2003 CMS Post Doctoral Symposium

Silicon Oxide in Metal Oxide Matrices: Synthesis, Characterization, and Applications as Energetic Nanocomposite Materials

Brady J. Clapsaddle, David W. Sprehn, Alexander E. Gash, Joe H. Satcher Jr., Randall L.Simpson

Chemistry and Materials Science Directorate and Energetic Materials Center, Lawrence Livermore National Laboratory

UCRL-PRES-154135

This Work was performed under the auspices of the U.S. Department of Energy by the University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

Energetic Nanocomposites: Thermite Reactions

Idealized energetic reactions :

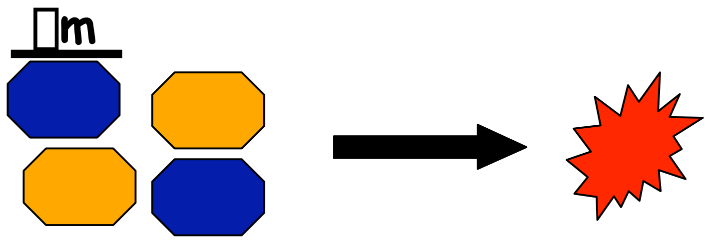
Thermite :

$$2Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe + \Delta H$$

Thermite with gas generator :

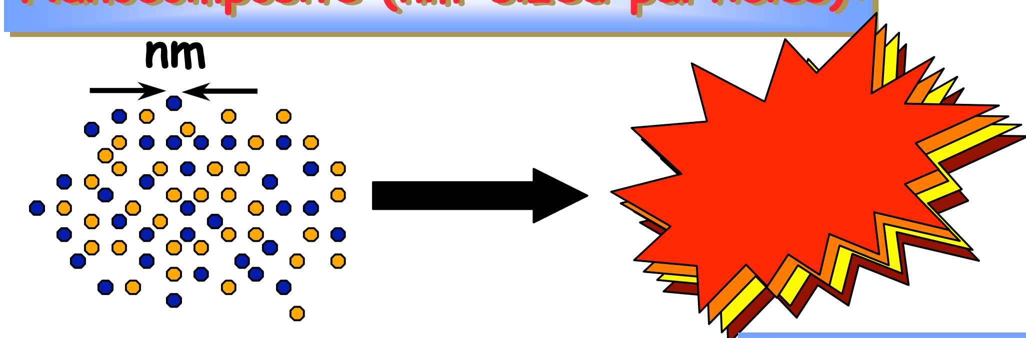
$$2Al + Fe_2O_3 + 3CF_2 \longrightarrow 2AlF_3 + 2Fe + 3CO + \Delta H$$

Conventional (μm-sized particles):



- mass transport an issue
- lower power
- energy lower (incomplete reaction)

Nanocomposite (nm-sized particles):



