Catalysis Today 81 (2003) 611–621

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Preparation and characterisation of chemisorbents based on heteropolyacids supported on synthetic mesoporous carbons and silica

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Abstract

The preparation of chemisorbents based on tungsto- and molybdophosphoric acids supported on two types of synthetic mesoporous carbons and two types of mesoporous silica is described. Strong solid acids with good accessibility to acid sites may potentially be effective adsorbents for the removal of basic molecular impurities, such as amines, from ultrapure manufacturing environments. Prepared materials were characterised by scanning electron microscopy, nitrogen adsorption, Fourier-transform infrared spectroscopy, powder X-ray diffraction, and equilibrium ammonia uptake. Composites of SBA-15 with heteropolyacids were synthesised. It was shown that the inclusion of HPAs into SBA-15 results in the loss of long range order. Adsorbents based on the HPAs impregnated into the supports with the open-pore morphology (Novacarb and SBA-15) were found to be promising materials. A composite of tungstophosphoric acid with sol–gel SiO_2 was found to have the highest ammonia uptake.

Keywords: Heteropolyacids; Clean room; Mesoporous materials; Chemisorption; Synthetic carbons

1. Introduction

The development of solid acid catalysts is an active and very important area of research, underpinning the development of future “green” chemical processes. There is significant need for new catalysts active in such reactions as Friedel–Crafts acylation and alkylation, esterification, and selective oxidation, which would substitute more conventional stoichiometric reactions known to generate large quantities of hazardous waste materials. At the same time porous solid acid materials of very similar physico-chemical and textural properties as solid acid catalysts may also find applications in separation processes.

Removal of molecular impurities from ultrapure manufacturing environments, such as in the manufacture of silicon wafers, is based on the use of acidic and basic chemisorbents [1]. At present, acidic chemisorbents are based on mineral acids, such as phosphoric and sulphuric acids, impregnated into activated carbon and dispersed in a polymer mesh filter. Sorbents based on supported liquid acids have a number of drawbacks. The formation of insoluble salts upon reaction with primary impurities restricts access to the

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0920-5861/03/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0920-5861(03)00159-7

remaining acid, thus decreasing the overall capacity of an adsorption bed. Furthermore, liquid sulphuric and phosphoric acids generate secondary oxide impurities, due to vapour pressure above liquid acids, and require installation of additional downstream filters. Using highly dispersed solid acids could potentially eliminate these drawbacks. The peculiarity of this application is that adsorbents must be efficient at very low concentration of pollutants, whereas high equilibrium capacity is of lesser importance. Therefore, the main focus of the development of such adsorbents should be on the acid strength and good accessibility to the acid sites.

There exist a large number of solid materials exhibiting varying degree of Brönsted acidity, ranging from natural acid-leached clays, amorphous silica–aluminas, meso-structured silicas such as MCM and SBA type materials, zeolites, free and supported heteropolyacids, and sulphated oxides [2]. Amongst these materials heteropolyacids supported onto mesoporous solids seem to be the most promising materials for this application. Heteropolyacids are strong Brönsted acids which already have found a number of commercial applications as catalysts (examples of two commercial applications of heteropolyacid catalysts: (a) direct hydration of propene to propanol; (b) acylation of anisole with acetic anhydride [3]), and are being actively investigated for new catalytic processes (see, e.g. [4]). Their applications as sorbents are much more limited [5]. It was shown in [6] that each Keggin unit of tungstophosphoric acid ($H_3PW_{12}O_{40}$, or W-HPA) is able to adsorb four molecules of ammonia irreversibly, which is higher than the proton content of the acid molecule. Thus, application of heteropolyacids as chemisorbents should ensure high sorbent capacity. However, in order to provide easy accessibility to adsorption sites it is necessary to obtain a highly dispersed acid and preferably use mesoporous supports providing easy pathways for convective and diffusional fluxes.

Preparation of supported heteropolyacids on a variety of support materials is widely reported (see, e.g. [7]). It was shown that the Keggin structure of HPAs is retained upon adsorption onto supports over a broad range of loadings. However, due to the interaction between the acid and the supports, the acidity of heteropolyacids may vary significantly. The acidity of HPAs supported onto carbons is generally lower than that of supported onto silica [7]. Preparation of heteropolyacids supported on a number of mesoporous solids was reported. Thus, it was shown that at loadings up to 23 wt% W-HPA supported onto MCM-41 by impregnation exhibits higher acidity than that of pure acid [8]. However, at higher loadings a significant distortion of the structure of the support and a decrease of acidity were observed. The low thermal stability of MCM-41 may potentially be disadvantageous for application in adsorption processes, as it precludes the use of thermal regeneration methods. Although the filters used in clean-room air purification systems are not regenerated, it is of general interest to develop materials that could be regenerated and re-used. It was shown that following thermal decomposition into β-MoO_3 oxide, the original structure of $H_3PMo_{12}O_{40}$ might be recovered by treatment in an atmosphere of steam [9]. Furthermore, the Keggin structure of tungstophosphoric acid may be regenerated by simple thermal treatment [10]. This may potentially provide a method of regeneration of adsorbents based on heteropolyacids. However, thermal stability and the nature of the supports become important. Compared with MCM-41, sol–gel derived mesoporous silica and SBA-15 are characterised by higher thermal stability. Furthermore, the sol–gel preparation method allows the making of heteropolyacid–silica composites with high acid loading [11].

