A calorimetric study of the acidity of bulk and silica-supported heteropoly acid $H_3PW_{12}O_{40}$

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Abstract

The acid strength of bulk and SiO_2-supported (10–60 wt%) $H_3PW_{12}O_{40}$ (PW) is characterised by differential scanning calorimetry of ammonia adsorption in a gas–solid system and by microcalorimetry of pyridine adsorption in a liquid–solid system (cyclohexane slurry). In both systems, the strength of PW in terms of the heat of adsorption of NH_3 or pyridine increases with increasing PW loading on silica, the bulk PW being the strongest acid. The temperature and the heat of NH_3 desorption are shown to indicate the acid strength, in full agreement with the heats of NH_3 adsorption. Attempts to measure the acidity of PW included in a sol–gel silica matrix have failed due to a large amount of water present in such systems.
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1. Introduction

Heteropoly acids (HPA), in particular those of the Keggin structure $H_{8-x}[X^{x+}M_{12}O_{40}]$ (X = P^{5+} or Si^{4+}, M = W^{6+} or Mo^{6+}), are strong Brønsted acids and extensively used as acid catalysts [1–4]. Their acidity has been the subject of many studies in the last three decades, and the strongest, 12-tungstophosphoric acid $H_3[PW_{12}O_{40}]$ (PW), has been the most studied (for a review, see [1–4] and references therein). The acid properties of bulk solid PW are well documented, including the nature of the acidity, the strength, the number, and the distribution of acid sites. These data have been mainly obtained from ammonia or pyridine adsorption microcalorimetry and temperature-programmed desorption (TPD) as well as from IR of adsorbed base probes. The most accurate and meaningful results have been obtained from the adsorption microcalorimetry that provides the heats of adsorption of base probe molecules as a function of coverage [5–11]. Silica-supported PW—the most important HPA-based solid acid catalyst—has also been frequently studied ([1–3] and references therein), though less systematically, especially regarding the effect of HPA loading on the acid strength. The limited data available [5,10] show that the acid strength decreases when HPA is supported on silica. PW included in a sol–gel silica matrix has attracted interest as a nonleaching solid acid catalyst suitable for reactions in polar media [12–15]. No data on the acidity of sol–gel HPA catalysts have been reported, however. The aim of this work is to characterise the acidity of bulk PW, silica-supported PW/SiO_2, and sol–gel $PW-SiO_2$ catalysts in gas–solid and liquid–solid systems using calorimetric techniques: differential scanning calorimetry (DSC) of NH_3 adsorption/desorption in gas–solid system and microcalorimetry of pyridine adsorption in liquid–solid system. The latter technique known as the Cal-ad method has been applied to characterise the acidity of bulk PW [8].

2. Experimental

2.1. Chemicals and catalysts

$H_3[PW_{12}O_{40}]$ hydrate from Aldrich and Aerosil 300 silica from Degussa were used. Pyridine (99.8%) and cyclohexane (99.5%), both anhydrous, were obtained from Aldrich and used as received. Other reagents and solvents were of analytical purity.

Silica-supported catalysts, 10–60% PW/SiO_2, were prepared by impregnating Aerosil 300 silica (S_{BET}, 300 $m^2\,g^{-1}$)

