USAXS STUDIES OF GROWTH OF NANOCRYSTALLINE CERIA IN REAL TIME

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2006 USERS MEETING, Argonne National Laboratory, Argonne, Illinois • May 1-5, 2006

Introduction

- Nano-CeO_2 has important potential applications:
  3-way catalysts for vehicle emissions, SOFC electrolytes, gas sensors, optical coatings, CMP slurries, etc.
- Solution-mediated "soft" chemistry routes provide control/selectivity under mild conditions, use less energy
- We need to understand conditions and timescales for nucleation and growth in order to predict and control particle size and other material characteristics
- In situ, real-time analysis of particle size and growth parameters are desired

Homogeneous Precipitation of Ceria (IV) Oxide

Reactants:

1. hexamethylenetetramine (HMT) $(CH_2)_6N_4$ [0.25 M]

polydentate ligand forms complexes with metal cations

2. cerium (III) nitrate hexahydrate $Ce(NO_3)_3{\cdot}6H_2O$ [0.02 M]

Chen & Chen *J. Am. Ceram. Soc.* **76**, 1577-83 (1995)

HMT hydrolyzes slowly in water to form ammonia and formaldehyde:

$$C_6H_{12}N_4 + 6H_2O \rightarrow 6CH_2O + 4NH_3$$
$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

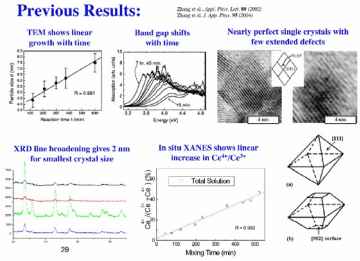
pH increase initiates homogeneous precipitation of cerium (IV) oxide:

$$Ce^{4+} + 2H_2O \rightarrow CeO_2 + 4H^+$$

HMT may also play role in oxidation of Ce^{3+} to Ce^{4+}

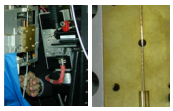
Previous Results:

Zhang et al., *Appl. Phys. Lett.* **80** (2002); Zhang et al. *J. App. Phys.* **95** (2004)



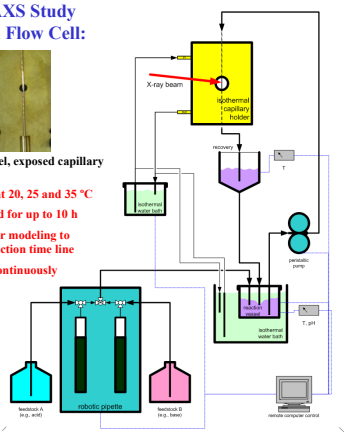
Experimental Approach

Real-time USAXS Study Using a Liquid Flow Cell:

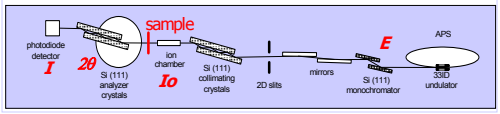


Installed capillary flow cel, exposed capillary

- isothermal experiments at 20, 25 and 35 °C
- reaction changes followed for up to 10 h
- periodic scans selected for modeling to represent observable reaction time line
- pH and temp recorded continuously



Bonse-Hart USAXS Camera at APS sector 33-ID



Data Reduction & Analysis

Data Reduction
- transmission
- air blank
- solution blank
- desmearing (& smoothing)
- incoherent background

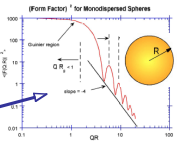
$$I(Q) = I_0\,\Omega\,t\,e^{-\mu t}\,\frac{d\Sigma}{d\Omega}(Q)$$

measured

$$\frac{d\Sigma}{d\Omega}(Q) = |\Delta\rho|^2 \int_0^\infty \left[F(Q,r)\right]^2 V(r)\, f(r)\, dr$$

scattering contrast

Spheres: $F(Q,r) = 3(Qr)^{-3}\left[\sin(Qr) - (Qr)\cos(Qr)\right]$



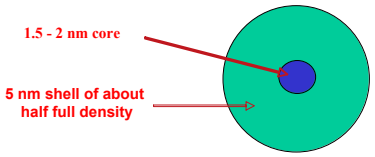
Form factors exist for other geometries, including core/shell.

