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A sol–gel preparation of silica coated zirconia microspheres as chromatographic support materials

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Four silica–zirconia composites were prepared using a sol–gel process and compared with zirconia, which was prepared under the same conditions but without the addition of sodium metasilicate pentahydrate. Spherical particles (1–2 μm) resulted which were free from aggregation and hollow spheres. Raman spectroscopy, differential thermal analysis, thermal gravimetric analysis and electron microscopy were used to evaluate the properties of these composites. Addition of the silica onto the zirconia microspheres prevented the formation of monoclinic zirconia and increased the temperature of crystallization into the tetragonal form. Calcination of the composites at 1300 °C produced zircon.

1. Introduction

Silica is the most common stationary phase support currently used in liquid chromatography. It is available as rigid particles possessing excellent mechanical strength and in a wide range of known particle sizes and pore sizes. Unfortunately, silica is limited to solvents with pH values between approximately 2 and 8. Undesirable adsorption towards basic species also occurs. The search for methods that stabilize the silica support [1, 2] or for alternative supports has been an area of continued research in chromatographic science.

A wide range of materials has been investigated in an attempt to develop a chemically stable support without the two disadvantages of silica mentioned. Polymeric stationary phases such as polystyrene–divinyl benzene, and other resins based on polyacrylate, hydroxylated polyether copolymers or poly (vinyl alcohol) are now commercially available. These polymeric stationary phases are stable over a wide pH range and have a highly homogeneous surface, free from silanol groups. The polymeric phases are, however, less mechanically stable; they exhibit swelling, which varies the pore size, and they are thermally unstable. Alumina has often been used as an alternative to silica, but complex adsorption mechanisms have limited its application in chromatography. Polymer-coated alumina stationary phases have, however, shown excellent pH stability [3, 4] but the heterogeneous nature of the pore sizes introduced additional problems [5].

Recently, zirconia has shown promise as a stationary phase support and Nawrocki *et al.* [6] have reviewed the area. Being a highly rigid support, zirconia is able to withstand the rigours of high-performance liquid chromatography and, also, zirconia is basic and hence is insoluble in alkaline media. Zirconia is also stable in acidic solvents to a pH as low as 1. The surface of zirconia is, however, highly heterogeneous, consisting of Lewis acid, Bronsted acid and Bronsted base sites. Hence a multitude of elution mechanisms can occur that may complicate the elution process but, because zirconia is highly resistant to solvent attack, a large choice of eluent modifiers can be added to the mobile phase at virtually any pH to control unwanted interactions [7–10]. As a result, the highly functional zirconia surface can be fully utilized to obtain high levels of selectivity. Several examples currently exist in the literature where this novel selectivity has afforded very interesting separations [7–12].

Kaneko *et al.* [13] have recently prepared mixed-phase silica and zirconia supports for chromatographic use. The support materials that were prepared by the coprecipitation of zirconyl chloride and sodium metasilicate were irregularly shaped and required grinding and sieving to the appropriate particle size. Modern chromatographic materials are, however, mainly spherical because of the resultant improvement in packing-bed stability. Hence the preparation of spherical particles would be preferred. Nevertheless the stationary phases were suitable to illustrate the separation of dimethyl phthlate and pyridine on silica–zirconia, silica–titania, silica–alumina and silica–magnesia supports. Their studies illustrated that varying selectivities were obtained for both compounds on each of the mixed-phase columns. Elution of pyridine was not observed on either the silica or the silica–zirconia columns. No information, however, was presented on the particle composition. No further publications dealing with the chromatographic applications on mixed-phase silica–zirconia stationary phases have since appeared and very little is known of their performance.

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Recent studies in the preparation of zircon ($ZrSiO_4$) has led to the development of methods for preparing spherical silica and zirconia composites. Ultrafine particles have been prepared using spray pyrolysis techniques with varying degrees of success. Ono *et al.* [14] prepared ultrafine spherical-like particles by spraying an aqueous solution of zirconyl nitrate hydrate ($ZrO(NO_3)_2 \cdot 2H_2O$) and silicone oil into an ultrahigh temperature inductively coupled plasma. Particle sizes were approximately 10–20 nm. Jada [15] used a spray pyrolysis technique to produce hollow zircon spheres with particle sizes between 2 and 8 μm. Calcination of these spheres at 250 °C produced mainly amorphous material. When heated to 600 °C, poorly defined tetragonal zirconia was observed, which became more predominant as the temperature increased. A phase change to zircon was observed on heating for 4 h at 1500 °C, contrary to the observation made by Ono *et al.* [14] who observed no change to zircon when their product was heated to 1500 °C.

