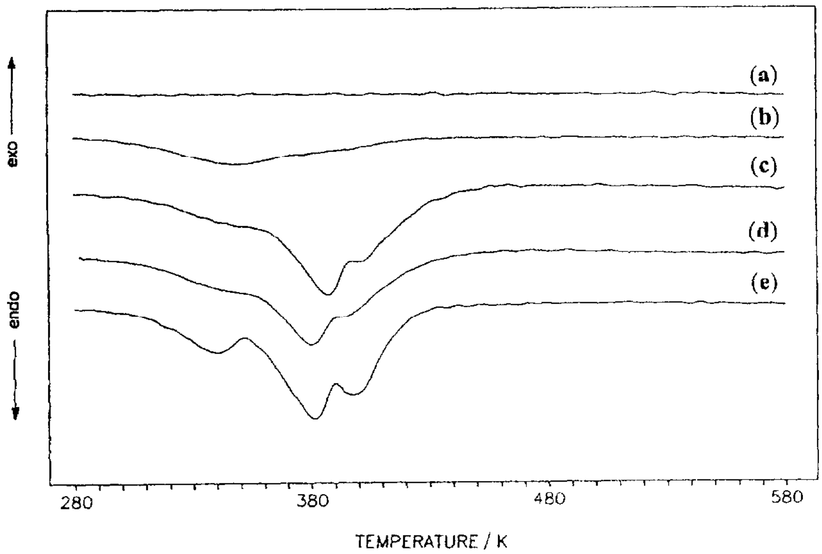

Fig. 4 DSC patterns of $H_3[PMo_{12}O_{40}]$ after several pretreatments; (a) heat treatment at 573 K; the heat treated sample after contact with air at room temperature (b) for 1 h, (c) for 23 h, (d) for 72 h, (e) as received

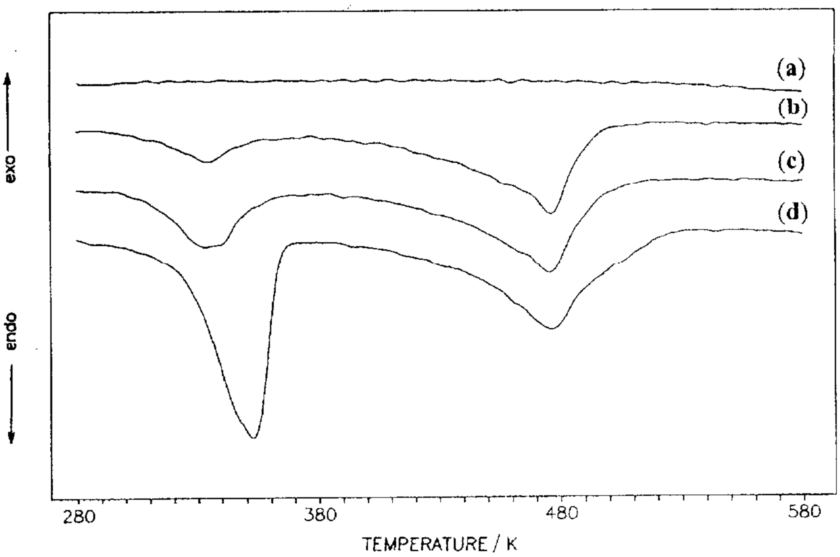

Fig. 5 DSC patterns of $H_4[SiW_{12}O_{40}]$ after several pretreatments; (a) heat treatment at 573 K; the heat treated sample after contact with air at room temperature (b) for 1 h, (c) for 23 h or 72 h, (d) as received

