

New fluorinated carbon support for catalysts

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Abstract

The adsorption of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ from water and organic solvents (acetone and acetonitrile) by carbon mesoporous materials (Sibunit and fluorinated Sibunit (F-Sibunit)) was studied. The concentration of Brønsted acidic sites in $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and 8% $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{F-Sibunit}$ was determined from ESR studies of the stable nitroxyl radical (4-hydroxy-2,2',6,6'-tetramethylpiperidin-*N*-oxyl (TEMPOL)) adsorbed from hexane. For $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and 8% $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{F-Sibunit}$, the concentration was equal to 4 and $12 \mu\text{mol g}^{-1}$, respectively. A correlation between the rate constant of cyclohexene dimerisation of in the hexane solution and the strength of HPA-support interaction was determined. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

Heteropoly acids (HPA, $\text{H}_m\text{XY}_{12}\text{O}_{40}$ with $m=3-4$; X = Si^{IV} , P^{V} ; Y = Mo^{VI} , W^{IV}) are used as homogeneous and heterogeneous acid catalysts [1,2] in order to obtain proton acidity. Heterogeneous HPA catalysts are prepared by supporting on a number of porous materials [3–6]. A variety of methods is used to characterise HPAs supported on SiO_2 , carbon, Al_2O_3 and MgF_2 [4,7,8]. According to ^{31}P NMR [9] and FTIR-spectra of HPA on SiO_2 , $\text{SiO}_2\text{-Al}_2\text{O}_3$ and Al_2O_3 [7,10], the primary Keggin structure is not destroyed upon adsorption, but some degradation can be observed on Al_2O_3 heated above 200°C . The acid strength of supported $\text{H}_3\text{PW}_{12}\text{O}_{40}$ is ranked as $\text{SiO}_2 > \text{Al}_2\text{O}_3 > \text{C}$, assuming interaction between HPA and carbon [2].

The nature of the interaction depends mainly on the concentration of impregnated solutions, the solvent used, the pH of the solution and the chemical nature of the support surface. For example, when $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ are supported from concentrated aqueous solutions on carbon, HPAs preserve their Keggin structure and appear highly

dispersed on the support. However, HPA impregnated from diluted solutions is partly decomposed [2].

Porous carbon materials such as activated carbons [8,10] or catalytic filamentous carbons [6,10] are extensively utilised for the preparation of supported heteropoly acid catalysts. Unfortunately, the acid strength of HPA supported on these materials is lower than that of bulk HPA. Fluorinated carbon materials were not used as support for HPA so far, though these materials possess an inert surface and a high specific surface area [11,12].

In this paper, we report the preparation of HPA/F-Sibunit catalysts, their characterisation by a combination of physical–chemical methods and the comparison of the catalytic properties of two various supported HPA-systems.

2. Experimental

2.1. Materials

$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 15\text{H}_2\text{O}$ (HPA) of chemical purity grade was recrystallized by ether extraction. The purity was controlled by ^{31}P NMR on an MSL-400 Bruker instrument. Hexane was purified by distillation. 4-hydroxy-2,2',6,6'-tetramethylpiperidin-*N*-oxyl, TEMPOL (SIGMA), was dissolved in hexane ($0.5\text{--}5 \text{ mmol L}^{-1}$).

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Table 1
The main characteristics of carbon materials

Carbon	D_{mean} (Å)	S_{BET} (m ² g ⁻¹)	ΣV_{pore} (cm ³ g ⁻¹)	a_{max} (mg g ⁻¹)			a_{irr} (mg g ⁻¹)		
				H ₂ O	Me ₂ CO	MeCN	H ₂ O	Me ₂ CO	MeCN
Sibunit	62	402	0.6	402	360	262	100	80	60
F-Sibunit	30–35	360–390	0.6	0	13	92	0	0	10

F-Sibunit (superstoichiometrical fluorocarbon material) was synthesised by a direct fluorination treatment of Sibunit with a gaseous mixture F₂/Ar = 1 : 3 at 320–330 °C [11]. The chemical composition of F-Sibunit corresponded to the general formula CF_{1.25} in accordance to the technical specification [12]. The main contaminations were H₂O (0.04–0.08 wt.%), HF (0.08–0.10 wt.%) and metals (0.08 wt.%). The common main characteristics (mean pore diameter D_{mean} , specific surface area S_{BET} and cumulative pore volume ΣV_{pore}) of the supports are presented in Table 1.