This paper reports initial results on the preparation and characterisation of heteropolyacids supported on SBA-15, sol–gel derived SiO_2 and two different synthetic mesoporous carbons, to be used for removal of basic molecular impurities (e.g. ammonia and amines) from air in ultrapure manufacturing environments.

2. Experimental

2.1. Support materials

Four different support materials were used in this study: mesoporous phenolic resin derived carbon (Novacarb^{TM}), mesoporous synthetic carbon (Sibunit^{TM}), mesoporous silica SBA-15 and sol–gel derived silica. Samples of Novacarb^{TM} were kindly provided by MAST Carbon (UK) in the form of microspheres with diameters in the range of 10–45 μm. Detailed information on the preparation and properties of Novacarb^{TM} can be found in [12]. Brominated Novacarb was prepared by direct contact with bromine gas in a three-neck flask at 673 K over 6 h in an atmosphere of argon to prevent oxidation of carbon. A 35% weight increase was observed following bromination. A sample of mesoporous carbon catalyst support Sibunit^{TM} was kindly provided by the Boreskov Institute of Catalysis (Novosibirsk, Russia). Sibunit was washed in water and ethanol, and dried under vacuum at 473 K for 2–3 h prior to impregnation.

Pure SBA-15 was prepared as described in [13]. In a typical synthesis 2 g of Pluronic (P123) co-polymer was dissolved in a mixture of 52.5 g H_2O and 12 g HCl (36.5 wt.%) at 313 K. 4.28 g of tetraethoxy silane (TEOS) was added dropwise and the resultant mixture was stirred for 24 h. After stirring the mixture was poured into a polypropylene bottle and aged in an oven for 24 h at 363 K. Following ageing the mixture was filtered, washed with deionised water and dried under atmospheric conditions for 48 h. Finally, plain SBA-15 samples were calcined in flowing oxygen. The calcination temperature was increased from ambient to 773 K at 1 K/min and kept at that temperature for 6 h.

Composites of SBA-15 with W-HPA and molybdophosphoric acid ($H_3PMo_{12}O_{40}$), or Mo-HPA, heteropolyacids were synthesised by adding the corresponding acid to a solution of Pluronic co-polymer, water and hydrochloric acid. Mo-HPA (0.3970 g) and W-HPA (0.3065 g) were used to prepare composites containing 0.5 mol% W-HPA and 1 mol% Mo-HPA. The amount of HCl in solution was adjusted to maintain pH $\approx$ 1. The calcination temperature of composite samples was kept below 723 K in order to avoid decomposition of heteropolyacids.

Sol–gel silica and HPA/silica composites were prepared as described in [11]. In a typical synthesis 4.62 g TEOS was dissolved at 353 K in a mixture of 2.753 g of ethylene glycol and 2.67 g of ethanol while stirring. The calculated amount of heteropolyacid, yielding 20 and 50 wt.% composites, was added to the solution. After stirring for 1 h, a mixture of 8 g ethanol, 2 g water and a catalytic amount of acetic acid was added to the solution. The solution was kept at 353 K under stirring until a clear transparent gel was obtained, typically after 3 h. The resulting gel was aged at ambient conditions for 24 h and dried under vacuum at 413 K for 3 h, followed by calcination in flowing oxygen at 723 K for 6 h. The calcination temperature was ramped from ambient to 723 K at 1 K/min.

2.2. Preparation of supported heteropolyacids

W-HPA and Mo-HPA were obtained from Fischer and purified by re-crystallisation prior to impregnation. Supported acids were prepared by adsorption from ethanol–water solutions (1:1 volumetric ratio of demineralised water and 96 wt.% ethanol) as described previously in [14]. Gently stirred samples were equilibrated for 72 h at ambient temperature. The amount of acid adsorbed was evaluated gravimetrically. Sibunit samples were dried in vacuum at 473 K for 2 h following impregnation. Samples of Novacarb, SBA-15 and sol–gel silica were dried in air at 473 K for 2 h. A list of prepared samples and characterisation results is shown in Table 1.

