Ceramic Spheres Derived From Cation Exchange Beads

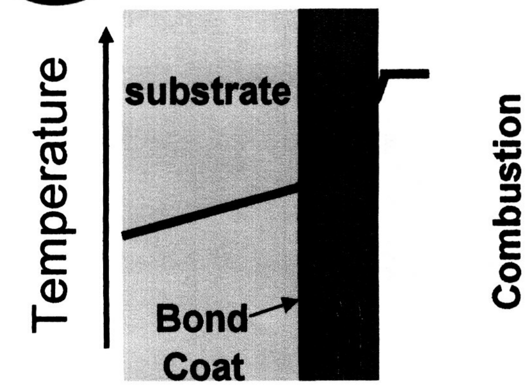
Fred Dynys

National Aeronautics & Space Administration

Glenn Research Center

Sponsored: Ultra Efficient Engine Technology (UEET)

Thermal Barrier Coating



Benefits:

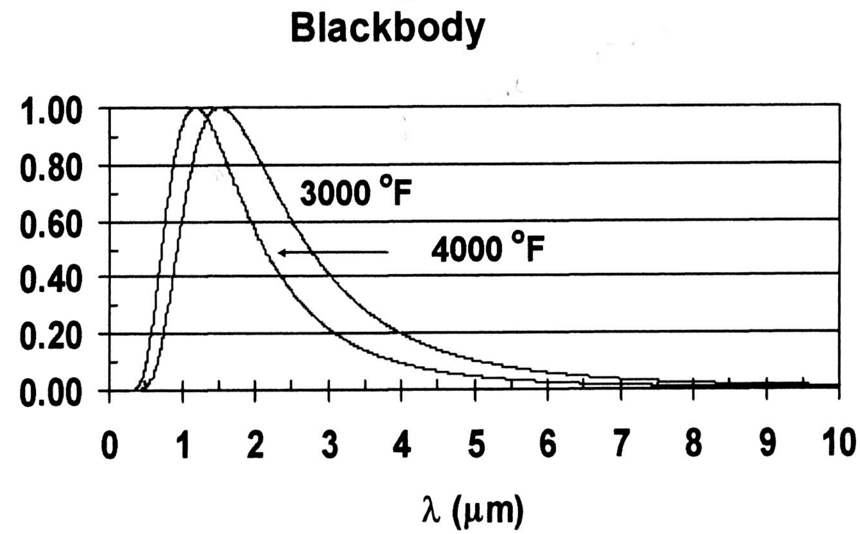
- •Reduce Substrate Temp. (150° F to 325°F)
- •Increase Combustion Temp.
- •Increase~~d~~ part life
- •Environmental Protection
- •Increase efficiency

Ultra Efficient Engine Technology (UEET)

- Reduce CO_2/NO_x 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.

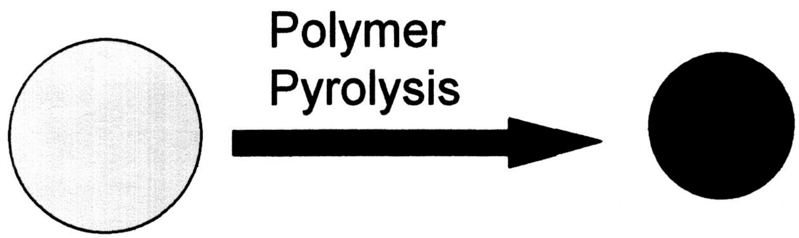
Template – Cation exchange beads -Polystyrene based polymer

Oxide – ZrO_2, $Y_3Al_5O_{12}$

Templating

A. Ion Exchange Reaction

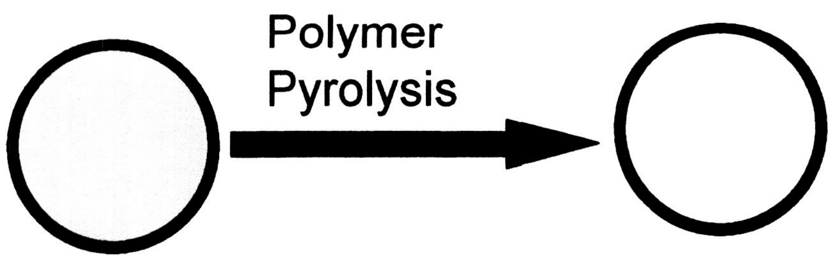
Aqueous Solution



Ceramic Sphere

B. Coat Sphere Surface

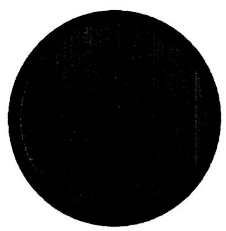
$M(OR)_n + H_2O$



Hollow Ceramic Sphere

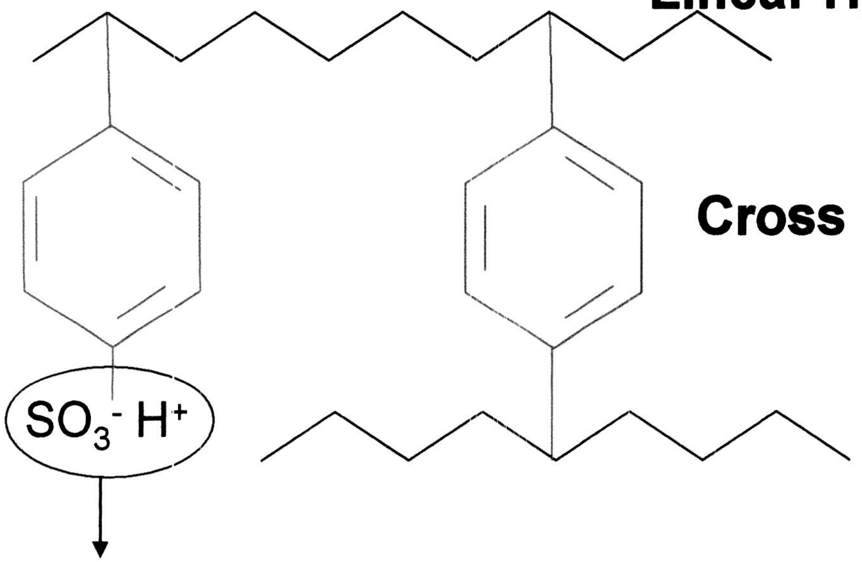
C. Composite Sphere

Methods A & B



- Optical Applications
- Environmental Coatings

Organic Cation Exchange Resin



Linear Hydrocarbon Chain - Polystyrene

Cross Linker - Divinylbenzene

Functional Groups – 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

$$2(R\text{-}SO_3)^- H^+ + ZrOCl_2 \longleftrightarrow (R\text{-}SO_3)_2^- ZrO^{-2} + 2HCl$$

