

## THERMAL BEHAVIOUR OF HYDRATED DODECATUNGSTOSILICIC ACID

A. Bielański<sup>1</sup>, J. Poźniczek<sup>1</sup> and M. Hasik<sup>2</sup>

<sup>1</sup>Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek, 30-239 Kraków, Poland

<sup>2</sup>Department of Materials Science and Ceramics, Academy of Mining and Metallurgy, Mickiewicza 30, 30-059 Kraków, Poland

(Received October 29, 1994)

### Abstract

The thermal behaviour of  $H_4SiW_{12}O_{40} \cdot 24.8H_2O$  ( $SiW_{12}$ ) was investigated by using DTA, TG and FTIR. Endothermic effects were observed at 40, 98 and 217°C, corresponding to the fusion of  $SiW_{12}$  in its own crystallization water, boiling of the solution and decomposition of the remaining tetrahydrate into anhydrous  $SiW_{12}$ , respectively. The mass of the sample remained constant on heating from about 250 to 400°C. Subsequently, it slowly decreased and reached a constant value at about 500°C. At 526°C a DTA peak appeared. There was an abrupt change in the FTIR spectrum of the sample heated to 550°C. The typical spectrum of the Keggin unit vanished and new bands at 807.5 and 1030  $cm^{-1}$  indicated the presence of free  $WO_3$  and  $SiO_2$ , respectively.

**Keywords:** dodecatungstosilicic acid, DTA-TG, FTIR

### Introduction

Heteropolyacids (HPAs) of the type  $H_{8-n}X^{n+}M_{12}O_{40}$ , exhibiting the typical structure of anions called Keggin units (K.U.), are interesting catalysts for acid-base type reactions and also in some cases for redox reactions. However, for any applications in gas-phase catalytic reactions, the thermal stability plays an essential role. To characterize the thermal behaviour of HPAs, in most cases differential thermal analysis (DTA) has been used [1-3]. More complete information is obtained if DTA is coupled with simultaneous thermogravimetry. It has been shown in the case of the  $H_{3+x}PM_{12-x}V_xO_{40}$  series ( $x=0, 1, 2, 3$ ) [4] that for the highly hydrated crystalline samples a DTA endotherm appears above 40°C. This corresponds to complete fusion of the sample (dissolution of the HPA in its own water of crystallization). The solution boiled at 110 to 130°C, depending on the composition of the sample. Total loss of crystallization water occurred below 170-200°C. The anhydrous acids  $H_{3+x}PM_{12-x}V_xO_{40}$  decomposed (dehy-

droxylated) at temperatures decreasing from 433°C for  $x=0$  to about 293°C for  $x=3$ . At still higher temperature, a weak but well reproducible exotherm appeared, which was not accompanied by any mass change. An analogous peak was reported by West [1] in the cases of dodecaphospho- and dodecasilicomolybdates and also dodecaphospho- and dodecasilicotungstic acids. As no parallel thermogravimetric measurements were carried out in that investigation, the authors could not differentiate between the process of dehydroxylation and the transformation at constant mass occurring at somewhat higher temperatures, which most probably led to decomposition of the dehydroxylated product into the trioxide of molybdenum or tungsten and oxides of phosphorus or silicon. Generally, the exothermic effect observed in [1] and also in our preliminary experiments is much more pronounced in the cases of dodecatungstophosphoric acid and dodecasilicotungstic acids than for the analogous molybdenum-containing HPAs. The aim of the present investigation was to study in more detail the thermal behaviour of  $H_4SiW_{12}O_{40}\cdot aq$  through the simultaneous use of DTA and TG analysis, and also to characterize the dehydration products by means of IR absorption measurements. It should be observed that dodecatungstic HPAs are thermally more stable than the analogous molybdic HPAs. They are also more resistant against reduction.

## Experimental

Before the experiments, dodecatungstosilicic acid  $H_4SiW_{12}O_{40}$  was kept over a saturated solution of sodium chloride. DTA and TG analyses were carried out with a Mettler TA-2 thermoanalyser and IR spectra were recorded with a Bruker IFS 48 spectrometer.

