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ACID SITES STRENGTH DISTRIBUTION IN HETEROPOLY ACIDS BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

Acid sites strength distributions (ASSD) in the heteropoly acids (HPAs) silicotungstic acid (STA), phosphotungstic acid (PTA) and phosphomolybdic acid (PMA) are investigated using differential scanning calorimetery (DSC). The strengths of the acid sites in these HPAs are grouped into weak, intermediate and strong, according to the temperature region in which presorbed triethylamine (TEA) desorbs. Such desorption appears in a DSC thermogram for a single group of acid sites with a definite strength as one or more exothermal effects. The ΔH value corresponding to these effects is taken to evaluate the relative quantities of acid sites. The percentage of strong acid sites in the HPAs studied is found to increase as the total number of acid sites increases, whereas the percentage of intermediate-strength acid sites is found to decrease.

INTRODUCTION

Considerable interest has been evoked recently by the unusual catalytic properties of heteropoly compounds for a variety of reactions [1–4]. While much of the work has been concerned with using heteropoly compounds as heterogeneous catalysts, there is also considerable interest in their use as homogeneous catalysts [5–7]. The heteropoly compounds of interest in most catalytic work are those which contain an anion possessing a cage-like structure (Keggin unit) with a central atom, e.g. P, Si, in a tetrahedron of oxygen atoms [8]. Twelve edge-sharing octahedra of oxygen atoms and a metal atom, e.g. Mo, W, surround and share oxygen atoms with this central tetrahedron.

PMA [9] and STA [10] are active catalysts used in the alkylation of benzene with olefins for detergent production. PWA and SWA are effective catalysts in methanol conversion, whereas PMA is less selective [11]. The reaction of epichlorohydrin with allyl alcohol is catalysed by PWA, PMA and SWA; the degree of conversion decreases in that order [6]. Isopropanol

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dehydration is catalysed by those HPAs in the order: PWA > STA > PMA, while in methacrolein oxidation PMA and SMA (silicomolybdic acid) were more active and selective than PWA and SWA [2].

The ASSD is a catalytic property of prime importance for solid acidic catalysts. However, this property has not been determined for HPAs. Hence, this work is primarily carried out to evaluate the ASSD in the HPAs PWA, PMA and STA using our DSC method in which TEA is absorbed on the solid acid followed by its desorption in the temperature-programmed furnace of a DSC unit [12]. The modification involving the nullification of the DSC effects of the solid acid itself has been used [13].

EXPERIMENTAL

Presorption of TEA on the HPAs

PWA, PMA and STA (BDH) were dried at 80 °C for 1 h before mixing thoroughly with dried TEA. Excess TEA was then driven out through heating at 80 °C for 30 min.

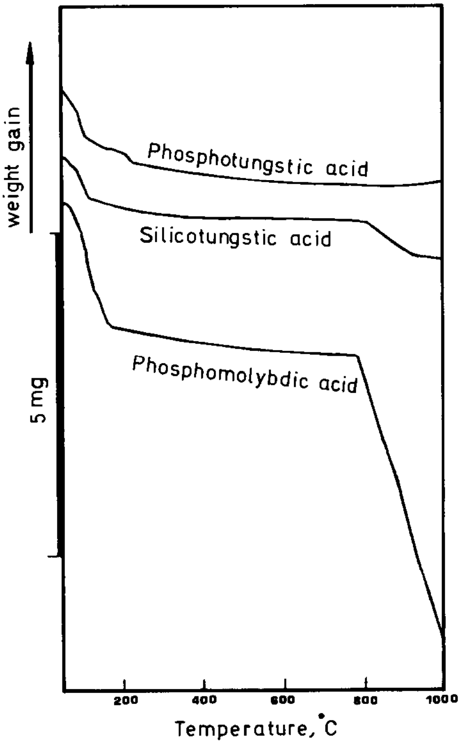

Fig. 1. TG thermograms for PTA, STA and PMA.