Kanno and Suzuki [16, 17] studied the preparation of spherical zirconia–silica particles by ultrasonic spray pyrolysis. The resulting particles were identified as tetragonal zirconia and amorphous silica. Particle sizes were of the order of 0.8–1.0 μm. Particles were free from agglomeration and no hollow spheres were observed, although "volcanic"-like deformations were observed on the particle surfaces. No zircon was observed, possibly because the samples were not heated to 1500 °C. A recent paper by Tartaj *et al.* [18] reported the preparation of zircon using an aerosol method. In their procedure, tetraethylortho-silicate and zirconium *n*-propoxide were used as precursors, the alkoxide being partially hydrolysed prior to introduction into an aerosol apparatus. The resulting spherical particles had good homogeneity and were amorphous. Calcination of the product up to temperatures of 950 °C gave rise to the segregation of silica and the crystallization of tetragonal zirconia. Monoclinic zirconia formation was detected after calcination at a temperature of 1300 °C, and crystallization into the form of zircon occurred with prolonged heating at 1500 °C.

Each of the aforementioned studies on the preparation of zirconia and silica composites have been primarily aimed at forming a uniform equimolar zircon material. In the current study the aim was to produce a zirconia–silica composite that had a uniform surface containing silica and zirconia functionality. As such, the important features of the material are its surface homogeneity, particle size and shape, and changes in selectivity that may be produced with the variations in silica content. The preparation of silica-coated zirconia microspheres using a sol–gel process whereby the surface of preformed zirconia is modified by the addition of various quantities of silica is described. Using this simple sol–gel method the need for complicated aerosol techniques is avoided and the surface concentration of silica is controllable. Chromatographic applications of the product will follow in further communications.

2. Experimental procedure

2.1. Chemicals and reagents

The surfactants Span 80, Brij 35 and Tween 85 were supplied by the Sigma Chemical Company Inc. Both sodium metasilicate pentahydrate, which was used as received and zirconyl chloride octahydrate (95%), which was recrystallized twice from concentrated HCl prior to use, were obtained from BDH Chemicals Ltd, Poole, UK. Urea and hexamethylenetetramine were supplied by the Aldrich Chemical Company Inc. Laboratory-grade heptane (May and Baker Aust. Pty. Ltd) and toluene (Selby Scientific Ltd, Milton Qld) were used as supplied.

2.2. Preparation of silica modified zirconia

Zirconyl chloride octahydrate (100 g) was dissolved in water (75 ml) with stirring for 1 h. The extent to which the zirconyl chloride octahydrate was hydrolysed was not determined. The resulting zirconium hydroxide solution was added to *n*-heptane (875 ml) stabilized by the addition of Span 80 (13.75 g), Tween 85 (4.15 g) and Brij 35 (3.12 g). The mixture was homogenized using a Janeke and Kunkel Ika-Werk Ultra-Turrax shear stirrer (John Morris Pty. Ltd Scientific Instruments) for 225 s at a speed calibrated to yield particles with a diameter of approximately 2 μm. Hexamethylenetetramine (87.5 g) and urea (87.5 g) were added to the mixture, which was then stirred for 48 h at room temperature (26–28 °C) [5]. The resulting spherical zirconia particles were washed with each of the following solvents (400 ml) in the order 50:50 pentane:hexane, 50:50 pentane:butanol, 50:50 butanol:ethanol, ethanol, 50:50 ethanol:water, water (twice) and finally methanol [5, 19]. The zirconia microspheres were then azeotropically dried in toluene and collected on a vacuum filter. The product was then divided into five portions of approximately 10 g and each portion was then rewashed twice in methanol (100 ml) and twice in water (100 ml). The zirconia was then suspended in water. Sodium metasilicate pentahydrate (70 g) that had been previously hydrolysed with water (106 ml) was then added to four of the zirconia suspensions in quantities of 7 ml (sample A), 21 ml (sample B), 42 ml (sample C) and 70 ml (sample D). The volume of each zirconia suspension was then made up to approximately 200 ml. These suspensions were then stirred for 36 h at 50–60 °C, allowing the water to evaporate slowly to a volume of less than 30 ml. Each product was then washed twice with water (100 ml) and collected by centrifugation. The composite materials were then resuspended in water and acidified with HCl and collected by centrifugation. This was repeated until the pH of the resuspended product was neutral. The product was then washed four times with water (100 ml) followed by two washings in methanol (100 ml). Finally the composites were azeotropically dried in toluene.