## Results and discussion

Figure 1 shows the results of thermal analysis of a sample of  $H_4SiW_{12}O_{40}$  previously kept for several days over a saturated solution of NaCl at room temperature. The DTA curve exhibits endothermic effects at 40, 98 and 217°C, and an exothermic one at 526°C. Two higher endotherms and the exotherm were also observed by earlier authors [1, 2, 5]. However, the lowest endotherm was not observed in [1, 2, 5] because the samples were partially dehydrated at room temperature (vacuum treatment, storage over conc.  $H_2SO_4$ ).

The lowest endotherm corresponds to the fusion of the sample (dissolution of  $H_4SiW_{12}O_{40}$  in its own water of crystallization) which was also observed visually. It is not connected with any appreciable loss in mass in the TG curve.

The second endothermic effect corresponds to the boiling of the saturated solution. The process is finished somewhat above 100°C by the simultaneous loss of 20.6  $H_2O$  molecules per K.U. The remainder represents an intermediate

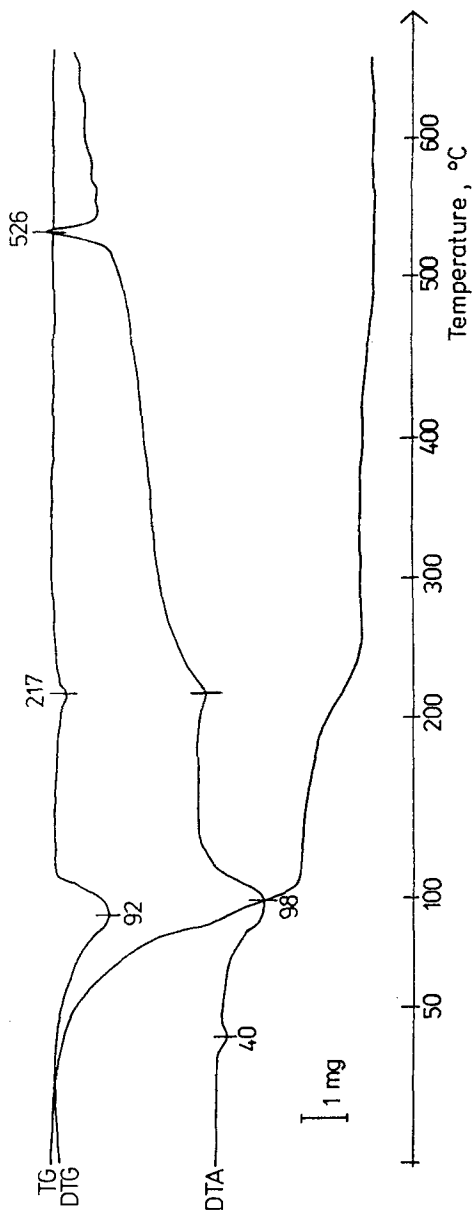


Fig. 1 Thermal curves of sample  $H_4SiW_{12}O_{40}$  previously kept over saturated solution of sodium chloride. Heating rate: 5 deg/min

hydrate, which decomposes on further heating above 115°C. This rapid stage of decomposition is accompanied by the third endotherm, at 217°C. As indicated by the TG curve, the mass of the sample remains constant on heating from about 250 to 400°C. It again slowly decreases above 400°C, and at about 500°C it reaches a final constant value assumed to correspond to the fully dehydroxylated HPA.

