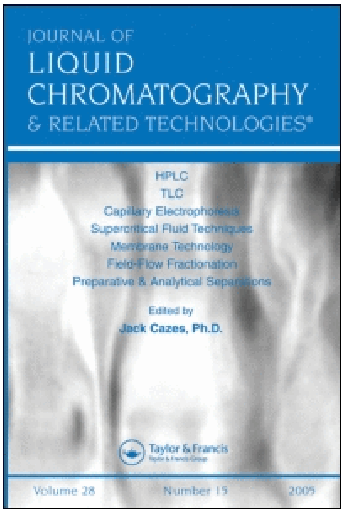

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THE DEVELOPMENT OF STATIONARY PHASE SUPPORTS FOR LIQUID CHROMATOGRAPHY. II. EXAMINATION OF THE PORE STRUCTURE OF ZIRCONIA-SILICA COMPOSITES USING NITROGEN SORPTION

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ABSTRACT

In this Part II of a two-part series, we examined the pore structure of zirconia-silica mixed oxide supports that were prepared using a variety of calcination conditions. Nitrogen sorption was used to evaluate the pore structure, offering a comparison to the size exclusion results presented in Part I. Pore volumes and surface areas of zirconia-silica composites, calcined in the presence of sodium chloride, were found to be higher compared to the composite calcined in the absence of sodium chloride. The pore diameter was observed to increase as the temperature of calcination increased.

INTRODUCTION

In Part I,[1] the pore structure of a range of zirconia-silica composites was examined using size exclusion chromatography (SEC). The advantage of size exclusion chromatography for such studies is that the actual chromatographic surface available for solute-stationary phase interactions is measured. The resulting size exclusion curve also serves to illustrate the usefulness of the surface for various molecular weight species, that is, whether the support would be suitable for macromolecular separations or more useful for small molecules only. In addition, SEC allows comparisons to be made between the column efficiencies of a range of different types of surfaces in order to establish the optimal surface preparation.

While size exclusion is useful for these studies, relatively few surfaces are characterised in this manner, nitrogen sorption being a far more popular technique. As some of the size exclusion curves in Part I yielded indistinct exclusion limits, indicating the surfaces had a macroporous component, we have sought to characterise further some of the supports using nitrogen sorption to establish a comparison. This study involves the analysis of the pore structure of the zirconia-silica composite that contains 10 mol % silicon (ZS10) calcined under various temperatures in both the presence of sodium chloride and in the absence of sodium chloride.[1]

EXPERIMENTAL

The preparation of the zirconia-silica composite was described in Part I.[1] In the present work, the composite referred to previously as ZS10 was calcined either as a pure powder or as a homogeneous mixture of composite and sodium chloride, according the procedure in Part I.

Nitrogen sorption experiments were performed by Particle and Surface Sciences Pty., Ltd. (Gosford, N.S.W. Aust. 2250) with fifty adsorption points and fifty desorption points being acquired at liquid nitrogen temperatures.

XPS experiments were carried out in ultrahigh vacuum using a Physical Electronics Industries PHI Model 560 surface analysis system. This system employs a double-pass CMA (20-270AR) with a perpendicular mounted dual (Mg/Mg) X-ray source. A single Mg Ka X-ray source was operated at 400 W and 15kV. The maximum energy resolution of the CMA was 1.2 eV, operated for the XPS analysis in the fixed analyser transmission (FAT) mode, with a pass energy of 25 eV for the Ag $3d_{5/2}$ emission. The electron binding energies

(E_B) were calibrated against the Au $4f_{7/2}$ emission at E_B = 84 eV.[2,3] Typical pressures during the analysis were between 5×10^{-8} and 5×10^{-7} Torr. Survey spectra were obtained over the range 0-1000 eV using a pass energy of 100 eV with an acquisition time of 2 minutes. Atomic concentrations were quantified using peak areas from 25 eV multiplex spectra (acquisition time 20 minutes) and experimentally derived elemental sensitivity factors.[4] Sample charging was referenced to the Cl s photoelectron peak.