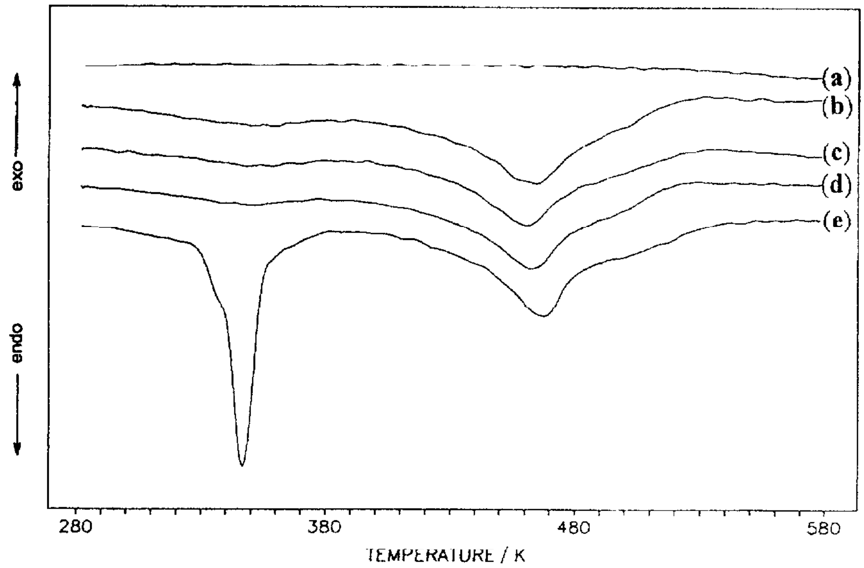

Fig. 6 DSC patterns of $H_3[PW_{12}O_{40}]$ after several pretreatments; (a) heat treatment at 573 K; the heat treated sample after contact with air at room temperature (b) for 1 h, (c) for 23 h, (d) for 72 h, (e) as received

SiW_{12} differs significantly. The original samples gave two peaks at around 350 and 470 K with the ratio of integrals found to be about 1/1. After the heat treatment the peaks reappeared in the case of SiW_{12}, however, the relative ratio of the peaks was found to be much lower (about 1/2). An even more characteristic change was observed with PW_{12}: after three days only the 470 K peak could be detected.

The partial reversibility of the observed reactions unequivocally indicates that it concerns the water content of the crystalline heteropoly acids. The DSC curves of the original acids allow the identification of different types of bonded water molecules. In the light of the literature data at least two different forms can be identified. The peak evolving close to 473 K can be assigned to water coordinated to the metal ions, while water released at lower temperature is thought to consist of adsorbed, so-called zeolitic water [21,22]. However, if one considers the relatively low surface area of the neat crystalline HPAs, the large amount of water released at low temperature (usually under 373 K) cannot be explained by a simple water desorption. Rather, as it is suggested by Misono [23, 24], a part of the water content provides a possibility to build a three-dimensional network in the HPA crystal through dioxonium ion ($H_5O_2^+$) bridges. This network maintains the secondary structure of the HPAs. As a rule, the primary structures are rather stable and rigid, while the secondary structure is flexible to a large extent. These water molecules can easily be substituted by polar compounds, thus they have a crucial role in the formation of the so-called *pseudoliquid phase*. We suggest, therefore, that these weakly bound water molecules are released at relatively low temperatures. Due to the flexible nature of the secondary structure several types may exist as it is observed in the case of the molybdenum containing acids: two peaks were found for $SiMo_{12}$, while three peaks were observed for PMo_{12} near 373 K. In contrast, water, evolving around 473 K is observed as a single peak in the case of SiW_{12} and PW_{12} and can be assigned to water directly coordinated to the metal ions in agreement with the literature [4, 18, 19].

The experimental evidences described above support this explanation. Like all figures clearly illustrate, DSC is found to be a sensitive method for characterization of the water content in the heteropoly acids. The DSC method provides the first thermoanalytical experimental evidence for the existence of different types of water in the secondary structure of heteropoly acids. It is also unambiguously pointed out that the acids deprived from their water content can completely rebuild the original structure in the case of molybdenum-containing acids, while only a partial reconstruction is possible in the case of tungsten-containing acids. The molybdenum-containing acids first introduce the absorbed water into their primary structure and then the flexible network is built forming the secondary structure. Surprisingly, the tungsten-containing acids, although absorb water and refill the primary positions, are not able to reform the *pseudoliquid region,* i.e., their secondary structure.

Conclusions

A systematic DSC study was carried out with four heteropoly acids of the Keggin type. The characteristic temperatures for the actual transformations (dehydration and thermal decomposition) were determined. DSC was found to be a convenient and sensitive method in the characterization of the water content of the heteropoly acids. The water loss was shown to be completely reversible with molybdenum-containing acids while the tungsten-containing heteropoly acids were able only partially to reform their secondary structure.

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