Preparation and Characterisation of Mesoporous, High Surface Area Zirconium(IV) Oxides

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High surface area, mesoporous zirconium(IV) oxides may be prepared by controlled heating of a surfactant–zirconium(IV) oxide composite in which the surfactant acts as a combined drying-control and scaffolding agent.

Recently, there has been interest in mesoporous silicates with well defined pore sizes, prepared by templating with surfactants and subsequent calcination.[1,2] The mechanism of formation of the silicate and aluminosilicate structures, the MCM-type materials, has been illuminated by the extension of the templating technique to other oxide systems such as WO_3 and PbO using cationic and anionic surfactants, respectively.[3] As part of a study to extend further knowledge of these systems, we have attempted to prepare high surface area, mesoporous zirconium(IV) oxide using a series of cationic surfactants (alkyltrimethylammonium halides) and to characterise the materials formed. Templated structures do not seem to form in this system; however, some ordering does occur which is explained by a newly proposed scaffolding mechanism.

Calcined hydrous zirconium(IV) oxide has low surface area and porosity since the drying of a hydrous metal oxide causes stress on the metal oxide framework by the capillary pressure at the liquid–vapour interface in the pores of the material. This stress tends to collapse the pores, reducing the surface area of the dried gel. The problem has been overcome by the preparation of zirconium(IV) oxide aerogels.[4] High surface area zirconium(IV) oxides have been prepared here by an alternative route. The first step to the preparation of the mesoporous zirconium(IV) oxide samples was the preparation of surfactant-exchanged hydrous zirconium(IV) oxide. The scaffolding and controlled-drying processes occur during heating of the materials at temperatures below *ca.* 570 K. Calcination to *ca.* 723–973 K in air oxidises the organic species resulting in a high surface area, mesoporous zirconium(IV) oxide, with BET surface areas of the calcined materials of 240–329 $m^2\ g^{-1}$ depending upon the chain length of the incorporated surfactant. Powder X-ray diffraction patterns of the materials exhibit broad, low-angle reflections indicating some ordering of the structure. There is no dependence of the scale of ordering on the chain length of the surfactant at room temperature; however, after calcination to 723 K and above, the ordering is a linear function of hydrocarbon chain length of the surfactant.

The preparation was as follows. To an aqueous solution of zirconyl chloride (0.01 mol in Zr^{IV}, 0.1 mol dm^{-3}, Aldrich) was added an aqueous solution of alkyltrimethylammonium halide (0.005 mol, 0.1 mol dm^{-3}). Aqueous ammonia was slowly added with continuous stirring to pH 11.4–11.7. The product precipitated a few moments after the addition of the base. The mixture was placed in a bath thermostatically maintained at 363 K. The reaction mixture was maintained at this temperature in a sealed vessel and continuously stirred for 90 h. After this time, the mixture was allowed to cool, filtered off under suction and washed with an excess of water and acetone until free of surfactant. The samples were washed repeatedly after filtering to ensure that no free alkyltrimethylammonium salts were present. The products were dried at 333 K for 20 h. The aliphatic hydrocarbon chain lengths of the surfactants used were C_8, C_{10}, C_{12}, C_{14}, C_{16} and C_{18}.

Simultaneous thermogravimetry–differential thermal analysis (Stanton-Redcroft STA 1000 using lidless, platinum pans with recalcined alumina as DTA reference) and Fourier-transform IR spectroscopy (Perkin Elmer 1100B spectrophotometer) indicated the presence of alkyltrimethylammonium in the samples. TG–DTA was used to estimate the amount of alkyltrimethylammonium incorporated in the zirconium(IV) oxide. The results are shown in Table 1. This technique has been used in the determination of incorporated surfactant in studies of WO_3–surfactant mesostructures.[3] All experiments were performed in static air at a ramp rate of 20 K min^{-1} to ensure the complete oxidation of the organic species.