2.3. Materials characterisation

Low temperature nitrogen adsorption experiments were performed using a Micromeritics ASAP-2010 volumetric system. Scanning electron microscopy (SEM) images were obtained using a JEOL 6310 system. Fourier-transform infrared (FT-IR) spectra were recorded using a Bruker Equinox 55 instrument in transmission mode (KBr pellets) and ATR mode (with a Golden Gate^{TM}, Specac, cell), using an MCT-A detector and resolution of 4 cm^{-1}. Powder X-ray diffraction (XRD) patterns were measured using a Bruker D8 powder diffractometer with Goebels mirrors.

2.4. Ammonia adsorption experiments

Breakthrough curves of ammonia were recorded using a custom-built setup equipped with a thermal conductivity detector (TCD). U-shaped quartz reactors of 10 and 5 mm ID were used. Sample of 0.3 g were loaded into a reactor with quartz beads and treated in flowing nitrogen at room temperature for approximately 2 h until a stable TCD signal was observed. The breakthrough curve was then recorded. In a typical experiment 2.1 vol.% ammonia in nitrogen and 70 ml/min flow were used. Total equilibrium ammonia uptake was calculated by integration of the breakthrough curves, less the free-volume of the reactor.

Table 1
Characterisation data for the supports and impregnation acids

	Starting solution (g[W]/l)	Starting solution (g[Mo]/l)	HPA loading (wt.%)	S_{BET}[a] (m^2/g)	Mesopore volume[b] (cm^3/g)	Micropore volume[c] (cm^3/g)	Equilibrium NH_3 sorption (mmol/g)
Novacarb	0	–	–	522.1	0.52	0.18	0.22
	–	110	20				1.37
	120	–	24	359.4	0.35	0.12	0.96
Novacarb brominated	0	0	–				0.56
	–	110	19				2.30
	120	–	16				–
Sibunit	0	0	–	286.1	0.23	0.02	0.05
	–	110	19				0.35
	120	–	22	149.1	0.17	0	0.47
SBA-15	0	0	–	321.1	0.38	0.01	0.89
	–	110	16	522.4	0.64	0.05	–
	120	–	16	421.9	0.52	0.04	1.67
SBA-HPA composite	–	–	0.5[d]				
	–	–	1.0[d]				
SiO_2–W-HPA composite	0	0	20				2.11
SiO_2 sol–gel	0	0	–	381.4	0.15	0.03	0.85
	–	110	33				1.29
	120	–	35	240.1	0.10	0.03	1.00

[a] Measured by nitrogen adsorption at 77 K.
[b] Calculated from desorption branch of isotherms using BJH method.
[c] Calculated using *t*-plot method.
[d] Expressed in mol%.

3. Results and discussion

3.1. Novacarb

Amongst the four support materials used, Novacarb shows the highest BET surface area at 522 m^2/g and mesopore volume 0.52 cm^3/g (see Table 1). This comparison is made between the pure support materials: the Mo-HPA impregnated SBA-15 exhibits higher BET surface area and mesopore volume. Novacarb also exhibits appreciable microporosity. This is clearly seen from the relatively high amount adsorbed at low relative pressures on the nitrogen adsorption isotherm (see Fig. 1). The mode of the pore-size distribution in the mesopore range for Novacarb is ca. 17.4 nm (see Fig. 2). The equilibrium loading of HPAs on Novacarb is ca. 20 wt.%. Reduction in the mesopore and micropore volumes after impregnation indicates that some W-HPA molecules are adsorbed in the microporous structure of Novacarb. However, the majority of the acid is located in the mesopores. According to the FT-IR data, the Keggin anion structure of W-HPA is retained upon adsorption on Novacarb (see Fig. 3). The fingerprint bands of the W-HPA Keggin anion at 795, 893, 983 and 1081 cm^{-1} are clearly seen on the spectrum of the supported acid.

The total equilibrium uptake of ammonia on pure Novacarb is relatively high. However, this is likely to be due to physical adsorption in the micropores. The equilibrium uptake of ammonia on the impregnated Novacarb samples corresponds to both reversibly, and irreversibly, adsorbed ammonia. This amount is slightly higher than could be expected from a simple sum of ammonia adsorbed by the support plus the total amount of ammonia adsorbed by the heteropolyacid. Vedrine and coworkers [6] have estimated that the total, reversible plus irreversible uptake of ammonia by W-HPA is about 7.7 molecules per Keggin anion, which in our case should give approximately 0.86 mmol/g of total uptake. Given that the accuracy

