SYNTHESIS OF SOL-GEL AND GEL-BASED MATERIALS AND THEIR USE FOR ADSORPTION OF ORGANICS

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Abstract. The development of mesoporous silicas containing organic functionality via templated sol-gel methodology has led to a great deal of interest, primarily as catalysts, but also in applications such as adsorbency.

It is possible to prepare materials with a mechanically stable silica backbone, with mesopores having narrow pore size distribution, and which can be coated with a wide range of functionality. They are promising adsorbents due to their controllable surface chemistry and their significant pore volumes.

We have also demonstrated that starch can be expanded to give a gel, which can be converted to a novel range of mesoporous carbons, with tuneable surface functionality, high surface area and good pore volume.

They display remarkable catalytic activity (for example, they can completely esterify succinic acid in *aqueous* environments). We believe that this unusual behaviour can be related to their adsorbency properties.

We present details of the properties of these materials, as well as preliminary results on their ability to adsorb a range of compounds.

Keywords: Mesoporous silicas, starch, starbon, mesoporous carbon, surface chemistry, adsorbency, organics.

1. Introduction

The synthesis of silicas with controlled regular porosity, high surface area has led to an explosion of interest in their use, primarily as catalysts, but also in many other applications such as sensors and as hosts for nanoparticles.[1]

It is well known that the rate of catalysis of liquid phase reactions with solid catalysts such as mesoporous silicas can depend not only on the intrinsic

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reaction step(s) but also on adsorption/desorption of reactants and products to/from the active site. Therefore, it is not only important to provide the silica with catalytically active sites, but also with the appropriate surface properties for the reaction. These may include modification of the polarity of the surface to improve adsorption/desorption processes, by the inclusion of second "spectator" groups, which are themselves devoid of catalytic activity. Given that such processes can deliver significant (order of magnitude in some cases) improvements in catalytic activity,[2] it seems reasonable that the same materials and the same approach might be used to adsorb organic species from solution.

2. Experimental

Materials were prepared by standard procedures.[6,7,9] Adsorbency experiments were carried out by stirring the adsorbent with the desired compound in distilled water at 298 K for 16 h, unless stated otherwise. The quantities adsorbed were determined by centrifugation and UV-vis analysis of the supernatant.

3. Results and Discussions

3.1. SYNTHESIS OF ORGANICALLY MODIFIED SILICAS

The basic templated synthesis of silicas, involving $(EtO)_4Si$ (TEOS), a micelle forming system such as a long chain amine, a quaternary ammonium salt or a block copolymer, and water can be carried out to give the micelle templated silica. This can be functionalised with a range of silanes to give surface organic groups (Figure 1a).

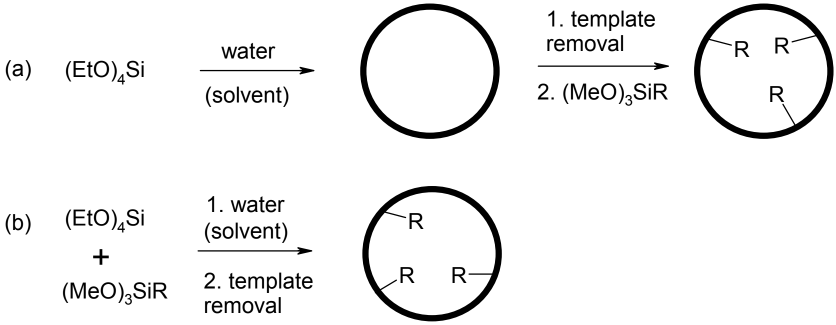

Figure 1. The two major routes for the preparation of organically modified micelle templated silicas. In route (b) it is possible to add more than one functional silane.

A shorter alternative incorporates the functional silane directly in the synthesis. This leads to organically functionalised silicas in one stage. (Figure 1b) The loading of groups is controlled by variation in the ratio of TEOS: organosilane; up to ca. 10–20% is possible, while preserving the templated structure, depending on the silane. Higher loadings (up to ca. 3.8 mmol g^{-1}) are possible but lead to amorphous materials.

It should be noted that the materials prepared from each of these two routes are not necessarily the same. Differences in behaviour have been noted, which have been ascribed to different distributions of silanes (in-pore vs. external[3]; clustering on hydrophobic patches[4] as opposed to evenly distributed; occluded within walls vs. on the surface[5]).