At still higher temperature, 526°C, a distinct exotherm appears, which is much more pronounced than that observed in the case of dodecamolybdophosphoric acid [4]. In the last period, above 400°C, the loss of 1.2 molecules of water per K.U. was observed, which indicated that partial dehydroxylation corresponding to 0.8 H<sub>2</sub>O/K.U. must have occurred at temperatures lower than 400°C. It should be stated that the loss in mass of the sample between 100 and 400°C corresponded to the departure of 5.2 H<sub>2</sub>O/K.U. If we subtract from this value 0.8 H<sub>2</sub>O/K.U., assumed to correspond to dehydroxylation, we obtain 4.4 H<sub>2</sub>O/K.U. as the composition of the intermediate hydrate H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>. The average value obtained from 3 independent runs was 4.2±0.5 H<sub>2</sub>O/K.U. The composition of the initial sample corresponded to the formula H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>·24.8H<sub>2</sub>O.

The primary products of dehydroxylation obtained at about 500°C is unstable and at a somewhat higher temperature is transformed into a more stable substance or substances; this is indicated by the DTA exotherm at 526°C. The first deflection from the DTA baseline was always observed when dehydroxylation was already in progress, and it was complete when the temperature of the peak was reached. This indicates a rather abrupt transformation of the primary dehydroxylation product.

In order to get more information concerning the nature of this transformation, the IR spectra of samples heated up to 440, 455, 480 and 550°C in the thermoanalyser were recorded. Similarly to the untreated sample, the samples heated at 440 and 455°C, were in the form of a white powder completely soluble in water. This may be taken as an indication that the strongly dehydroxylated samples can be reversibly rehydrated. The sample heated up to 480°C was light-yellow in colour and was not completely soluble in water. The sample heated up to 550°C was yellow and was apparently not soluble in water, which is an indication that the HPA was transformed into insoluble products.

The roughly estimated degree of dehydroxylation of the samples heated up to 450 and 480°C was not less than 20% and 23%, respectively. The dehydroxylation of the sample heated up to 550°C, which reached constant mass, was assumed to be complete.

Figure 2 shows that the IR spectrum (KBr technique) of the sample heated to 450°C exhibited all the characteristic bands of the K.U. observed for the non-heated sample. They agree well with the spectra listed in [6], where an interpre-

tation of the bands is also given. The spectrum of the sample heated to 480°C was not changed in the region below 1030 cm<sup>-1</sup>. However, a diffuse band ap-