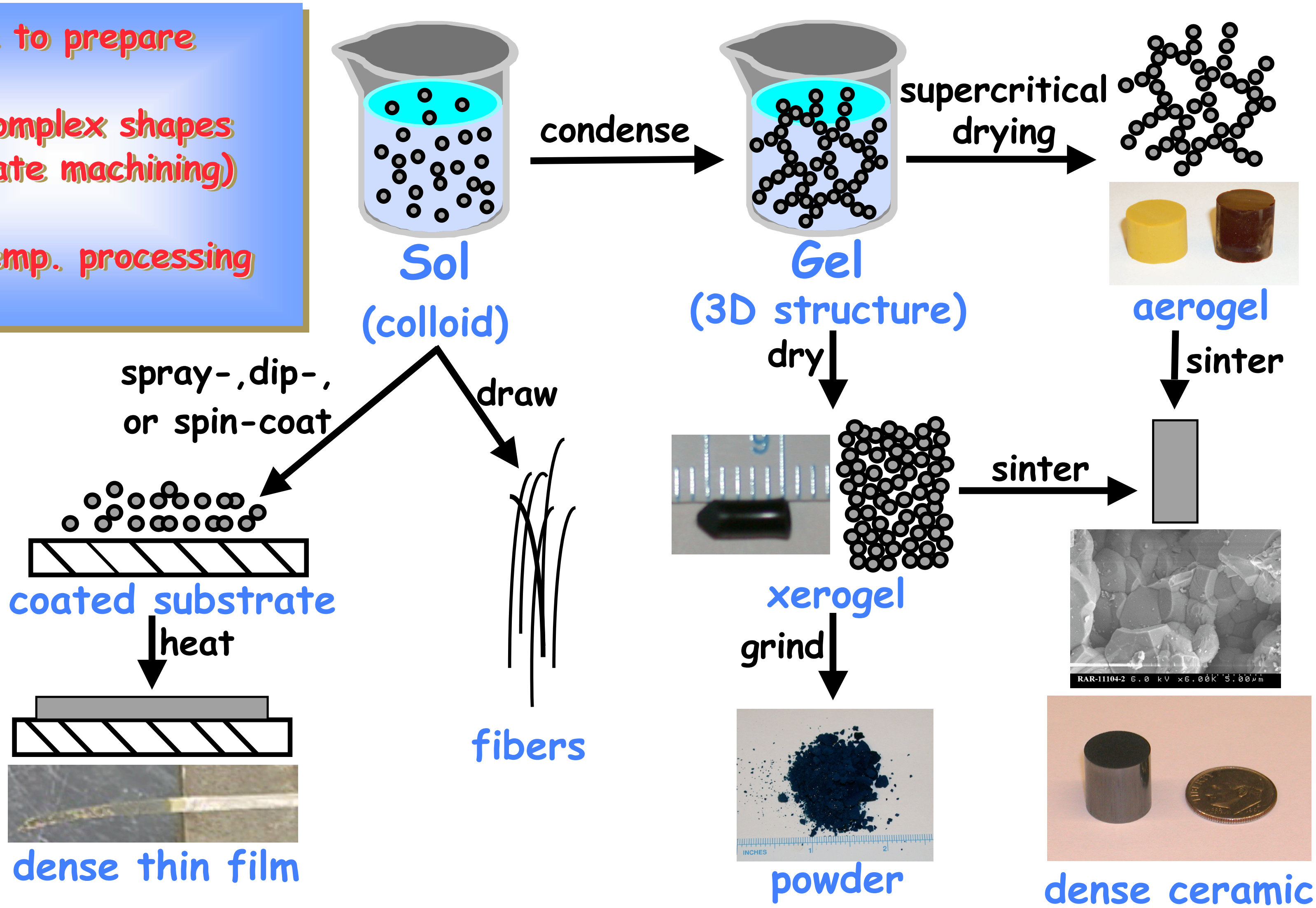
- mass transport minimized
- higher power (faster rxn)
- higher total energy

> Nanostructuring is potentially a means of making materials with high power and high energy

Tillotson, T. M. *et. al.* J. Non-Cryst. Solids **2001**, *285*, 338.

The Sol-gel Methodology: Inherently "Nano"