General Remarks

- Reversible Reaction
- Maintain Charge Neutrally
- pH Independent - Strong Acid Functional Group – SO_3^-
- pH dependent - Weak Acid Functional Group – COO^-
- Number of groups determined exchange capacity equivalents/volume
- Cation Selective

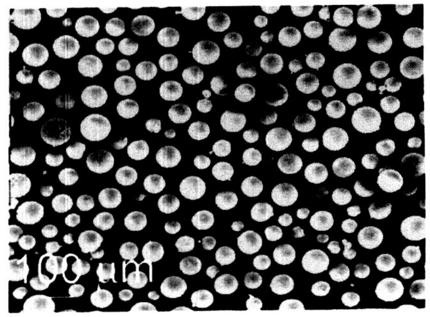
  Valence – $M^{+3} > M^{+2} > M^{+1}$

  $Ba^{+2} > Pb^{+2} > Sr^{+2} > Ca^{+2} > Ni^{+2} > Cd^{+2} > Cu^{+2} > Zn^{+2} > Mg^{+2} > UO_2^{+2}$

Procedure - Ion Exchange

1. 0.1-0.3 M Salt Solution – $ZrOCl_2$, $MgCl_2$, $AlCl_3$
2. Dowex 50x4 Beads - SO_3^-
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

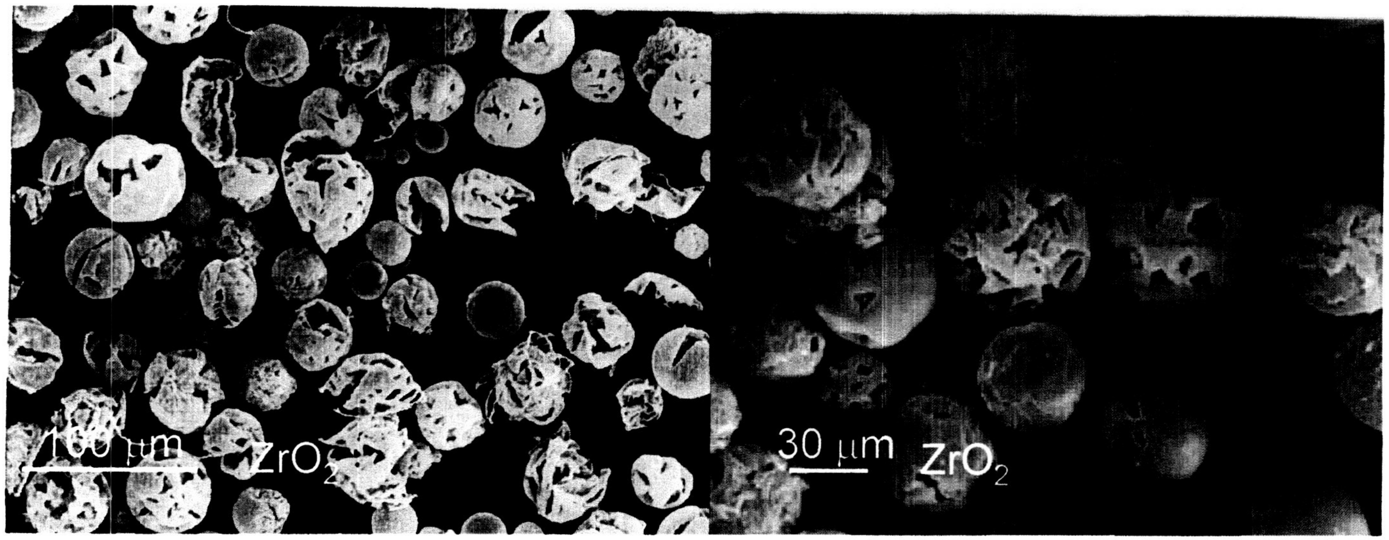
       → ≥6 °C/min – 800-1000 °C – Air



Process Variables

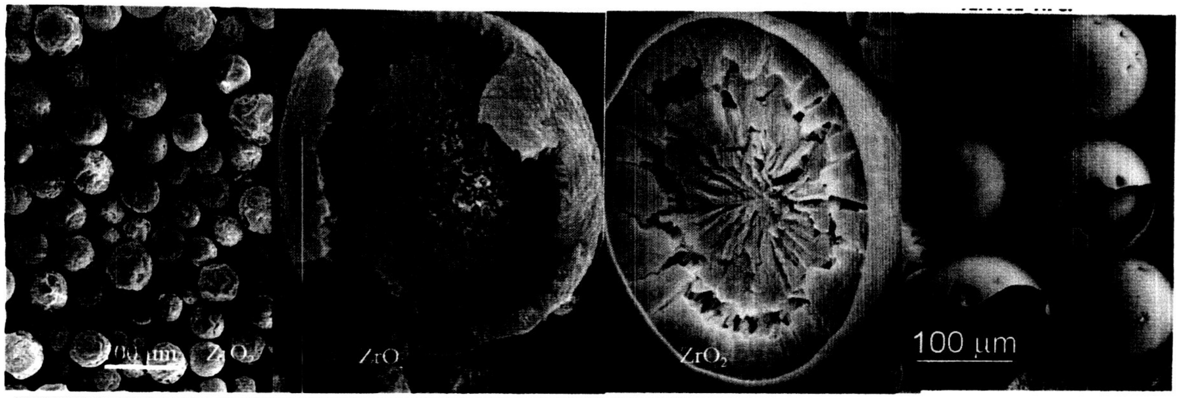
- Calcination Heating Rate $<6^{\circ}C/min$
- Ion Exchange Time <18 Hrs.