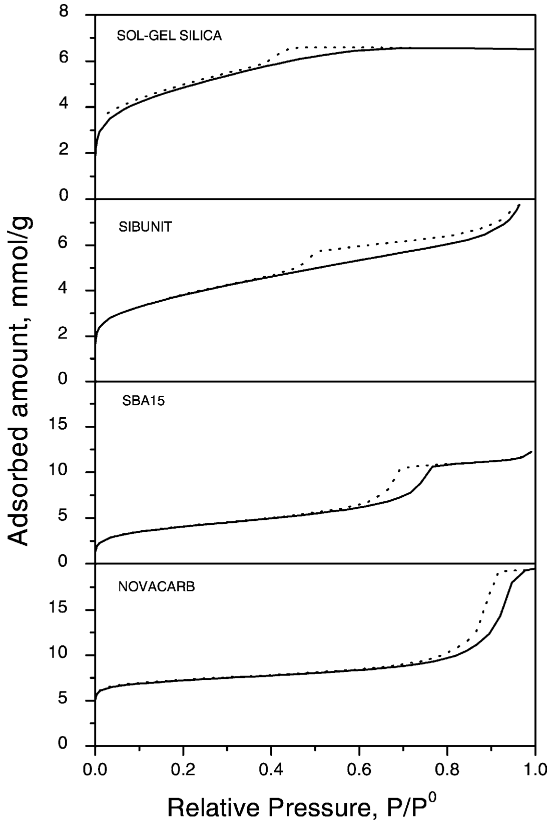

Fig. 1. Nitrogen adsorption–desorption isotherms measured at 77 K.

of gravimetric measurements of HPA loading is quite low, this agreement between the data is very reasonable.

The brominated Novacarb was prepared in order to modify the surface chemistry of carbon. Halogenation of carbon surfaces is used to increase the hydrophobicity of carbon surface, thus altering interaction with polar substances, as well as prevent ageing (oxidation) of carbon surface (see, e.g. [15]). Bromination should result in the formation of fairly labile C–Br bond, and may potentially influence interactions between carbon and heteropolyacids.

The FT-IR spectra of brominated Novacarb shows a band at 1400 cm^{-1}, an increased band at 1709 cm^{-1} and a broad band with a maximum at 1035 cm^{-1}, in comparison to the spectra of the parent Novacarb sample (see Fig. 3). The band at 1577 cm^{-1} present in both samples could be assigned to C=O groups of surface quinine groups [16,17]. An increase in the band at 1709 cm^{-1} (C=O groups of carboxylic acids or lactones) and 1035 cm^{-1} (C–O stretch in ether groups) indicate oxidation of carbon during the bromination reaction. Although reaction of bromination was performed in the atmosphere of argon, some oxygen may have been present in the reaction vessel, resulting in slight oxidation of carbon surface. The band at 1400 cm^{-1} is probably due to symmetrical stretching of $-COO^-$. The band for C–Br stretching could be expected in the frequency range of 600–500 cm^{-1} [18], and could not have been registered in our experiments.

The loading of HPAs on brominated Novacarb is slightly lower than that on the untreated support, indicating that bromination does not have any beneficial effect on the adsorption of heteropolyacids. There is a more significant effect of bromination on the ammonia uptake on both the brominated support and the acid loaded brominated samples. This could be attributed to two factors: (i) an increased acidity of carbon surface, indicated by FT-IR results and (ii) a reaction between ammonia and bromine, resulting in the formation of either NH_4Br or more complex adducts. The available experimental data does not permit to elucidate the true nature of the effect and requires more careful examination of the heats of adsorption and desorption of ammonia.

3.2. Sibunit

Sibunit is a mesoporous carbon support prepared by depositing pyrolytic carbon onto carbon black particulates, followed by controlled gasification of defective pyrolytic carbon, but mainly of carbon black [19]. The resulting open hollow shells are formed into granular particles. Preparation of W-HPA supported onto several Sibunit samples is reported in a recent paper [20]. The Sibunit sample used in this work is characterised by lower BET area, lower mesopore volume and smaller pore diameter, compared to most samples used in [20]. The mode of the pore-size distribution for Sibunit was determined to be 4 nm. The morphology of Sibunit is significantly different from that of Novacarb. Sibunit has virtually zero microporosity. The hysteresis of nitrogen adsorption–desorption on Sibunit shows a long plateau on the desorption branch (see Fig. 1). This type of hysteresis may originate from narrow pore necks, whereas the abrupt nature of