Adsorption measurements were carried out in a periodically agitated reactor held at a constant temperature (± 0.1 °C). The carbon-containing Sibunit and fluorinated Sibunit (F-Sibunit) supports were pre-washed in an appropriate solvent and dried in air. The adsorbent (2 g) was loaded into the reactor and the HPA solution (10 ml, 10–150 g L⁻¹) was added. Samples of the solutions (0.1 mL) were taken at certain time intervals. After dilution, the HPA concentration in the solution was determined from UV–vis spectra (Specord UV–vis M-40 instrument, $\nu = 32000\text{--}42000$ cm⁻¹, error of measurement $\pm 10\%$). The irreversible adsorption (a_{irr}) was determined by boiling 0.5 g of the 8% HPA-support in a pure solvent (10 mL) followed by separation of the sediment by vacuum filtration and burning of the sample at 900 °C in a muffle furnace. The a_{irr} value was calculated from the amount of the solid residue.

2.2. Techniques

Infrared spectra were recorded on a BOMEM-MB-102 spectrometer in 250–4000 cm⁻¹ range (compressed pellets of 2 mg catalysts plus 500 mg KBr).

The porous structure of the supports was determined from the adsorption isotherm of N₂ (77 K). The specific surface area (S_{BET}) was calculated by the Brunauer–Emmett–Teller (BET) method.

Samples for transmission electron microscopy (TEM) were prepared by ultrasonic dispergation of HPA/C in hexane followed by deposition of the suspension onto a standard Cu grid covered with a holed carbon film. TEM studies were carried out at a JEM-2010 TEM (JEOL).

The amount of proton sites was determined from curves given by TEMPOL on solid samples (error $\pm 15\%$). The equilibrium concentration of TEMPOL in hexane solution was measured by ESR. ESR spectra (room temperature) were recorded at 9.5 GHz at a ERS-221 spectrometer in

cylindrical glass tubes ($d = 4$ mm). These spectra were quantified by double integration and the concentration of TEMPOL was calculated from a calibration procedure (error $\pm 10\%$). Before measurement, samples were heated in oxygen atmosphere at 200 °C during 2 h.

2.3. Dimerisation of cyclohexene

The dimerisation of cyclohexene was carried out at 40 °C in a glass thermostated vessel equipped with a stirrer and reflux condenser. Before the test, the samples were heated in oxygen atmosphere at 200 °C during 2 h. The reactor was charged with the mixture of hexane:cyclohexene 10:1 mol/mol (30 ml) and the catalyst (1 wt.% based on cyclohexene). The products were analysed by GLC (3 m column packed with 5% SE-30 on Chromatone N-AW-DMCS, 150 °C, decane was used as internal standard).

3. Results

3.1. Adsorption of H₃PW₁₂O₄₀ on F-Sibunit

The experimental data of maximal (a_{max}) and irreversible (a_{irr}) adsorption of HPA on Sibunit and F-Sibunit from water and organic solvents (Me₂CO and MeCN) are presented in Table 1. The adsorption isotherms of HPA are shown in Fig. 1. Fig. 1 shows that at the very beginning