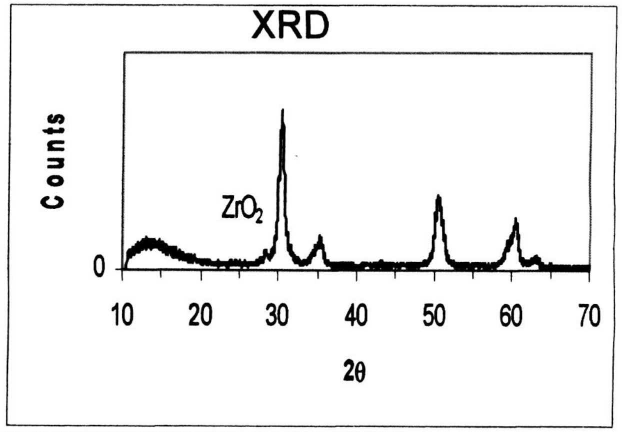
→ Defective Spheres

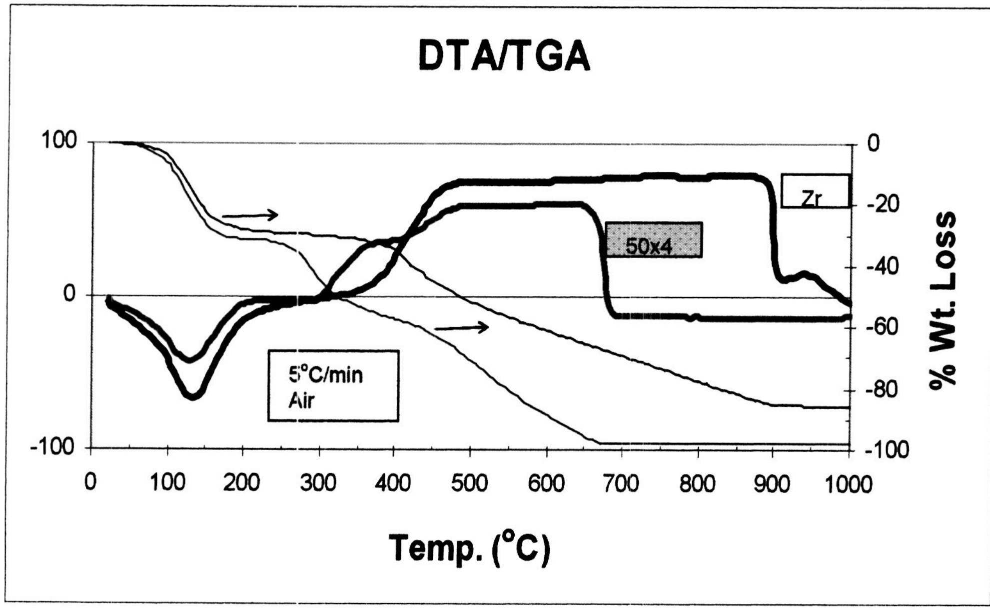


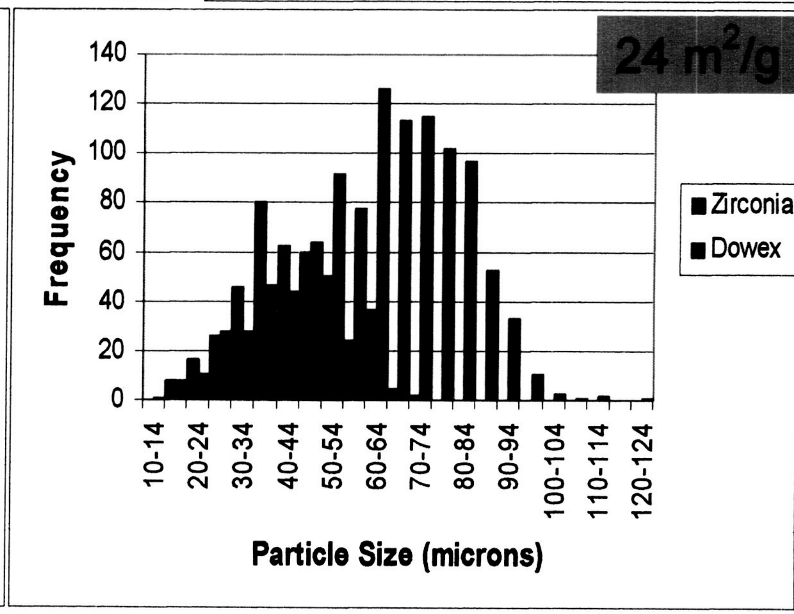
Single Step Calcination

ZrO_2



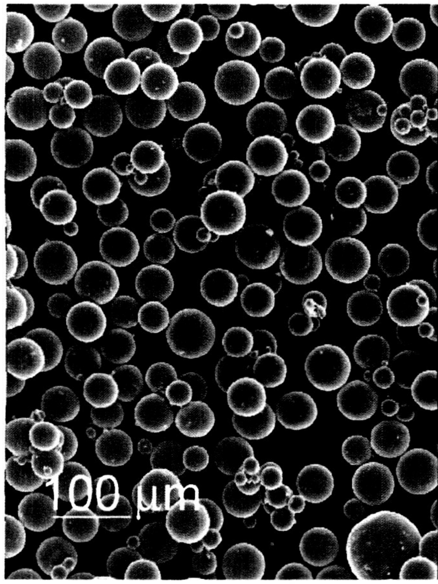


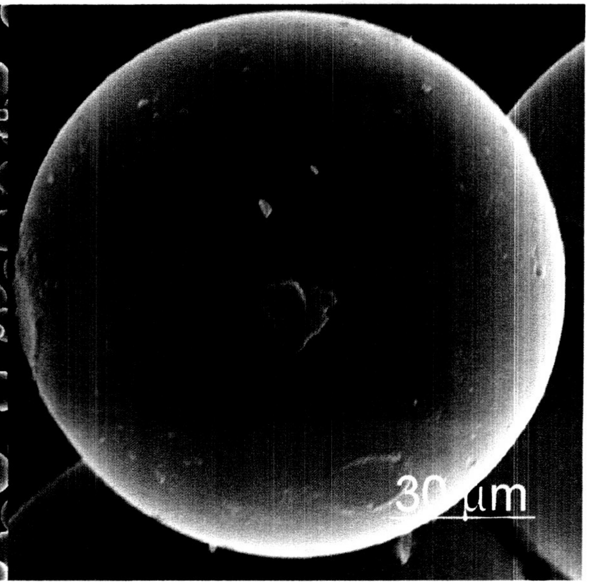


