Ceramic Spheres Derived From Cation Exchange Beads

Fred Dynys
National Aeronautics & Space Administration
Glenn Research Center

Sponsored: Ultra Efficient Engine Technology (UEET)
Thermal Barrier Coating

Benefits:
- Reduce Substrate Temp. (150°F to 325°F)
- Increase Combustion Temp.
- Increased part life
- Environmental Protection
- Increase efficiency

Ultra Efficient Engine Technology (UEET)

- Reduce CO₂/NOₓ emission by increasing engine operating temperature → 3000 °F (1649 °C)

Radiation Barrier Coating

- Porous Coating to Reduce Photon Conduction
- Max. Scattering - Pores → 1-4 μm
- Hollow/Porous Ceramic Spheres
Objective

Establish a simple templating process to produce hollow ceramic spheres with a pore size 1 to 10 μm.

Template – Cation exchange beads -Polystyrene based polymer

Oxide – ZrO₂, Y₃Al₅O₁₂
A. Ion Exchange Reaction
   Aqueous Solution

B. Coat Sphere Surface
   $M(OR)_n + H_2O$

C. Composite Sphere
   Methods A & B

Templating

Polymer Pyrolysis

Ceramic Sphere

Polymer Pyrolysis

Hollow Ceramic Sphere

• Optical Applications
• Environmental Coatings
Organic Cation Exchange Resin

Linear Hydrocarbon Chain - Polystyrene

Cross Linker - Divinylbenzene

Functional Groups – SO$_3^-$, COO$^-$, PO$_3^{2-}$, AsO$_3^{2-}$, SeO$_3^-$

Cross Linking
• Swelling
• Regulates Pore Size – Ion Mobility
• Randomness in crosslinking produces disordered structure
Ion Exchange

\[ 2(\text{R-SO}_3^-) \cdot \text{H}^+ + \text{ZrOCl}_2 \rightleftharpoons (\text{R-SO}_3^-)_2 \cdot \text{ZrO}^{2-} + 2\text{HCl} \]

General Remarks

• Reversible Reaction
• Maintain Charge Neutrally
• pH Independent - Strong Acid Functional Group – \(\text{SO}_3^-\)
• pH dependent - Weak Acid Functional Group – \(\text{COO}^-\)
• Number of groups determined exchange capacity equivalents/volume
• Cation Selective
  Valence – \(\text{M}^{+3} > \text{M}^{+2} > \text{M}^{+1}\)
  \(\text{Ba}^{+2} > \text{Pb}^{+2} > \text{Sr}^{+2} > \text{Ca}^{+2} > \text{Ni}^{+2} > \text{Cd}^{+2} > \text{Cu}^{+2} > \text{Zn}^{+2} > \text{Mg}^{+2} > \text{UO}_2^{+2}\)
Procedure - Ion Exchange

1. 0.1-0.3 M Salt Solution – ZrOCl₂, MgCl₂, AlCl₃
2. Dowex 50x4 Beads – SO₃⁻
3. Ion Exchange Time ≥18 Hrs.
4. Liquid/Solid Separation
5. Wash
6. Calcination
   1. Single Step → ≥6 °C/min – 600-900 °C – Air
   2. Double Step → 800-1000 °C – Inert
      → ≥6 °C/min – 800-1000 °C – Air
Process Variables

- Calcination Heating Rate < 6°C/min
- Ion Exchange Time < 18 Hrs.

Defective Spheres

![Image showing defective spheres](image-url)
Single Step Calcination

ZrO₂

DTA/TGA

XRD

24 m²/g

Particle Size (microns)
Double Calcination
ZrO₂ – Step 1 - Inert

XRD

TGA

Carbide Spheres
1400 - 1600 °C
Inert
Zr₄C₂S₂
Double Calcination

ZrO₂ – Step 2 – Air
MgO/Al₂O₃ Spheres

Single Step Calcination
MgAl$_2$O$_4$/Y$_3$Al$_5$O$_{12}$ Spheres

**MgAl$_2$O$_4$**
- Phase Formation
  - 1050 °C 12 hrs.
  - 600 °C 5 hrs.

**Y$_3$Al$_5$O$_{12}$/Y$_4$Al$_2$O$_9$ minor**
- Phase Formation
  - 1200 °C 48 hrs
  - 1200 °C 12 hrs
  - 1150 °C 12 hrs
  - 600 °C 6 hrs

Molar Ratio
- AlCl$_3$/MgCl: 2/1
- AlCl$_3$/Y(NO$_3$)$_3$: 5/3
Hollow TiO$_2$ Spheres

2,4-pentanedione
Ti(OC$_3$H$_7$)$_4$
Isopropanol

Drip

Ti(OC$_3$H$_7$)$_4$ + H$_2$O

2,2,4-trimethyl pentane
Span 80

Coated Beads

- Solid/Liquid Separation
- Air Dry
- Calcine - ≥6 °C/min - 600-800 °C - Air
Hollow TiO$_2$ Spheres

![Images of hollow TiO$_2$ spheres with XRD and particle size distribution graphs.]

XRD

- Count vs. 2θ
- Peaks indicating anatase phase

Frequency vs. Particle Diameter (mm)

- Coated Beads
- TiO$_2$

42 m$^2$/g
Al$_2$O$_3$ Coated ZrO$_2$ Spheres
Single Step Calcination

Phase Formation
- 1300 °C  12 hrs.
- 1200 °C  12 hrs.
- 1100 °C  12 hrs.
- 600 °C     5 hrs.
Summary

- Ion exchange using cation exchange beads can be used as shape forming template to make simple and complex oxides.
- Ion exchange method produces porous ceramic spheres with a unique structure; Inner sphere surrounded by a outer sphere.
- Porous spheres contained elongated pores with a pore width of 0.5 – 3 μm.
- Calcination rate and ion exchange time are important process parameters.
- Cation exchange beads can be utilized as a micro-reactor to form hollow ceramic spheres.
- Cation exchange bead size regulates the pore size of the hollow ceramic sphere.
- Composite particles can be formed by combining both templating methods.