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with an aqueous solution of PW [16]. The mixture was stirred overnight at room temperature, followed by drying using a rotary evaporator. The catalysts were calcined at $150\,°C/0.5$ Torr for 1.5 h, unless stated otherwise, and stored in a desiccator over P_2O_5. Pure silica, SiO_2, was prepared by stirring Aerosil 300 with water at room temperature overnight, followed by drying using a rotary evaporator, and calcined at $150\,°C/0.5$ Torr for 1.5 h. Sol–gel catalysts, PW-SiO_2, were prepared by hydrolysis of tetraethoxysilane in aqueous ethanol in the presence of PW using the Japanese [12] or Hungarian [13] procedure. The hydrolysis of $(EtO)_4Si$ was carried out at $40\,°C$ for 1 h then at $80\,°C$ for 3 h. The amount of PW charged corresponded to 10–20 wt% PW loading in anhydrous PW-SiO_2 catalysts, $H_2O/(EtO)_4Si = 5$ mol/mol, the $EtOH/(EtO)_4Si$ molar ratio was 0.7 (Japanese method) or 2.7 (Hungarian method). The resulting hydrogel was dehydrated at $45\,°C/24$ Torr, calcined at $150\,°C/0.5$ Torr/1.5 h, ground, extracted with hot water ($80\,°C$, 3 h), and finally, unless stated otherwise, heated at $150\,°C/0.5$ Torr/1.5 h and stored in a desiccator over P_2O_5. The W and P content in the catalysts was determined by ICP. This procedure allowed a maximum PW loading of 16–18 wt% to be obtained for the sol–gel catalysts; excess PW was washed out during aqueous extraction. It should be noted that when the hydrogel was extracted by 1 mol/L aqueous H_2O_2, practically all PW was washed out. The sol–gel SiO_2 was prepared by hydrolysis of ethanol solution of tetraethoxysilane ($H_2O/EtOH/(EtO)_4Si = 5/2.7/1$ (mol)) in the presence of H_2SO_4 as a catalyst. The mixture was stirred at $40\,°C$ for 1 h and then at $80\,°C$ for 3 h. The resulting hydrogel was dehydrated at $45\,°C/24$ Torr, calcined at $150\,°C/0.5$ Torr/1.5 h, ground, extracted with hot water ($80\,°C$, 3 h), washed with water until pH 7 and, finally, heated at $150\,°C/0.5$ Torr/1.5 h. No remaining H_2SO_4 was found in the sol–gel SiO_2 by ICP of sulfur. The salt $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW) was prepared by precipitation of PW with Cs_2CO_3 from aqueous solution [12]. For microcalorimetric studies of pyridine adsorption, the catalysts were pretreated at $165\,°C/0.5$ Torr/4 h to allow comparison with the results reported by Drago and co-workers [8]. Catalyst characterisation is given in Table 1.

2.2. Techniques

Surface area and porosity of PW catalysts were measured by nitrogen physisorption on a Micromeritics ASAP 2000 instrument. Before the analysis, the samples were evacuated overnight at $250\,°C$. Thermogravimetric analyses (TGA) were performed using a Perkin Elmer TGA 7 instrument under nitrogen flow. Diffuse reflectance IR spectra were recorded on a Nicolet NEXUS FTIR instrument using powder mixtures of catalysts with KBr.

Ammonia adsorption onto PW catalysts was measured using Setaram TG-DSC 111 differential scanning calorimeter in a flow system. The sample weight was 30–80 mg. The gases (N_2 and NH_3, 99.99% purity) were passed through molecular sieve traps before entering the system. Prior to adsorption, the catalyst samples were pretreated in the DSC cell at a specified temperature (300 or $350\,°C$) under N_2 flow (35 ml/min) for 1 h until constant weight. Then ammonia was fed in the gas flow for 1 h (50:50 NH_3:N_2 molar ratio, 35 ml/min). The heat evolved upon NH_3 adsorption was measured, and the amount of NH_3 adsorbed was obtained from TG. This allowed the average molar heat of adsorption, $-\Delta H_a$, per mole of NH_3 adsorbed to be obtained. Generally, the reproducibility of ΔH_a was within ± 5 kJ/mol. After adsorption, the sample was purged with pure N_2 for 1 h at the same temperature. Then the desorption of NH_3 was performed by ramping the temperature up to $800\,°C$ at a rate of $10\,°C$/min. The temperature of NH_3 desorption, T_d, and the heat consumed thereupon were measured. These values corresponded to decomposition of the salt $(NH_4)_3PW_{12}O_{40}$, with the Keggin structure collapsing (see below). The heat of desorption (decomposition), ΔH_d, per mole of PW was calculated.