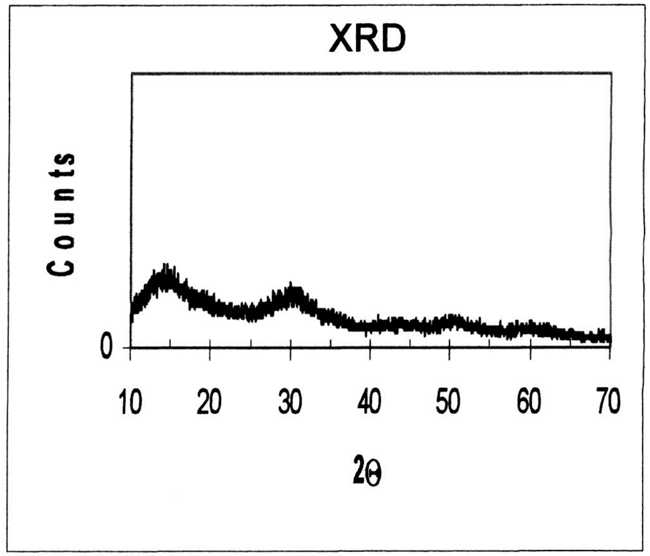


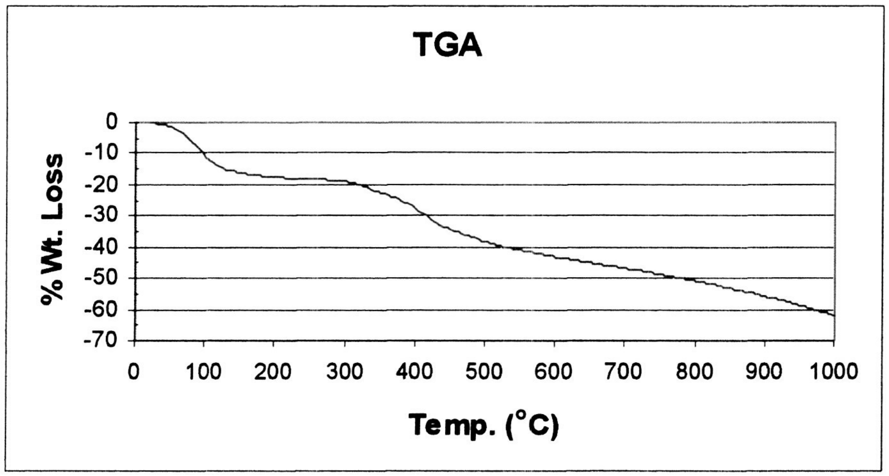
Double Calcination

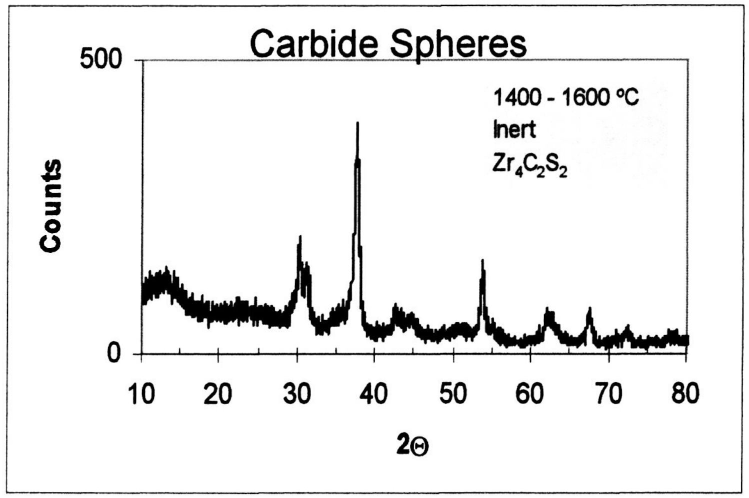
ZrO_2 – Step 1 - Inert





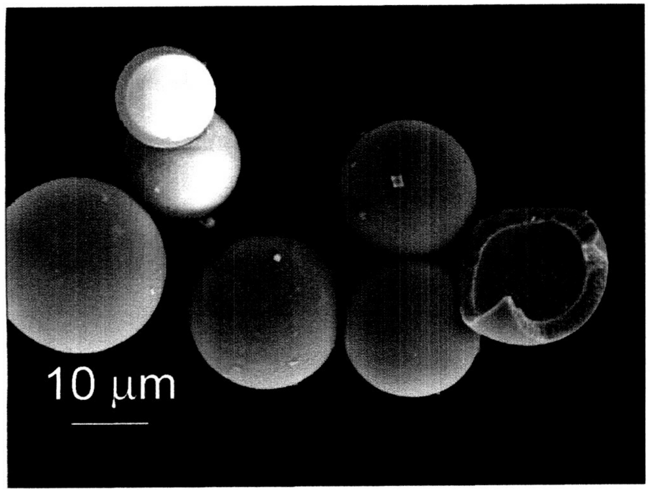


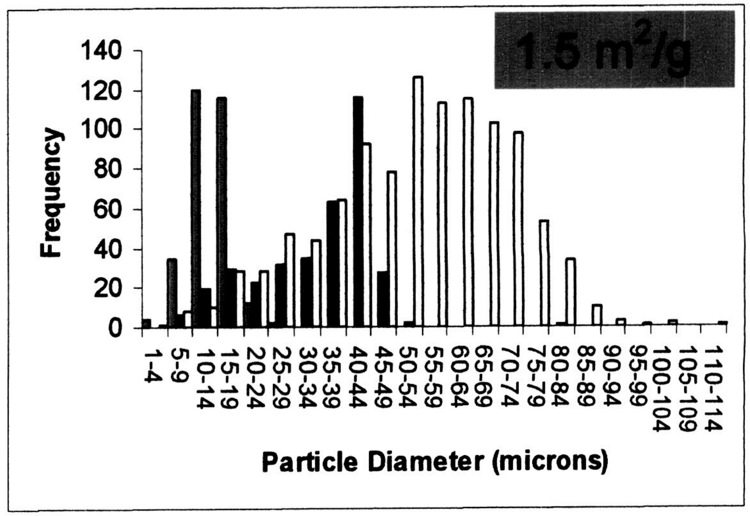