Each material was then subjected to calcination. The materials were initially heated to 260 °C and an aliquot was taken. The materials were then reheated sequentially for 3 h to 420, 520, 605, 730, 850, 920 and 1000 °C and then for 20 h at 1300 °C. Aliquots were taken at each temperature.

2.3. Particle analysis

Scanning electron microscopy (SEM) was carried out using a JEOL 35CF JSM scanning electron microscope coupled with Tracor X-ray facilities. Elemental analysis was performed by firstly mounting the samples in resin and grinding the surface to a highly polished flat surface. The sample plug was then coated lightly with carbon and analysed using the Tracor X-ray facilities on the scanning electron microscope at 25 keV.

The zirconia and silica composites were subjected to thermogravimetric analysis (TGA) and differential thermal analysis (DTA) using a Setaram TGA 92 at heating rates of 5 °C min^{-1}.

Raman spectra were obtained using either a Perkin–Elmer system 2000 Fourier transform (FT)–Raman spectrometer or a Renishaw Raman microscope system 1000. The FT–Raman spectrometer was equipped with a quartz beam splitter and a continuous-wave Spectron Laser Systems SL301 neodymium-doped yttrium aluminium garnet laser emitting at 1064 nm and an $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$ detector operated at ambient temperature. The mirror velocity was 0.2 cm s^{-1}, and strong Beer–Norton apodization was used. A notch-type Rayleigh filter was installed to provide an extended scan range from 3600 to 100 cm^{-1}. Typically, 200 scans were recorded at a resolution of 4 cm^{-1} and laser power of 400 mW. All FT–Raman spectra were corrected for instrumental effects. Raman spectra obtained on the Renishaw Raman microscope were excited by a helium–neon laser operating at 633 nm, producing 8 mW at the sample, or by a Renishaw laser diode operating at 780 nm, producing 1 mW at the sample. The Renishaw system 1000 used a 612 × 480 charge-coupled device array, giving a resolution of 2.5 cm^{-1} when coupled to the 50 × microscope objective. Good signal-to-noise ratios were routinely obtained with total measurement times in the vicinity of 60 s for the crystalline samples. Any data manipulations were accomplished with the GRAMS 386 (Galactic Inc., Salem NH) software package.

3. Results and discussion

3.1. Electron microscopy

Silica-coated zirconia microspheres were prepared using a straightforward sol–gel procedure. The particle size was controllable by the rate of shear stirring [19] and the addition of silica onto the surface of the zirconia could be adjusted to various concentrations. The procedure involved the initial preparation of zirconia microspheres, which were then washed, collected and resuspended in water, and the addition of the hydrolysed sodium metasilicate produced a highly alkaline solution. With heat and constant stirring, the water evaporates with the consequent formation of silica-coated zirconia microspheres. The extent of the silica coverage may be controlled by varying the quantity of hydrolysed sodium metasilicate initially added. Table I presents the zirconia–silica surface composition data obtained for each sample using SEM and Tracor X-ray analysis. These results were obtained by the random analysis of five particles for each sample. Multiple analyses were also conducted on an individual particle in each sample on at least three locations across the surface. An examination of the homogeneity of the entire sample involved the analysis of several hundred spheres. The results in Table I clearly indicate that no significant difference exists between the surface modification of individual particles and that of the bulk sample. The variation in composition across the surface of individual particles is not significantly different from the variation over randomly selected particles. In fact the variation across the surface of a single particle was in most instances less than the variation between particles. The results in Table I show that a controlled amount of silica can be added to the zirconia surface up to at least a 1.2 mole ratio of Si to Zr. Lower than expected surface modification was obtained for the sample