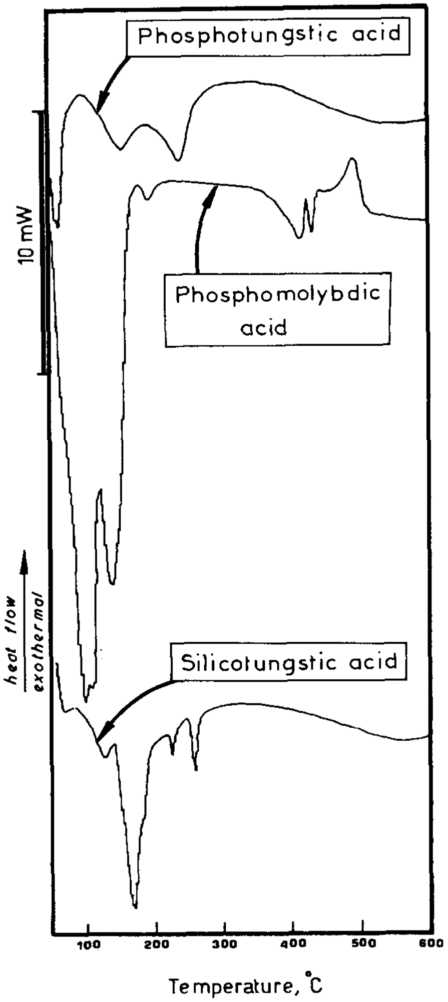

Fig. 2. DSC thermograms for PTA, PMA and STA.

TG Measurements

The dried HPAs were measured by a Mettler thermobalance system 3000 under the following conditions: initial temperature, 50 ° C; rate 20 K min^{-1}; final temperature, 1000 ° C; plot, 11 cm; full-scale range, 10 mg (Fig. 1); mass, different.

DSC Measurements

The TEA-free HPAs were measured using the conventional DSC procedure (reference cell always empty) (Fig. 2). The TEA-presorbing HPAs were analysed using the nullifying method, adopted by the present authors [13] in which the reference cell contains an equal weight of the same HPA (TEA-free). All DSC measurements were carried out at atmospheric pressure and no purge gas was used. A Mettler DSC-30 unit (system TA 3000) was used under the following conditions: initial temperature, 50 °C; rate, 20 K min^{-1}; final temperature, 600 °C; plot, 10 cm; full-scale range, 25 mW; mass, 10.0–10.5 mg.

RESULTS AND DISCUSSION

TG and DSC for the HPAs

Figure 1 shows the thermogravimetric behaviour of the HPAs under study throughout the temperature region 50–1000 °C. From 50 ° to approximately 300 ° C, the weight loss appearing in TG thermograms is due to the dehydration of these HPAs. The weight loss in this dehydration region was found to be 12.69, 12.97 and 21.56% for PTA, STA and PMA, respectively. Using these values the number of water molecules per each HPA formula were calculated and found to correspond to 23.20, 22.95 and 46.97 for PTA, STA and PMA, respectively. However, the formula water molecules are 24 and 48

TABLE 1

TG and DSC data obtained from Figs. 1 and 2

HPA	DSC effect range (°C)	Peak max. (°C)	ΔH ($J\,g^{-1}$)	Water molecules (calcd.)	Formula water (%)	TG water (%)	TG water molecules (calcd.)
PTA ($12WO_3 \cdot H_3PO_4 \cdot xH_2O$)							
	50–105	84	19	5			
	105–200	179	31	8			
	200–288	259	42	11			
	50–288		Total 92	24	–	12.69	23.25
PMA ($20MoO_3 \cdot 2H_3PO_4 \cdot 48H_2O$)							
	50–130	100	225	28			
	130–181	148	152	19			
	181–205	195	7.8	1			
	50–205		Total 385	48	21.93	21.56	46.97
STA [$(SiO_2 \cdot 2H_2O)12WO_3 \cdot 22H_2O$]							
	50–140	125	16	5			
	140–210	170	51	16			
	210–240	220	3.2	1			
	240–270	250	6	2			
	50–270		Total 76.3	24	13.19	12.97	22.95

for STA and PTA, respectively. Hence, a calculated value of 23.25 for PTA may also be equal to 24 molecules. Figure 1 also shows that PTA does not suffer any weight change between 288 and 1000 ° C, whereas STA and PMA start a high temperature weight loss at 810 and 780 ° C, respectively. This is due to structural decomposition. Such high thermal stability of the HPAs under study is a characteristic of prime importance for catalysts used in reactions carried out at relatively high temperatures.

The DSC thermograms obtained for the HPAs under study (Fig. 2) indicate that their dehydration takes place in a stepwise fashion since several endothermic DSC effects appear in the dehydration regions. The TG thermograms (Fig. 1) do not exhibit enough sensitivity to reveal such dehydration steps. Figure 2 also shows that PTA ends its dehydration at a higher temperature than PMA and STA (Table 1). Such higher dehydration thermal stability of PTA may be due to the fact that the cation in this HPA is $H_5O_2^+$ which is hydrogen-bonded to the outer oxygen atoms of the neighbouring anions [14]. However, in the DSC thermogram of PMA two small endothermic effects followed by a small exothermic effect in the 350–500 ° C region appear. These effects which are not associated with any TG weight loss (see Fig. 1) may be due to some solid-state interactions probably owing to structural complexity (see formula, Table 1).

