Ceramic Spheres Derived From Cation Exchange Beads

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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

- Optical Applications
- Environmental Coatings
Organic Cation Exchange Resin

Linear Hydrocarbon Chain - Polystyrene

Cross Linker - Divinylbenzene

Functional Groups – \( \text{SO}_3^-, \text{COO}^-, \text{PO}_3^{2-}, \text{AsO}_3^{2-}, \text{SeO}_3^- \)

Cross Linking

- Swelling
- Regulates Pore Size – Ion Mobility
- Randomness in crosslinking produces disordered structure
Ion Exchange

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

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.
Single Step Calcination

$\text{ZrO}_2$

**XRD**

**DTA/TGA**

- **Frequency**
  - Zirconia
  - Dowex

- **Particle Size (microns)**
  - 10-14
  - 20-24
  - 30-34
  - 40-44
  - 50-54
  - 60-64
  - 70-74
  - 80-84
  - 90-94
  - 100-104
  - 110-114
  - 120-124

- **Counts**
  - 10
  - 20
  - 30
  - 40
  - 50
  - 60
  - 70

- **Temp. (°C)**
  - 0
  - 100
  - 200
  - 300
  - 400
  - 500
  - 600
  - 700
  - 800
  - 900
  - 1000

- **% Wt. Loss**
  - 0
  - 20
  - 40
  - 60
  - 80
  - 100

- **Zr**

- **5°C/min Air**

- **100 μm**
Double Calcination

ZrO$_2$ – Step 1 - Inert

XRD

TGA

Carbide Spheres

1400 - 1600 °C
Inert
Zr$_4$C$_2$S$_2$
Double Calcination

ZrO₂ – Step 2 – Air

Particle Diameter (microns)

Frequency

TGA

% Pt Loss

Temp. (°C)

XRD

Counts

2θ

10 m²/g

Cubic
Monoclinic
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.

Molar Ratio

AlCl$_3$/MgCl

2/1

Y$_3$Al$_5$O$_{12}$/Y$_4$Al$_2$O$_9$ minor

Y$_4$Al$_2$O$_9$

Phase Formation

- 1200 °C 48 hrs
- 1200 °C 12 hrs
- 1150 °C 12 hrs
- 600 °C 6 hrs

Molar Ratio

AlCl$_3$/Y(NO$_3$)$_3$

5/3
Hollow TiO₂ Spheres

2,4-pentanedione
Ti(OC₃H₇)₄
Isopropanol

Drip

Ti(OC₃H₇)₄ + H₂O

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

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

XRD

Counts

0 10 20 30 40 50 60 70

2θ

anatase

Frequency

0 50 100 150

10-14

20-24 30-34 40-44 50-54 60-64 70-74 80-84 90-94

Particle Diameter (mm)

42 m$^2$/g

- Coated Beads
- TiO$_2$
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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