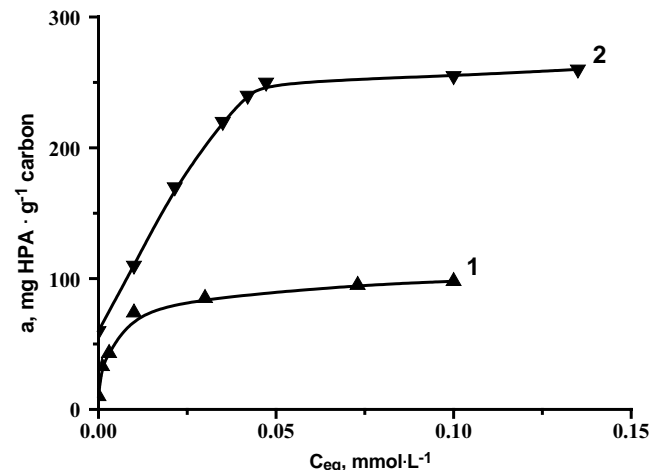


Fig. 1. Adsorption isotherms of HPA on (1) F-Sibunit and (2) Sibunit, from MeCN at 20 °C.

of the isotherms the adsorption is irreversible from aqueous, acetone and acetonitrile solutions. The phenomenon of irreversible HPA adsorption on hydrophilic supports is known [4,6]. Our results confirm that HPA cannot completely be desorbed from the Sibunit surface even in boiling water and methanol [4]. It indicates both the strong interaction between HPA molecules and the Sibunit support surface and the capsulation of sufficiently large HPA molecules onto landing places of about 100 Å [3,6,8,13]. In the case of the hydrophobic F-Sibunit this problem was not studied.

The solvent nature affects the adsorption values (Table 1). Adsorption of HPA on Sibunit from organic solvents decreases as the solvent polarity ($\text{H}_2\text{O} > \text{Me}_2\text{CO} > \text{MeCN}$) increases. This correlation is in accord with the competitive adsorption of the solvent molecules and HPA molecules on the outer surface of Sibunit. It was assumed that HPA adsorbs on the hydrated surface because water plays the binding role in the formation of the crystal structure of HPA [2]. On the other hand, the maximal (a_{max}) adsorption of HPA on F-Sibunit from these three solvents decreases in the inverse order: $\text{MeCN} > \text{Me}_2\text{CO} > \text{H}_2\text{O}$. The interaction strength of the solvent molecules with the surface groups of F-Sibunit is unknown yet, but it probably changes in the same order.

According to the IR spectra (Fig. 2), the structure of the Keggin anion $[\text{PW}_{12}\text{O}_{40}]^{3-}$ remains unchanged on the F-Sibunit surface. At the same time, the IR-spectrum of F-Sibunit corresponds to the known spectra for $\text{CF}_{(1+x)}$ [12,15] and does not significantly change after HPA adsorption. The IR-spectrum of 8% $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{F-Sibunit}$

sample exhibits the absorption bands at $\nu(\text{W-O-W}) = 826, 898 \text{ cm}^{-1}$, $\nu_{\text{as}}(\text{W=O}) = 982 \text{ cm}^{-1}$ and $\nu_{\text{as}}(\text{PO}_4) = 1080 \text{ cm}^{-1}$, which can be attributed to HPA with a Keggin structure [14]. IR-shifts of the corresponding bands from 805 to 826 cm^{-1} , from 890 to 898 cm^{-1} and from 1090 to 1080 cm^{-1} may be caused by the interaction of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ with the functional groups of the F-Sibunit surface and are similar to the known data for carbon materials [6]. At the same time, additional bands are observed in $1360\text{--}1400 \text{ cm}^{-1}$ and $1520\text{--}1640 \text{ cm}^{-1}$ regions, which correspond to the surface groups of carbon (carboxylic, lactonic, etc.).