Template removal is an important consideration, not just from the point of view of green chemistry (recovery and reuse of template) but also because a considerable amount of chemistry can take place in the washing stage. We have found that solvent extraction of template (in our case 1-aminododecane, leading to the HMS series of mesoporous silicas) is successful where the solvent has a significant H-bonding capacity. This disrupts H-bonding interactions between the template head group and the silanols on the surface and allows the template to be removed and reused.[6] Alcohols, acetone and acetic acid are all effective. Importantly, alcohols react with the silanols, possibly catalysed by the amine template, to generate surface SiOR species (Figure 2). Thus, template removal with methanol leads to 3.2 mmol g^{-1} loading of SiOMe, with larger alcohols (up to C_8) still giving >2 mmol g^{-1}. Thermal stability is good – those which can readily eliminate alkenes (e.g. 2-propyl) being lower (ca. 400°C) than those with less stabilised alkene products (e.g. linear alkyl) which decompose at ca. 500°C. Methanol begins to decompose around 700°C via a different mechanism, possibly by elimination of HCHO. Hydrolytic stability of small R groups is relatively low, but larger groups such as hexyl or benzyl give materials of pronounced hydrophobicity, and are water stable, at least at lower temperatures.

A further opportunity to modify the surface of silica materials comes from the possibility of removing template by reaction of the as-synthesised material with a silane. This can migrate into the template-filled pore, cap the silanol and thus disrupt the H-bonding interaction with the template, which can then be readily removed by non-polar solvents such as toluene under conditions where the template would otherwise remain in pore. Functional silanes (i.e. $(MeO)_3SiR$) can be added to attach a second silane to the surface, as can Me_3Si groups to improve hydrophobicity and lower polarity.

In particular, we have recently found that the incorporation of CF_3SiMe_3 directly into the synthesis mixture provides material with exceptional hydrophobicity, far more than more conventional silylating agents such as Me_3SiCl

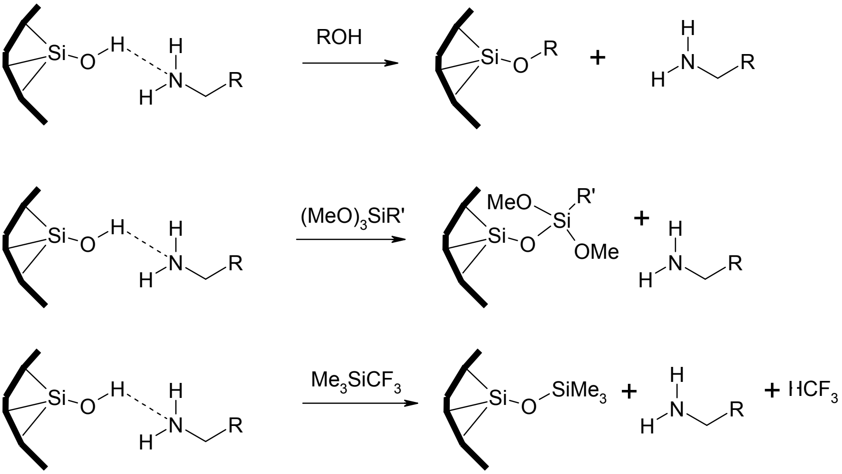

Figure 2. Strategies for reactive template removal.

or $Me_3SiNHSiMe_3$.[7] Thus, it is possible to produce extremely hydrophobic materials directly from an aqueous synthesis gel, without the need for subsequent treatment. Thermal analysis indicates that no water is present on the surface after template extraction (weight loss $\leq 150^\circ C$ is $<0.2\%$)

We have utilised these strategies for the preparation of a series of silica materials with differing surface chemistries, and have applied them to the adsorption of small molecules from water.

The adsorption of phenols from water is a system often studied for adsorption processes.[8] We studied the adsorption of phenol from water at $25^\circ C$ (initial concentration of phenol 1,000 ppm). After 16 h, samples were centrifuged and the supernatant analysed for phenol. The results are given in Figure 3.

The more polar materials are poor adsorbents of phenol, with no adsorption for silica itself or for HMS-Et, which has limited stability in water, and is likely to lose Et groups rapidly. The benzyl system, the most hydrophobic of the alcohol-extracted systems works very well, and surprisingly, the acetone extracted system has some activity. However, the CF_3SiMe_3 system displays excellent activity, adsorbing more than its own mass. Clearly, the best systems allow very effective removal of phenol from aqueous environments into the non-polar pore system.