A Setaram C80 heat flux Calvet-type microcalorimeter was used to measure the differential heat of adsorption of pyridine on PW catalysts in anhydrous cyclohexane slurry. The microcalorimeter had two identical stainless-steel mixing vessels equipped with stirrers, one for the sample and the other as a reference, placed in a calorimetric block that controlled the temperature with an accuracy $\pm 0.01\,°C$. The mixing vessels comprised an upper chamber (2.9-ml volume) and a bottom chamber (2.5-ml volume) separated by a thin Teflon membrane. The experiments were carried out in isothermal mode at $50\,°C$. All operations, including weighing catalyst samples, loading the vessels, and pretreating catalysts and solvent, were carried out under a dry nitrogen atmosphere. In a typical experiment, a 0.2–1 g catalyst sample and 1 ml of anhydrous cyclohexane were placed in the bottom chamber. In the case of supported and sol–gel PW catalysts, the chamber was heated at $50\,°C$ for 30 min to remove excessive air adsorbed. There was no need to do so for nonporous bulk PW. The chamber was then sealed off with the Teflon membrane and connected to the upper vessel body. The upper chamber was filled with a solution of pyridine in cyclohexane (1 ml) and locked. The reference vessel was filled in the same manner, but without the catalyst. Both vessels were then placed into the calorimeter and allowed to equilibrate (usually 3–4 h). Once equilibrium was attained, the experiment was started by bringing the catalyst in contact with pyridine. This was done by breaking the membranes with stirrer shafts and activating the stirrers. The heat associated with the membrane breaking and mixing was negligible, less that 2% of the heat of pyridine adsorption. Typically, the calorimetric measurement was complete in 30–40 min. Immediately after that, while the temperature in the vessel was $50\,°C$, a 1-ml sample of cyclohexane solution was taken from the chamber to determine the amount of free pyridine in solution. This was done by UV–vis spectroscopy using a Varian Cary 50 spectrophotometer in a 1-cm quartz cuvette at a pyridine absorption band of 252 nm ($\varepsilon = 1818$ L/

Table 1
Catalyst characterisation

Catalyst[a]	S_{BET}[b] (m^2/g)	Pore size[c] (Å)	Pore volume[d] (cm^2/g)	H_2O content[e] (wt%)			W content[f] (wt%)
				(a)	(b)	(c)	
PW	8	74	0.02	4.3	1.0	2.6	
60% PW/SiO_2	86	146	0.32	4.0	1.1	2.6	45.7 (46.0)
40% PW/SiO_2	143	110	0.39	4.0	1.4	2.7	32.4 (30.6)
30% PW/SiO_2	154	147	0.56	3.6	1.1	2.4	23.7 (23.0)
20% PW/SiO_2	205	144	0.74	3.3	1.1	2.4	14.1 (15.3)
10% PW/SiO_2	266	97	0.65	2.7	1.2	2.4	7.1 (7.6)
SiO_2	285	145	1.03	2.6	1.2		–
Sol–gel SiO_2	109	16	0.04	4.6	6.5		–
Sol–gel 11% $PW-SiO_2$[g,h]	160	16	0.05	9.0	3.4	5.9	8.5
Sol–gel 15% $PW-SiO_2$[g,k]	393	18	0.18	8.8	3.2	6.1	11.5
CsPW	119	29	0.09	1.8	0.3		66.4 (67.2)

[a] Catalysts pretreated at 150 °C/0.5 Torr for 1.5 h; PW loadings from the preparation stoichiometry refer to anhydrous catalysts.
[b] Measured after evacuation at 250 °C.
[c] From BET isotherm.
[d] Single-point adsorption total pore volume at a relative pressure $p/p_0 = 0.97$–1.0.
[e] Weight loss from TGA: (a) from 30 to 300 °C and (b) from 300 to 650 °C after pretreatment at 150 °C/0.5 Torr for 1.5 h; (c) from 30 to 300 °C after pretreatment at 165 °C/0.5 Torr for 4 h.
[f] W content in anhydrous catalysts from ICP; in parentheses from the preparation stoichiometry.
[g] PW content in anhydrous catalysts from ICP.
[h] Prepared by method [13].
[k] Prepared by method [12].

(mol cm)). The amount of pyridine adsorbed onto the catalyst was found by difference between the initial and the unadsorbed amount of pyridine. The measurements were carried out at [Py]/[PW] < 1 mol/mol, and in most cases all the pyridine introduced was adsorbed on PW. From the total adsorption heats and the amount of pyridine adsorbed the differential heats of adsorption per mole of pyridine adsorbed were calculated.

