Reversible adsorption of perfluorocarboxylic acids by chemically modified surfaces

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Attempted derivatisation of ω-aminopropyltrimethoxysilated Aerosil-200 with perfluorocarboxylic acids leads to a complex surface architecture involving both the amide and the perfluorocarboxylate–ammonium salt pair which can be reversibly bound.

Chemically modified silica gels are widely used in chromatography, heterogeneous catalysis and as reagents for the removal of metal ions. Bonded ω-aminoalkyl groups are among the most common surface groups and these can easily be introduced by treatment of the material with ω-aminoalkyltrialkoxysilanes.[1,2] Subsequent derivatisation of the amino groups can lead to various interesting and useful surface functionalities. It has been reported, for example, that various thermally stable aliphatic and aromatic acids will react directly with ω-aminoalkylsilicas at elevated temperatures under vacuum without the need for solvent.[3] As part of our research on chemically modified silicas[4] and on fluorinated materials,[5] we have used this methodology to prepare silica-based materials with surface-bound close-packed perfluorocarbon groups in which there is considerable interest especially in the context of low-energy surfaces.[6–8] This is a good example of clean synthesis since it avoids the use of solvents. Remarkably, we have found that a stable surface architecture is generated based on both the expected perfluorocarboxylic amide and the intermediate alkylammonium perfluorocarboxylate that seems to be independent of the perfluoroalkyl chain length. The latter can be selectively decomposed thermally to leave a simple surface amide which can readsorb fresh perfluorocarboxylic acid to reform the original surface structure.

Aminopropylsilica (AMPS) was prepared from aerosil (nonporous amophous fumed silica, 180 $m^2 g^{-1}$ surface area by BET N_2 adsorption) by reaction with aminopropyltrimethoxysilane in toluene *via* triethylamine catalysis, followed by thorough toluene washing and air curing at 110 °C as described elsewhere.[1] The resulting material has a loading of organic groups of *ca.* 1.0 mmol g^{-1} (by elemental analysis) and a surface area of 140 $m^2 g^{-1}$ corresponding to a surface coverage of *ca.* 4.3 molecules per nm.[2] All of the residual trimethoxysilyl groups have been hydrolysed (by FTIR and ^{13}C CP MAS NMR). The AMPS (1 g, 1 mmol of NH_2) was then ground together with a fivefold excess (relative to N on the surface) of various perfluorocarboxylic acids, R_FCO_2H (R_F = C_7F_{15}, $C_{11}F_{23}$, $C_{15}F_{31}$) and the mixtures were placed in a vacuum pistol and slowly heated from 20 to 130 °C under a vacuum of 0.2 mbar, and finally left at 130 °C for 16 h. The resulting materials were then washed with acetone to remove any unreacted acid, and dried in air. Diffuse reflectance FTIR of these materials show broad carbonyl bands centred at 1680 cm^{-1} with shoulders on the high wavenumber side. The rest of the spectra are difficult to resolve but strong absorbances in the 3500–2500 cm^{-1} region are apparent, presumably due to hydrogen-bonded NH and OH stretching modes. *In situ* heating of the materials results in a marked change at 200–300 °C with the carbonyl stretching regions reduced to single bands at *ca.* 1720 cm^{-1} and a complete loss of activity at *ca.* 1680 cm^{-1}. There is also a reduction in the intensity of the broad OH/NH stretching bands in the region < 3000 cm^{-1}. The appearance of two bands at 3375 and 3200 cm^{-1} indicates a regeneration of some free NH_2 groups. The positions of the single carbonyl bands after heating the materials correspond very closely to those of the unsupported perfluorocarboxylic amides and the bands at *ca.* 1680 cm^{-1} are consistent with perfluorocarboxylate salts. Simultaneous thermogravimetry–evolved gas FTIR of the $C_7F_{15}CO_2H$-treated material (as an example) shows a mass loss at *ca.* 230 °C due to evolution of CO_2 and a highly fluorinated compound (probably $C_7F_{15}H$). Further heating results in a second loss of equal mass at *ca.* 420 °C due to evolution of a compound which shows strong CF activity but has a more complex IR spectrum than the fluoro compound evolved earlier. Simultaneous TG–DTA shows that both of these mass losses are enthalpic (Fig. 1). Mass spectrometric analysis of the evolved gases at various temperatures from the perfluorooctanoic acid derived material shows slightly different behaviour. Under vacuum, a fragment derived from loss of $C_7F_{15}CO_2H$ at *ca.* 200 °C is now evident. The next intense section of ions observed at *ca.* 430 °C corresponds to a compound with a highest *m*/*z* of 454 [$C_7F_{15}CONH(CH_2)_3^+$]. It can also be noted that the independently prepared salt $C_7F_{15}CO_2NPr^nH_3$ decomposes at 250 °C, close to the temperature of the first mass loss observed from the analogous fluorinated material.

An alternative route to the perfluorocarboxylic amide derivatised silica would be to react the AMPS with the appropriate acid chloride (although in the absence of an HCl scavenger this can only be expected to be 50% efficient at best due to the concomitant formation of chemisorbed propylammonium chloride). In this way we prepared the perfluorooctyl-derivatised material which gave only one major mass loss at *ca.* 430 °C along with a weaker peak at 200 °C due to the propylammonium chloride.

The thermal desorption and evolved gas analysis results are consistent with a complex surface structure involving the expected amide and the intermediate alkylammonium salt.

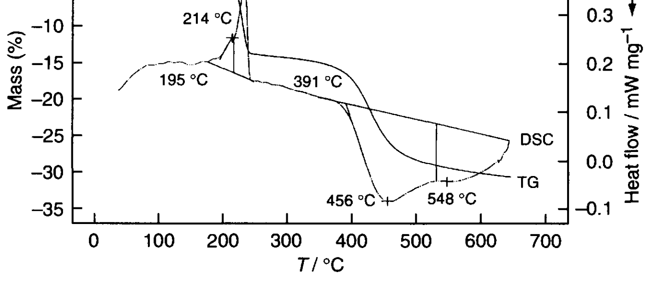

Fig. 1 TG–DSC trace of perfluorocarboxylic acid-derivatised aminopropylaerosil: (*a*) thermogravimetry trace, (*b*) differential scanning calorimetry trace

Heating of this material releases the more loosely held salt before the chemisorbed amide is destroyed. The partially amide-derivatised silica (prepared by heating the complex material to remove the perfluorocarboxylic acid) is actually slightly less easily wetted by surfactant solution (2% aqueous sodium dodecyl sulfate) than the complex material. It has also been found that the former material readsorbs fresh perfluorocarboxylic acid on mixing and heating as in the original preparation. In this way the spectral and thermal characteristics of the complex material are restored. It is interesting to note that attempts to prepare similar materials based on the analogous hydrocarbon carboxylic acids always gave the simple amide-derivatised material only.

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