TABLE I Surface analysis results illustrating the mole ratio of Si to Zr for each of the zirconia composites

Sample	Particle composition (mole ratio of Si) (standard deviation)			
	Volume of hydrolysed sodium metasilicate added (ml)	Composition measured from five individual particles	Composition across the surface of a single particle	Average surface composition[a]
A	7	0.39 (0.02)	0.42 (0.04)	0.36 (0.004)
B	21	0.92 (0.02)	0.90 (0.01)	0.89 (0.02)
C	42	1.13 (0.06)	1.11 (0.006)	1.15 (0.05)
D	70	0.82 (0.02)	0.82 (0.006)	0.78 (0.02)
E	0	1.13×10^{-2} (5.29×10^{-3})	1.17×10^{-2} (8.45×10^{-3})	1.44×10^{-2} (1.03×10^{-2})

[a] Average represents the composition of a large number of spheres.

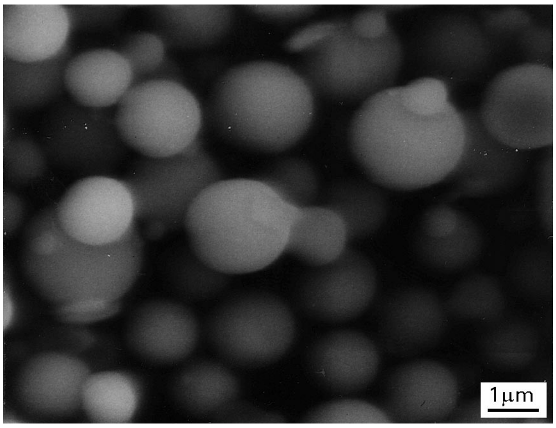


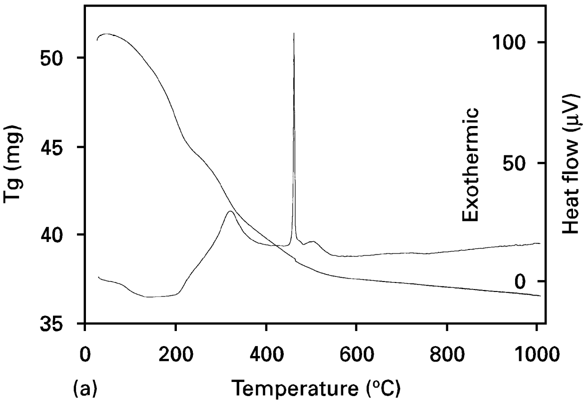
Figure 1 A scanning electron micrograph of the zirconia–silica composite containing a 1.13 mole ratio of Si (Table I, sample C) obtained at an accelerating voltage of 15 keV. (Magnification, 6000x.)

prepared by the addition of 70 ml of hydrolysed sodium metasilicate and this result is the focus of further investigation. Insignificant levels of Si were present in the uncoated zirconia (Table I, sample E).

The average particle size and distribution, obtained by SEM measurements on at least 300 spheres was 1.26 µm ± 36.5% for the uncoated zirconia. Although this distribution is slightly larger than ideal for chromatographic use, suspension and decantation of the fines considerably improves the product. The overall particle size increased slightly with silica coating; for example the sample containing a 0.42 mole ratio of Si (Table I, sample C) had an average particle size of 1.41 µm ± 44%. Whilst all samples were examined by electron microscopy, only the electron micrograph of the zirconia composite containing a 1.13 mole ratio of Si (Table I, sample C) calcined at 520 °C is illustrated in Fig. 1. There was no evidence of aggregation, and only a very small number of fractured particles were observed in any of the products. Furthermore, the precipitation of amorphous silica was not observed. Calcination at temperatures above 920 °C did, however, cause agglomeration of the silica-coated zirconia samples, possibly because the silica fused at these temperatures. The uncoated zirconia showed no such agglomeration.