The sum of ΔH values obtained for all DSC effects in the dehydration region for each HPA (Fig. 2) may be taken to correspond to the total number of water molecules in a HPA. These values are 76, 92 and 385 J g^{-1} (Table 1) for STA, PTA and PMA, respectively (ratio = 1.00 : 1.21 : 5.06). The ΔH values corresponding to individual DSC peaks in the dehydration region can be taken as a measure for the number of water molecules removed in one step (Table 1).

Correlation of the TG and DSC data (Table 1) may reveal some inconsistencies, e.g. the TG weight loss ratio cannot exhibit a linear relationship with the corresponding ΔH values. This may indicate that HPAs have individual characteristics that affect their heat capacities and thermal conductivities [15]. This situation seems different from another group of solid acids, i.e. zeolites, where our previous study [16] on the TG–DSC relationship for zeolitic water proved its linearity.

ASSD in HPAs via DSC

HPAs are largely used at the present time for catalysing a multitude of chemical reactions. Some of these reactions require mild acidity in the catalysts employed, whereas others require strong acid sites. Hence, knowledge of the ASSD in HPAs should be an important aid in making the proper choice of a HPA catalyst for a given reaction.

In the present work, our recently published method for measuring ASSD in solid catalytic materials such as alumina and silica–alumina [12] and

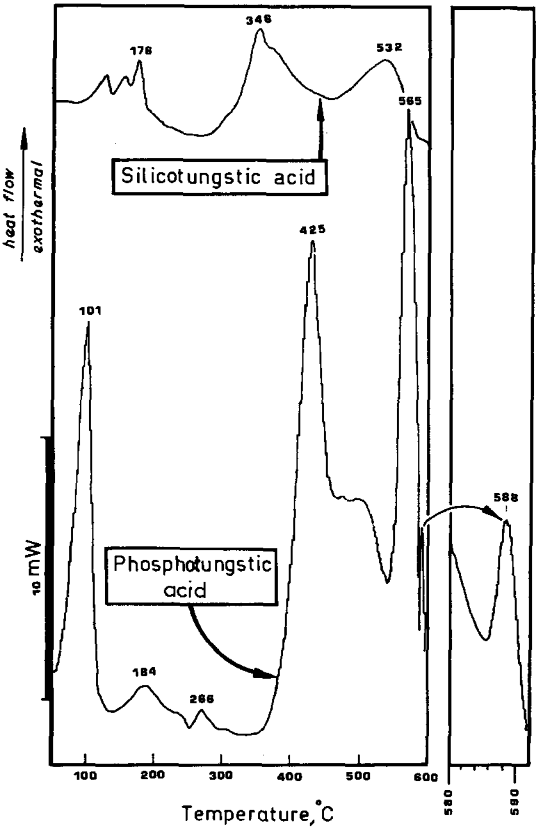

Fig. 3. DSC thermograms for TEA-desorption from STA and PTA.

zeolites [13] is used. Since the DSC effects obtained for the HPAs under study (Fig. 2) appear to overlap the DSC effects obtained for TEA desorbed from those HPAs (Figs. 3 and 4), the nullifying method used in case of ASSD measurement in zeolites [13] is employed herein.

In this study, ASSD may be classified according to our previous observations while determining ASSD in the most strongly acidic zeolites "mordenites" [17] into weak acid sites (50 to ~250 °C), intermediate strength acid sites (~250 to ~450 °C) and strong acid sites (~450 to ~600 °C).

All of the DSC effects appearing in Fig. 2 for the HPAs under study are completely nullified through use of a reference cell containing TEA-free HPA having the same weight of the corresponding TEA-presorbing HPA in the sample cell (Figs. 3 and 4). In these figures, the thermograms obtained give only exothermic peaks that indicate chemisorption of the TEA molecules on the acid sites and that physisorbed molecules are completely absent. Since the thermograms in Figs. 3 and 4 were all obtained using equal sample weights (±0.5%) and equal heat flows, the total number of acid sites in a HPA is relative to the sum of DSC effects in the thermogram obtained for