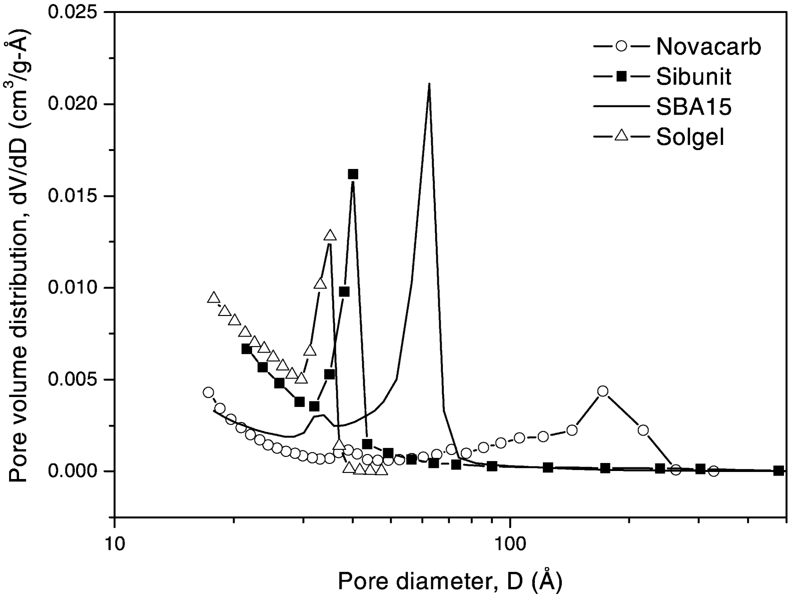

Fig. 2. Pore-size distributions calculated from nitrogen adsorption data using the BJH method.

hysteresis for Novacarb is indicative of a more open-pore structure.

The amount of HPAs adsorbed onto Sibunit is similar to that in the case of Novacarb. The maximum HPA loading found in this work is lower than that in [20]. However, these results cannot be compared directly due to the differences in the solvent and the concentration of the starting HPA solutions used in the two studies. An ethanol–water solution with the maximum concentration of acid ca. 120 g[W]/l was used in this study, whereas Likholobov et al. [20] used a methanol solution and 150 g[W]/l acid concentration.

Pure Sibunit adsorbs very little ammonia. This is due to the absence of microporosity and, possibly, due to lower surface functionality. The total ammonia uptake registered for the HPA loaded Sibunit is also quite low. Using the data of Vedrine and coworkers [6], the total ammonia uptake on samples with this HPA loading could be estimated to be ≈0.5 mmol/g. The low ammonia uptake observed for HPA impregnated Sibunit is possibly due to the strong interaction between HPA molecules and the carbon surface. This is supported by the data that between 12 and 25% of total HPA loading is irreversibly adsorbed onto Sibunit [20].

3.3. SBA-15

Fig. 4 shows the SEM images of synthesised SBA-15 mesoporous silica. The larger magnification image clearly shows hexagonal particles organised into rope-like structures, which are further agglomerated into elongated particles of length of the order of 0.1 μm. Similar structures were reported in earlier papers on SBA-15 [13,21]. The material synthesised in this work is characterised by a BET surface area of 321 m^2/g, which is low compared to literature data. However, the shape of the nitrogen adsorption–desorption hysteresis (see Fig. 1) is characteristic of a narrow pore-size distribution in the mesopore region [22]. The mode of the pore-size distribution was found by the Barrat–Joyner–Halenda (BJH) method to be 6.3 nm and the mesopore volume was determined as 0.38 cm^3/g. The hexagonal structure of synthesised SBA-15 was confirmed by recording the XRD patterns (see Fig. 5). The *d*-spacing of (1 0 0) planes in pure SBA-15 is 9.4 nm.

Apart from pure SBA-15 materials, two composite materials with HPAs were synthesised in an attempt to incorporate HPA anions into the walls of mesoporous silica. At high HPA concentrations in the synthesis