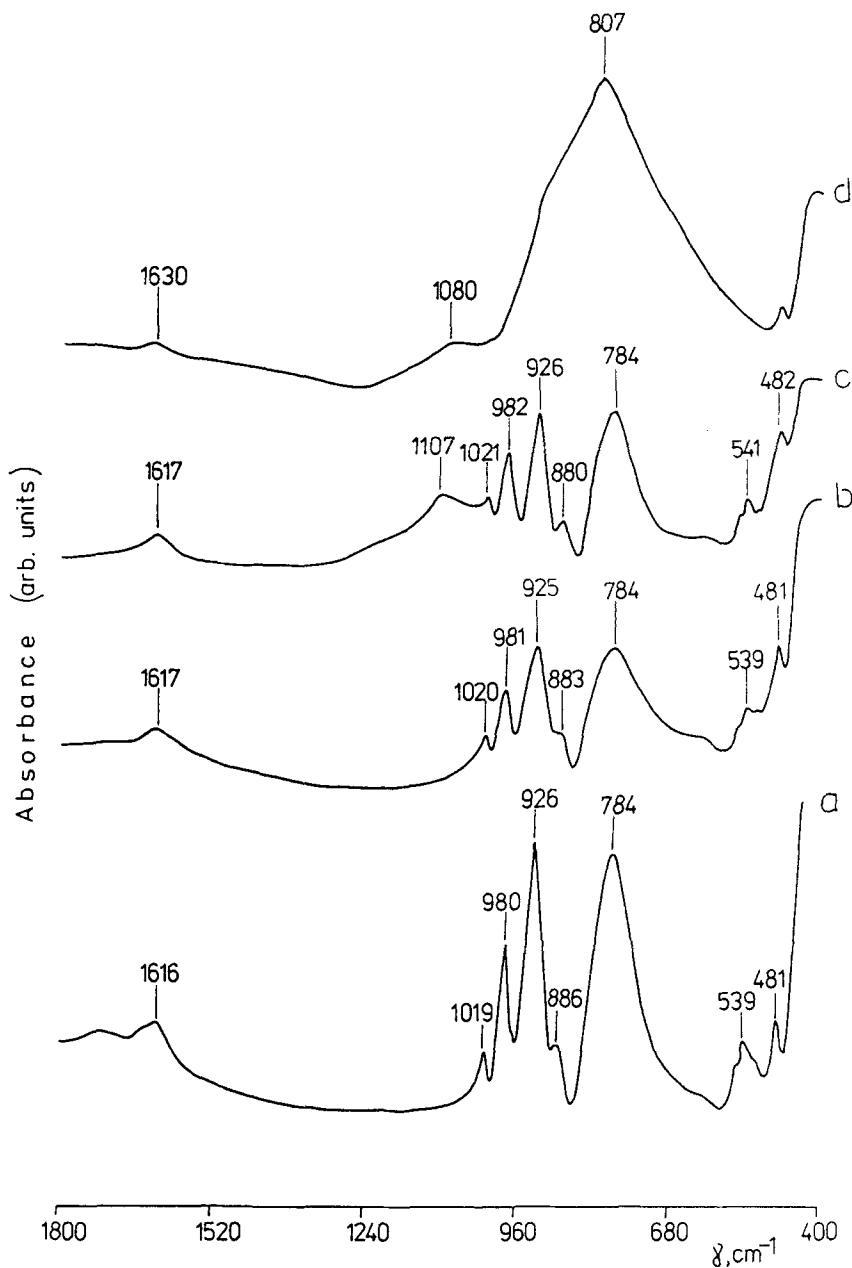
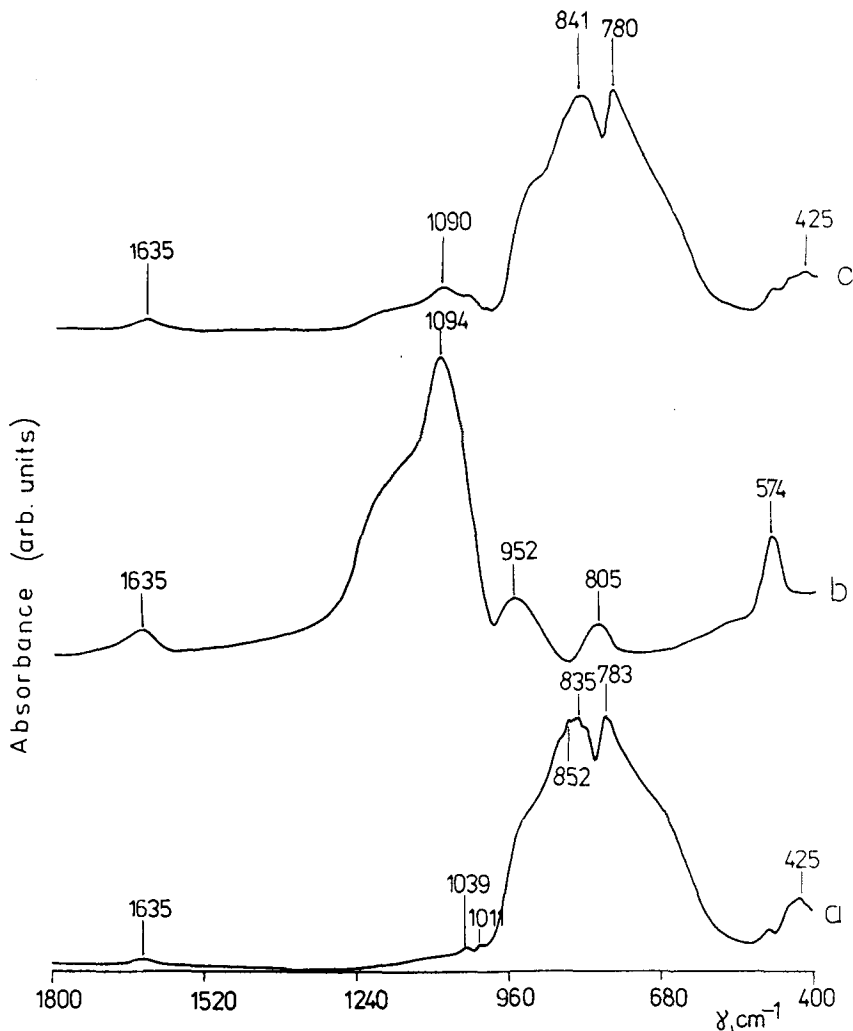