For ease of discussion, the composite materials will be referred to using the same nomenclature as in Part I, that is, ZS10-700NaCl, refers to the composite material calcined at 700°C with sodium chloride and ZS10-810 refers to the same material calcined at 810°C without sodium chloride.

RESULTS AND DISCUSSION

In the present study, a zirconia-silica composite was prepared with a silicon concentration of 10.2 mol %. This material displayed a phase transition (Zr_a-Zr_t) at 837°C. Calcination at temperatures below the Zr_a-Zr_t phase transition temperature gave an amorphous product, while calcination at temperatures greater than the Zr_a-Zr_t phase transition temperature transformed this material to the tetragonal crystal phase. The tetragonal phase has previously been shown to undergo phase stabilisation as a result of silicon doping.[5]

Previous work has shown that calcination of zirconia in the presence of sodium chloride is conducive to the formation of cylindrical shaped pores that improve mass transfer into and out of the pore structure.[6] Studies on zirconia-silica composites have also indicated that the addition of sodium chloride during calcination improves the pore structure.[7] However, little is known regarding the shape of the porous network and work to date indicates that the pore structure is complex and depends on the silicon concentration and the thermal history of the material. The pore structure of the ZS10 composite was examined after calcination at various temperatures in the presence of sodium chloride. The same material was calcined at one temperature in the absence of sodium chloride.

Nitrogen sorption isotherms of each composite material are depicted in Figure 1. Examination of the composites calcined in the presence of (1:1 w/w composite:sodium chloride) shows that the nitrogen adsorption/desorption isotherm for the sample ZS10-600NaCl (Figure 1, curve a), was a type IV isotherm with a type H_2 hysteresis loop,[8] indicative of pores consisting of bodies with wide cavities having restricted pore entrances. Increasing the temperature

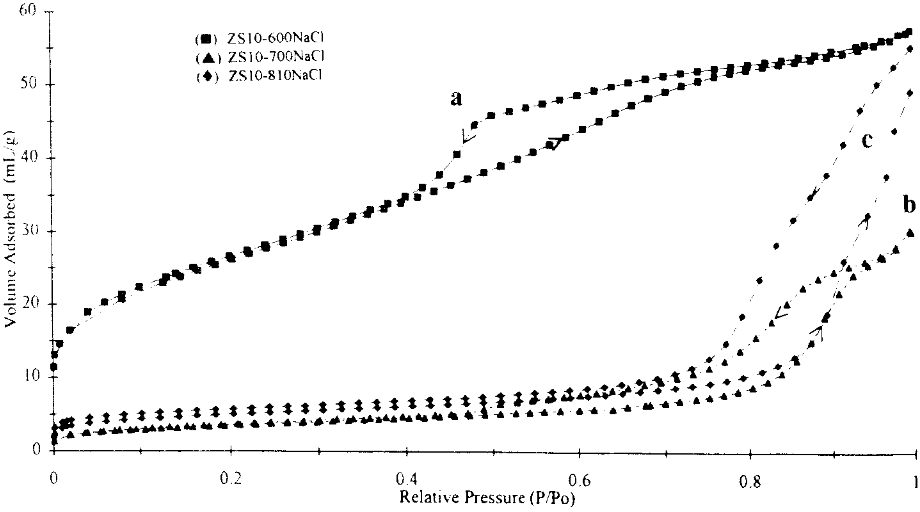

Figure 1. Nitrogen sorption isotherms of the zirconia-silica composite materials, calcined in the presence of sodium chloride. (a) ZS10-600NaCl, (b) ZS10-700NaCl, (c) ZS10-810NaCl.