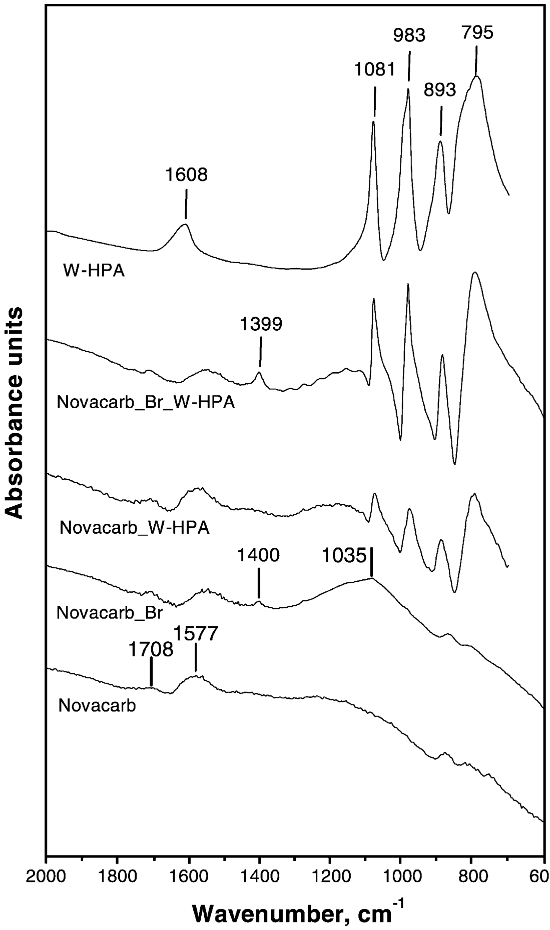

Fig. 3. FT-IR spectra of pure W-HPA, Novacarb, brominated Novacarb and Novacarb impregnated with W-HPA.

solution both acids react with Pluronic surfactant. Therefore, only very small concentrations of HPAs could be used, resulting in 0.5 mol% W-HPA/SBA and 1.0 mol% Mo-HPA/SBA composites. According

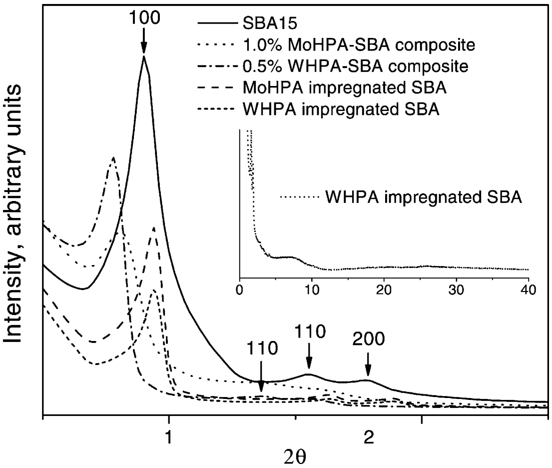

Fig. 5. XRD patterns of SBA-15, 1.0% Mo-HPA/SBA composite, 0.5% W-HPA/SBA composite, Mo-HPA impregnated SBA-15 and W-HPA impregnated SBA-15.

to the XRD patterns for the composite materials, diffraction from (1 0 0) planes is shifted to lower 2θ angles, indicating an increase in *d*-spacing, possibly due to swelling of the surfactant micelles arising from the strong interaction between the HPAs and surfactant. At the same time the lower intensity diffraction from (1 1 0) and (2 0 0) planes appear as broad peaks, indicating the loss of long range order.

Impregnation of heteropolyacids onto pure SBA-15 resulted in an increase in BET surface area and meso- and micropore volumes, compared to those of pure SBA-15 (see Table 1). The XRD spectra of SBA-15 impregnated with W-HPA and Mo-HPA reveal a shift of the pattern to larger 2θ angles, i.e. a decrease in *d*-spacings. This is probably due to restructuring of silica during the step of adsorption of HPAs from water–ethanol solution. The XRD spectra showed no

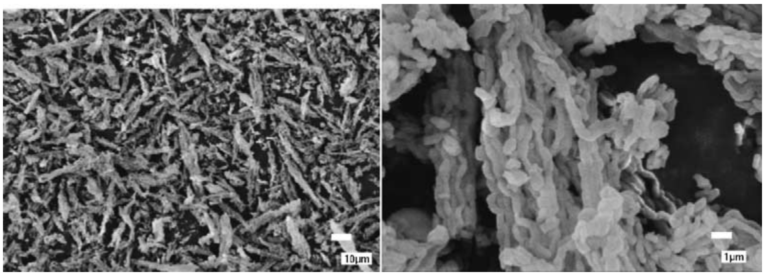

Fig. 4. SEM images of calcined SBA-15 at two magnifications.