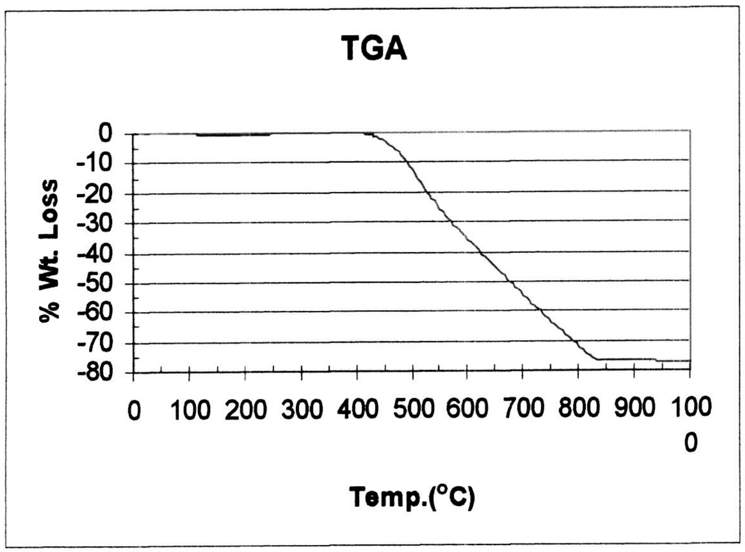


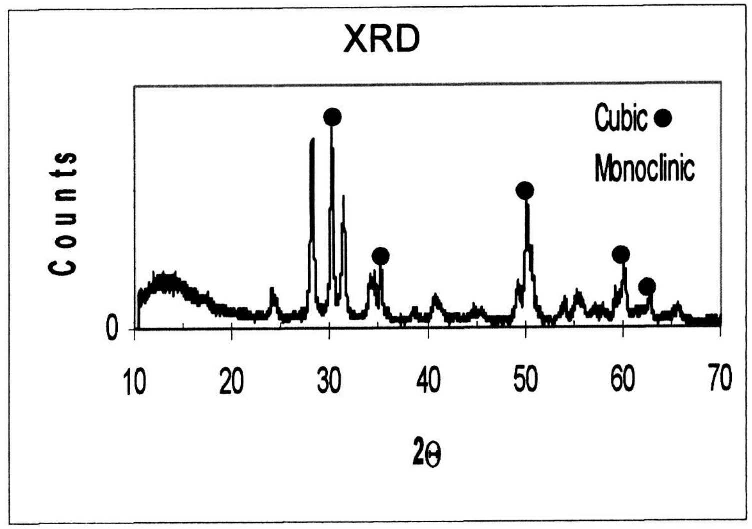
Double Calcination

ZrO_2 – Step 2 – Air



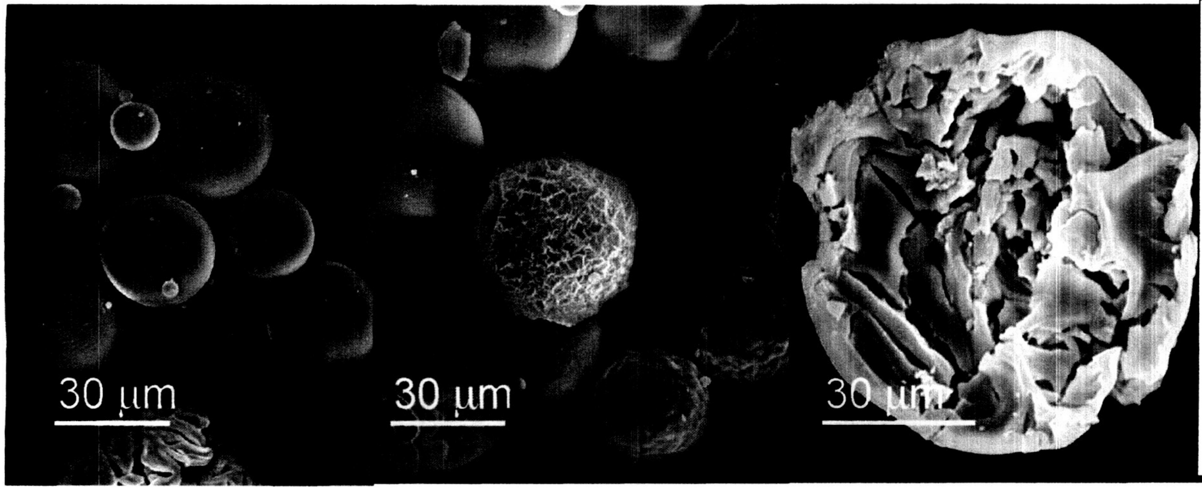


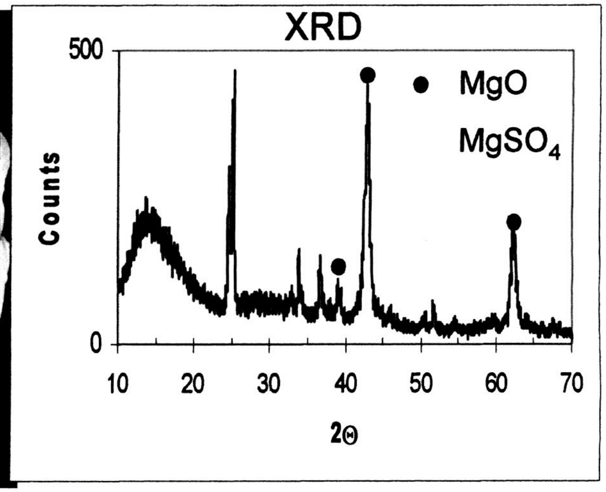


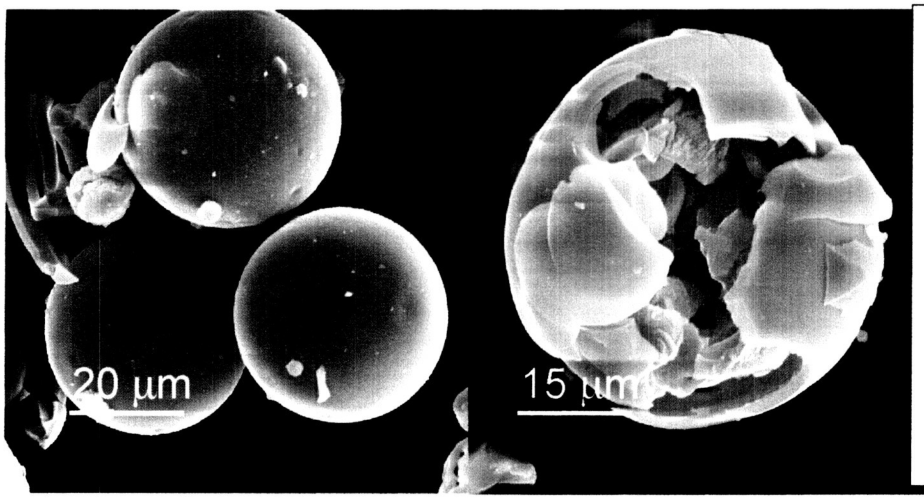


