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DSC STUDY OF CHEMICALLY MODIFIED POROUS SILICA POWDERS

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ABSTRACT

Differential Scanning Calorimetry was used to characterise silica samples following their reaction with n-octylmethyldichlorosilane by means of the fluidised bed technique. It was found that the observed thermal effects varied with the progressive increase in octylsilyl groups bonded into the silica surface in a regular manner.

INTRODUCTION

The fluidised bed technique for the preparation of chemically bonded reversed phases for use in High Performance liquid Chromatography (HPLC) has been described previously [1]. Stepwise silanisation and hydroxylation of porous silica gel with n-octylmethyldichlorosilane under controlled reaction conditions apparently produces a dense-layered C8 chemically bonded stationary phase. The chromatographic properties of these phases have been studied for a variety of solutes [2]. The aim of this study was to determine whether DSC could be used to characterise the modified silica surfaces.

EXPERIMENTAL

Samples were prepared to contain various loaodings of octylsilyl bonded phases [2]. Elemental analysis of the bonded phases was

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performed at the University College Microanalysis Laboratory, London.

For the DSC investigation the Perkin-Elmer DSC7 system was used. Samples (1 mg) were heated in an atmosphere of pure oxygen (flowrate about 40 cm^3/min) in uncovered Aluminium crucibles. An empty pan was used as the reference. Samples were heated in the tempoerature range 140 to 300°C with a heating rate of 5°C/min.

RESULTS

Values of the percentage carbon load for the ten samples are given in Table 1. These values show an increase in the carbon load with the reaction step and thus represent an increase in the number of layers of the octylsilyl groups bonded into the silica support. A plot of reaction step number against the carbon load (Fig. 1) gave a linear relationship after the third step. This observation has been discussed fully in a previous paper [2].

TABLE 1
Carbon load (in % W/W) for ten recation steps

Reaction step number	1	2	3	4	5	6	7	8	9	10
Carbon load (% W/W)	7.58	9.69	11.14	12.28	12.69	14.43	14.90	15.80	16.79	17.45

Fig 1

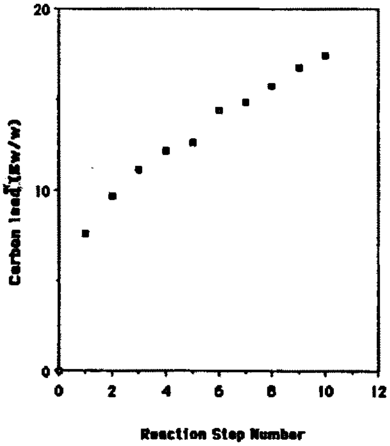


Fig. 1 - Carbon load (in % W/W) as a function of the reaction step.

Fig 2

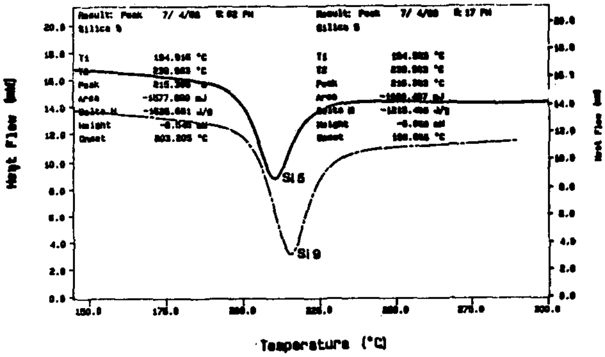


Fig. 2 - DSC curves of silica after stepwise silanisation (Si 5 and Si 9, 5 and 9 treatments with n-octylmethyldichlorosilane, respectively)

In all the ten samples studied a single exothermic peak was observed where the average onset temperature was 200°C and the peak maximum occurred at 211°C (Fig. 2). Peak area and enthalpy change were calculated using the PE 7700 computer and the following variations were found:

- the peak area increased in a linear manner with the reaction step number (Fig 3) which corresponds to an increase in carbon load on the silica surface,
- the enthalpy changes also varied linearly with the percentage carbon load on the bonded phase as shown in Fig. 4.