of calcination altered the form of the isotherm hysteresis. The sample ZS10-700NaCl (Figure 1, curve b) had a type IV isotherm with an intermediate H_1-H_2 hysteresis loop that exhibited slight asymptotical behaviour as the relative pressure approached unity. This isotherm was similar to the isotherm observed for a zirconia sample calcined at 650°C without sodium chloride,[6] except for the asymptotical approach to the relative pressure $P/P_0=1$. Increasing the temperature of calcination to 810°C, as for the sample ZS10-810NaCl (Figure 1, curve c), resulted in the formation of a type IV isotherm again with an intermediate type H_1-H_2 hysteresis loop. This isotherm exhibited a very small degree of low pressure hysteresis which can be explained either by the surface containing microporous regions or possibly as the result of nitrogen chemisorption onto the surface. The latter can be discounted, since the sample is unlikely to behave differently to other samples prepared from the same composite. The nitrogen sorption isotherm of the composite calcined at 810°C in the absence of sodium chloride was a type IV with a H_3 hysteresis loop as shown in Figure 2. The close proximity of the desorption branch to the adsorption branch indicates that this surface contained pores with entrances that offer very little restriction. The presence of the hysteresis loop in the low relative pressure region ($P/P_0 \approx 0.42$) and extending to the high relative pressure region indicates the surface had a broad pore size distribution.

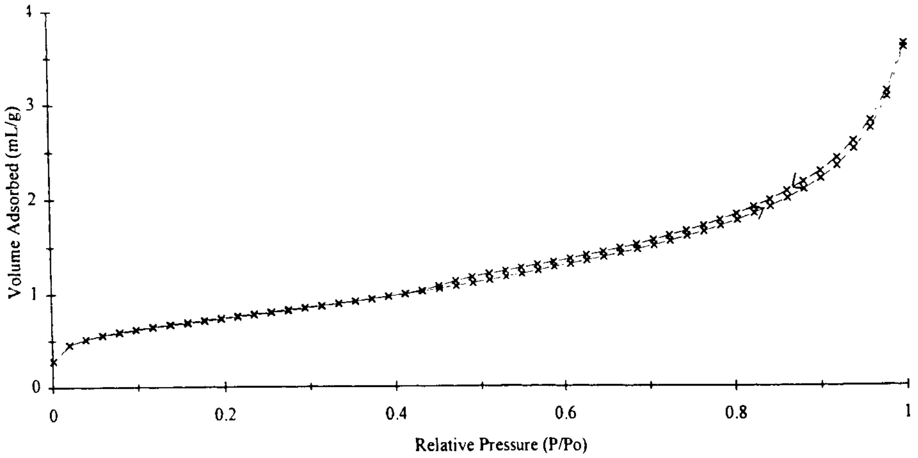

Figure 2. Nitrogen sorption isotherm of the zirconia-silica composite calcined without sodium chloride at 810°C.

Table 1

Surface Areas and Pore Volumes Calculated From the Nitrogen Sorption Isotherms of Each Composite Material

Sample	V_m	C	V_p (mLg^{-1})	$S_{a(BET)}$ (m^2g^{-1})	$S_{a(t\text{-}plot)}$ (m^2g^{-1})	S_{micro} (m^2g^{-1})
ZS10-600NaCl	21.75	83.16	0.0890	94.7	77.2	17.5
ZS10-700NaCl	2.91	104.98	0.0472	12.7	10.7	2.0
ZS10-810NaCl	3.98	2138	0.0863	17.4	13.0	4.4
ZS10-810	0.62	92.38	0.0056	2.7	2.8	-0.1

Surface areas of the zirconia composites were calculated from the BET equation in the range of linearity P/P_0 (0.05-0.3). The estimation of the volume of adsorbed nitrogen associated with a monolayer capacity (V_m) and the value of C were derived from a multipoint BET plot and are presented in Table 1. BET surface areas ($S_{a(BET)}$), calculated assuming the cross sectional area of the nitrogen molecule to be 0.162 nm^2, are shown in Table 1 together with the specific pore volumes of each adsorbent (V_p).