Fig. 2 IR spectra of  $H_4SiW_{12}O_{40}$  samples: a) not heated; b) heated up to 450°C; c) heated up to 480°C; d) heated up to 550°C

peared at  $1107\text{ cm}^{-1}$ . The spectrum of the sample heated to  $550^\circ\text{C}$  was entirely different and indicated that the K.U. had vanished completely. It contained a strong and asymmetric band at  $807.5\text{ cm}^{-1}$  and a weak, very diffuse one at  $1080\text{ cm}^{-1}$ . Comparison with Fig. 3 allows assignment of the former to free  $\text{WO}_3$  and of the latter (similarly as the  $1030\text{ cm}^{-1}$  band in the  $480^\circ\text{C}$  sample) to the lattice vibration of  $\text{SiO}_2$ . Thus, the IR spectra confirm the decomposition of  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  into its component oxides and permit interpretation of the exotherm at  $526^\circ\text{C}$  in the DTA curve as being due to the spontaneous transformation of a



**Fig. 3** IR spectra of samples: a)  $\text{WO}_3$  (BDH Laboratory Reagent untreated); b)  $\text{SiO}_2$  (Mallinckrodt. silicic acid  $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ ) heated at  $550^\circ\text{C}$  for 2 h; c) mechanical mixture of  $\text{SiO}_2$  and  $\text{WO}_3$  (molar ratio 1:12)

highly disordered primary dehydroxylation product into a mixture of  $\text{WO}_3$  and  $\text{SiO}_2$ .

## References

- 1 S. F. West and L. F. Audrieth, *J. Phys. Chem.*, 59 (1955) 1069.
- 2 B. K. Hodnett and J. B. Moffat, *J. Catal.*, 88 (1984) 255.
- 3 G. A. Tsigdinos, *Topics Current Chem.*, 76 (1978) 1.
- 4 A. Bielański, A. Małecka and J. Poźniczek, *J. Thermal Anal.*, 35 (1989) 1699.
- 5 E. Ya. Rode, *Zh. Neorg. Khim. (USSR)*, 3 (1958) 2707.
- 6 C. Rocchiccioli-Deltcheff, R. Thouvenot and R. Franck, *Spectrochim. Acta*, A32 (1976) 587.

**Zusammenfassung** Mittels DTA, TG und FTIR wurde das thermische Verhalten von  $\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot 24\cdot 8\text{H}_2\text{O}$  ( $\text{SiW}_{12}$ ) untersucht. Bei 40, 98 und 217°C wurden endotherme Effekte beobachtet, die dem Schmelzen von  $\text{SiW}_{12}$  im eigenen Kristallwasser, dem Sieden der Lösung und der Zersetzung des verbleibenden Tetrahydrates in wasserfreies  $\text{SiW}_{12}$  entsprechen. Die Masse der zurückbleibenden Probe bleibt während des Erhitzens von 250 bis 400°C konstant. Anschließend nimmt sie leicht ab und erreicht bei 500°C einen konstanten Wert. Bei 526°C tritt ein endothermer Peak auf. Beim Erhitzen der Probe auf 550°C tritt eine plötzliche Änderung im FTIR-Spektrum auf. Das typische Spektrum der Keggin-Einheit verschwindet und neue Banden bei 807.5 und 1030  $\text{cm}^{-1}$  weisen auf die Anwesenheit von freiem  $\text{WO}_3$  und  $\text{SiO}_2$  hin.