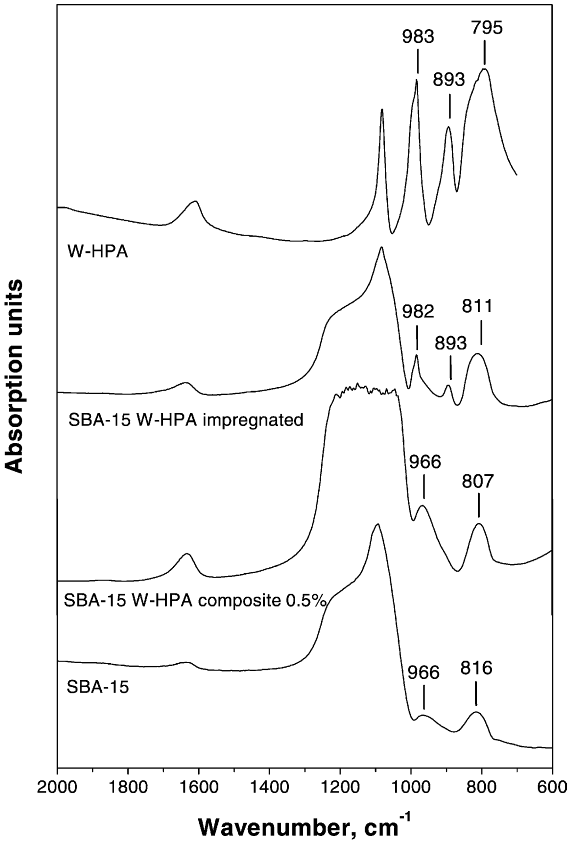

Fig. 6. FT-IR spectra of pure SBA-15, SBA-15 HPA composite and SBA-15 impregnated with W-HPA.

pattern of crystalline HPAs [23] (see inset of Fig. 5), which is probably due to (i) too low a quantity of heteropolyacid for detection, (ii) molecular distribution of heteropolyanions or (iii) too small crystallites of HPA for detection. However, the FT-IR spectrum of the W-HPA impregnated sample (see Fig. 6) clearly shows the fingerprint bands of the Keggin anion, which indicates that the heteropolyacid structure is preserved upon impregnation.

The total equilibrium uptake of ammonia by pure SBA-15 is considerably higher than that of the carbons. This is likely to be due to the acidity of silica itself, as mesopore and micropore volumes of SBA are lower than those for carbon. The total uptake of ammonia by W-HPA impregnated SBA-15 is higher than could be expected from analogous considerations as applied to carbons. However, as was demonstrated in [8], the acidity of the HPA/MCM-41 system depends on acid loading and exhibits maxima at ca. 23 wt.% HPA loading. It is feasible that a similar phenomenon is present in the case of HPA/SBA-15 system and is responsible for the high uptake of ammonia.

3.4. Sol–gel SiO_2

Pure sol–gel SiO_2 was synthesised according to a literature recipe [11]. This material is characterised by a relatively low mesopore volume 0.15 cm^3/g compared to both carbons and SBA-15, but it has a higher micropore volume than SBA-15 and Sibunit. The BET surface area of synthesised sol–gel SiO_2 material was found 381 m^2/g, which is higher than that reported in [11]. Due to the morphology of sol–gel derived materials the adsorption–desorption hysteresis exhibits a long plateau on the desorption branch (see Fig. 1). Similar hysteresis was observed in the case of Sibunit. The morphology of the two materials can probably be described by the spherical pores with narrow opening, which is responsible for long desorption hysteresis.

Similar to the results obtained in [11], impregnation of HPAs results in a decrease in BET surface area. Comparison between the relative changes in the mesopore and micropore volumes of pure support and impregnated support indicates that all the HPA is located within mesopores.

The total equilibrium uptake of ammonia by the pure SiO_2 support is very similar to that of SBA-15 despite the differences in morphology, which indirectly supports our hypothesis that the acidity of silica itself might be responsible for the uptake of ammonia. However, the amount of ammonia uptake by the impregnated samples is considerably lower than that on SBA-15 and similar to the uptake by samples of Novacarb with a much lower HPA loading.

A significantly higher ammonia uptake was measured on the sample of W-HPA/SiO_2 composite containing 20 wt.% acid. This result seems to be in contradiction to the conclusions obtained in [11] that HPA/SiO_2 sol–gel composites have lower acidity compared to the impregnated samples. It was concluded in [11] that after calcination at 723 K the Keggin anion of W-HPA in the composite material is decomposed. However samples containing 20% W-HPA were shown to have catalytic activity in the reaction of 1-butene isomerisation. The FT-IR spectra