3.2. Differential thermal analysis

Figs. 2a and b illustrate the TGA and DTA of the uncoated zirconia and the zirconia–silica sample containing a 0.92 mole ratio of Si (Table I, sample B), respectively. The uncoated zirconia showed a sharp exothermic "glow" peak at 467 °C in its DTA, which previous workers have attributed to a phase change from amorphous zirconia [6, 20–23] to a metastable tetragonal phase, after which the zirconia undergoes a further phase change to a monoclinic form. No evidence of this phase change was present on any of the silica-coated zirconia samples. The DTA of the sample that contained a 0.92 mole ratio of Si-coated zirconia composite showed an exothermic peak at 871 °C (Fig. 2b). Tartaj *et al.* [18] suggested that this



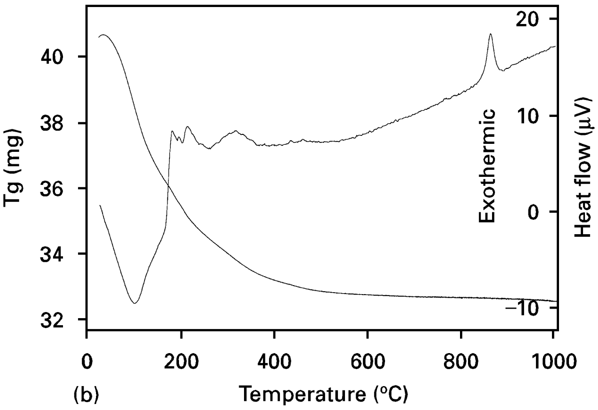


Figure 2 DTA of (a) the uncoated zirconia and (b) the zirconia–silica composite containing a 0.92 mole ratio of Si (Table I, sample B) (temperature gradient, 5 °C min^{-1}).

peak may be due to the crystallization of zirconia in the tetragonal form. Whilst each of the silica-modified samples showed the presence of a similar peak, the temperature at which it occurred increased as the concentration of silica increased. Each DTA for all samples showed an endothermic peak at around 100 °C attributed to the loss of water, and an exothermic region attributed to the loss of toluene and hydrocarbon impurities up to almost 400 °C. Previous workers [22] concluded that no phase change occurred within this temperature range. TGA data show a large mass loss within this temperature range, which supports the above conclusions.

3.3. Raman spectroscopy

Vibrational spectroscopy has been used extensively to characterize zirconia, titania, silica and their composites [20, 24–27]. Raman spectroscopy has several advantages over infrared techniques in the study of the structure of materials, particularly with respect to its sensitivity to crystallinity and the ease of sampling. Here Raman spectroscopy was used to identify the on set of crystallization and to characterize the structure of both modified and unmodified zirconia spheres.

Raman spectra of samples calcined at 260 and 420 °C (temperatures below the onset of crystallization according to DTA) showed no discernible peaks. Both FT–Raman and Raman microscopy measurements on these low-temperature samples were dominated by fluorescence or other emission processes, despite the long excitation wavelength used. The inherently weak Raman scattering from amorphous silica and zirconia was swamped by fluorescence presumably arising from residual solvent impurities not yet expelled by heat. This contrasted with the infrared and Raman spectral study of Lee and Condrate [25] where zirconia–silica glasses were prepared by a sol–gel process. These workers observed broad profiles and were able to discern bands in their spectra at 954, 600, 550, 490 and 400 cm^{-1}, which were variously assigned to SiOH and Si–O bending vibrations and silicate defect bands. Of particular interest was the band at 954 cm^{-1} which they assigned to Zr–O–Si linkages, which will be discussed later.

At higher temperatures, Raman spectra were routinely obtained on samples calcined above the phase transition temperatures as indicated by the DTA results. Fig. 3 illustrates Raman spectra obtained for the unmodified zirconia sample as the temperature increased from 520 to 1300 °C. At 520 °C, a Raman spectrum (Fig. 3a) consistent with tetragonal zirconia was obtained, with major peaks at 646, 461, 317 and 266 cm^{-1}. However, a small amount of monoclinic zirconia was present as can be seen by the peaks at 550, 475, 380 and 190 cm^{-1}. As the temperature increased, the tetragonal phase changed to monoclinic zirconia and, above 730 °C, only monoclinic zirconia was observed. The intensity and the sharpness of the monoclinic peak increased as the temperature increased. This indicates that there is considerable crystal growth occurring as the temperature rises. Raman spectra obtained from unmodified zirconia calcined at the temperature associated with the exothermic glow peak in the DTA supports the conclusion that this peak is associated with the phase change from amorphous zirconia to the metastable tetragonal phase. It is worth noting that the metastable tetragonal zirconia changed to monoclinic zirconia after standing at room temperature (about 30 °C) for 14 days. This is possibly why mixed reports have appeared in the literature concerning the crystal phase of zirconia associated with the phase change at the exothermic glow peak (see, for example, [20] and references cited therein).