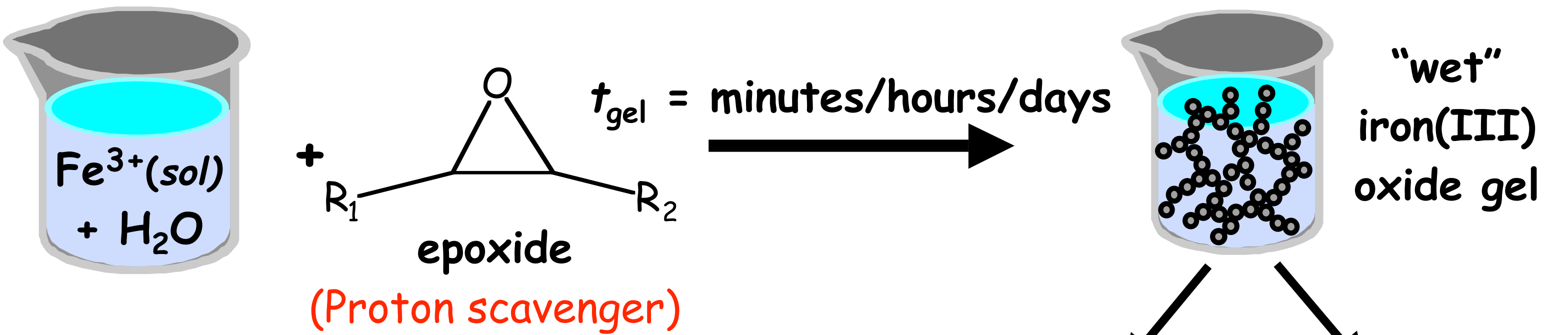
- Simple to prepare
- Cast complex shapes (eliminate machining)
- Low temp. processing

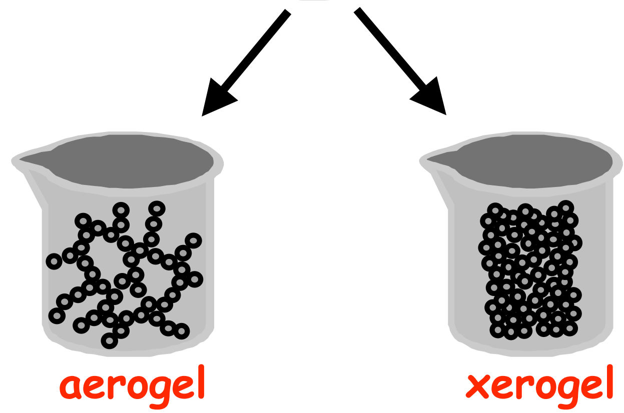


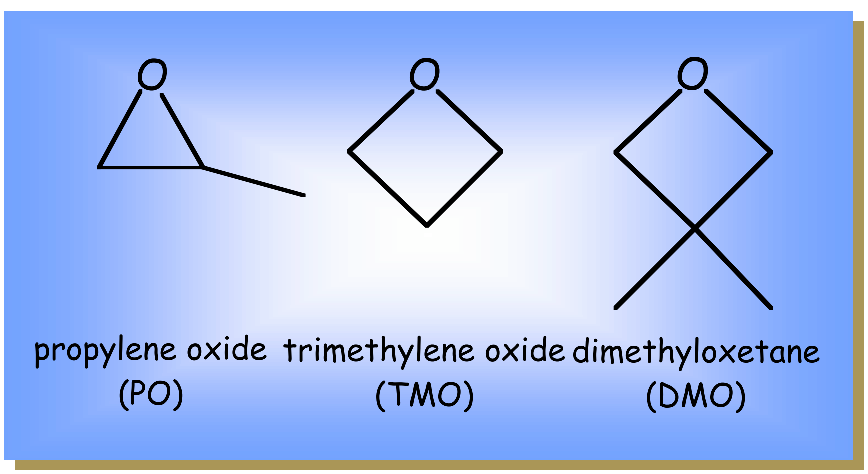
Brinker, C.G.; Scherer, G.W. Sol-Gel Science, Academic Press; New York, 1990.

