Nonporous Zirconia as a Novel Stationary Phase Support

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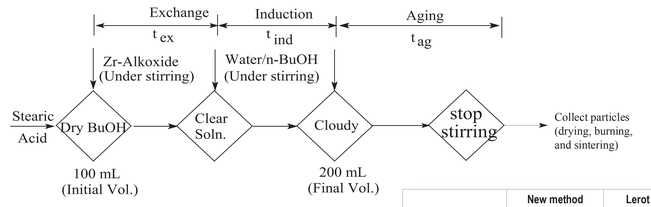
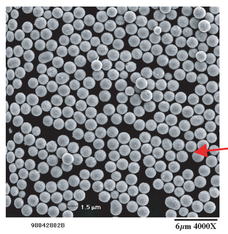
Novel Synthetic Route to Nonporous Zirconia



- Zirconia particles are stable the entire pH range (1-14)
- Nonporous particles were synthesized using a new synthetic route, with distinct advantages over the Lerot method

	New method	Lerot method
Reactant concentration (M) $Zr(OPr^n)_4$ H_2O Stearic acid	0.1M 0.42M 0.016M	0.1M 0.35M 0.016M
Post-treatment	(1) dilution before filtration (2) filtration	(1) centrifugation
Aggregation Particle size Induction time Chromatographic applicability	**no aggregation** 1.8 micron ~35min **yes**	severe aggregation 1.8 micron less than 2 minutes no

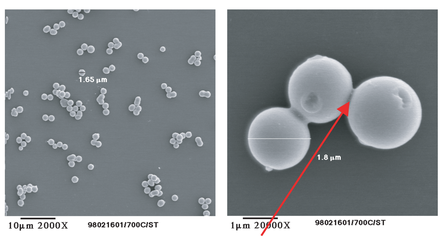
New Method



It is very important to dilute and filter instead of using centrifugation for particle collection.

The resulting particles are monodisperse, spherical and nonaggregated.

Lerot Method



Collection by centrifugation causes "necks"and particle aggregation

Reproducibility

Batch No.	Weight of ZrO_2(g)	Surface area[a] (m^2/g)
1	0.11351	1.78
2	0.10284	1.87
3	0.12012	1.82
4	0.10967	1.87
5	0.11064	1.76
Average	---	1.82
Standard Deviation	---	0.0505

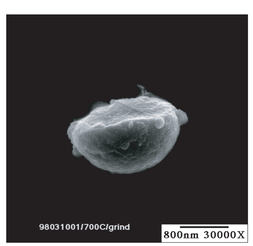
Good Batch-to-batch reproducibility

Only 2.9 times theoretical area of 1.65 micron spheres--easily accountable by surface texture

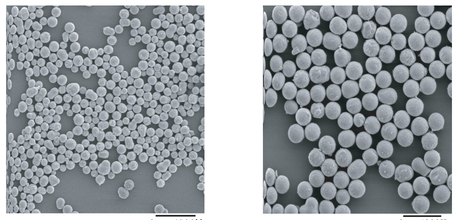
[a] Based on using porous zirconia of known surface area (by BET) as standard
[b] The particle size is 1.65 micron, the density of zirconia is 5.8 g/ml, theoretical surface area is 0.63 m^2/g

Particle Cross-Section

The nonporous nature of the particles was verified by grinding a sample and looking at the interior of a broken particle.



New Method Allows Tuning of Particle Size



(a) (b)

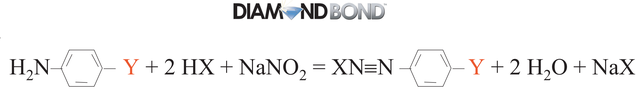
SEM photograph of particles synthesized using ACS butanol. Synthesis conditions: $[Zr(OPr^n)_4]$ = 0.1 M, [H2O] = 0.42 M, (a) [decanoic acid] = 0.016 M, Induction time = 31 min, Aging time = 60 min, (b) [eicosanoic acid] = 0.016 M, Induction time = 31 min, Aging time = 150 min.. Post synthetic treatment: dilution and filtration.

