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 – ZrO$_2$, Y$_3$Al$_5$O$_{12}$
Templating

A. Ion Exchange Reaction
   Aqueous Solution
   Polymer Pyrolysis
   Ceramic Sphere

B. Coat Sphere Surface
   \( M(OR)_n + H_2O \)
   Polymer Pyrolysis
   Hollow Ceramic Sphere

C. Composite Sphere
   Methods A & B

- Optical Applications
- Environmental Coatings
Organic Cation Exchange Resin

Linear Hydrocarbon Chain - Polystyrene

Cross Linker - Divinylbenzene

Functional Groups – SO₃⁻, COO⁻, PO₃²⁻, AsO₃²⁻, SeO₃⁻

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

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

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 – \( M^{+3} > M^{+2} > M^{+1} \)
  \( \text{Ba}^{+2} > \text{Pb}^{+2} > \text{Sr}^{+2} > \text{Ca}^{+2} > \text{Ni}^{+2} > \text{Cd}^{+2} > \text{Cu}^{+2} > \text{Zn}^{+2} > \text{Mg}^{+2} > \text{UO}_2^{+2} \)
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
Single Step Calcination

ZrO$_2$

DTA/TGA

XRD

24 m$^2$/g

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

[Images of electron micrographs and XRD scans showing patterns and graphs with data points for TGA and Carbide Spheres]
Double Calcination
ZrO$_2$ – Step 2 – Air

TGA

XRD

Particle Diameter (microns)

Counts

Cubic
Monoclinic
MgO/Al₂O₃ Spheres

Single Step Calcination

XRD

Counts

MgO

MgSO₄

2θ

Counts

Al₂O₃

2θ
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(O$_3$C$_3$H$_7$)$_4$
Isopropanol

Drip

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

2,2,4-trimethyl pentane
Span 80

Coated Beads

- Solid/Liquid Separation
- Air Dry
- Calcine - $\geq 6 \, ^\circ\text{C/min} - 600-800 \, ^\circ\text{C} - \text{Air}$
Hollow TiO$_2$ Spheres

![Image of Hollow TiO$_2$ Spheres]

- XRD
- Frequency vs Particle Diameter (mm)
- 42 m$^2$/g

- Coated Beads
- TiO2
**Al₂O₃ Coated ZrO₂ 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.
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