New Approach Uses Epoxide Addition for Synthesis of Gels

Does *not* use alkoxides as starting material

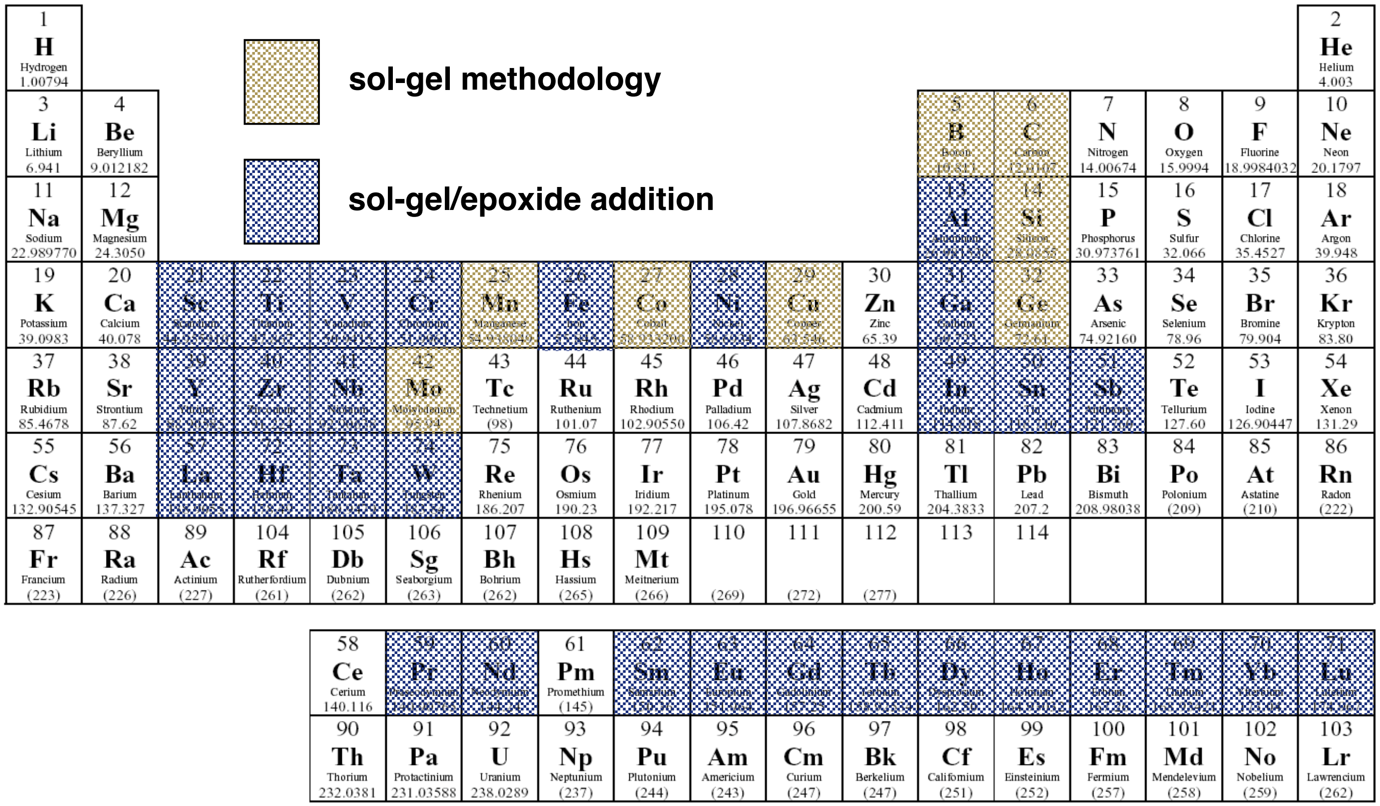






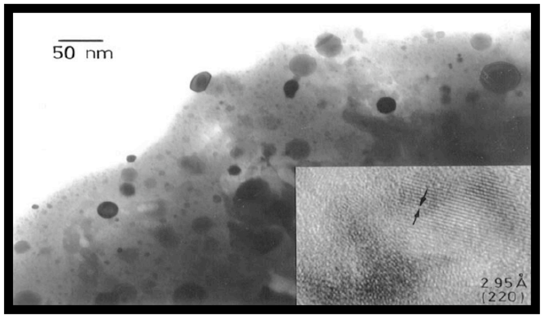
1. Gash, A. E.; Tillotson, T. M.; Satcher, J. H. Jr.; Hrubesh, L. W.; Simpson, R. L. *Chem. Mater.* **2001**, *13*, 999.
2. Gash, A. E.; Tillotson, T. M.; Poco, J. F.; Satcher, J. H. Jr.; Hrubesh, L. W.; Simpson, R. L. *J. Non-Cryst. Solids* **2001**, *285*, 22.

