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Development of Ceramic Based Stationary Phases for Chromatography

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Motivation & Goal

Preparative chromatography is still mainly performed with silica-based retention phases. [1,2] Unfortunately, the small stability range of silica, approximately pH 2–8, limits the possible parameter space of chromatographic protocols. In order to fully protonate or deprotonate common product types (i.e. amino acids), or to routinely clean and reuse the columns (typically with concentrated sodium hydroxide solutions), stationary phases with stability ranges outside pH 2–12 would be desired. [1,3] Previous work shows promising results with other oxide materials, such as alumina (Al_2O_3), titania (TiO_2), or zirconia (ZrO_2). [4]

Materials & Methods

Porous spheres of zirconia, alumina and titania were produced either by a precursor route or by controlled agglomeration (PICA method, [5]) of nanoparticle dispersions. In the former approach, aqueous solutions of nitrate or chloride salts with organic monomers (urea and formaldehyde) were either dispersed by agitation or dispensed dropwise (by one of two different dispenser types) into a curing bath based on silicone or mineral oil. Variation of the viscosity of the oil phase, dispersants and heating rate led to a set of different particles.

Alternatively, the dispersed phase contained alginate instead of monomers while the continuous phase contained calcium hydroxide, both to coagulate the alginate and to precipitate the precursor salts.

After calcination of the particles, surface modifications with different polymers were performed. Particle sizes and pore sizes were compared in the prepared state and after surface modification. The stability against dissolution of various materials was tested in buffer solutions at pH 1 and pH 12. According to these trials, zirconia, alumina, titania, and ceria were selected. Non-oxidic materials such as silicon carbide or silicon nitride were excluded due to the low stability of the former and the non-sinterability of the latter.

Results

A first set of experiments using agitation synthesis ("water in oil") aimed at the preparation of particles of ZrO_2 or yttrium doped ZrO_2 (zirconia, YSZ).

After sintering, these particles exhibited specific surface areas around 50 m^2/g. Considering the density of zirconia, which is approximately 2.5 times larger than the density of silica, this compares to a silica of approx. 125 m^2/g (Fig. 1).

Due to difficulties with reproducibility, this approach was abandoned in favor of other methods.

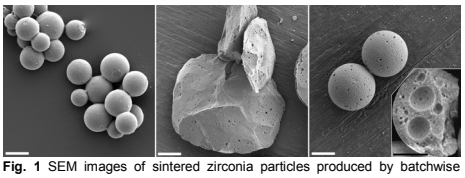

Fig. 1 SEM images of sintered zirconia particles produced by batchwise emulsification under different conditions. The scale bars correspond to 10 µm. The inset on the rightmost image represents a cross section of a particle.

The first dispenser used a piezo driven nozzle, allowing the production of particles in the desired size range of 10-30 µm. Producing small amounts (ca. 50-100 mg) of monodispersed spheres could be achieved with this system at moderate rates (ca. 100-3000 Hz).

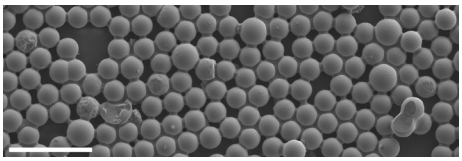

Fig. 2 Sintered zirconia particles produced by piezo-driven dispensing. The scale bar corresponds to 100 µm.

Not regarding these good results, Fig. 2, the system was slow, the dispensing conditions were often instable and had strict limits on the viscosity of the dispensed liquid.

The second dispenser used was a state of the art flow vibration tool. Using similar precursor routes as for the agitation synthesis, it was possible to produce monodisperse spheres with a diameter of ca. 70 µm after sintering (Fig. 3); smaller spheres would be accessible using a smaller die.

In order to increase pore volume, experiments with pore formers have been conducted. The increase in pore size is apparent using two different models, DFT and BJH, but the absolute values are quite different between these two models (Fig. 3). Further experiments in order to normalize these models would be required for a quantitative result.

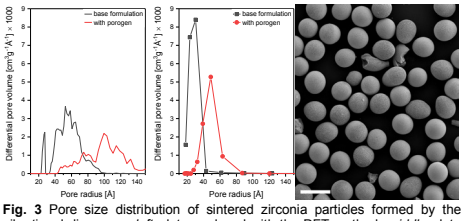

Fig. 3 Pore size distribution of sintered zirconia particles formed by the vibrational dispenser. *left*: data analyzed with the DFT-method; *middle*: data analyzed with the BJH method; *right*: SEM image, scale bar 100 µm.

The particles formed by the PICA method (polymerization-induced colloidal aggregation) are the smallest among the different preparation routes. On the other hand, due to the more physical nature of particle formation, this method is relatively insensitive towards the type of material and yields highly porous particles with narrow particle size distribution (Fig. 4). The method is only limited to particles dispersible in water without further dispersants.