3. Results and discussion

3.1. TG-DSC for ammonia adsorption/desorption

Water control is essential for acidity characterisation. The content of water in the catalysts was measured by TGA and is given in Table 1. Fig. 1 shows the TGA for PW catalysts and silica supports. The bulk PW pretreated at 300 °C contains practically no hydration water. The constitutional water, 1.5 H_2O (1.0 wt%) per Keggin unit (KU), is lost in the range of 450–550 °C upon PW decomposition. The SiO_2 support and PW/SiO_2 retain traces of hydration water ($\leqslant 0.5$ H_2O per KU) after pretreatment at 300 °C. In contrast, the sol–gel SiO_2 and sol–gel $PW-SiO_2$ catalysts remain highly hydrated, giving up water continuously up to 700 °C and higher. It was, therefore, impossible to prepare such catalysts in an anhydrous form.

The results of the TG-DSC study of NH_3 adsorption on bulk PW and PW/SiO_2 together with the TPD of NH_3 are given in Table 2. Most adsorption measurements were done at relatively high temperatures 300–350 °C to exclude ammonia physisorption and reduce equilibration time and ad-

sorption on silica. Such conditions favour NH_3 adsorption on strong acid sites. Figs. 2–4 show typical TG-DSC profiles. During the first 0.5 h, the temperature was increased up to 300 °C and held for 1 h to equilibrate the system. Then NH_3 was introduced, resulting in a weight gain accompanied by an exotherm. At a time $t = 2.5$ h, NH_3 supply was stopped. At $t = 3.5$ h, the TPD was started, resulting in a weight loss and an endotherm at $t \approx 4.5$ h. The total number of NH_3 molecules adsorbed per KU was close to the theoretical value of 3.0, although generally slightly higher than that. This was probably due to the presence of traces of water in the catalysts (Table 1), providing additional proton sites. The heats of adsorption, $-\Delta H_a$, given in Table 2 are the av-

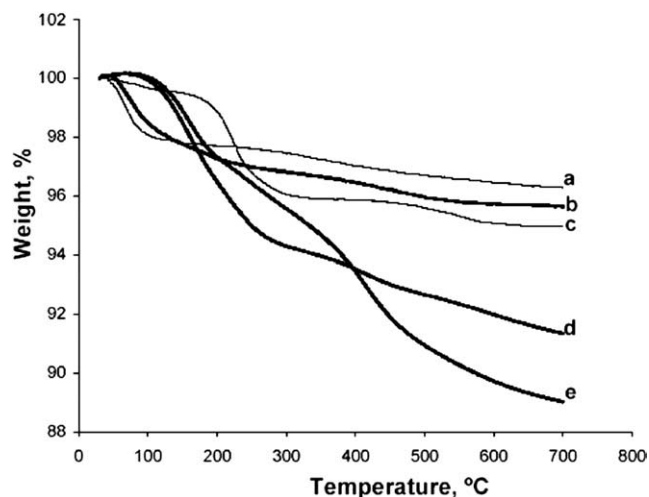Fig. 1. TGA for PW catalysts and supports: (a) SiO_2; (b) 20% PW/SiO_2; (c) bulk PW; (d) sol–gel 15% $PW-SiO_2$; (e) sol–gel SiO_2.

Table 2
TG/DSC for ammonia adsorption/desorption

Catalyst	Adsorption			Desorption	
	T (°C)	NH_3/PW (mol/mol)	$-\Delta H_a$ (kJ/mol)	T_d (°C)	ΔH_d (kJ/mol)[a]
PW[b]	150	3.2	133	637	491
PW[c]	300	3.1	148	632	448
60% PW/SiO$_2$[c]	300	3.8	134	601	396
40% PW/SiO$_2$[c]	300	3.1	122	582	312
30% PW/SiO$_2$[c]	300	4.0	117	580	234
20% PW/SiO$_2$[c]	300	3.7	102	575	164
10% PW/SiO$_2$[c]	300	3.0	76	576	[d]
SiO$_2$[c]	300	None	1.5[e]		
PW[f]	350	2.8	152	655	415
30% PW/SiO$_2$[f]	350	3.8	115	592	282
20% PW/SiO$_2$[f]	350	3.0	94	588	[d]
SiO$_2$[f]	350	None	0.1[e]		
CsPW	350	0.7	107	623	[d]

[a] Per mole PW.

[b] Catalyst pretreated at 300 °C/2 h under N$_2$, followed by stabilisation at 150 °C/1 h and NH$_3$ adsorption at 150 °C/1 h.

