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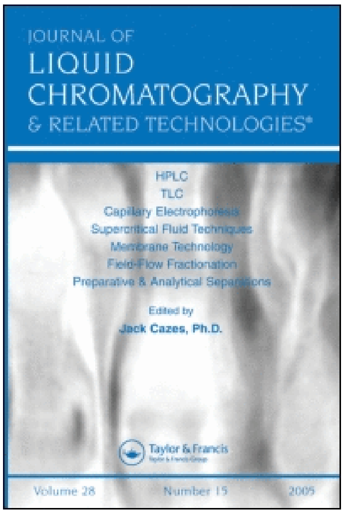

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THE PORE STRUCTURE OF ZIRCONIA FOR LIQUID CHROMATOGRAPHY

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ABSTRACT

Interest in zirconia as a chromatography support has increased considerably recently because of its chemical inertness and its promise as a useful support, particularly in biological systems. While studies have mainly focused on applications using zirconia or the control of complex elution behaviour that is often observed on this surface, many of the papers presented have not considered the importance of using materials with optimised pore structures. As a result, the efficiency of some separations may have been compromised. In this review we focus on what is perhaps the most important feature of such supports, namely, the pore structure and recent developments in this area. We have not attempted to review the many applications of zirconia in chromatography as they have been comprehensively reviewed by Nawrocki and co-workers in 1993[1] and again as a new material for biotechnology in 1994.[2] In these reviews the usefulness of zirconia was demonstrated by the many applications that were referenced, particularly with respect to the chromatography of biological species.

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Studies on the Pore Structure of Zirconia

Several recent studies have been made of the pore structures on zirconia prepared for liquid chromatography or for use as catalysts.[3-11] Zirconia for chromatography may be prepared using sol-gel type technology where, for instance, the zirconia is formed in an oil-water emulsion from polymerisation of, say, a zirconium salt. The resulting zirconia is collected and subjected to a multisolvent washing process. Another process for the preparation of zirconia for chromatography is that of microencapsulation or polymer induced colloid aggregation (PICA), where microspheres are formed from the aggregation of nanospheres that congregate together through the attraction between polymer functional groups attached to the nanospheres. Each of these procedures have been detailed in the literature and will not be reviewed further[1,12] and references cited therein.

Mercera and co-workers[3] prepared zirconia for use as a catalyst by a sol-gel procedure, and whilst the particle size was not considered from a chromatographic aspect the pore structure was examined in detail and this warrants further discussion. Zirconyl chloride in ammonia at a constant pH of 10.0 was used to precipitate ZrO_2 particles that were then ground to a mesh size of approximately 100 μm. The pore structure of the zirconia that was calcined for 15 hours at six different temperatures was examined using nitrogen sorption and over the temperature range of 110°C to 850°C each zirconia showed a type IV isotherm. As the temperature of calcination increased the hysteresis loop gradually changed from a type H2 to a type H1. This was an indication that narrow necked pores with wide bodies, the so called 'ink bottle' shaped pores, were becoming more cylindrical as the temperature of calcination increased. Pore size distributions were unimodal and showed that as the temperature of calcination increased the most frequent pore radius increased. The zirconia heated to 110°C, however, was microporous and microporosity was not eliminated from the surface until the sample was calcined at temperatures higher than 650°C. Surface areas were shown to decrease rapidly with thermal treatment; a 100 fold decrease in the surface area (from 289 m^2g^{-1} to 2.9 m^2g^{-1}) being observed as the temperature of calcination was increased from 110°C to 850°C.

Differential thermal analysis and X-ray diffraction studies showed that the material calcined at 110°C was amorphous, whereas after calcination at temperatures greater than 450°C it displayed some crystallinity either as the metastable tetragonal phase and/or the monoclinic phase. Even after the onset of crystallisation the decrease in surface area over the temperature range 450°C to 850°C was in the order of 40 fold (111.1 m^2g^{-1} to 2.9 m^2g^{-1}). The pore volume also decreased rapidly with thermal treatment, primarily as a result of the progressive pore widening and the subsequent loss of microporosity. The loss in pore volume was particularly rapid after calcination above 650°C, for instance the pore volume at 110°C was 0.185 mLg^{-1}, that at 650°C was 0.0527 mLg^{-1} and at 850°C the pore volume was 0.010 mLg^{-1}.