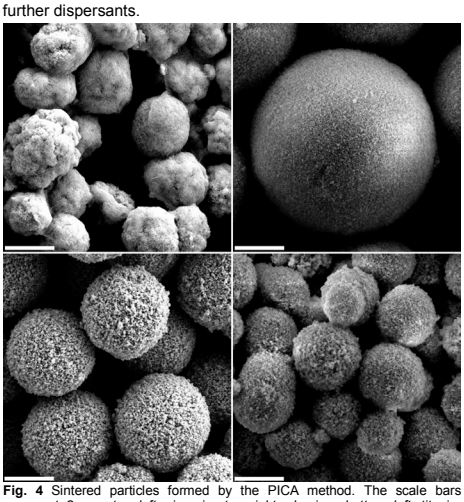

Fig. 4 Sintered particles formed by the PICA method. The scale bars represent 2 µm. *top left*: zirconia; *top right*: alumina; *bottom left*: titania; *bottom right*: ceria.

Again, the pore volumes calculated by the BJH method are significantly higher than those derived from DFT (Tab. 1, Fig. 5). The main reason for that is the absence of pore size information in the DFT data above about 150 Å (i.e. the pore volume of pores larger than 150 Å is not taken into account). The DFT also predicts unrealistic average pore sizes around 19 Å for TiO_2 and CeO_2 which are not consistent with the particle sizes. All in all, the values of the BJH appear more consistent and reliable here to be considered as guidelines.

Although the sintering conditions were kept constant for all samples, the extent of sintering of the different materials is expected to vary. In combination with the different densities of the materials (with respect to SiO_2, Al_2O_3: 1.7 times, TiO_2: 1.9 times, CeO_2: 3.3 times larger density) this leads to some differences in specific surface area and pore volumes.

Tab. 1 Specific surface area (BET), total pore volume, and peak pore size as determined by N_2 adsorption on sintered PICA samples.

Material	[m^2/g] BET	[m^3/g] DFT	[m^3/g] BJH	R [Å] DFT	R [Å] BJH
Zirconia	56	0.147	0.219	100	45
Alumina	115	0.280	0.676	100	90
Titania	38	0.065	0.300	18.9	126
Ceria	54	0.104	0.320	18.9	127

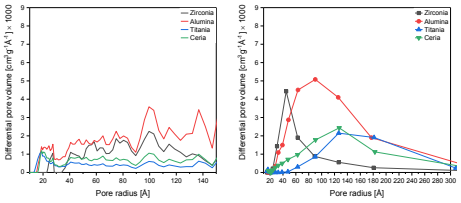

Fig. 5 Pore size distribution of sintered particles formed by the PICA method. *left*: data analyzed with the DFT-method; *right*: data analyzed with the BJH method.

Conclusions

Several methods for producing spheres by batchwise emulsification were tested. The one using the precursor route produced spheres of relatively narrow size distribution around the targeted sphere size range of 10-30 µm. Nevertheless, gel-casting formulations using dispersions with alginate based binders or PICA type reactions may be more promising for producing and controlling the targeted pore size distribution. As long as perfect monodispersity is not the highest priority, batch emulsification is clearly the method of choice for practical production of spheres in the targeted size range and screening of materials with different pore size distributions.

Through the PICA process high yields of various, practically monodispersed, oxide spheres could be achieved. Underneath the initial simplicity of the process, surprising difficulties arose: The increase of sphere size to the 10–30 µm range requires more development and the control of pore size distribution requires new concepts as well. So-far, the PICA process seems to be rather a "black box" system, where it is unclear which handles exist to influence particle size or porosity.

Since dispensing methods offer inherent control over the droplet size (and thus finally the particle size), they are an attractive option to close the "size gap" opened by the above discussed methods. On the other hand, it has to be considered that when dispensing the rate of sphere production is highly dependent on the sphere diameter. For example, producing the same mass of spheres with diameters of 10 µm would take a factor of 10^3 longer than for 100 µm spheres.

Irrespective of the type of dispenser system, one of the main obstacles at present for production of spheres by dispensing is the curing and collection of the spheres. Fusing or aggregation of not fully cured droplets (in flight, on the interface to the curing liquid, in the curing liquid) has to be avoided. Although some parameters to influence this seem obvious (i.e. dispensing frequency, surface tension of the curing liquid, curing speed), finding practical solutions to this issue is not trivial.

Website of the group "Ceramic Materials"

Literature

[1] H.A. Claessens, M.A. van Straten, *J. Chromatogr. A*, **2004**, *1060*, 23-41.

[2] V. Žižkovský, R. Kučera, J. Klimeš, *J. Pharmaceut. Biomed.*, **2007**, *44*, 1048-1055.

[3] C. McNeff, L. Zigan, K. Johnson, *et al.*, *LC-GC*, **2000**, *18(5)*, 514-529.

[4] J. Nawrocki, C. Dunlap, *et al.*, *J. Chromatogr. A*, **2004**, *1028*, 1-62.

[5] a) P.W. Carr *et al.*, United States Patent 5540834, **1996**.
b) R.K. Iler *et al.*, United States Patent 3855172, **1974**.