The results in Table 1 show that the monolayered capacity (V_m) decreased rapidly as the calcination temperature increased from 600°C to 700°C, with a slight increase as the calcination temperature increased to 810°C. The C value for the sample ZS10-810NaCl was very large and this is consistent with the sample exhibiting low pressure hysteresis and having a significant microporous structure. BET surface areas of the material calcined in the presence of sodium chloride decreased rapidly from 94.7 m^2g^{-1} at 600°C to 12.7 m^2g^{-1} at 700°C before increasing to 17.4 m^2g^{-1} at 810°C. A similar trend was apparent in the pore volumes where at 600°C the pore volume was 0.089 mLg^{-1} decreasing to almost half this value at 700°C (0.0472 mLg^{-1}). After calcination at 810°C, the pore volume (0.0863 mLg^{-1}) was almost the same as the material calcined at 600°C.

These results are not consistent with previous studies on zirconia calcined with sodium chloride, which showed that the surface area decreased with increasing calcination temperature, while little variation was observed in the pore volume.[9] They are, however, consistent with the results reported in Part I[1] where a study on the same composites employed size exclusion chromatography to evaluate the chromatographically available surface area and pore volume. Although the precise values of the surface areas and pore volumes presented in Part I were different from the above results, the same trends are apparent.

Calcination of the composite without the sodium chloride produced a material with very different surface properties. The results in Table 1 show that the pore volume of the ZS10-810NaCl composite was over 15 times greater than the pore volume of the ZS10-810 composite and the surface area likewise was over 6 times higher. Similar results were obtained when size exclusion chromatography was used to evaluate the surface area and pore volume. That is, the surface area of the ZS10-810NaCl material was six times higher than the surface area of the ZS10-810 material, although the pore volume was only three times higher. This is a clear illustration of the effect sodium chloride has on the surface structure of such materials and is an important consideration when designing surfaces with maximum surfaces areas and pore volumes.

When determining the pore size and the distribution of adsorbents it is imperative to consider which of the isotherm branches are used. Unless the process of adsorption and desorption is completely reversible, both adsorption and desorption data will lead to an error in the estimation of the correct pore size distribution. The use of adsorption data will ultimately lead to an over estimation of the pore size distribution,[10,11] while the desorption branch is prone to errors associated with slow solute diffusion, as a result of restricted pore entrances. Hence, the results from the adsorption branch are indicative of the width of the pore bodies, whilst the desorption data is indicative of the width of the pore entrance. The results from the desorption branch would, therefore, result in a bias towards the smaller pores.[10] The pore dimensions obtained from pore size distribution plots derived from the adsorption branch of the sorption isotherm are given in Table 2. These results show that for the samples calcined in the presence of sodium chloride, the mean pore size increased as the temperature of calcination increased. No maximum was observed for the material calcined at 600°C, indicating the pore size was distributed in the microporous to lower mesoporous region. The high surface area and pore volume of this material supports this result. By increasing the calcination temperature to 700°C, the mean pore diameter increased to 17.4 nm with a small distribution being apparent around 7 nm (Figure 3). Calcination at 810°C further increased the mean pore diameter to 21.0 nm and the distribution was essentially unimodal. The pore size distribution of the ZS10-810 material was broadly distributed with a peak maximum of approximately 3.4 nm. However, the peak was skewed significantly to the macroporous region.

The pore diameters determined from the desorption data are also given in Table 2. The results in Table 2 show that a significant decrease in the mean pore size results for the samples ZS10-810NaCl and ZS10-700NaCl when the desorption branch is considered. This indicates that the pore entrances are restricted and supports the conclusion that the isotherms contain a degree of H_2 type hysteresis. These pores, therefore, appear to contain body cavities in the order of 21 nm in diameter with necks in the order of 10 nm diameter. The results of the pore size distribution for the sample ZS10-600NaCl should be viewed cautiously as the nitrogen sorption method becomes less appropriate as the microporous region is approached. The sample ZS10-810 had almost identical adsorption and desorption pore size distributions, illustrating the reversible nature of the sorption process within this pore structure. The difference in magnitude between the pore diameters, when measured using nitrogen sorption and size exclusion chromatography, are quite significant and this result will be considered in the following discussion.