New Approach Uses Epoxide Addition for Synthesis of Gels



- Extremely versatile method
- Expands sol-gel chemistry to more of the periodic table

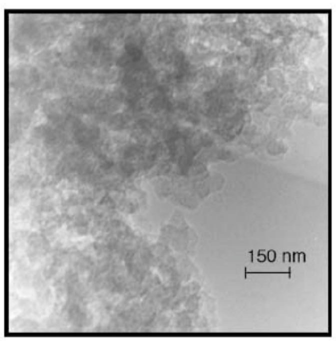
Fe-Si Mixed Oxide Composites



Morales et. al. - Instituto Ciencia de Materiales Madrid

Sol-gel synthesis using TEOS and $FeCl_3 \cdot 6H_20$ results in materials of Fe/Si = 0.2 - 0.4. Further heat treatment (200 - 400 °C) results in the formation of □-Fe_2O_3 and □-Fe_2O_3 domains.

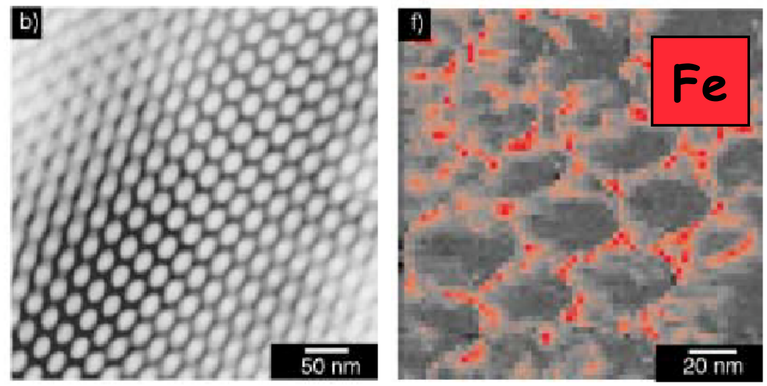
Langmuir, **1997**, *13*, 3627 - 3634.



Baiker et. al. - Swiss Federal Institute of Technology

Sol-gel synthesis using TMOS/TEOS and $FeCl_3 \cdot 6H_20$ results in materials of Fe/Si ≈ 0.1. Dispersion and crystalline phase of Fe(III) oxide depends on heat treatment (200 - 900 °C).

J. Mater. Chem., **2002**, *12*, 619 - 630.

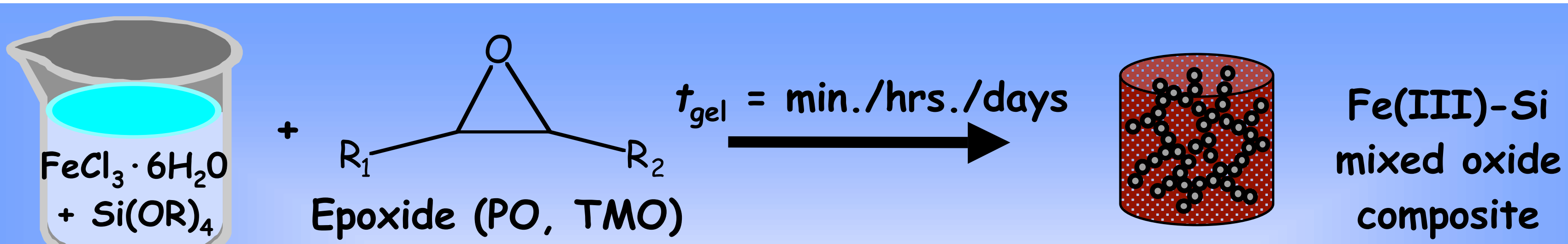


Wiesner et. al., Cornell University

Polymeric structure directing agent results in □-Fe_2O_3 doped, Fe/Si=0.3-1, ordered mesoporous aluminosilicates from aluminum, silicon, and iron(III) alkoxides.