Fig 3

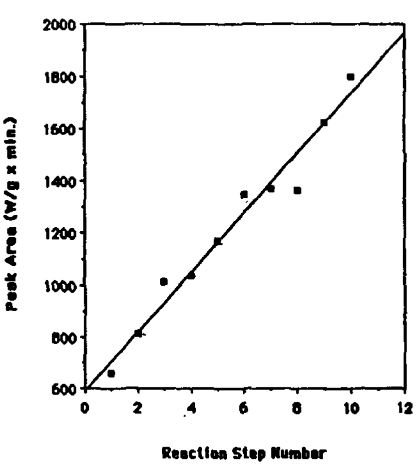


Fig 4

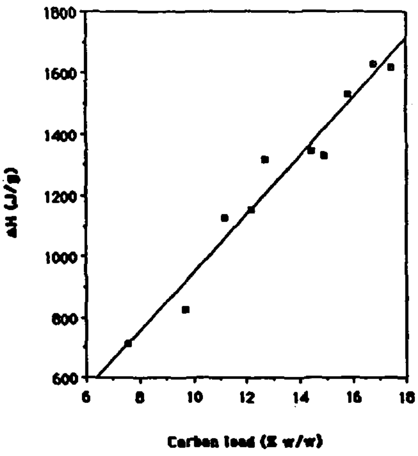


Fig. 3 - Area of DSC peak (in W/g x min) as a function of the reaction step.
Fig. 4 - Enthalpy change (in J/g) as a function of the carbon load.

Fig 5

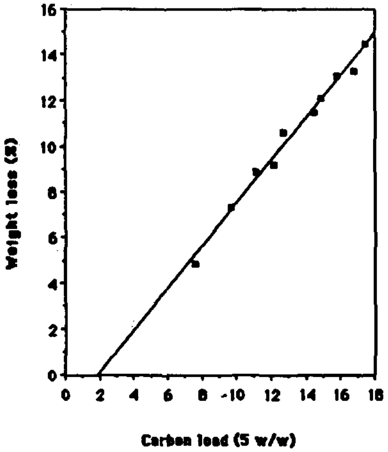
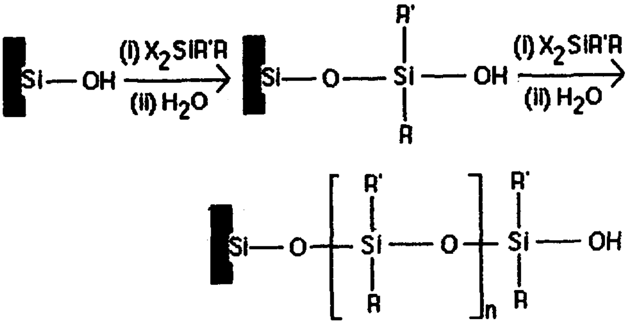


Fig. 5 - Weight loss (in %) as a function of carbon load.

- the percentage weight loss obtained by weighing the samples before and after heating increased gradually after the third step with the reaction step number and hence the carbon load (Fig. 5).

DISCUSSION

The reproducibility of the exothermic effect for the chemically modified silica indicates that this reaction is due to the oxidative degradation of the octylsilyl groups which are attached to the silica surfaces via siloxane bonds in the following manner:



$$\mathrm{Si{-}OH} \xrightarrow[\text{(II) } H_2O]{\text{(I) } X_2SiR'R} \mathrm{Si{-}O{-}}\overset{R'}{\underset{R}{Si}}\mathrm{{-}OH} \xrightarrow[\text{(II) } H_2O]{\text{(I) } X_2SiR'R}$$

$$\mathrm{Si{-}O}\left[\overset{R'}{\underset{R}{Si}}\mathrm{{-}O}\right]_n\overset{R'}{\underset{R}{Si}}\mathrm{{-}OH}$$

where X = Cl, R' = CH_3, R = $CH_3(CH_2)_7$ and n = 0, 1, 2, ---- depending on the number of the reaction steps.

The linear dependence of the exothermic reaction, as shown by the peak area/enthalpy/weight looss measurements, on the carbon loading of the silica surfaces makes its valuable indicator of the number of layers of the organic groups attached to the surface.

Further work will be carried out to determine H values for the oxidation of known alkoxysilane groups. This will assist in not only understanding the H values obtained in the present study but also in determining the size and nature of the functional groups attached to the silica matrix. Hence the H values could be used as a quality control test on commercially available reversed phases.

CONCLUSIONS

DSC studies of chemically modified silica samples under oxidising conditions have demonstrated that it is possible to characterise the samples and further work involving the calibration of H values will define the exact nature of the functional groups present.

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