[c] Catalyst pretreated at 300 °C/1 h under N$_2$, followed by NH$_3$ adsorption at 300 °C/1 h.

[d] ΔH_d was impossible to measure accurately.

[e] No NH$_3$ adsorbed; ΔH_a in kJ per mole SiO$_2$.

[f] Catalyst pretreated at 350 °C/2 h under N$_2$, followed by NH$_3$ adsorption at 350 °C/1 h.

Fig. 2. TG-DSC for ammonia adsorption/desorption on PW.

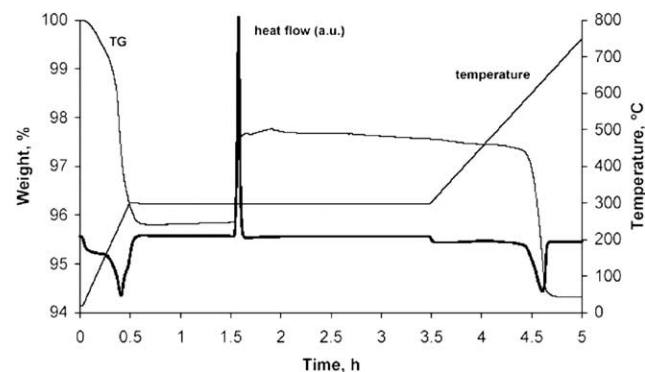Fig. 3. TG-DSC of ammonia adsorption/desorption on 60% PW/SiO$_2$.
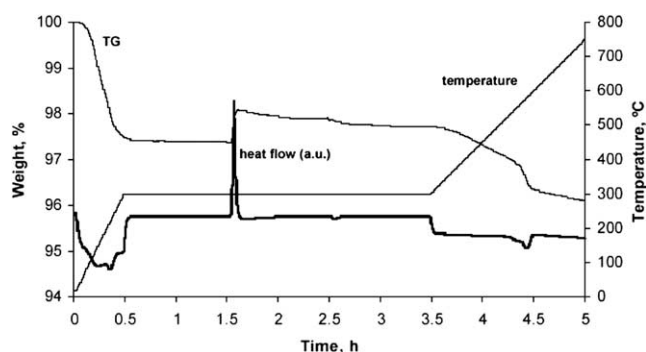
Fig. 4. TG-DSC of ammonia adsorption/desorption on 30% PW/SiO$_2$.

erage molar heats (per mole NH$_3$ adsorbed) corresponding to the formation of stoichiometric salt (NH$_4$)$_3$PW$_{12}$O$_{40}$. As expected, these values are lower than the differential heats at zero NH$_3$ adsorption, $-\Delta H_a^*$, due to heterogeneity of acid sites. For bulk PW, the $-\Delta H_a^*$ have been found to be 150–200 kJ/mol, depending on the pretreatment temperature [5–7]. Our value $-\Delta H_a = 133$ kJ/mol (Table 2) for bulk PW at 150 °C is close to the average molar heats calculated from [5,6].

No weight gain upon NH$_3$ adsorption on pure SiO$_2$ was observed at 300–350 °C, but a small exotherm was registered (Table 2). This can be explained by the formation of SiNH$_2$ groups [17]:
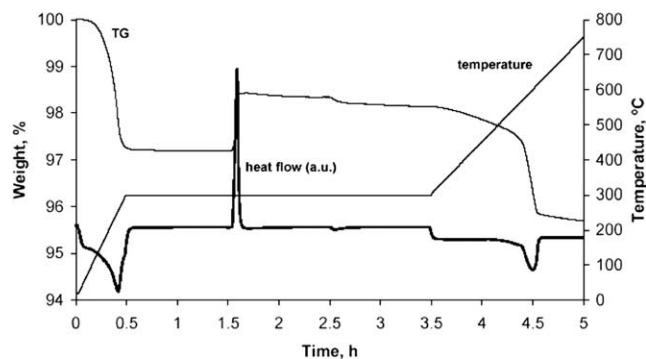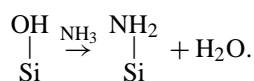
$$\underset{Si}{\overset{OH}{|}} \xrightarrow{NH_3} \underset{Si}{\overset{NH_2}{|}} + H_2O.$$

From ^{1}H MAS NMR, the number of silanol groups, SiOH, in 20% PW/SiO$_2$ reduces more than three times compared to that in the pure silica due to interaction with PW and acid-catalysed dehydroxylation of the silica surface [18]. It was assumed, therefore, that the formation of SiNH$_2$ groups would not play a significant role in the case of PW/SiO$_2$ catalysts and could be neglected.