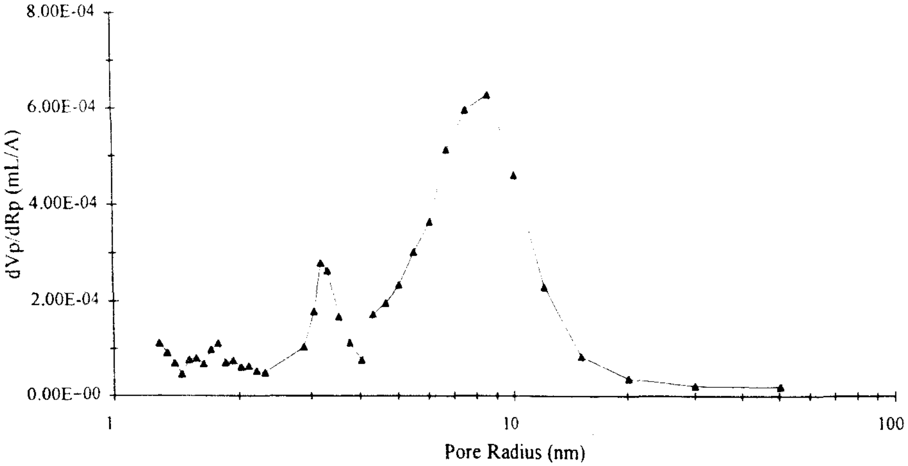

Figure 3. Pore size distribution plot of the ZS10-700NaCl sample obtained from the nitrogen adsorption branch of the isotherm.

Table 2

Pore Size of Each Support Determined from the Adsorption and Desorption Branches of the Nitrogen Isotherms

Sample	Mean R_p (nm) Adsorption Branch	Mean R_p (nm) Desorption Branch
ZS10-600NaCl	no maximum	3.0
ZS10-700NaCl	17.4	10.0
ZS10-810NaCl	21.0	10.0
ZS10-810	Very broad distribution (maximum at 3.4 nm)	Very broad distribution (maximum at 3.4 nm)

In addition to pore size distribution plots, valuable information regarding the pore size can be obtained from normalised cumulative pore size frequency plots. For example, Figure 4 shows the normalised cumulative pore size frequency plots determined from the adsorption branch of the nitrogen sorption isotherms for each of the composites. These curves clearly illustrate

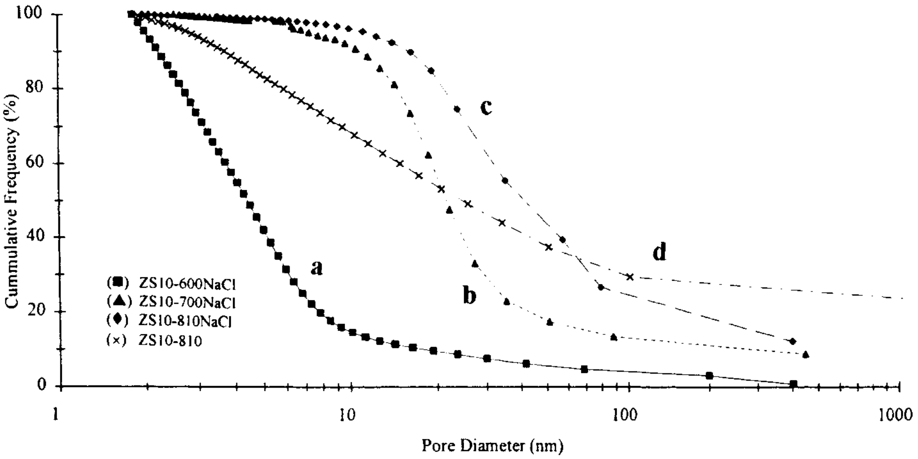

Figure 4. Cumulative pore frequency plots derived from the nitrogen sorption isotherms depicted in Figure 1 and Figure 2. (a) ZS10-600NaCl, (b) ZS10-700NaCl, (c) ZS10-810NaCl, (d) ZS10-810.