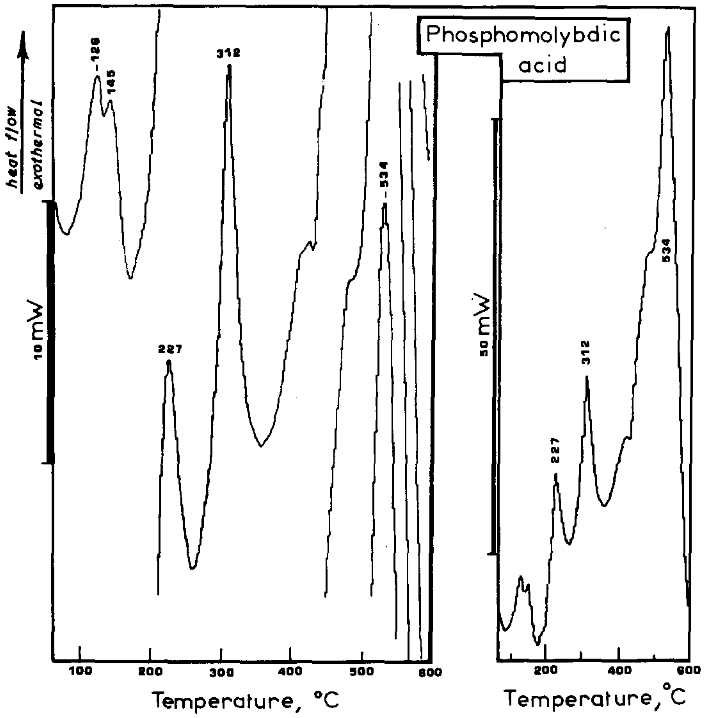

Fig. 4. DSC thermogram for TEA-desorption from PMA (intensity comparable with that in Fig. 3).

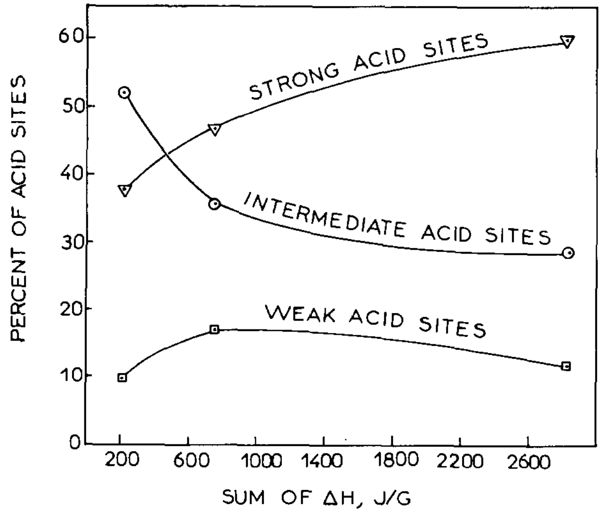

Fig. 5. Change of ASSD with total acidity in the HPAs.

TABLE 2

ΔH for acid sites groups in the heteropoly acids STA, PTA and PMA

Temperature range (°C)	ΔH (J g^{-1})	Ratio	%	Strength
STA				
100–200	21		10.0	Weak
270–450	109		52.2	Intermediate
450–580	79		37.8	Strong
Total	209	1.0		
PTA				
50–140	112		17.4	Weak
140–255	19			
255–280	3		35.8	Intermediate
350–460	266			
460–537	162		46.8	Strong
537–585	190			
Total	752	3.60		
PMA				
80–175	87		11.7	Weak
175–260	243			
260–358	416		28.5	Intermediate
358–430	380			
430–600	1694		59.8	Strong
Total	2830	13.54		

TEA desorption from this HPA. So, the total ΔH values obtained for TEA desorption from the acid sites in STA, PTA and PMA are, respectively, 209, 752 and 2830 J g^{-1}, i.e. in the ratio 1.0 : 3.6 : 13.5. Nevertheless, the presence of other DSC effects beyond 600 °C (the available maximum) cannot be ruled out.

As mentioned above, the whole temperature range in a thermogram is divided into three groups indicating the DSC effects of acid sites with different strengths. Each group may exhibit a number of peaks, each of which signifies a subgroup of acid sites (Table 2). For PTA and PMA, such subgrouping occurs in two of the peaks (Figs. 3 and 4, respectively; Table 2), whereas for STA such subgrouping appears only in the weak sites group (50–250 °C, Fig. 3) while in the two stronger regions single broad effects appear.

In zeolites, the high temperature DSC effects (strong acid sites) are always much less in quantity than the intermediate-strength DSC effects [17,18] (Lewis acid sites). However, in HPAs it would appear that based on ΔH values, the percentage of strong acid sites increases as the number of total acid sites in a HPA increases, whereas the percentage of intermediate-strength acid sites decreases (Fig. 5 and Table 2).

Since some specific catalytic reactions require milder acid sites whereas others require stronger ones, this study may help in the choice of a proper HPA catalyst, taking into consideration the amount of HPA per chargestock employed.

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