Angewandte Chem. Int. Ed., **2003**, *42*, 1526 - 1530.

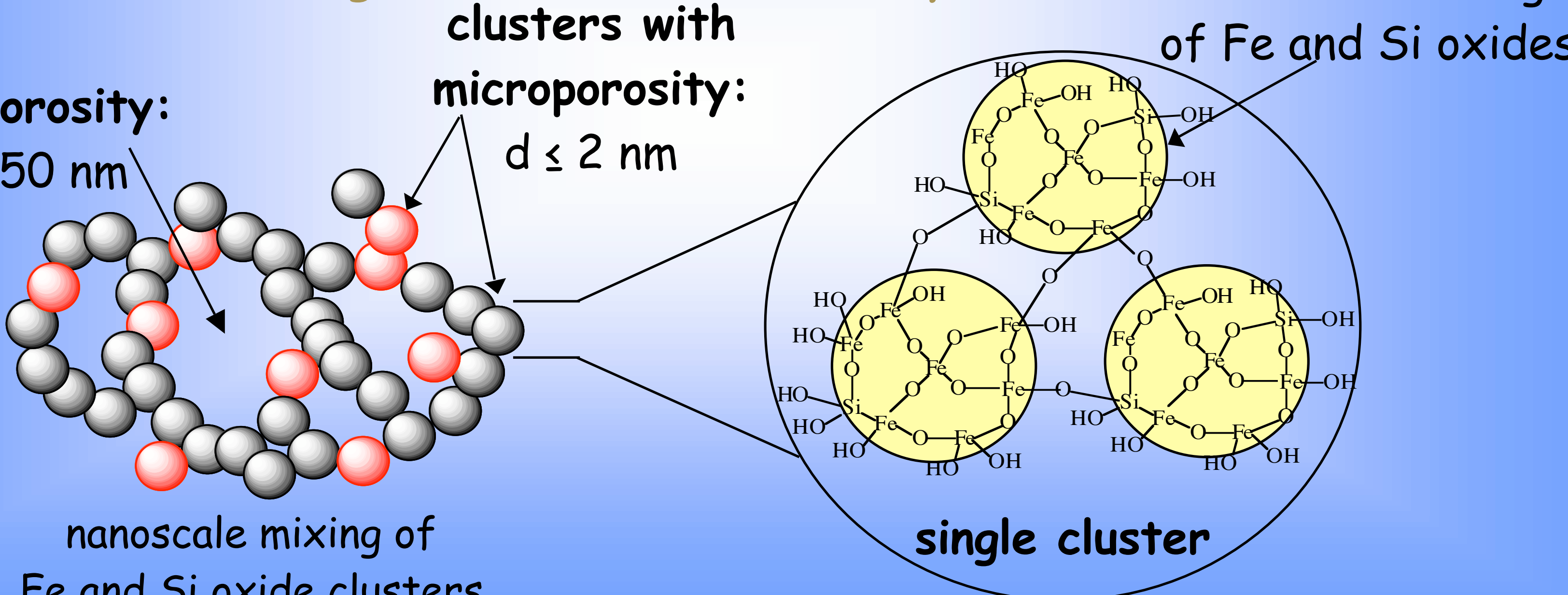
Fe-Si Mixed Oxide Composites: Epoxide Addition



Epoxide (PO, TMO)
(Proton scavenger)

R = ethyl (TEOS)
or methyl (TMOS)

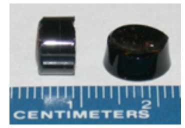
Microstructure of Sol-gel Fe-Si Oxide Nanocomposites:



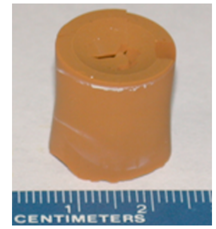
nanoscale mixing of
Fe and Si oxide clusters