The molar heat of NH$_3$ adsorption on PW/SiO$_2$ decreases monotonously with decreasing the PW loading, both at 300 and 350 °C (Table 2), and so does the acid strength, the pure bulk PW being the strongest acid in the PW/SiO$_2$ system. This is in agreement with the previous reports [5,10]. Although the average molar heats of adsorption do not reflect the heterogeneity of acid sites, they provide a useful estimate of the average acid strength of PW that can be used for correlation with catalytic activities. It should be noted that solid HPAs possess quite uniform acid sites [1–4]; thus, the molar heats of adsorption, which are easier to obtain than the differential heats of adsorption, may well represent the strength of most acid sites in PW catalysts.

The temperatures (T_d) and heats (ΔH_d) of NH$_3$ desorption are given in Table 2. The heats are given per mole PW. The desorption occurs at 570–660 °C along with decomposition of the Keggin structure. No bands characteristic of the Keggin structure were observed in the IR spectra of catalysts after desorption. The weight loss upon desorption was greater than the amount of NH$_3$ adsorbed and consistent with the decomposition of PW structure to evolve 3NH$_3$ + 1.5 H$_2$O per KU (ammonia partly evolves as N$_2$ [19]). Hence,

the ΔH_d values should be considered as the heats of decomposition of the salt $(NH_4)_3PW_{12}O_{40}$. These heats accumulate the heats of NH_3 desorption (endothermic) and PW decomposition (exothermic), the former being greater than the latter. The decomposition of PW and its NH_3 salt has been discussed elsewhere [4,19]. The TPD results are in good agreement with the results on NH_3 adsorption. Like the $-\Delta H_a$, both T_d and ΔH_d decrease with decreasing PW loading, hence correctly reflecting the trend of the acid strength. Thus T_d and ΔH_d, along with ΔH_a, can be used to predict the catalytic activity of PW catalysts.

Separately, from DSC, we estimated the enthalpies (kJ/mol) and temperatures of PW decomposition for bulk PW, 60% PW/SiO_2, and 30% PW/SiO_2 to be respectively -240 (599 °C), -250 (582 °C), and -160 (568 °C); in parentheses are the exotherm peak top temperatures. This indicates that PW becomes less stable when supported on silica due to interaction with the support.

The salt $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW) possesses weaker proton sites than the bulk PW, in agreement with the literature [1], but stronger than 20% PW/SiO_2. This is evidenced from the values of ΔH_a and T_d (Table 2).

Figs. 5 and 6 show the TG-DSC profiles for sol–gel SiO_2 and 15% $PW-SiO_2$. Both samples did not reach equilibrium upon thermal treatment, losing water continuously. When the samples were brought in contact with NH_3 ($t \approx 1.5$ h), the loss of water increased sharply, showing an exothermic effect, probably due to base catalysed dehydration to form a
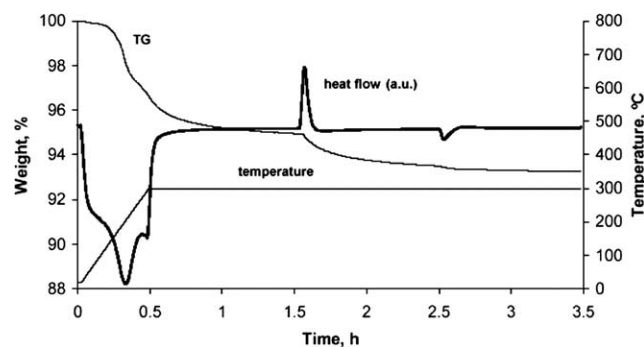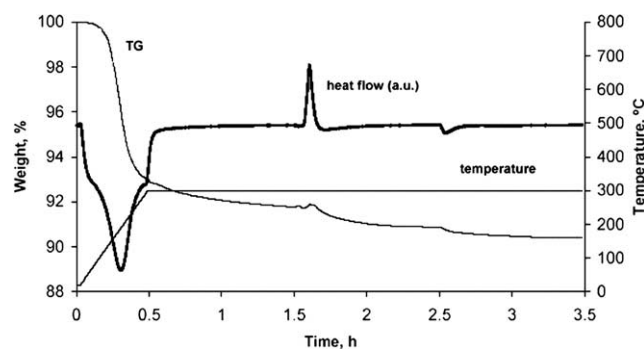
stronger silica network.