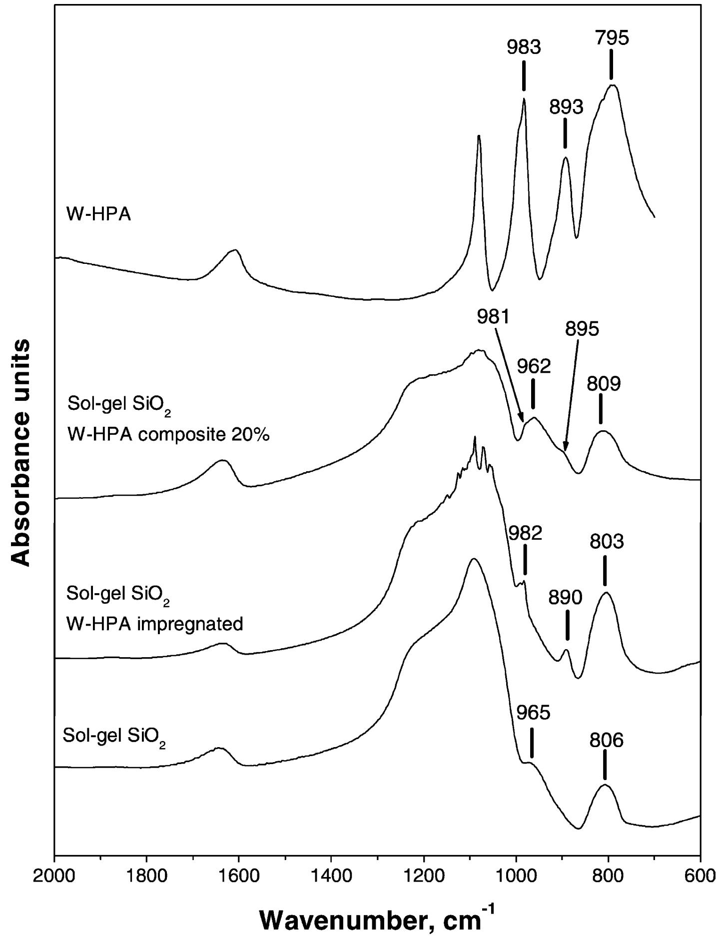

Fig. 7. FT-IR spectra of pure sol–gel derived SiO_2, SiO_2–W-HPA composite and SiO_2 impregnated with W-HPA.

of 20% W-HPA/SiO_2 composite sample does not show clearly resolved W-HPA bands (see Fig. 7). However, weak shoulders at 980 and 895 cm^{-1} are likely to be due to the W-HPA bands at 983 and 893 cm^{-1}, respectively. The bands of heteropolyacids at 1081 and 795 cm^{-1} are masked by stronger absorption of silica at the same wavenumbers. Therefore, the Keggin structure of the acid seems to be at least partially retained. However, at this stage there is no sufficient data to explain why W-HPA/SiO_2 composite material shows such a high ammonia uptake.

It is useful to provide a comparison of the adsorption capacity of materials prepared in this study with that of conventional adsorbents. However, equilibrium uptake, although an important parameter, is not the key function for the specific application in the air purification in clean rooms. Therefore, it would not be possible to make selection of the best material for this specific application based on this information alone.

A recent systematic study of ammonia adsorption on a number of adsorbents [24], aimed at developing adsorbents for a pressure swing adsorption process of separation of ammonia, provides some data for comparison. Thus, in this study the highest ammonia uptake ca. 2.3 mmol/g, at the partial pressure of ca. 2.1 kPa, was measured on the brominated sample of Novacarb impregnated with Mo-HPA acid. At a similar pressure, the highest ammonia uptake ca. 6.7 mmol/g was reported on microporous synthetic zeolite 13X with the mean pore diameter of 0.85 nm and BET surface area of 430 m^2/g [24]. Ammonia uptake on a mesoporous silica–gel (ca. 1.68 mmol/g) with the mean pore diameter of 10 nm and BET surface area of 238 m^2/g was considerably higher than that on the sol–gel derived silica prepared in this work (0.85 mmol/g).

4. Conclusions

Four different mesoporous supports were impregnated with tungstophosphoric acid $H_3PW_{12}O_{40}$ (W-HPA) and molybdophosphoric acid $Mo_3PW_{12}O_{40}$ (Mo-HPA). Characterisation of the morphology of supports showed that mesoporous synthetic carbon Novacarb^{TM} and template-derived mesoporous silica SBA-15 have relatively narrow pore-size distributions and open porous structures, whereas mesoporous carbon Sibunit^{TM} and sol–gel derived SiO_2 both have bottle-neck type pores.

Between the two mesoporous carbons, the open-pore morphology and larger pore size of Novacarb seem to be beneficial for ammonia uptake. Between the two silicas the impregnated samples show comparable performance in ammonia uptake, although SBA-15 showed slightly higher uptake. It was shown that inclusion of heteropolyacid molecules into the SBA-15 framework results in a significant loss of structure, even at very small concentrations of HPAs. At the same time, the incorporation of HPAs into HPA/SiO_2 composites via the sol–gel technique seems to give a material with the highest total ammonia uptake amongst the materials studied. This phenomenon could not be explained in this study without further characterisation.

Further study is under way to characterise the performance of these materials in the removal of ammonia and amines from air streams at very low concentrations. These results, as well as results on ammonia TPD and regeneration of heteropolyacid based chemisorbents will be presented in a forthcoming paper.

Acknowledgements

This work was funded by the Engineering and Physical Sciences Research Council via grant GR/R18697/01. AL is grateful to Steve Tennison, MAST Carbon, for providing carbon support materials and for many useful discussions.

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