Raman spectra of the silica-modified zirconia samples showed that all samples remained amorphous until the calcination temperature exceeded the temperature of the exothermic peak observed in the DTA. At calcination temperatures higher than the exothermic peak, all silica–zirconia samples underwent a slow crystallization into tetragonal zirconia. Fig. 4 illustrates this transformation for the lowest silica-modified zirconia material (Table I, sample A). A very small amount of monoclinic zirconia was apparent at 1000 °C as evidenced by small peaks at around 190 and 380 cm^{-1}. Although not presented here, all samples showed the same transition, corresponding to the exothermic peak from the DTA, but no evidence of monoclinic zirconia was apparent for the zirconia–silica composites containing the higher silica loading. As the calcination temperature increased, the crystallinity increased, as evidenced by the sharper peaks and more intense spectra overall. By evaluating the resolution of the peaks of each sample at comparable temperatures it was noted that increased silica content decreased apparent crystallinity. This is

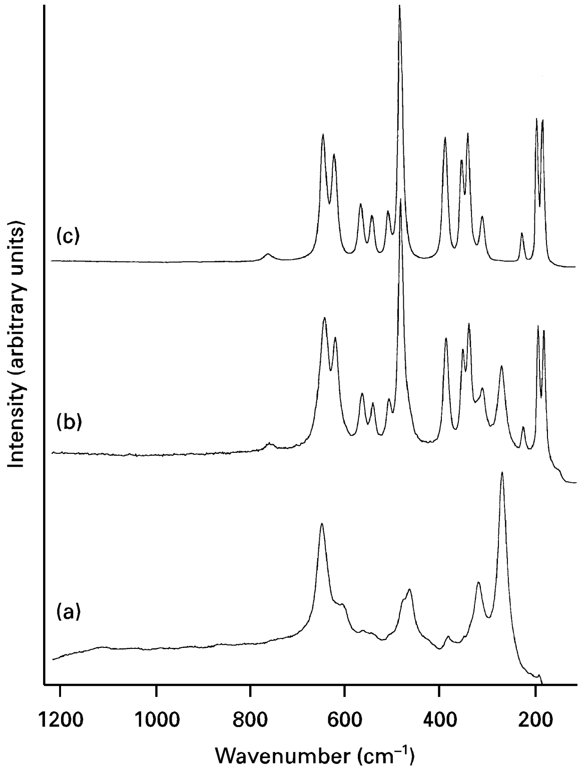


Figure 3 Raman spectra of the unmodified zirconia sample after calcination at temperatures of (a) 520 °C, (b) 605 °C and (c) 1000 °C.