TEM data (Fig. 3) show that the HPA is adsorbed on the surface of F-Sibunit in two main forms: isolated molecules less than 20 Å in size and clusters of ca., 35–50 Å in size. HPA aggregates larger than 100–150 Å are not observed, which can be explained by the pronounced hydrophobic properties of the F-Sibunit surface, preventing the formation of the large hydrophilic aggregates. Such conclusion is confirmed by the known aggregation of HPA on hydrophilic surfaces of SiO_2 and active carbons [4]. Recently, it was shown that the large crystals of HPA are only formed on specifically oxidised carbon films [4] as a result of the capsulation process during the preparation of HPA supported on hydrophilic surface of active carbons.

According to [12,15] the main motif of F-Sibunit nanostructure involves sp^3 corrugated fluorographite-like C–F nets forming more or less ordered layers lying 6.3–6.7 Å apart. F-Sibunit $\text{CF}_{1.25}$ is superstoichiometric fluorocarbon material and excessive fluorine atoms are located in

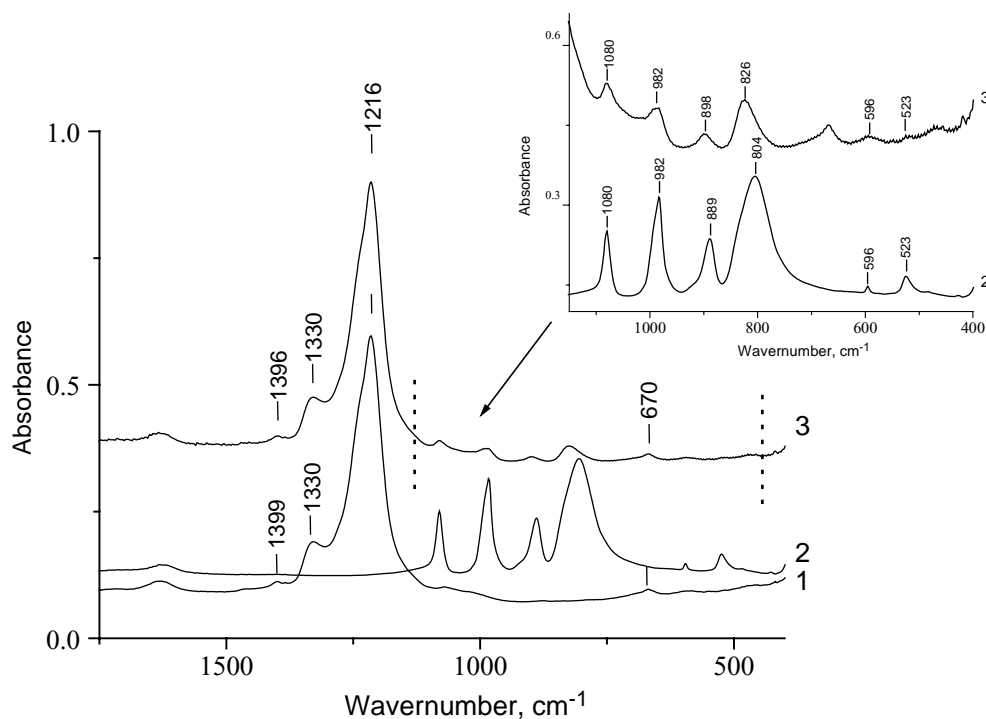


Fig. 2. IR spectra of (1) F-Sibunit, (2) HPA and (3) 8%HPA/F-Sibunit.

