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Core-shell polymer aerogels prepared by co-polymerisation of 2,4-dihydroxybenzoic acid, resorcinol and formaldehyde

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ABSTRACT

DHBARF polymer aerogels were prepared from mixtures containing a fixed stoichiometric amount of formaldehyde (F) and varying proportions of resorcinol (R) and 2,4-dihydroxybenzoic acid (DHBA), with the objective of combining the advantages of high mesopore volume and solids content of RF aerogels with the ion exchange capacity of DHBAF aerogels. The results show that surface area, pore volume, pore size and ion exchange capacity vary in a systematic fashion as the composition of the synthesis mixture is altered. It was found that up to a DHBA mole fraction of about 0.5 preferential phase separation of RF occurred and lead to the formation of primary particles consisting of an RF core and a rough DHBAF shell. When DHBAF and DHBARF aerogels were prepared using the same %DHBA, it was found that the addition of R to the synthesis mixture resulted in increased values of surface area, mesopore volume and mean diameter while simultaneously maintaining the ion exchange capacity of the wet gel. The optimum compromise was found for a DHBARF aerogel with core-shell structure prepared using 5% DHBA and 5% R. Under these conditions the ion exchange capacity was at its maximum value of slightly higher than 2 meq g^{-1}, the surface area was ~850 $m^2\,g^{-1}$, the mesopore volume was ~2 $cm^3\,g^{-1}$ and the mesopore mean diameter was ~17 nm.

1. Introduction

Polymer aerogels have most frequently been obtained by sol–gel polymerisation of formaldehyde (F) and another reactive monomer which, in the majority of work so far published, has been resorcinol (R) [1–5]. A number of papers have also described the preparation of polymer aerogels from alternative co-monomers, including cresols [6–8], melamine [8–11], and polyurethanes [12,13], as well as post synthesis modification with isocyanates as a means to improve the mechanical resistance of the aerogel monoliths [14]. It has also been shown that organic aerogels can be successfully prepared by co-polymerisation of formaldehyde with 2 or more different co-monomers, namely phenol/melamine [15] or phenol/melamine/cresol [8]. Fast microwave synthesis has been developed [16,17] and a review of the patent literature has also been published [18]. Most of these materials do not contain metals. If required these can be introduced by adding salts or complexes to the synthesis mixture [19–23]. An alternative is to introduce ion-exchange properties during synthesis by using a co-monomer containing an appropriate non-reacting functional group. An example is 2,4-dihydroxybenzoic acid (DHBA). The carboxyl group of DHBA does not react during co-polymerisation with formaldehyde and a number of studies have shown that metals, such as Fe, Ni and Cu, can readily be introduced by ion exchange of the wet gel before the supercritical drying step [24–29]. Carbonisation of the metal containing polymer aerogel then results in a carbon aerogel containing metallic nanoparticles which show catalytic activity, for carbon nanotube growth [26], for example, and which can also alter the molecular sieve properties of the carbon aerogel [27].

It might be expected that the amount of metal which can be introduced into the polymer aerogel would be related to its surface area, mesopore volume and possibly mesopore width. The latter are generally lower for DHBAF (2,4-dihydroxybenzoic acid – formaldehyde) aerogels in comparison with RF (resorcinol – formaldehyde) aerogels prepared under similar conditions. Another difference between DHBAF and RF is that the solids content of the synthesis mixture is limited to a maximum of about 20% in the former case, compared to values of at least 50% for RF polymer aerogels. This can be a disadvantage as shrinkage of the gel during supercritical drying is much more significant when the solids content is low.

The objective of the present work was to try to overcome the difficulties mentioned and combine the advantages of higher mesopore volume and solids content of RF aerogels with the ion exchange capacity of DHBAF aerogels, by co-polymerisation of mixtures of resorcinol and 2,4-dihydroxybenzoic acid in the presence of formaldehyde in order to form DHBARF (2,4-dihydroxybenzoic acid – resorcinol – formaldehyde) aerogels.

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2. Experimental

We have prepared polymer gels from mixtures containing a fixed stoichiometric amount of formaldehyde, varying proportions of resorcinol and 2,4-dihydroxybenzoic acid, and a DHBA/catalyst ratio of 100. The gels were prepared under basic conditions. In the present work 2 series of DHBARF aerogel samples were prepared from reaction mixtures containing total solids content, *S*, of 10% or 20%, where $S = 100(m_F + m_R + m_{DHBA})/m_W$, where W is water and *m* is mass. Samples of DHBAF aerogels were also prepared, with solids content of 10% or 20%, as well as RF aerogels with solids content between 4% and 20%. Solids content of 4–20% corresponds to ratios R/W or DHBA/W of approximately 0.03–0.14 and dilution ratios [30] of approximately 12–2. In all cases the aerogels were in the form of small tubes about 1–2 cm in length and about 5 mm in diameter and comparatively rigid. From the weight and dimensions of the tubes, the bulk density was estimated to be approximately 0.1–0.3 g cm^{-3}, in agreement with previously published results for similar aerogels [31].

In a typical procedure 111.2 mmol of DHBA and/or *R* were suspended in 92.00 mL of distilled water and the stoichiometric quantity of K_2CO_3 added to neutralise the acid. The mixture was stirred for 30 min to assure complete dissolution. Subsequently, 8.00 mL of formaldehyde (35% aqueous solution) and 0.0645 g of K_2CO_3 (the catalyst for the polymerisation) was added and the mixture stirred for 24 h at 298 K, during which time a sol formed. At the end of this period, aliquots of 2 mL were transferred to glass tubes which were stoppered and packed into an autoclave which was heated for 72 h at 353 K in a Memmert model EU 200 oven. At the end of this period each tubular hydrogel was transferred to a test tube and covered completely with distilled water. The gels were left for 3 days, with daily exchange of the liquid phase. They were then left for 3 days in 0.1 M hydrochloric acid, 0.1 M iron (III) nitrate or 0.1 M nickel (II) chloride, followed by a further 3 days in distilled water, with daily exchange of the liquid phase in all cases. Finally, the aqueous phase was substituted by acetone during 3 days and the gels supercritically dried in CO_2 using a Quorum Emitech E3000 Jumbo Series supercritical drying apparatus.