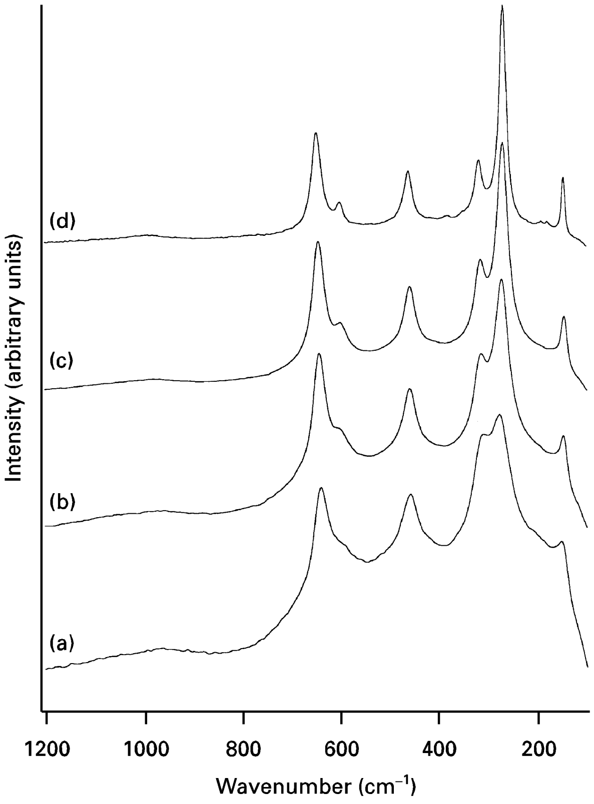


Figure 4 Raman spectra of the zirconia–silica composite containing a 0.39 mole ratio of Si (Table I, sample A) after calcination at temperatures of (a) 730 °C, (b) 850 °C, (c) 920 °C and (d) 1000 °C.

supported by the DTA which showed an increasing transition temperature with increasing silica content.

Below 1300 °C all peaks, except a broad weak band at 1000 cm^{-1} that appeared in the composite samples, could be attributed to either the monoclinic or the tetragonal crystal phases of zirconia. The intensity of the 1000 cm^{-1} band increased with increasing Si content. This band is also a dominant band in the spectra of silica precipitated in the absence of zirconia and can be assigned to a SiOH bonding vibration of the hydroxyls on the amorphous silica. An assignment to a Zr–O–Si vibration observed at 975 cm^{-1} observed by Lee and Condrate [25] in mixed silica–zirconia composites is not supported because the relative proportion of this bond to the bulk silica and zirconia would not change with increasing silica thickness once a monolayer coverage had been exceeded.

Above 1300 °C the FT–Raman spectra of the mixed silica–zirconia samples were partially masked by a large fluoresence signal that was not previously evident in the spectra of the samples calcined at lower temperatures. Even so, a sharp peak could be discerned at 1006 cm^{-1}, suggesting that zircon had been formed. Further calcination at 1300 °C for 20 h resulted in a stronger Raman signal but no reduction in the fluorescence. However, by using the Raman microscope, with 780 nm excitation, Raman spectra free from broad underlying fluorescence were obtained as shown in Fig. 5, which illustrates the spectra of the zirconia–silica composites containing a 0.39 mole ratio of Si (Table I, sample A) and 1.13 mole ratio of Si (Table I, sample C) and naturally occurring zircon (Australian Mineral Association). The spectra of samples that contained 0.39, 0.88 and 1.13 mole ratios Si (Table I, samples A, B and C) all showed sharp bands at 1006, 973, 436, 355 and 221 cm^{-1} that are characteristic of zircon as can be seen in Fig. 5 when compared with the native zircon. The sample with a 0.39 mole ratio of Si (Table I, sample A), however, also shows peaks consistent with a mixture of monoclinic phase zirconia and zircon (Fig. 5c). Incomplete conversion to the mineral zircon is not unexpected as the amount of silica in the sample is well below the required 1:1 stoichiometry. The tetragonal phase of zirconia is no longer present after calcination at this temperature, but rather the monoclinic phase predominates. Of further interest in these spectra is the presence of strong peaks above 1200 cm^{-1} that are too high to be reasonably assigned as Raman modes of zirconia or silica. Recently a note of warning was sounded in the literature [28] regarding possible infrared luminescence occurring as an artefact in the FT–Raman spectra of apatites and other inorganic minerals. Accordingly a thorough check of the anti-Stokes region was undertaken to determine whether these anomalous bands were of Raman origin. No bands other than those of zirconia and zircon could be detected. The anomalous bands occur in both the synthetic and the native zircon but are entirely absent when either 633 or 1064 nm excitation is used. It would therefore appear that these additional bands arise from far-red excited luminescence.