the differences between each surface. While the ZS10-700NaCl (curve b) and ZS10-810NaCl (curve c) materials exhibited very similar cumulative frequency plots, indicating that these materials were essentially mesoporous, the cumulative frequency plots of the ZS10-600NaCl (curve a) and ZS10-810 (curve d) materials were very different. The plot for ZS10-600NaCl showed that the pore structure consisted of pores that mostly had a maximum diameter below 10 nm. The plot for ZS10-810 showed that the pore size was broadly distributed from the small mesoporous region to the macroporous region. Size exclusion experiments also indicated that the pore size distribution for the same sample was very broad. This is in stark contrast to the material calcined at the same temperature with sodium chloride (compare curves c and d). The normalised cumulative pore size distribution plots shown in Figure 4 illustrate further the significant differences between the salt impregnated composites and that of the composite calcined without the salt. Not only are surface areas and pore volumes increased by the inclusion of salt, but the pore size distribution is narrowed quite dramatically.

To evaluate the mesoporous contribution to the surface area, t-plots were calculated from the Harkins-Jura expression using Gemini 2375 V4.01 software (Particle and Surface Sciences Pty., Ltd., Gosford, N.S.W. Aust. 2250) and these results are presented in Table 1. Inspection of the t-plot derived surface areas in Table 1 shows that the ZS10-600NaCl sample had a significant microporous contribution as also illustrated in the cumulative pore size frequency plots in Figure 4. After calcination at 700°C, this microporous region was essentially eliminated as shown by the results in Table 1. Curiously, the microporous region increased after the sample was calcined at 810°C. Such a difference between these two samples may not be significant when the pore size distribution plots and the cumulative frequency plots are viewed. Minimal microporous contribution was apparent for the sample calcined in the absence of the sodium chloride. The low surface area and pore volume, together with the shape of the sorption isotherm and hysteresis loop for the sample ZS10-810, clearly indicates that the pores are shallow and with a broad distribution of pore sizes.

The results from this work have determined several important findings. Firstly, the presence of sodium chloride in the composite matrix during calcination serves to increase substantially the surface area and pore volume of the support. Such a result is important from a chromatographic aspect because a higher surface area usually equates to a higher degree of separation, provided mass transfer into the porous network is efficient. A high pore volume allows size separation to be improved by the extension of the linear region of a size exclusion curve. Hence, the peak capacity is improved. Furthermore, the modification of the stationary phase in LLC is improved due to the greater depth of the pores. Hence, the usefulness of such surfaces in these types of chromatography is enhanced. Sodium chloride served to decrease the pore size distribution, compared to the same material calcined without the sodium chloride.

Despite the improvements in the surface area and pore volume, the shape of the nitrogen sorption isotherms and the resulting hysteresis loops suggested that the necks of the pore entrances were still restricted. Such a result was not observed when zirconia stationary phases were calcined in the presence of sodium chloride. In that case, 'ink bottle' shaped pores were transformed to cylindrical shaped pores that were ideal for chromatography. The isotherm and hysteresis loop obtained for the zirconia-silica composite ZS10-810 showed that adsorption and desorption was almost reversible, indicating very few restricted pore entrances. However, when examined in context, the results also show that the surface area and the pore volume were very low, even despite the presence of a significant percentage of small mesopores. As a result, this surface probably resembled a surface containing shallow dishlike pores that, in reality, would offer little as a chromatographic adsorbent.

A second important finding was that, when using composite materials of this type studied here as chromatographic stationary phases, evaluation of the surface and knowledge of the materials' thermal history is of the utmost importance to ensure the surface is suitable for chromatography. The increase in surface area and pore volume as the surface is heated from 700°C to 800°C is an excellent example of why the thermal history should be known. Such a result is contrary to the expected trends in pore structure observed when calcining inorganic materials. As yet we can not fully understand this effect and it remains the focus of future work.