The more polar benzoic acid was also investigated, and the trend obtained was the opposite, with the more polar materials adsorbing the acid much better than the more hydrophobic systems. It should be noted that the quantities adsorbed were significantly lower in all cases (Figure 4).

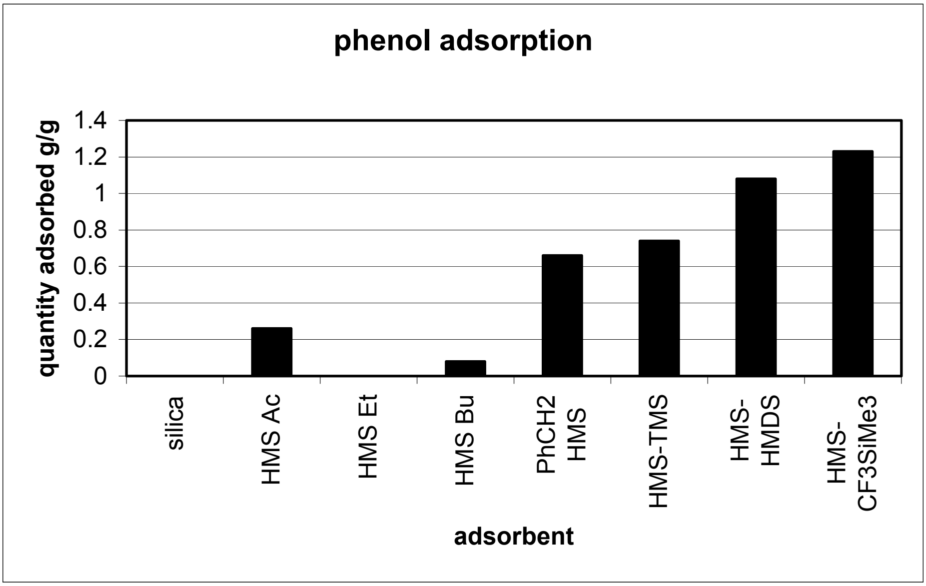

Figure 3. Phenol adsorption over a range of silicas. HMS-Ac – acetone extracted micelle templated silica (no surface functionalisation; HMS-Et (EtOH extracted, 2.4 mmol/g loading of SiOEt); HMS Bu (toluene/1-BuOH extracted, 2.2 mmol/g loading of SiOBu; $PhCH_2HMS$ – micelle templated silica extracted with toluene/$PhCH_2OH$, 2.1 mmol/g loading. The three to the right were synthesised by variations of the bottom route in Figure 2 using Me_3SiCl (TMS), $Me_3SiNHSiMe_3$ (HMDS) and CF_3SiMe_3 respectively.

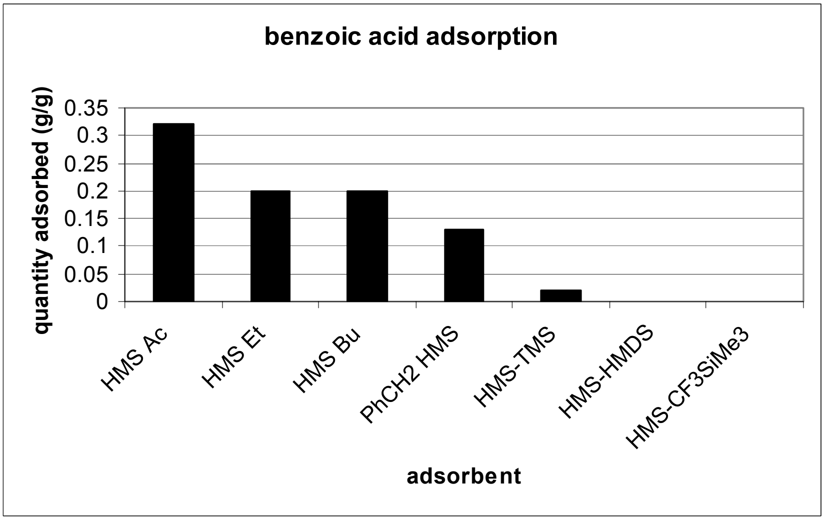

Figure 4. Adsorption of benzoic acid from water with modified silicas.

3.2. STARBONS

Starbons[9] are prepared from starch by expansion and acid catalysed carbonisation. Carbonisation can take place from 200°C to 1,000°C. As this temperature increases the materials are converted from a hydrophilic hydroxylic polysaccharide to a partly carbonised material with carbonyl functionality as well as hydroxylic, through to more aromatic-rich materials. Throughout this process, surface area remains broadly constant at ca. 100–130 m^2 g^{-1} and the pore diameter is also relatively constant at ca. 10 nm.