Using a PICA method, Sun et.al.[4] synthesised zirconia with a particle size of 3.5 μm after sintering. The calcination process involved initial drying of the sample at 170°C for 16 hours under vacuum followed by calcination in a muffle furnace at 700°C for three hours and then a further three hours at 900°C. An electron micrograph of the surface of this support indicated that the particles were formed through the aggregation of smaller nanospheres. Nitrogen sorption experiments were performed to measure the porous structure, and the specific surface area was determined to be 13 m^2g^{-1}. The shape of the adsorption/desorption isotherm was not given, however, the large difference in the pore size distributions measured from the desorption branch (20 nm) and compared with the adsorption branch (40 nm) indicated that the entrances to the pores were restricted. These particles were then coated with polybutadiene and tested in a reversed phase mode for the separation of benzene, toluene, and ethylbenzene. Although separation was obtained to baseline between the three solutes, peak widths were quite significant, which could either be due to the slow mass transfer into and out from the pore entrances or a result of the polymeric stationary phase coating and no discussion was presented regarding this factor.

Lorenzano-Porras and co-workers[5] investigated the pore structure of a zirconia prepared using an oil-emulsion process evaluating several different methods of surface analysis. The nitrogen adsorption/desorption isotherm of this zirconia was a type IV with a hysteresis loop intermediate between H2 and H3. This type of hysteresis loop suggests the presence of network effects where the desorption from a given pore is influenced by the state of the neighboring pore spaces.[5] The steepness of the desorption branch indicated that the throats connecting the cavities were relatively uniform.

The pore size distribution measured from the adsorption branch of the nitrogen sorption isotherm indicated the surface was bimodal with a distribution of mesopores between 10 nm and 40 nm and a larger distribution of macropores between 40 nm and 100 nm. The pore size distribution measured from the desorption branch was essentially unimodal and distributed between 10 nm and 30 nm. The surface area of this support measured from the nitrogen sorption was 12.3 m^2g^{-1}.

Mercury porosimetry indicated restricted pore openings with some pore bodies as wide as 100 nm having pore entrances only 60 nm in diameter. The results indicated that 80% of the pores were assigned to be behind throats less than 60 nm in diameter. The porosity determined from mercury porosimetry and the nitrogen sorption experiments agreed to within 7%. NMR spin relaxation was also used to evaluate the porous structure and the mean pore diameter was determined to be 38 nm. The authors concluded that since the nitrogen sorption experiments and the mercury porosimetry were compromised by pore restrictions the NMR spin relaxation experiments provided another method to examine the pore structure, which was not influenced by such interferences. This study highlighted the importance of multiple analysis methods for the evaluation of surfaces and the care that should be exercised when interpreting results.

Lorenzano-Porras and co-workers then investigated the differences in the pore structure of zirconia that were prepared using two different methods of synthesis.[6] They compared a PICA zirconia to the oil-emulsion zirconia discussed in the previous paragraph.[5] Evaluation of the PICA zirconia using nitrogen sorption determined that the material had a surface area of 11 m^2g^{-1} with a narrow range of pores between 35 nm and 55 nm. The pore size distribution calculated from the desorption branch indicated that 70% of the pores lay behind throats less than 10 nm to 25 nm in diameter. However, the pore size distribution calculated from mercury porosimetry indicated that the major contribution to the total pore volume corresponded to pores with throats that were 50 nm - 60 nm in diameter, with a small contribution from throats less than 25 nm in diameter. Pores with bodies larger than 100 nm were observed to contain throats as small as 60 nm in diameter and in some instances, pores with throats smaller than 10 nm were observed. NMR spin relaxation indicated that the volume averaged pore diameter of the PICA zirconia was 38 nm.

The authors noted that nitrogen sorption and mercury porosimetry illustrated that significant differences in pore structure were observed between the two materials, but NMR spin relaxation showed that the two materials were indeed quite similar with respect to the average pore diameter. They are currently investigating the effect of fines on the final pore structure analysis.