A third finding to come from this study was that the size exclusion results obtained in Part I and the nitrogen sorption results in Part II were not always consistent. To a certain degree, this is to be expected, particularly with regard to the magnitude of the surface area and pore volume. In the size exclusion results, the surface area and pore volume available for solute interaction are determined in a chromatographic sense, where pore access of a solute in a flowing system is examined. This is certainly different from that of a nitrogen molecule, which has substantially less steric hindrance. In general, however, the relativity of surface areas and pore volumes remained essentially uniform for each of the stationary phases analysed, while some major discrepancies were observed in the pore diameters.

The mean pore diameter of the ZS10-600NaCl sample using nitrogen sorption was 3 nm (desorption branch) compared to 13.5 nm determined from the size exclusion studies (Part I).[1] The size exclusion result is a reflection on the chromatographically available surface and this excludes the contribution of the smaller pores into which the smallest solute probe (benzene) does not have access. The reduction in surface area using the size exclusion method (20.8 m^2g^{-1}), compared to the nitrogen sorption method (94.7 m^2g^{-1}), also accounts for the micropores and smaller mesopores. As a result, the mean pore diameter measured using size exclusion is skewed towards the larger pore sizes. The most significant differences were observed for the ZS10-700NaCl and ZS10-810NaCl supports. The nitrogen sorption results indicated that the pore diameters increased with increasing calcination temperature, whereas the size exclusion results showed that the pore size decreased substantially between 700°C and 800°C. Size exclusion results indicated that the mean pore diameters of the ZS10-700NaCl and ZS10-810NaCl materials were 39.8 nm and 27.0 nm, respectively. By comparison, nitrogen sorption measurements on the same materials gave mean pore diameters of 17.4 nm and 21.0 nm, respectively. The difference between the mean pore diameters of the ZS-810NaCl sample is less significant, particularly when you consider the size exclusion result is likely to be skewed towards the larger pore diameters. However, the difference in the two values for the ZS10-700NaCl material is significant.

In an attempt to explain these results, we have considered that the particles undergo a process of homogenisation during thermal treatment. As these composites were prepared using a process that coated zirconia microspheres with silica, a homogenisation process would result in a migration of silicon through the particle as the temperature increased. Previous studies have shown that prolonged thermal treatment at 1300°C transformed the segregated zirconia (ZrO_2) and silica (SiO_2) phases to zircon ($ZrSiO_4$).[5] Such a process certainly could result in a complicated pore restructuring. However, in the present study, samples were heated to temperatures not exceeding 810°C and for periods of only one hour. While Raman spectroscopy is sensitive to crystal structure changes, little information was obtained from the previous work regarding the slow migration of silica and/or zirconia during the thermal treatment unless a crystal phase change occurred. Hence, to observe subtle changes in the surface structure, a surface sensitive technique was required that could allow the analysis of both silica and zirconia at the surface. In order to evaluate this, X-ray photoelectron spectroscopy (XPS) was used, where the relative concentration of silicon and zirconium at the surface of the particle was measured on the samples ZS10-700NaCl, ZS10-810NaCl, ZS10-700, and ZS10-810. These results are shown in Table 3.

The results in Table 3 show a significant change in the relative concentration of silicon and zirconium in the samples calcined in the presence of sodium chloride over the temperature range from 700°C to 810°C. This corresponds to a migration of silicon away from the surface or (in other words) a mixing of the silica/zirconia phases, indicating particle homogenisation is occurring, which could conceivably lead to a complicated pore restructuring. No significant variation was observed in the relative concentrations of silicon or zirconium for the samples calcined without the sodium chloride. The increased particle homogenisation of the samples calcined in the presence of sodium chloride is consistent with the decrease in temperature associated with the crystallisation from the amorphous state to the tetragonal state recorded using Raman spectroscopy in Part I.[1]

Having demonstrated that a homogenisation process is occurring over this temperature range, an explanation is possible for the different pore diameters obtained for the ZS10-700NaCl composite discussed above. Two effects may be occurring: the formation of mesopores and the blocking of pore entrances. An examination of the shape of the size exclusion curves for samples ZS10-700NaCl and ZS10-810NaCl in Part I,[1] Figure 5, reveals that the exclusion limits are quite indistinct, suggesting the presence of a broad macroporous distribution. However, the nitrogen sorption results for the same materials do not support this. Alternatively, the variation in the elution of the high molecular weight polystyrenes may be due to slow solute diffusion out from the