- These SEMs show the influence of increasing the chain length of the carboxylic acid from decanoic acid (C_{10}) to eicosanoic acid (C_{20}) on particle size (from 0.5 to 2.8 micron).
- In this set of experiments, we show that different size monodisperse, spherical particles can made by changing the length of the carboxylic acid used

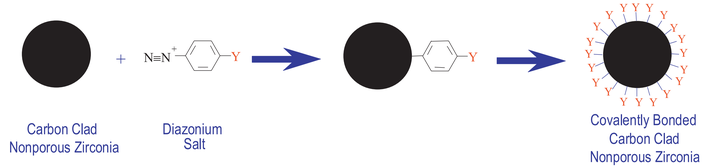
Synthesis of Covalently Bonded Carbon-Clad Nonporous Zirconia Particles

DIAMONDBOND

Step 1

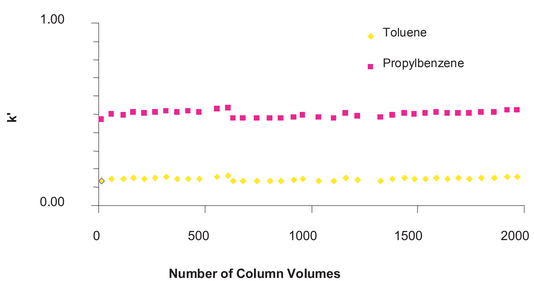


Step 2



Carbon Clad Nonporous Zirconia — Diazonium Salt — Covalently Bonded Carbon Clad Nonporous Zirconia

Bonded Materials are Ultra-Stable

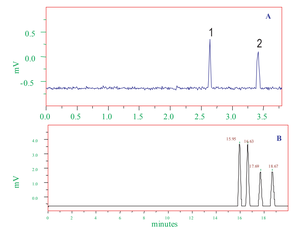


Stability testing of vinylbenzene modified carbon clad NPZ crosslinked with polybutadiene coating.

LC Conditions:
Column: 50 x 4.6 mm id.; Mobile Phase: 5/95 ACN/Water;
Flow Rate: 1 mL/min; Detection: 254 nm; Temperature: 200 °C, 1 microliter injection.

Fast Chromatography Using Non Porous Zirconia Phases

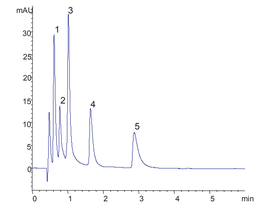
Ultra High Pressure LC



A: Separation of benzene (peak 1) and resorcinol (peak 2). Conditions: **5,000 psi** inlet pressure; 25 cm x 75 micron i.d fused silica column packed with **2.0 micron PBD-coated nonporous zirconia**; water/acetonitrile (64:40, v/v). Plate number for benzene is **61,000 N/m.**

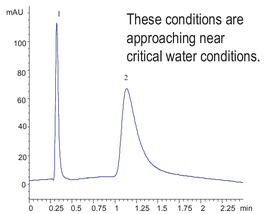
B:Separation of biphenyl, fluorene, fluoranthene, anthracene (peaks 1-4, respectively). Conditions:**15,000 psi** inlet pressure; 31 cm x 100 µm i.d. fused silica column packed with **1.0 micron PBD-coated nonporous zirconia**; Acetonitrile/ 10 mM H_3PO_4, pH = 4.0 in water (70:30, v:v); Plates per meter for these four compounds are: **N_1=183,000; N_2=195,000; N_3=191,000; N_4=179,000, respectively.**

Fast Separations Using Bonded Carbon Clad NPZ



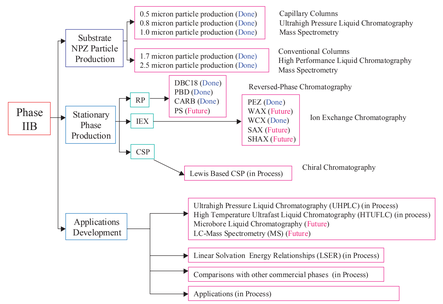
LC Conditions:
Column: **Diamondbond-CNPZ-C18** 50x4.6 mm; Mobile Phase: 35/65 Acetonitrile/Water; Flow rate: 1.0 mL/min.; Temperature: 30 °C; Injection volume: 1 µL
Analytes: 1 - Benzene, 2 - Toluene, 3 - Ethylbenzene, 4 - Propylbenzene, 5 - Butylbenzene

Separations in 100% Water



LC Conditions:
Column: **Carbon clad zirconia**; Mobile phase, 100% water; Column temperature, 200 °C; detection at 254 nm; flow rate=1.0 ml/min.
Analytes: phenol (peak 1) and 2,4,6 trichlorophenol (peak 2)

SBIR Grant Details



Conclusions

- A method was developed for the reproducible production of monodisperse nonporous zirconia particles in the size range of 0.8 to 2.8 microns
- Gentle collection protects size distribution. SEM results show that the particles are spherical and monodisperse
- These particles are stable between pH 1 to 13 and up to 200°C under HPLC conditions
- The synthesized particles are nonporous as demonstrated by SEM of a cross section and by confocal microscopy
- Ultra-fast high temperature separations are possible with little or no toxic waste production
- Nonporous zirconia particles can be carbon clad and surface modified through diazonium salt coupling reactions to create a new class of chemically and thermally stable bonded phase nonporous stationary phases for fast high temperature liquid chromatography
- *Acknowledgement: National Science Foundation Grant # DMI-990871*