Size exclusion chromatography[7] using polystyrene probes for the PICA zirconia from reference[6] and the oil emulsion zirconia from reference[5] illustrated that the inclusion limit of the size exclusion curve obtained using the PICA zirconia was not as distinct as that for the size exclusion curve obtained using the oil emulsion zirconia. The PICA material also had a smaller pore volume. Significant differences in pore volumes were reported between the size exclusion method and the nitrogen sorption experiments; the authors attributing this to an error as large as 10% in the nitrogen sorption measurements. The effect of the dextran coatings on the PICA zirconia and the oil-emulsion zirconia indicated that the oil-emulsion prepared zirconia was susceptible to pore blocking,[8] but did not alter the size exclusion behaviour on the PICA zirconia. However, whichever technique was used to evaluate the surface, the results showed that both surfaces contained a pore structure that was not ideal for chromatography as solute molecules undergo slow mass transfer within the pore system as a result of the restriction at the pore entrance. Dunlap et.al.[8] concluded that the PICA zirconias appeared to be better candidates for chromatographic stationary phase supports. This is due, no doubt, in part to the fact that the PICA generated zirconia produced a product with a much finer particle size distribution, which is an important feature of a chromatographic support.[6]

Although several examples detailing the pore structure of zirconias for chromatography have been presented, none of these studies have aimed to control, specifically, the pore structure for chromatography. For zirconia to truly become a useful chromatographic support the pore structure should be controlled so that a wide range of pore sizes can be produced; the way the pore size of silica based supports have been. In a series of recent publications by Shalliker and co-workers[9-11] such an approach to the development of porous zirconia was adopted.

In these papers, methods for controlling the pore structure of zirconia suitable for chromatography were reported. The zirconia in this work was prepared using a sol-gel procedure and the pore structure was examined using nitrogen sorption experiments[9] and size exclusion chromatography.[10,11] The zirconia was prepared from zirconyl chloride, which was dissolved in water and dispersed in a surfactant stabilised oil, polymerisation being induced by base catalysis. Control of the pore structure was achieved through judicious selection of calcination conditions. A sample of zirconia that was treated at 450°C for one hour was shown to have a type IV nitrogen sorption isotherm with a type H2 hysteresis loop. Increasing the calcination temperature gradually changed the hysteresis loop to that of an intermediate H2-H1 loop. As was the case with the study by Mercera and co-workers[3] the shape of the hysteresis loop indicated the pore openings were restricted by narrow necks. However, it is likely that the longer calcination period used by Mercera et.al.[3] decreased the extent of narrow necked pores eventually producing surfaces that showed a H1 hysteresis loop compared with the H2-H1 hysteresis loops observed by Shalliker et al.[9]

Mean pore diameters were consistently larger than the most frequent pore diameters reported by Mercera et.al.[2] and consequently the surface area of the zirconia calcined at 450°C was approximately half that of the zirconia calcined at the same temperature by Mercera and co-workers (51.9 m^2g^{-1} compared to 111.1 m^2g^{-1}). However, the surface area of the zirconia prepared by Shalliker and co-workers was more stable as a function of temperature. Thus at 810°C the surface area of the zirconia prepared by Shalliker et. al.[9] was 6.5 m^2g^{-1} compared to 2.9 m^2g^{-1} for the sample of zirconia prepared by Mercera et.al.[3] Pore volumes were also observed to decrease rapidly as a result of the progressive pore widening. Microporosity was essentially eliminated after calcination at temperatures higher than 600°C, but even then because of restricted pore entrances, these zirconias were deemed to be inappropriate as a chromatographic surface.

To address this problem, Shalliker and co-workers calcined the zirconia in the presence of sodium chloride at 810°C. The resulting zirconia had a type IV nitrogen sorption isotherm with a type H1 hysteresis loop, indicating the nitrogen desorption from the pore structure was effectively unhindered. The resulting mean pore diameter of the zirconia calcined in the presence of sodium chloride (38.8 nm) was slightly larger than the same material calcined without the salt (34.3 nm). However, the surface area was over twice as high (15.4 m^2g^{-1} compared to 6.5 m^2g^{-1}) and the pore volume was three times greater (0.0802 mLg^{-1} compared to 0.0262 mLg^{-1}). This study indicated that by using salts during calcination to influence the final pore structure, pore accessibility, pore volume, and surface area could all be improved.