Fe-Si Mixed Oxide Composites: Epoxide Addition

Fe/Si = 1 nanocomposites



xerogel



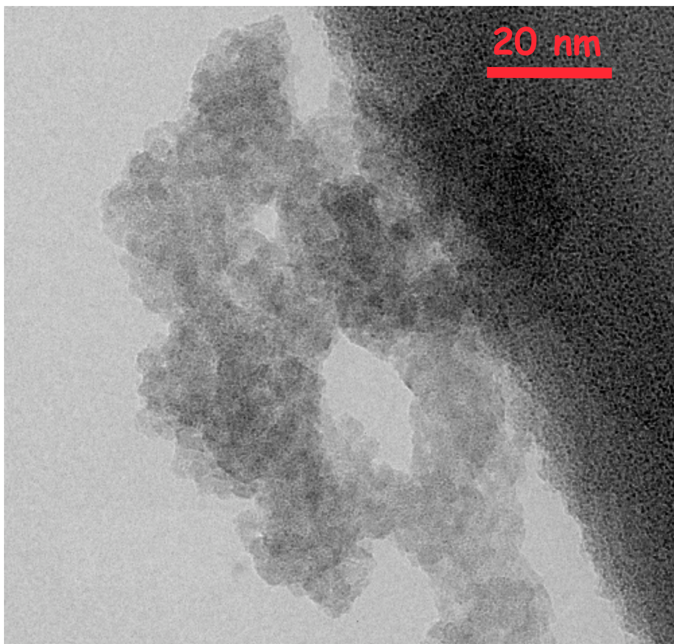
aerogel

calc. Fe/Si (mol/mol)	silica precursor	epoxide	t_{gel} (hr)	actual Fe/Si (mol/mol)	surf. area (BET; m^2/g)	pore vol. (mL/g)	avg. pore diam. (nm)
5	TMOS	PO	0.5	5.3	401	4.10	29
2	TMOS	PO	0.6	2.0	432	3.74	28
1	TMOS	PO	9	1.0	389	1.63	18
5	TEOS	PO	0.8	5.3	359	4.82	30
2	TEOS	PO	0.8	2.3	395	3.26	27
1	TEOS	PO	14	1.1	422	1.76	15
5	TMOS	TMO	60	4.9	375	4.79	24
2	TMOS	TMO	75	2.3	410	3.42	26
1	TMOS	TMO	144	1.1	383	2.24	20
5	TEOS	TMO	66	5.1	450	5.38	28
2	TEOS	TMO	85	2.3	429	4.19	31
1	TEOS	TMO	228	1.1	382	2.19	19