We have used these materials, in a sulfonated form, as solid acid catalysts for esterifications.[10] Remarkably, they catalyse esterifications in water. Diethyl succinate can be formed from succinic acid and ethanol in water in almost 100% yield. This is invaluable in the valorisation of fermentation-derived feedstocks, where isolation from the broth is expensive and difficult. Organic transformations (especially to water-insoluble products) in situ is an important short-cut to key products.

We believe that the key to this activity is its ability to partition acids (and alcohols) into the pores, to the (partial) exclusion of water, so that catalysis actually occurs in a low-water environment.

Thus, we have looked at the adsorption of acids from water onto starbon. (Figures 5, 6). Since there is a marked dependence of reaction rate on preparation temperature, and since the optimum preparation temperature for succinic acid esterification is 400°C (the materials is designated starbon 400), we studied the adsorbency using 400°C starbon.

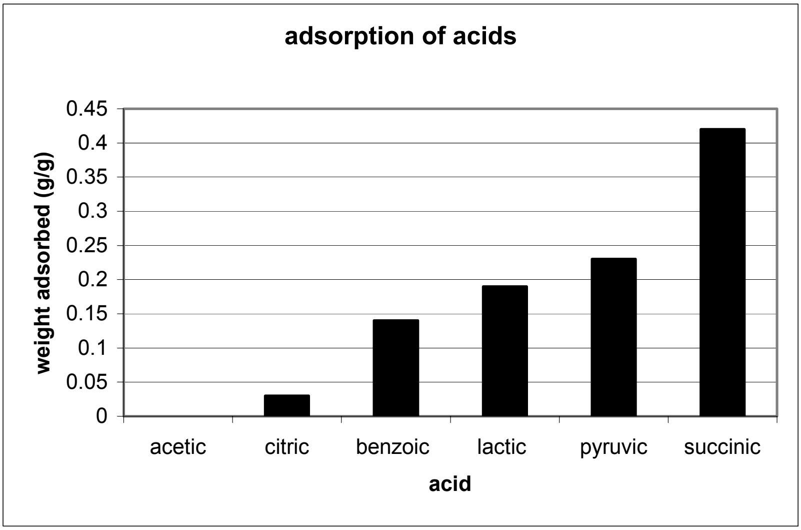

Figure 5. Adsorption of acids from water onto Starbon 400.

Figure 5 shows that succinic acid is adsorbed onto the material more than the others. Succinic acid appears to be less well adsorbed onto other starbons, consistent with the theory that adsorption is a key step in catalysis.

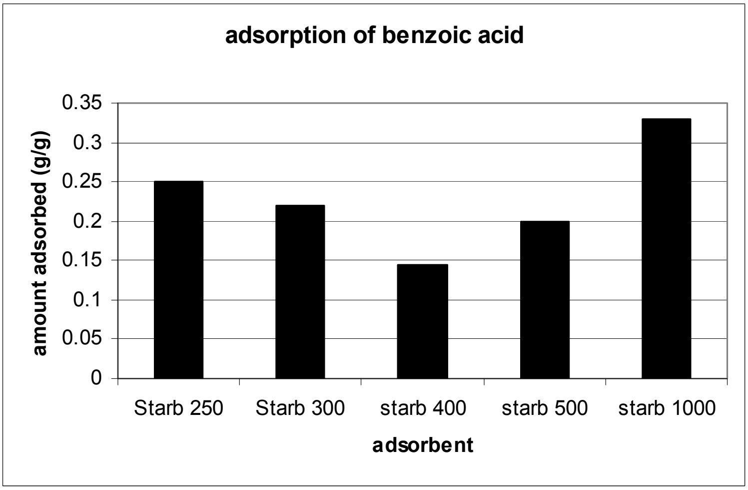

Figure 6. Adsorption of benzoic acid on starbons.

4. Conclusions

Control over surface chemistry can be readily achieved in micelle templated silicas by a combination of in situ synthetic strategies during the sol-gel synthesis of the materials, and appropriate template removal strategies. Materials can be designed to have optimum activity by a combination of appropriate active sites and surface polarity and hydrophobicity modification. Likewise mesoporous carbons can be prepared from expanded starch and thermal treatment, which allows excellent of control over surface chemistry.

Initial results on adsorbency, have shown that appropriately modified materials can display interesting adsorbency effects on simple systems.

Acknowledgements

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