Shalliker and Douglas[10] then proceeded to optimise the pore structure for chromatography. A range of different pore size zirconias were prepared and comparisons made of calcination in the presence of salts to that of calcination in the absence of salts. Size exclusion chromatography was used to evaluate the chromatographically available pore structure. The effects of salt concentration, calcination temperature, and calcination, period, were all investigated. Zirconias calcined in the presence of sodium chloride produced size exclusion curves with shapes that approached a classical size exclusion curve. The pore volumes were larger and more precise exclusion and inclusion regions were recorded than for zirconias calcined without the salt.[10,11] For zirconia calcined for one hour at 810°C, the mean pore size was found to increase as the concentration of salt increased up to a limiting value (Table 1). No explanation was offered concerning this limiting value. Surface areas remained almost uniform regardless of the salt concentration, while the pore volume increased, again up to a limiting value.

Table 1

The Pore Dimensions of Zirconias Calcined with Various Concentrations of Sodium Chloride

Zirconia	P_d(nm)[1]	Log σ[2]	Vp (mL)[3]	Sa (m^2g^{-1})[4]	H (m)[5]
Zr810NaCl(4:1)[6]	34.0	0.423	0.1004	12.2	$8.1x10^{-5}$
Zr810NaCl(2:1)	42.0	0.396	0.1310	12.4	$8.1x10^{-5}$
Zr810NaCl(1:1)	45.0	0.400	0.1324	11.8	$7.5X10^{-5}$
Zr810nAcL(1:2)	35.5	0.381	0.1136	12.8	$8.5x10^{-5}$
Zr600NaCl(1:1)	19.0	0.387	0.1159	24.4	$6.8x10^{-5}$
Zr700NaCl(1:1)	28.1	0.378	0.1343	19.2	$6.4x10^{-5}$
Zr810NaCl(1:1)	45.0	0.400	0.1324	11.8	$7.5x10^{-5}$
Zr700	20.0	0.567	0.0511	10.2	$1.0x10^{-4}$
Zr700NaCl(1h)	28.1	0.378	0.1343	19.2	$6.4x10^{-5}$
Zr700NaCl(5h)	31.6	0.468	0.1178	14.9	$5.1x10^{-5}$

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[1] P_d pore diameter, [2] standard deviation of the normal distribution of the pore size distribution plot, [3] V_p pore volume, [4] S_a surface area, [5] Height equivalent to a theoretical plate, [6] Number (i.e. 810) refers to temperature of calcination, NaCl refers to calcination in the presence of sodium chloride.

Maximum column efficiency was obtained for a zirconia calcined in a 1:1 (w/w) zirconia:sodium chloride mix. The mean pore size was observed to increase with increasing calcination temperature. The surface area, quite fortuitously, decreased linearly with increasing temperature and no specific relationship was observed for the change in pore volume. The most efficient calcination temperature was found to be 700°C (Table 1). The height equivalent to a theoretical plate for a zirconia calcined in a 1:1 zirconia:salt mix for one hour at 700°C was $6.4x10^{-5}$ m while in comparison zirconia calcined under the exact same conditions but without the salt was observed to have a theoretical plate height of $1.0x10^{-4}$ m. The surface area of the zirconia calcined without the salt was almost half that of the zirconia calcined with the salt, while the pore volume was almost one third that of the zirconia calcined with the salt.[10]

Impregnation with salt during calcination was also shown to decrease the pore size distribution. Increasing the calcination period from one hour to five hours decreased the pore volume and surface area and slightly increased the mean pore diameter. However, column efficiency was shown to increase during this extended calcination period as H decreased from $6.4\mathrm{x}10^{-5}$ m to $5.1\mathrm{x}10^{-5}$ m. It was reasoned that such an improvement in the efficiency, despite a decrease in surface area and pore volume, was most likely to be associated with an improvement in the pore opening.[10]

Future Studies

The indications are that zirconia will become an important support for liquid chromatography. Shalliker and Douglas[9-11] have shown, using sol-gel derived zirconia, that the control of the pore size is a matter of judicious selection of calcination conditions. Carr and co-workers[4-8] have shown that the PICA method for the preparation of zirconia allows very uniform particle size distributions to be obtained and it is reasonable to conclude that the combination of calcination of PICA zirconia in the presence of salts may prove to be the method of choice for the preparation of zirconias with pore sizes optimised for a particular separation problem.

An important point, which should be made, is that new users of zirconia should pay particular attention to the pore structure, as this ultimately will have a bearing on the final efficiency of the separation process. A wide variety of pore structures may be achieved using various techniques for the preparation of zirconia. Importantly, however, control of the pore size is possible and indeed should be encouraged during the synthesis of support materials.

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