After supercritical drying with CO_2 the resulting polymer aerogels were characterised by N_2 adsorption at 77 K using a Quantachrome Quadrasorb automated N_2 adsorption analyser. Prior to determination of the N_2 isotherms the samples were outgassed at 373 K using a Quantachrome Masterprep outgassing station. The N_2 at 77 K isotherms were analysed by the BET and α_s methods in order to confirm that the materials were non-microporous and to calculate their surface areas. The BJH method was used to estimate the total mesopore volume and size distribution.

An estimate of the concentration of free OH groups on the surface of the gels was obtained by preparing suspensions of the metal exchanged gels in 0.1 M NaOH in sealed erlenmayer flasks, leaving to equilibrate at 25 °C for 24 or 48 h, and determination of the excess NaOH by back titration with 0.1 M HCl.

An estimate of the ion exchange capacity of the freshly prepared gels was determined directly by chemical analysis of Fe and Ni, which was carried out by ActaLabs, Canada. We presume that the ion exchange capacity also gives an estimate of the concentration of free CO_2H groups which were present in the wet gel before ion exchange.

3. Results and discussion

3.1. Textural properties

The N_2 at 77 K isotherms determined on the RF and DHBAF aerogels were similar to previously published results [28,32]. For the DHBARF aerogels, representative N_2 at 77 K isotherms and corresponding mesopore size distributions are given in Fig. 1. All of the isotherms were found to be Type IV, but the precise shape of the hysteresis loop and the overall level of uptake varied as the relative amounts of DHBA and R used for the synthesis were varied. The results of the isotherm analyses are summarised in Figs. 2–4, where the values of BET surface area, BJH mesopore volume and BJH mesopore mean diameter are represented as a function of %R for the RF aerogels and %DHBA for the DHBAF and DHBARF aerogels. Results obtained for samples in the H, Fe and Ni forms are not discriminated as very similar experimental results were obtained in each case, indicating that the ion exchange procedure does not significantly alter the inherent structure formed during polymerisation of the gels.

It can be seen from Fig. 2 that for the RF and DHBAF aerogels the surface areas of most samples were in the range of 550–700 $m^2\,g^{-1}$, increasing approximately linearly with increasing % solids in the synthesis mixture. The surface areas of the DHBARF aerogels were generally significantly higher, being in the range 700–900 $m^2\,g^{-1}$ and decreasing as the %DHBA increased. During synthesis phase separation of small primary particles occurs. These may continue to grow and will eventually aggregate to form the characteristic open gel structure. At higher % solids content aggregation will occur while the particles are smaller and the surface area should be higher, as observed with the RF and DHBA aerogels. The higher surface areas of the DHBARF aerogels could therefore be an indication of a greater degree of surface roughness, particularly at lower ratios of DHBA to R.

The results in Figs. 3 and 4 show that the RF aerogels had mesopore volumes and mean diameters of around 2–5 $cm^3\,g^{-1}$ and 15–35 nm, respectively, which are values in the range typical for these materials [29,33,34]. Both mesopore volume and mean diameter decreased linearly with increasing % solids in the synthesis mixture. Similar tendencies were found with the DHBAF aerogels, although the variations were less significant. Of greater significance is that the values of mesopore volume and mean diameter were about 1 $cm^3\,g^{-1}$ and 10 nm, respectively, which are values much lower than those found with the RF aerogels. In the case of

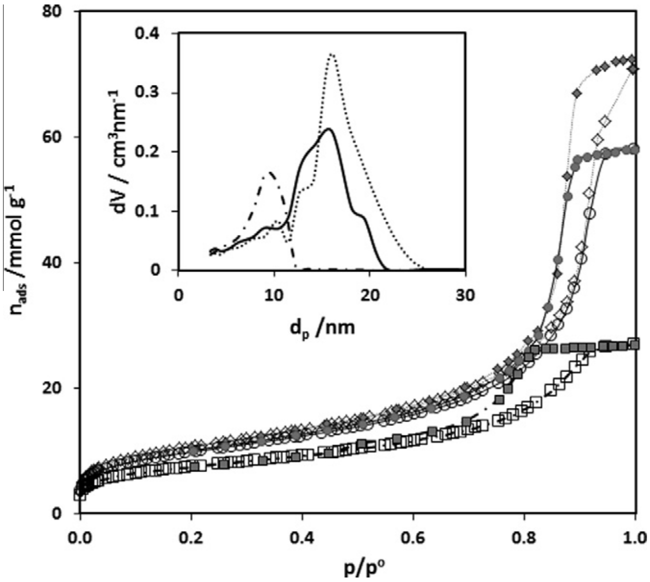

Fig. 1. N_2 at 77 K adsorption isotherms and corresponding BJH mesopore size distributions (inset) determined on Ni exchanged polymer aerogels prepared with varying proportions of resorcinol and 2,4-dihydroxybenzoic acid and 10% total solids content. Open symbols – adsorption. Shaded symbols – desorption. DHBA/R: lozanges + dotted – 4/6; circles + solid – 5/5; squares + dot-dash – 10/0.