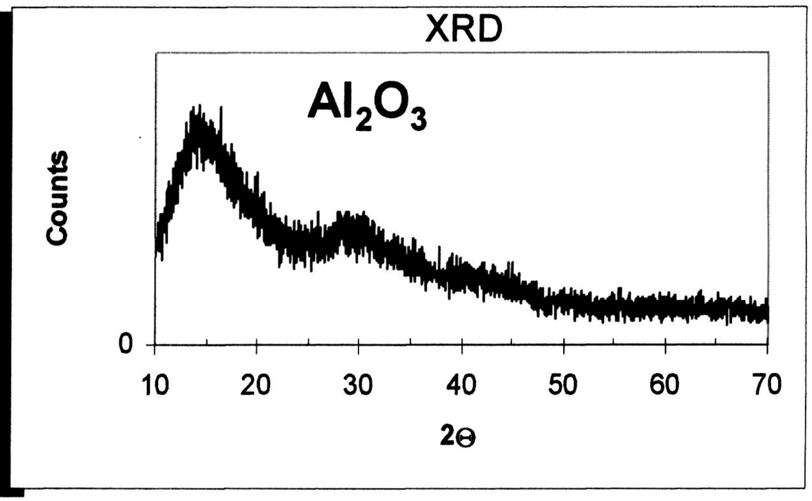
MgO/Al$_2$O$_3$ Spheres

Single Step Calcination

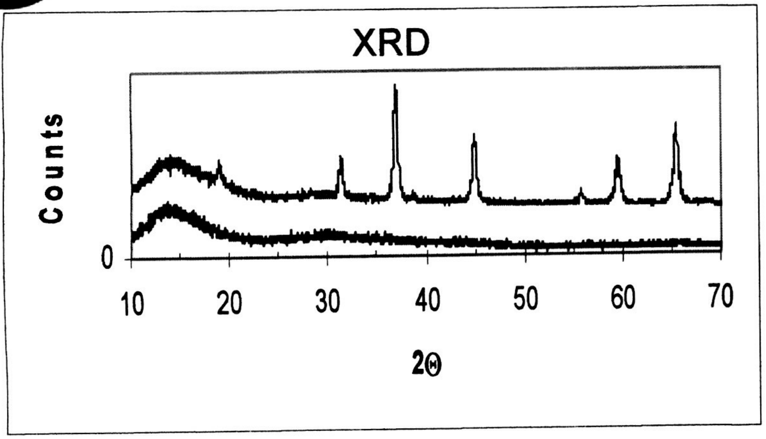








$MgAl_2O_4/Y_3Al_5O_{12}$ Spheres



$MgAl_2O_4$

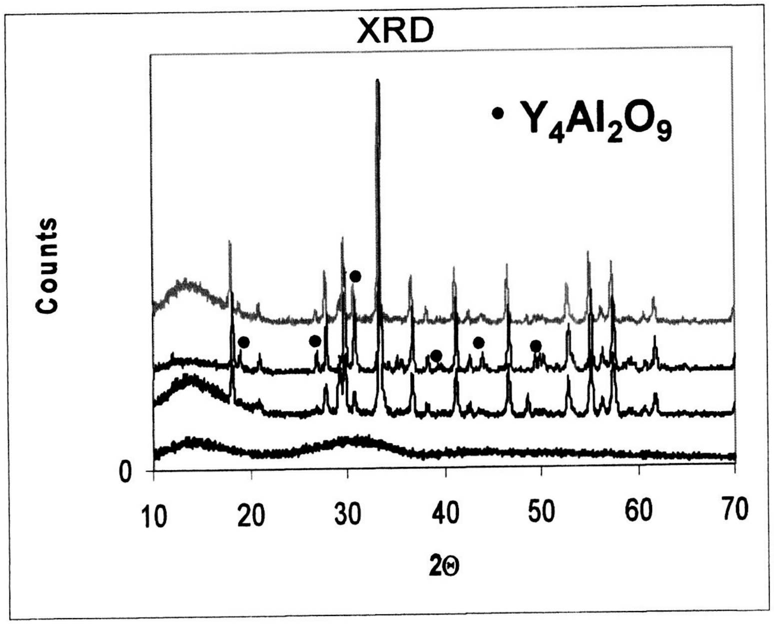
Phase Formation

- 1050 °C 12 hrs.
- 600 °C 5 hrs.