$$\underset{Si}{\overset{OH}{|}} + \underset{Si}{\overset{OH}{|}} \rightarrow Si{\overset{O}{\diagdown}}Si + H_2O$$
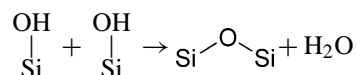
No weight gain for the sol–gel SiO_2 was observed (Fig. 5). A weight gain due to NH_3 adsorption was observed for 15% $PW-SiO_2$ (Fig. 6), but it could not be quantified because of the simultaneous water loss. This did not allow the heat of adsorption or desorption for the sol–gel $PW-SiO_2$ catalysts to be obtained.

3.2. Microcalorimetry for pyridine adsorption

In microcalorimetric studies, which are performed under equilibrium conditions, it is generally assumed that the base probe adsorbs on the strongest acid sites present in the catalyst [20]. The previous study [8] of pyridine adsorption on a PW slurry in cyclohexane by the Cal-ad method, combining a calorimetric titration and adsorption isotherm, has found the most acidic protons to have the enthalpies of -137 kJ/mol. Under such conditions, in contrast to the NH_3 adsorption in a gas–solid system, only a quarter of PW protons were accessible for pyridine adsorption. Our Cal-ad results for pyridine adsorption are summarised in Table 3. The PW catalysts were pretreated at 165 °C/0.5 Torr/4 h (Table 1) to allow comparison with the previous results for bulk PW [8]. Fig. 7 shows the differential heat of pyridine adsorption on the bulk PW as a function of the amount of pyridine adsorbed per KU. In the range of Py/PW = 0.14–0.70 mol/mol, the acidity of PW was almost uniform, with $-\Delta H_a^* = 135 \pm 5$ kJ/mol at zero adsorption. This is in good agreement with the value of 137 kJ/mol reported earlier [8]. The adsorption heats for 10–60% PW/SiO_2 catalysts were measured at a low pyridine adsorption, Py/PW = 0.07–0.46 mol/mol. These values can be taken as the differential heats at zero adsorption ($-\Delta H_a^*$) within the measurement error (± 5 kJ/mol). For SiO_2 (evacuated at 165 °C), the value of $-\Delta H_a^* = 28$ kJ/mol obtained in this work is close to the 23 kJ/mol for SiO_2 evacuated at 200 °C from [8].

The differential heats of pyridine adsorption for bulk PW and PW/SiO_2 decrease as the PW loading decreases in

Fig. 5. TG-DSC of ammonia adsorption on sol–gel SiO_2 at 300 °C.

Fig. 6. TG-DSC of ammonia adsorption on sol–gel 15% $PW-SiO_2$ at 300 °C.

Table 3
Microcalorimetry for pyridine adsorption onto PW catalysts in cyclohexane at 50 °C

Catalyst[a]	Py/PW (mol/mol)	$-\Delta H_a^*$ (kJ/mol)
PW	0.14–0.70	135 ± 5
60% PW/SiO_2	0.376	123
40% PW/SiO_2	0.068	88
30% PW/SiO_2	0.146	87
20% PW/SiO_2	0.242	58
10% PW/SiO_2	0.455	44
SiO_2	0.004[b]	28
Sol–gel 11% $PW-SiO_2$	0.847	86
Sol–gel SiO_2	0.006[b]	110