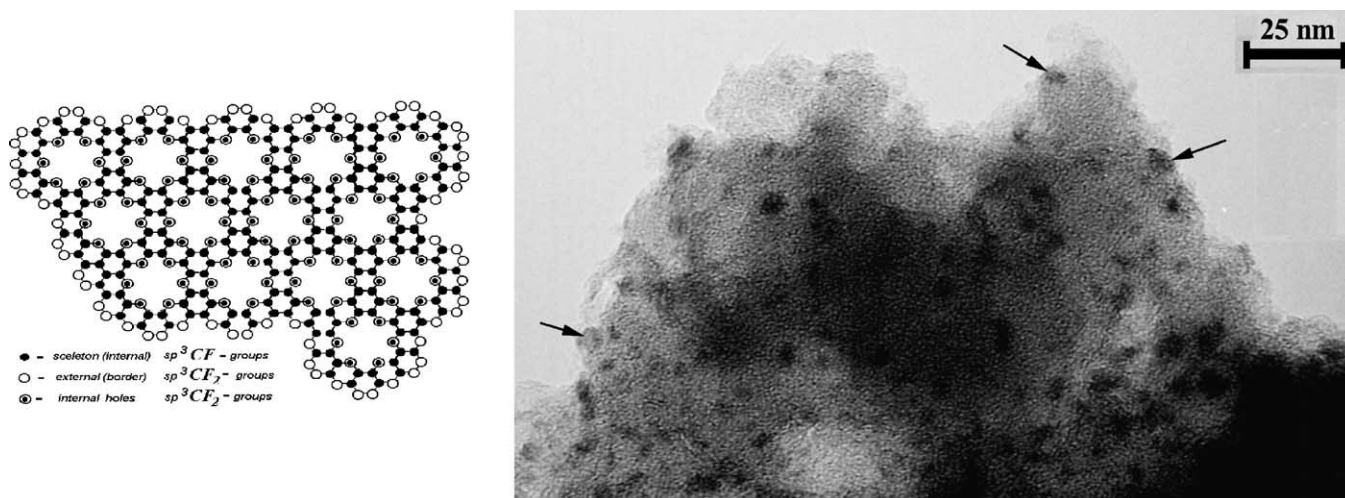


Fig. 3. The structure of F-Sibunit $CF_{1.33}$ monolayer [12,15] and a micrograph of 8% HPA supported on F-Sibunit.

Table 2

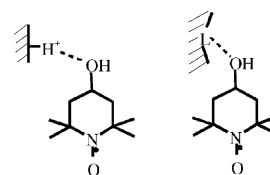
Dimerisation of cyclohexene catalysed by HPA at 40 °C (hexane : cyclohexene = 10 : 1 mol/mol, catalyst = 1 wt.%)

Catalyst	k_{cat} ($10^3 M^{-1} s^{-1} g^{-1}$)	K_{HPA} ($10^3 M^{-1} s^{-1} g^{-1}$)	k_{H^+} ($M^{-1} s^{-1} \mu mol^{-1}$)	H^+ ($\mu mol g^{-1}$)
HPA	1.2	1.2	300	4
8% HPA/F-Sibunit	0.5	6.3	42	12
F-Sibunit	0	0	0	0
8% HPA/Sibunit	0	0	0	15

isolated CF_2 -groups, distributed in the edge defects and mainly in holes of the fluorographite-like monolayers. Presence of CF_2 -groups is demonstrated by 1330 cm^{-1} band in FTIR-spectra (Fig. 2). Idealised scheme of F-Sibunit $CF_{1.33}$ structure is shown in Fig. 3. Each regular hole having a formula $C_{18}F_{24}$, consists of six sp^3 - CF_2 -groups and 12 sp^3 -C-F-groups and the minimal size of such six-centred hole is about 7.5 \AA . As it was shown [12,16], the chemical activity of CF_2 - and C-F-groups is very similar and in hydrolysis reactions it leads to elimination of HF and origin of C-OH, C=O and other carbonyl-contained groups on the surface of this fluorocarbon material (e.g. carboxyles or lactones). FTIR-spectra of F-Sibunit (Fig. 2), contains weak and broadened bands in regions of 670 , 1040 – 1090 , 1400 , 1460 and 1600 – 1650 cm^{-1} , corresponding to above-mentioned functional groups [12].

3.2. Surface acidity and catalytic activity of HPA/F-Sibunit

A TEMPOL molecule adsorbs on a Brønsted or Lewis acid site [17,18]. Most probably a TEMPOL molecule can be adsorbed via coordination of the hydroxyl group. Therefore, the concentrations of both types of acid sites can be estimated by adsorption of TEMPOL.