The powder X-ray diffraction patterns of the alkyltrimethylammonium-exchanged zirconium(IV) oxide samples before calcination exhibit single, broad, low-angle reflections (Spectrolab CPS Series 3000 120, using Ni-filtered Cu-Kα radiation). The *d*-spacings of these reflections are lower than those reported in the literature for templated materials[2] and are independent of the hydrocarbon chain length of the incorporated surfactant. There are no higher-order Bragg reflections observed in the powder patterns. After calcination of the materials to 723 K, the powder X-ray diffraction patterns exhibit similar, single, broad peaks at low 2θ values with the scale of the ordering depending directly upon the chain length of the incorporated alkyltrimethylammonium cation. The *d*-spacings,

Table 1 Thermogravimetric analysis of the amount of incorporated alkyltrimethylammonium species, BET surface area and total pore volume (V_p) of the calcined zirconium(IV) oxides as functions of calcination temperature (*T*) and chain length of incorporated alkyltrimethylammonium cation. The labels refer to Z, zirconium(IV) oxide, C_x, the chain length of incorporated alkyltrimethylammonium and a or b, distinct preparations of materials using hexadecyltrimethylammonium cations (C_{16} chain)

Entry	Zr : Surfactant ratio of precursor (TG)	*T*/K	BET surface area/$m^2\ g^{-1}$	V_p/ $cm^3\ g^{-1}$
ZC_8	1 : 0.082	723	238 ± 3	0.30
ZC_{10}	1 : 0.106	723	310 ± 5	0.47
ZC_{12}	1 : 0.131	723	274 ± 1	0.24
ZC_{14}	1 : 0.183	723	300 ± 1	0.29
$ZC_{16}{}^a$	1 : 0.260	723	312 ± 3	0.34
$ZC_{16}{}^b$	1 : 0.251	723	329 ± 4	0.33
ZC_{18}	1 : 0.341	723	313 ± 3	0.60

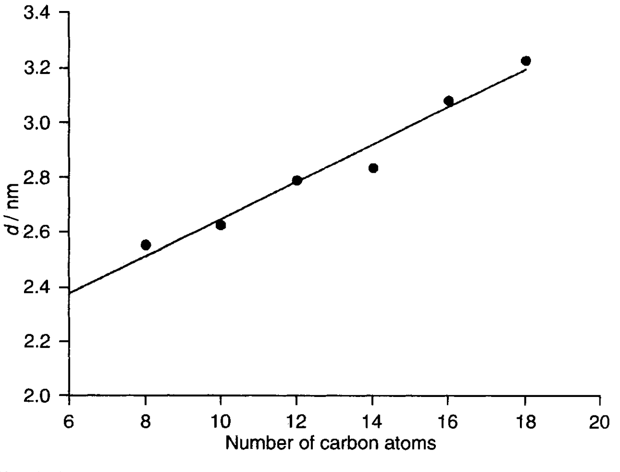
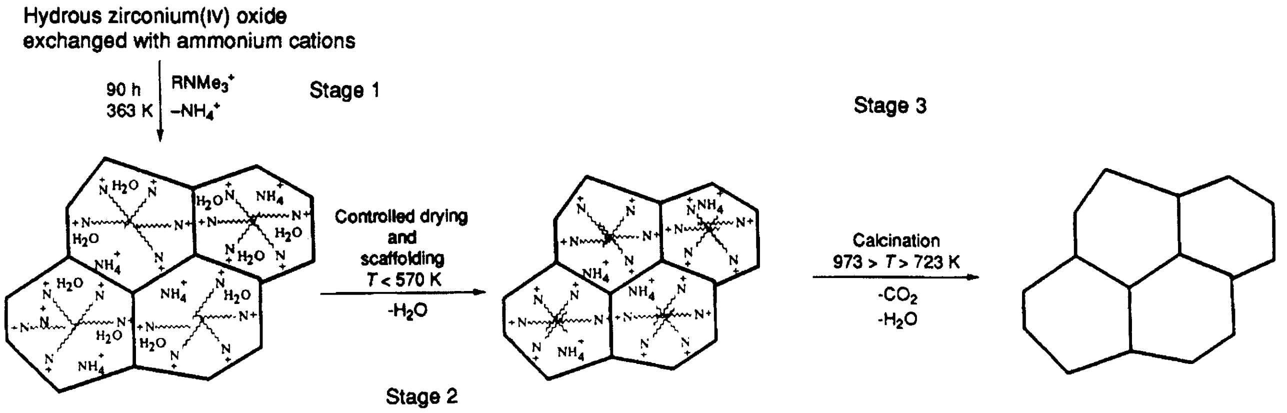


Fig. 1 *d*-Spacing of the low-angle powder X-ray diffraction reflections of the materials as a function of chain length of alkyltrimethylammonium cation after calcination in air at 723 K



Scheme 1 Representation of the proposed scaffolding mechanism in long-chain alkyltrimethylammonium incorporated hydrous zirconium(IV) oxide. See text for a fuller explanation.

as a function of chain length of exchanged alkyltrimethylammonium cation, are shown in Fig. 1. The graph approximates to a straight line, showing that the scale of ordering of the structure of the materials after calcination is directly dependent upon the size of the alkyl group of the incorporated cation.