[a] Catalysts pretreated at 165 °C/0.5 Torr/4 h (Table 1).
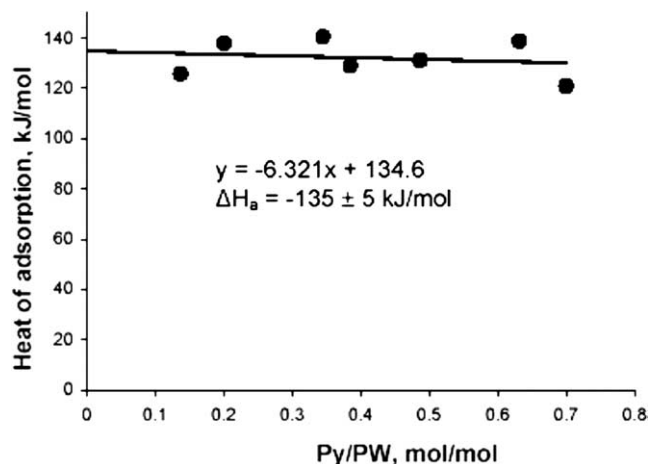[b] Per mole SiO_2.

Fig. 7. Differential heat of pyridine adsorption on PW in cyclohexane at 50 °C.
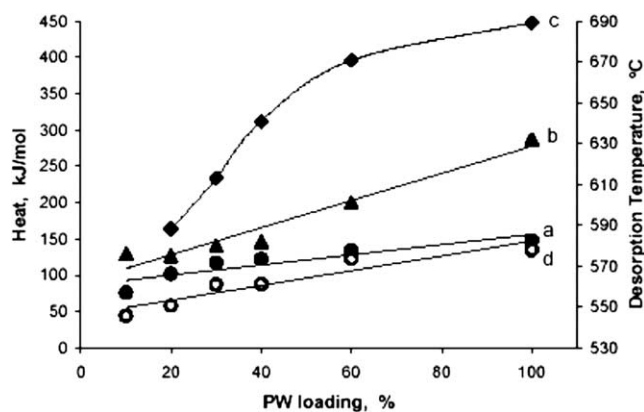

Fig. 8. Adsorption and desorption parameters for PW/SiO$_2$ vs PW loading: (a) heat of NH$_3$ adsorption; (b) temperature of NH$_3$ desorption; (c) heat of NH$_3$ desorption; (d) differential heat of pyridine adsorption.

agreement with the acid strength trend. Thus the Cal-ad results are fully consistent with those obtained by TG-DSC. Fig. 8 plots the values of $-\Delta H_a$, T_d, and ΔH_d obtained using NH$_3$ and pyridine as probe molecules versus the PW loading.

The heats of pyridine adsorption obtained for sol–gel SiO$_2$ and 11% PW-SiO$_2$ are far greater than those for silica and silica-supported 10% PW/SiO$_2$ (Table 3). This can be explained by the hydration of pyridinium cations by excess water present in these samples [8,10]. It is therefore impossible to compare the acid strength of silica-supported and sol–gel PW catalysts.

The heats of adsorption of base probes can be correlated with the activity of PW catalysts. Fig. 9 shows a relation between the catalytic activity, $RT \ln r$, of PW/SiO$_2$ in Fries rearrangement of phenyl acetate in liquid phase [15] and the heats of adsorption of NH$_3$ or pyridine. The activity, r, is
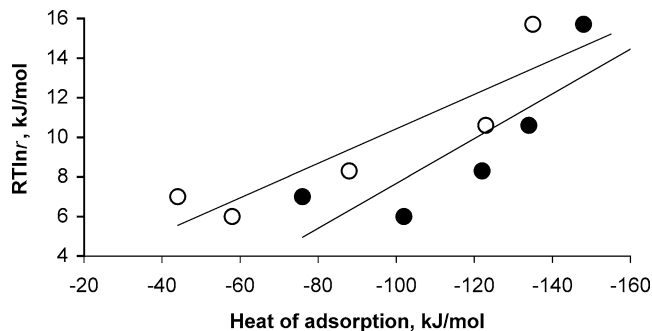

Fig. 9. Plot of the catalytic activity of PW/SiO$_2$ in Fries reaction of phenyl acetate (in dodecane, 130 °C, 10–100% PW on SiO$_2$) [15] vs the heat of adsorption of NH$_3$ (solid circles) and pyridine (open circles).

a turnover frequency (min^{-1}) per surface proton site calculated assuming a PW molecule cross section of 144 Å^2 per one H$^+$. Both heats give satisfactory Brønsted-type plots, the more relevant and accurate heats of pyridine adsorption provide better fit. This indicates that the reaction occurs via the surface-type catalysis rather than bulk-type catalysis [1].

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