For the volume-size distribution *f (r)*, apply an assumed form such as:
- **lognormal, Gaussian, LSW, etc.**
- **use least squares method to minimize fit error (χ^2)**

Or, solve for *f(r) dr* by a regularization method such as MaxEnt:
- **maximize configurational entropy of solution while min. error**

Multimodal Population Model with Core/Shell Structure

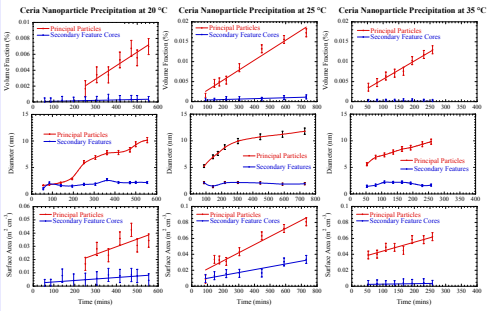
- Cannot fit USAXS data using a *single particle population* model
- Simple homogeneous spheres cannot reproduce high-Q behavior
- Two main populations present throughout the observation time at all temperatures*
  a) "*principal*" (high volume, larger size) is full density CeO_2;
  b) "*secondary*" (lower volume, finer size) is full-density CeO_2 **core**, in ~ 5 nm thick shell with ~ half the core density .
- Populations appear to act independently
- Two additional minor populations at large size required to account for low-Q scattering (may be associated with precipitates formed on capillary surface in beam)
- **except 20 °C for earliest times where a single core/shell population may exist*



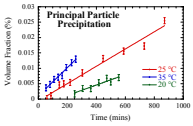
model for "secondary" scattering population

Results

Main Precipitation Characteristics versus Isothermal Reaction Time at 20, 25, 35 °C



Growth Kinetics of Principal Population



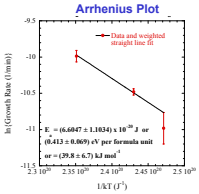
Volumetric Growth Rates (% min^{-1}):

20 °C: (1.70 ± 0.37) x 10^{-5}
after t_0 = (131 ± 97) minutes

25 °C: (2.81 ± 0.12) x 10^{-5}
after t_0 = (21.3 ± 18.9) minutes

35 °C: (4.60 ± 0.53) x 10^{-5}
after t_0 = (- 22.3 ± 19.3) minutes

Arrhenius Plot

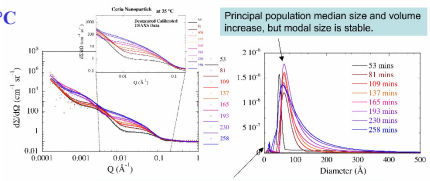


Estimated Activation Energy

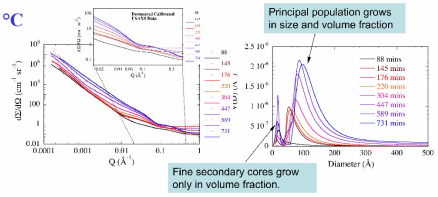
E_a = (39.8 ± 6.7) kJ mole^{-1}

Results (continued)

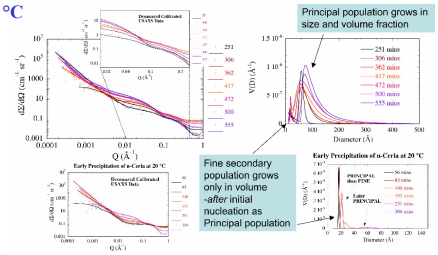
35 °C



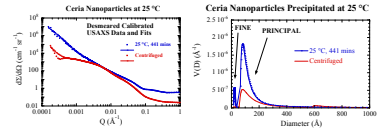
25 °C



20 °C



Effect of Selective Centrifuging: Fine Features not Enhanced



Fine features NOT a completely independent population but mostly associated with larger "principal population" particles

NOT OBSERVED IN PREVIOUS EXPERIMENTS

Conclusions

A single particle population model does not fit the data.

The multicomponent model suggests two main populations with the fine (2 nm) features having core/shell structure.

The principal population diameter agrees with TEM/XRD.

The two populations appear to act independently with regard to size, volume fraction, and surface area growth.

But…centrifuge experiments suggest most secondary features are associated with the growing principal particles.

At early times, fine "secondary" features may be critical nuclei with the shell an initial reaction volume around a nucleation site; later on, these may be on the surface of a growing principal particle.

The 20 °C data capture a transition between a single fine population with likely core/shell structure, and a linear growth regime with two populations: one growing in size and the other fixed.

Additional experiments were conducted with varying Ce^{3+} concentration, and will be used to determine the order of reaction.

Reference: A.J. Allen; "Characterization of Ceramics by X-ray and Neutron Small-Angle Scattering," J. Am. Ceram. Soc., **88**, 1367-1381 (2005).

Acknowledgements: The UNICAT facility at the Advanced Photon Source (APS) is supported by the Univ of Illinois at Urbana-Champaign, Materials Research Laboratory (U.S. DOE, the State of Illinois-IBHE-HECA, and the NSF), the Oak Ridge National Laboratory (U.S. DOE under contract with UT-Battelle LLC), the National Institute of Standards and Technology (U.S. Department of Commerce) and UOP LLC. The APS is supported by the U.S. DOE, Basic Energy Sciences, Office of Science under contract No. W-31-109-ENG-38. Columbia University research efforts are supported by the NSF MRSEC Program under Award No. DMR-0213574 and by the U.S. DOE under DE-FG02-05ER15730.

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