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 – ZrO$_2$, Y$_3$Al$_5$O$_{12}$
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 – $\text{SO}_3^-$, $\text{COO}^-$, $\text{PO}_3^{-2}$, $\text{AsO}_3^{-2}$, $\text{SeO}_3^{-}$

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

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

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

ZrO₂

XRD

DTA/TGA

24 m²/g

Particle Size (microns)
Double Calcination
ZrO$_2$ – Step 1 - Inert

TGA

Carbide Spheres

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

ZrO$_2$ – Step 2 – Air
MgO/Al₂O₃ Spheres

Single Step Calcination

NASA
Molar Ratio
AlCl₃/MgCl₂
2/1

MgAl₂O₄
Phase Formation
1050 °C 12 hrs.
600 °C 5 hrs.

Y₃Al₅O₁₂/Y₄Al₂O₉ minor
Phase Formation
1200 °C 48 hrs
1200 °C 12 hrs
1150 °C 12 hrs
600 °C 6 hrs

XRD
Counts
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 TiO₂ Spheres

Particle Diameter (mm)

Frequency

XRD

anatase

Counts
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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