Adsorption of TEMPOL on HPA samples from hexane was studied (Table 2, Fig. 4). No adsorption of TEMPOL on F-Sibunit was detected in the range 0 – $1\text{ }\mu\text{mol mL}^{-1}$ (Fig. 4, curve 1), whereas TEMPOL adsorbed from hexane on bulk $H_3PW_{12}O_{40}$ and 8% $H_3PW_{12}O_{40}$ /F-Sibunit gives L-curves (“Langmuir” type [19]) with the plateau at a level of adsorption of 4 and $12\text{ }\mu\text{mol g}^{-1}$, respectively (Fig. 4, curves 2–3). The specific surface area of bulk HPA is about $4\text{ m}^2\text{ g}^{-1}$, which corresponds to a surface density of 0.6 acid sites per 100 \AA^2 and a nearest-neighbour separation between these sites of $\sim 14\text{ \AA}$. Such a distance is close to the nearest-neighbour separation in bulk $[PW_{12}O_{40}]^{3-}$ (11 – 15 \AA) [20]. The concentration of the acid sites in supported HPA is higher than in bulk HPA due to the higher dispersion of the HPA aggregates (Fig. 3) after adsorption on F-Sibunit. However, the determined concentration in 8% HPA/F-Sibunit is lower than expected ($27 \times 3\text{ }\mu\text{mol g}^{-1}$), which can be explained by the interaction of the HPA protons with hydrolysed surface groups of F-Sibunit (C-OH

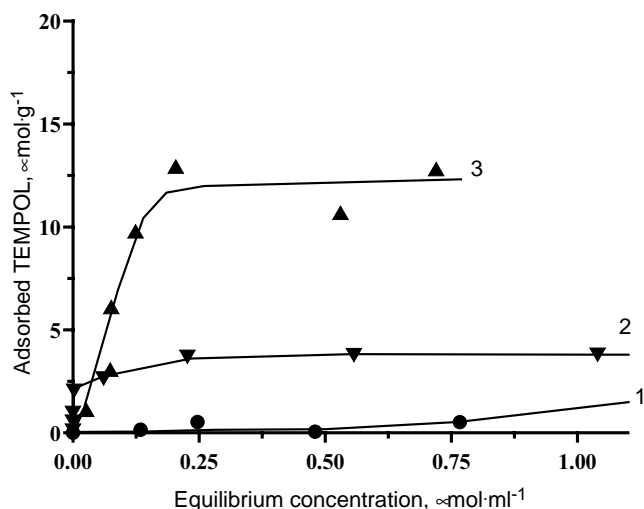
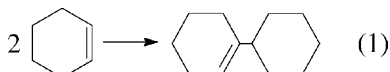


Fig. 4. Adsorption isotherms of TEMPOL on samples from hexane solution at room temperature (25 °C) on (1) F-Sibunit, (2) HPA and (3) 8% HPA/F-Sibunit.

and C=O) [16]. This interaction corresponds to the IR region 800–1100 cm^{-1} (Fig. 2).

3.3. Catalytic activity of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ /Sibunit and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ /F-Sibunit

The activity of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and 8% $\text{H}_3\text{PW}_{12}\text{O}_{40}$ /F-Sibunit in reaction (1) is presented in Table 2.



The rate constants k_{HPA} and k_{H^+} were calculated using the known values of second-order rate constants (k_{cat}) and the amount of surface protons (H^+) for bulk and supported HPA, respectively. The activity based on the total amount of HPA protons in the catalyst is denoted by k_{HPA} . The activity based on the amount of the surface protons is denoted by k_{H^+} . We see that the rate constants (k_{HPA}) of 8% $\text{H}_3\text{PW}_{12}\text{O}_{40}$ /F-Sibunit is higher than that of bulk HPA. The reason of the higher catalytic activity (k_{HPA}) is the formation of finely dispersed HPA species on the carbon surface. A similar correlation was observed when HPA is supported on SiO_2 [2].