Molar Ratio

$AlCl_3/MgCl$

2/1



$Y_3Al_5O_{12}$/ $Y_4Al_2O_9$ minor

Phase Formation

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

Molar Ratio

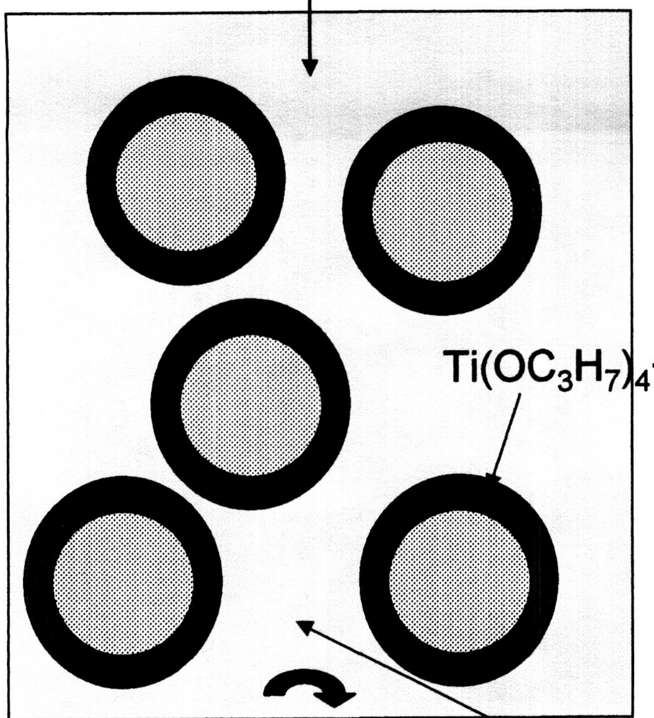
$AlCl_3/Y(NO_3)_3$

5/3

Hollow TiO_2 Spheres

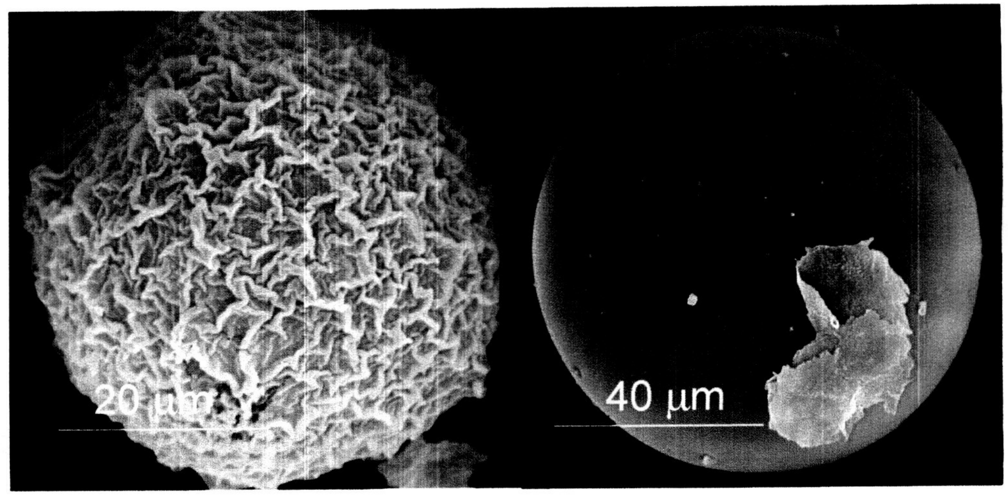
2,4– pentanedione
$Ti(OC_3H_7)_4$
Isopropanol

Drip



$Ti(OC_3H_7)_4 + H_2O$

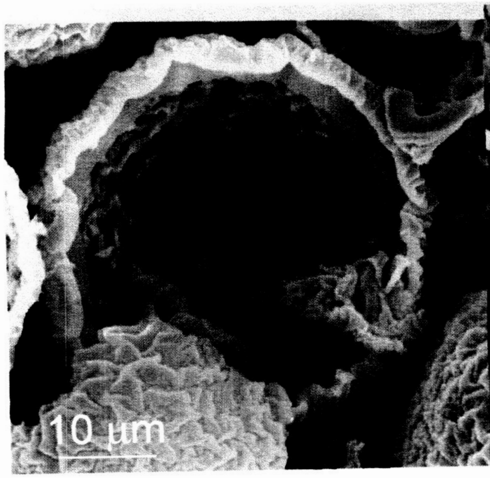
2,2,4-trimethyl pentane
Span 80

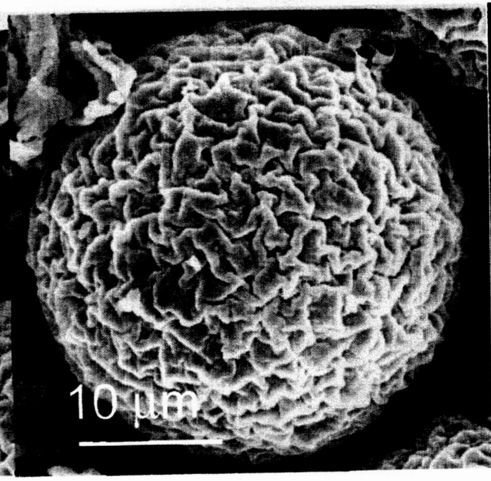


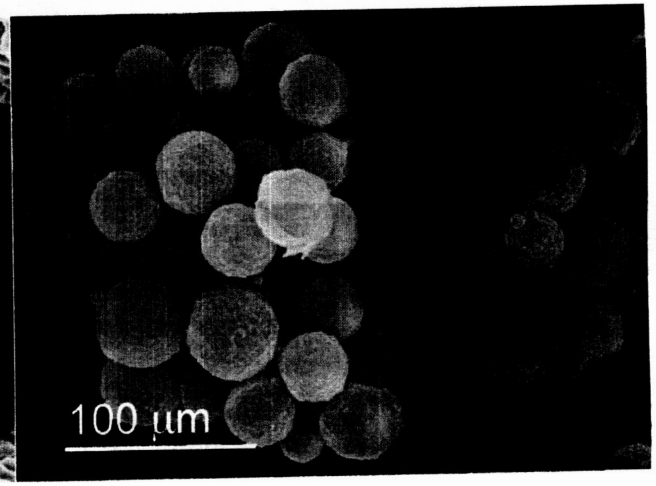
Coated Beads

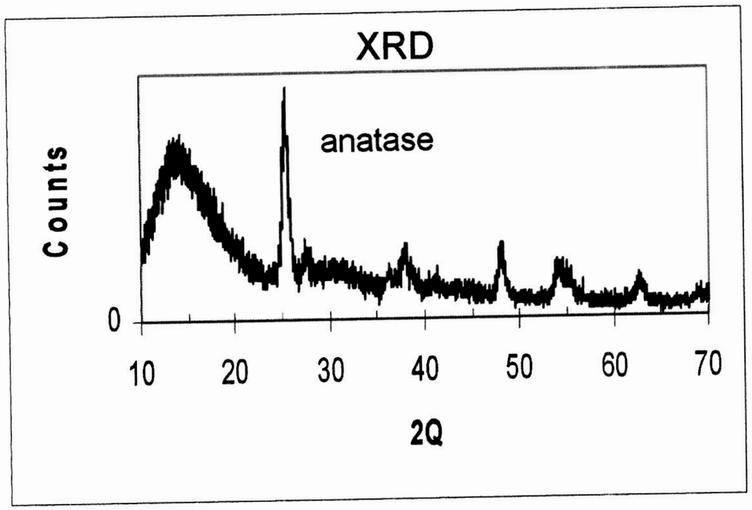
- Solid/Liquid Separation
- Air Dry
- Calcine - ≥6 °C/min – 600-800 °C – Air