Table 3

Relative Concentration (±10%) of Silicon and Zirconium on the Surface of the Sample ZS10 After Calcination at the Specified Temperatures With and Without Sodium Chloride Impregnation

Sample	%Si	%Zr
ZS10-700	14.69	14.02
ZS10-810	13.78	14.98
ZS10-700NaCl	15.38	10.28
ZS10-810NaCl	12.15	14.29

pores. Such a process is supported by the nitrogen sorption results, which indicate that the pore necks are restricted. The apparently larger pore diameter of the ZS10-700NaCl support may result if the diffusion of the polystyrenes is inhibited to a greater degree than when eluting from the pores on the ZS10-810NaCl support. The shape of the size exclusion curve in the high molecular weight region supports this, as the exclusion limit on the ZS10-810NaCl material has become more distinct (Part I, Figure 5). The analysis based on nitrogen sorption does not lead to an over estimation of the mean pore diameter that is as dramatic as the size exclusion result because the magnitude of the inhibition towards the diffusion of nitrogen molecules is less significant than for a high molecular weight polystyrene molecule. Both techniques do, however, depict a significant reduction in the surface area and pore volume associated with the ZS10-700NaCl support that is abnormal in comparison to the ZS10-600NaCl and ZS10-810NaCl supports. Further evaluation of the pore structures of these supports, using microscopic studies, are being undertaken. We emphasise that the same sample of ZS10-700NaCl was measured by both size exclusion and nitrogen sorption experiments, ruling out any differences associated with the synthesis of different batches.

Regardless of the cause of the discrepancy between the nitrogen sorption and size exclusion results, these studies have shown the importance of evaluating the performance of the supports in a chromatographic situation. If only nitrogen sorption was used to characterise the support in terms of identifying a suitable support for a given separation problem, then an incorrect assessment may have been made. Furthermore, very little is known regarding the performance of these supports as chromatographic stationary phase materials. Knowledge of the thermal history is, therefore, very important. We consider, also, that further studies are required to obtain the optimal calcination conditions to produce supports that do not contribute to slow solute diffusion throughout the porous network. We believe that this may be obtained by using extended calcination times rather than the short periods used in the present work.

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REFERENCES

1. R. A. Shalliker, G. K. Douglas, J. Liq. Chromatogr. & Rel. Technol., **21(12)**, 1749-1765 (1998).

2. R. J. Bird, T. Swift, J. Electron Spectrosc. & Relat. Phenom., **21**, 227 (1980).

3. M. P. Seah, Surf. Interface Anal., **14**, 488 (1989).

4. R. J. Ward, B. J. Wood, Surf. Interface Anal., **18**, 679 (1992).

5. R. A. Shalliker, L. Rintoul, G. K. Douglas, S. C. Russell, J. Mater. Sci., **32(11)**, 2949 (1997).

6. R. A. Shalliker, G. K. Douglas, P. R. Comino, P. E. Kavanagh, Powder Technology, **91(1)**, 17 (1997).

7. R. A. Shalliker, G. K. Douglas, L. Rintoul, P. R. Comino, P. E. Kavanagh, J. Liq. Chromatogr. & Rel. Technol., **20(10)**, 1471 (1997).

8. K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, T. Siemieniewska, Pure Appl. Chem., **57(4)**, 603 (1985).

9. R. A. Shalliker, G. K. Douglas, J. Liq. Chromatogr. & Rel. Technol., **20(11)**, 1651 (1997).

10. J. C. P. Broekhoff, in **Preparation of Catalysts**, B. Delmon, P. Grange, P. Jacobs, G. Poncelet, eds., Elsevier, Amsterdam, 1979, pp. 663-683.

11. J. C. P. Broekhoff, B. G. Linsen, in **Physical and Chemical Aspects of Adsorbents and Catalysts**, Academic Press, London, 1970, Ch. 1.

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