Nitrogen adsorption isotherms (determined at 77 K by means of a Micromeritics Gemini 2370 Surface Area Analyser) of calcined zirconium(IV) oxide–alkyltrimethylammonium materials exhibited type IV behaviour, typical of mesoporous materials.[5] All adsorption experiments were performed in triplicate. BET surface areas and other BET parameters were calculated from five points in the relative pressure range 0.10–0.30 assuming a cross-sectional area of 0.162 nm^2 for the nitrogen molecule. The total pore volume of the materials (V_p) was estimated from the upper plateau in the nitrogen adsorption isotherm, or from the amount of nitrogen adsorbed at P/P^0 = 0.95, assuming a liquid density of nitrogen at 77 K of 0.808 g cm^{-3}. The desorption branch of the isotherm exhibited various types of hysteresis, depending upon the calcination temperature. Calcination at 723 K invariably resulted in type H2 hysteresis.

The derived BET surface areas of the calcined materials varied with calcination temperature and with the method of preparation. The maximum reproducible surface area for a zirconium(IV) oxide prepared in this study is 329 m^2 g^{-1} for a zirconium(IV) oxide–hexadecyltrimethylammonium calcined at 723 K. This value compares favourably with the BET surface areas of both precipitated zirconium(IV) oxide and zirconium(IV) oxide aerogels calcined at these temperatures.[4] As far as we are aware these values are the highest observed BET surface areas of zirconium(IV) oxide calcined at these temperatures. Table 1 gives values of BET parameters and total pore volume (V_p) for the materials prepared in this study.

In the system described here, incorporation of alkyltrimethylammonium ions into the zirconium(IV) oxide gel by cation exchange and subsequent calcination leads to high surface area, high porosity solids. Surfactants incorporated into hydrous zirconium(IV) oxide act as chemically bound, drying control chemical additives: similar systems are effective in reducing the shrinkage of gels.[6,7] In the present system, the incorporated surfactants reduce the surface tension of pore water with which they come into contact, regardless of the ordering of the surfactant cations in the material. As a result, the surface area of the calcined mesoporous material is predicted to be proportional to the chain length of incorporated surfactant.

Alkyltrimethylammonium cations do not directly determine the scale of the ordering (by XRD) at room temperature. However, during heating the material shrinks under the influence of capillary pressure until the steric interaction between the incorporated organic cation and the Zr–O–Zr network prevents further shrinkage. The result is a scaffolding, rather than a templating, effect with the scale of ordering after calcination determined by the effective size of the incorporated cation. The proposed controlled-drying and scaffolding mechanism shows a cross section of the zirconium(IV) oxide gel (Scheme 1). Stage 1 involves incorporation of alkyltrimethylammonium cations within the hydrous zirconium(IV) oxide with some ammonium ions and water molecules being retained. Stage 2 involves initial heating of the organic/inorganic material. The water molecules are lost on drying, the structure shrinks but the drying-control effect of the surfactant reduces the tension on the porous zirconium(IV) oxide. The dehydroxylation reactions of the hydrous zirconium(IV) oxide proceed, giving a partially ordered, scaffolded structure prevented from collapsing by the surfactant. The dehydroxylation reaction has the result of fixing the structure so that the heating off (a process involving some oxidation) of the surfactant scaffold does not result in its collapse. At a higher temperature, in Stage 3, the organic species are heated off leaving mesoporous zirconium(IV) oxide.

The results presented here do not support a templating mechanism occurring in the zirconium(IV) oxide–alkyltrimethylammonium systems as occurs in the silicate system. Instead, after calcination there is an ordering of regions of the materials owing to a scaffolding mechanism, with the *d*-spacing of the calcined zirconium(IV) oxide being a linear function of the chain length of the incorporated surfactant. The drying-control effect of the surfactant also leads to higher surface area zirconium(IV) oxides, with nitrogen adsorption properties similar to those of calcined aerogels.[8] We suggest that the mechanisms proposed here may be extended to a wide range of metal oxides.

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