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 emissions 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

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

**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.
Single Step Calcination

ZrO₂

[Image of XRD graph]

[DTA/TGA graph]

[Particle size distribution graph]

24 m²/g
Double Calcination

ZrO₂ - Step 1 - Inert
MgO/Al$_2$O$_3$ Spheres

Single Step Calcination

XRD

Counts

MgO
MgSO$_4$

Counts

Al$_2$O$_3$
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

• Y₄Al₂O₉
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 - $\geq$6 °C/min – 600-800 °C – Air
Hollow TiO$_2$ Spheres
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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