However, the k_{H^+} value is lower for 8% $\text{H}_3\text{PW}_{12}\text{O}_{40}$ /F-Sibunit than for bulk HPA (Table 2). It indicates that the acid strength of the proton sites of HPA/F-Sibunit is lower than that of the bulk sites. It is evident that the interaction of HPA with surface groups of F-Sibunit (discussed above) results in a decrease of acid strength.

Two samples: 8% $\text{H}_3\text{PW}_{12}\text{O}_{40}$ /Sibunit and 8% $\text{H}_3\text{PW}_{12}\text{O}_{40}$ /F-Sibunit are similar with regard to the concentration of acid sites (Table 2). It seems to be likely that this similarity together with the apparent differences in the catalytic activities of these samples (Table 2) indicates the greater acid strength of the proton sites in 8%

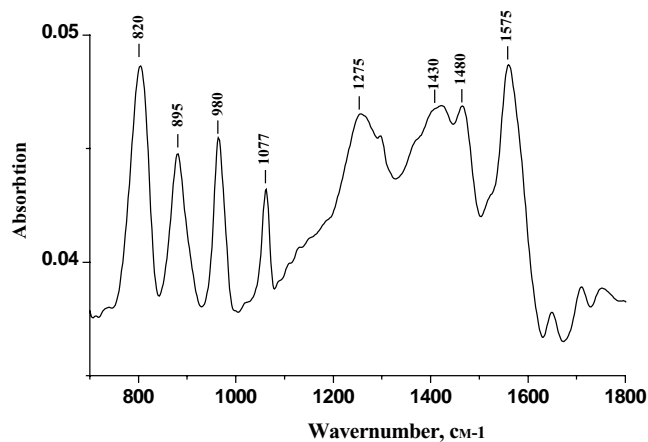


Fig. 5. IR spectra of 8% HPA/Sibunit [6].

$\text{H}_3\text{PW}_{12}\text{O}_{40}$ /F-Sibunit than that in 8% $\text{H}_3\text{PW}_{12}\text{O}_{40}$ /Sibunit. Although, according to IR spectroscopic data (Fig. 5), the structure of the Keggin anion $[\text{PW}_{12}\text{O}_{40}]^{3-}$ remains unchanged on the Sibunit surface as well as in the case of 8% $\text{H}_3\text{PW}_{12}\text{O}_{40}$ /F-Sibunit, the additional IR bands at 1100–1300 and 1400–1600 cm^{-1} point to both the interaction of HPA with the surface groups of Sibunit (carboxylic, lactonic, etc.), resulting in the formation of the intermolecular hydrogen bond (owing to the π -electron interaction) and partial oxidation of the Sibunit surface by the adsorbed HPA molecules [6]. Since this interaction is much stronger in the case of HPA supported on Sibunit, 8% HPA/Sibunit becomes inactive in dimerisation of cyclohexene.

4. Conclusion

HPA/F-Sibunit catalyst can be successfully prepared by irreversible adsorption from acetonitrile solution.

The structure of the Keggin anion $[\text{PW}_{12}\text{O}_{40}]^{3-}$ remains unchanged on the F-Sibunit surface. Two forms of HPA are observed on the F-Sibunit surface: isolated molecules less than 20 Å in size and clusters of ca. 50 Å in size. For $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and 8% $\text{H}_3\text{PW}_{12}\text{O}_{40}$ /F-Sibunit, the concentration of Brønsted acidic sites, detected by ESR studies of TEMPOL adsorption, is equal to 4 and 12 $\mu\text{mol g}^{-1}$, respectively.

The acidity of supported HPAs depends on the nature of surface species and on the strength of the HPA-support interaction. The $\text{H}_3\text{PW}_{12}\text{O}_{40}$ /F-Sibunit exhibits higher catalytic activity in the reaction of cyclohexene dimerisation than bulk HPA.

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