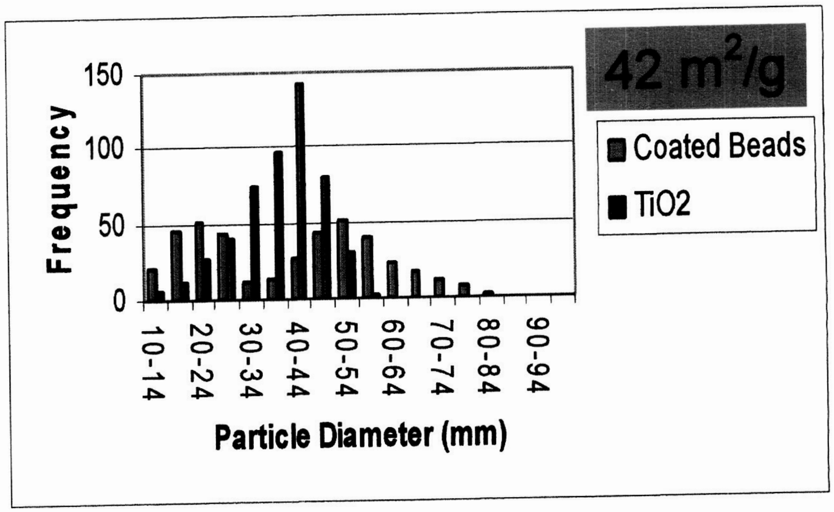
Hollow TiO_2 Spheres





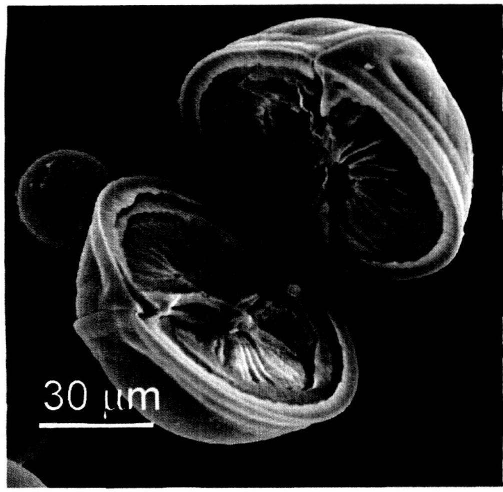


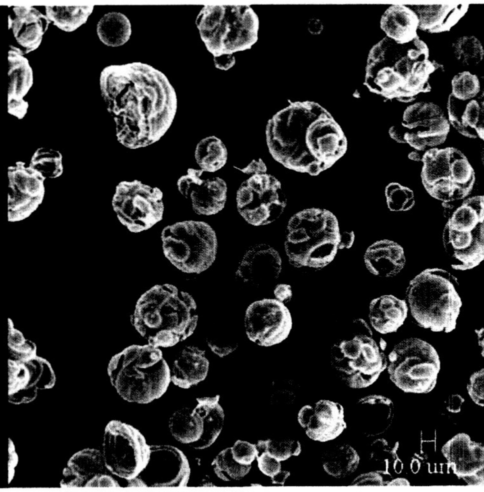


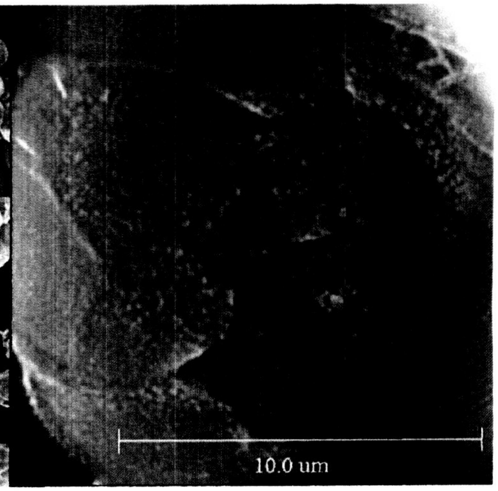


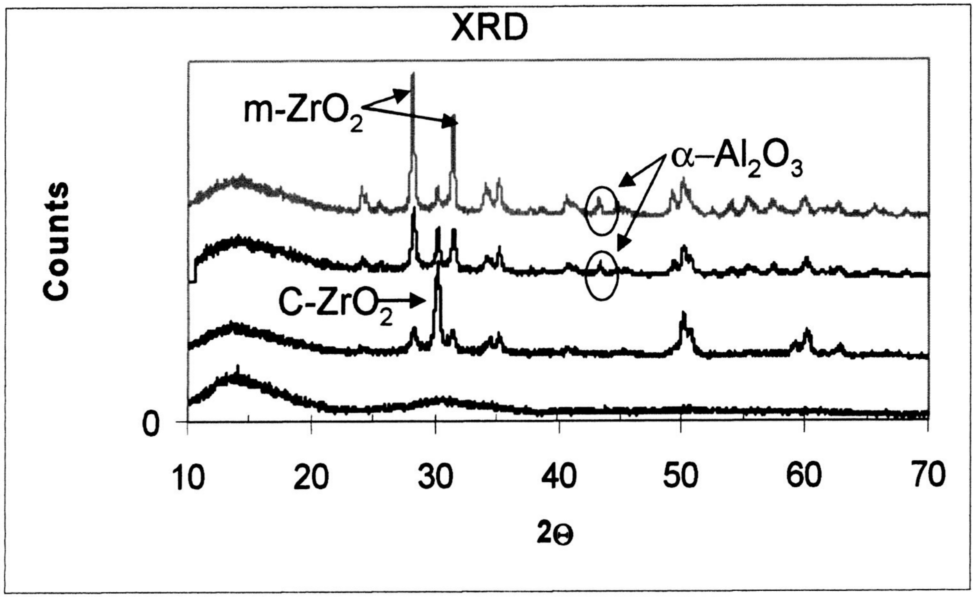
Al_2O_3 Coated ZrO_2 Spheres

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.

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