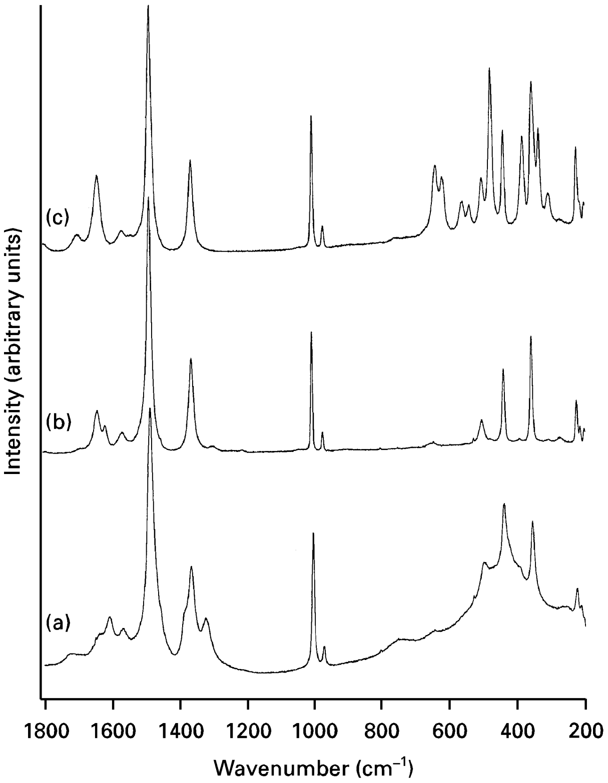


Figure 5 Raman spectra illustrating the formation of zircon from the zirconia–silica composites: (a) naturally occurring zircon; (b) 0.92 mole ratio Si (Table I, sample B) after calcination at 1300 °C for 20 h; (c) 0.39 mole ratio Si (Table I, sample A) after calcination at 1300 °C for 20 h.

Although spectra could be more rapidly recorded using the Raman than the FT–Raman technique, the Raman microscopy spectra of the composite spheres proved more susceptible to spectral artefacts, perhaps owing to the similarity in the particle size and the laser beam waist which, when using a 50x microscope objective, is diffraction limited and approaches 1 μm in diameter. However, the ability of the Raman microscope to record quality spectra of zircon, a task which proved difficult using FT–Raman techniques, illustrates the usefulness of having a range of excitation wavelengths from which to choose. The Raman microscope may also find application in the measurement and comparison of the spectra of individual particles that may be easily distinguished under the microscope. Furthermore, by coupling the Raman microscope to a temperature-controlled hot stage and suitable transfer optics the phase changes of these materials could be monitored *in situ*. This experiment is not possible using an FT–Raman spectrometer with near-infrared excitation as the near-infrared detector is soon swamped by thermal background above 200 °C.

Despite the fact that our aim was to prepare silica-coated zirconia microspheres that would exhibit unique chromatographic qualities, some rather interesting physical properties have been observed. In particular, the surface layer of silica dramatically influences the phase change from amorphous zirconia to its crystalline form. Both the temperature of crystallization and the form of crystallization have been influenced. Interestingly, the formation of zircon has been observed at higher temperatures, even though the silica is initially added only onto the surface layer of the zirconia microspheres. Hence during the calcination it is clear that rearrangements of atoms within the crystal lattice have occurred to produce a homogeneous composite as opposed to the surface-layered silica–zirconia composite. This variation in physical properties will make chromatographic applications on these supports a very interesting proposition, in terms of selectivity changes both with different concentrations of silica and also with variations in surface effects as the temperature of calcination is varied.

4. Conclusion

A straightforward method of spherical particle preparation has been described that allows the synthesis of mixed zirconia–silica supports using a sol–gel procedure. The addition of silica onto the surface of the support can be varied and this will have a marked effect on the chromatographic selectivity. Individual spheres within each sample contained a consistent Si-to-Zr atomic ratio and no evidence of hollow spheres was apparent. For the higher silica loadings, the addition of silica onto the surface of the zirconia prevented the formation of monoclinic zirconia and delayed the crystallization of the tetragonal form to temperatures greater than 700 °C. This temperature of crystallization was also dependent on the silica loading. As the temperature of calcination reached 1300 °C, Raman spectra revealed the presence of zircon in all the silica-coated composites. In the composite with the low mole ratio of silicon to zirconium (0.39 mole ratio of Si), zircon was present together with monoclinic zirconia. However, in the composites with mole ratios approaching or exceeding unity, no monoclinic zirconia was observed.

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