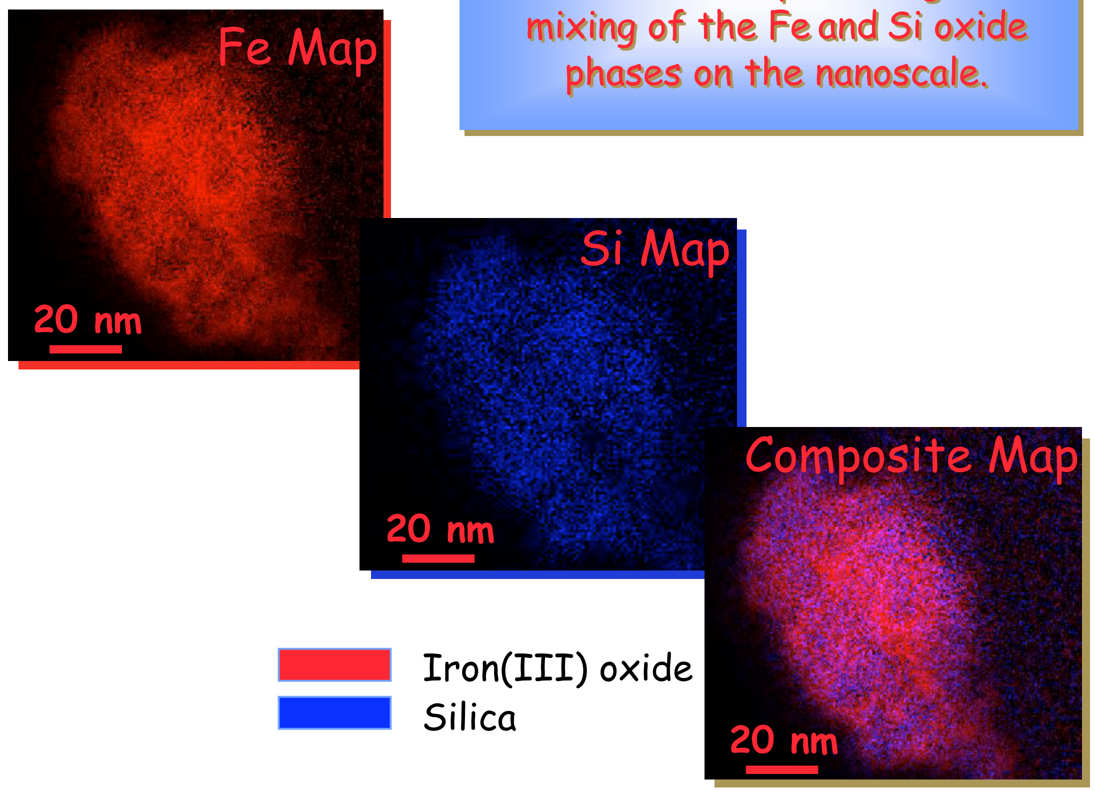
Clapsaddle, B. J. *et. al.;* Submitted to J. Non-Cryst. Solids, May 2003.

Dispersion of Fe and Si Oxides: TEM & EFTEM

TEM Micrograph: Fe-Si Oxide Aerogel Nanocomposite (1:1 (mol:mol) Fe:Si)



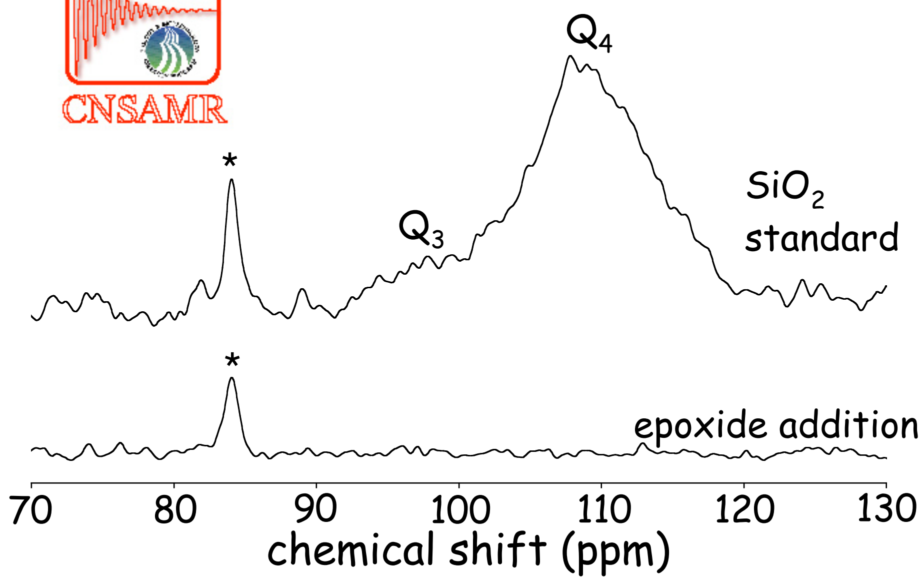
Energy Filtered Transmission Electron Micrographs: Elemental maps show good mixing of the Fe and Si oxide phases on the nanoscale.



Clapsaddle, B. J. *et. al.;* Submitted to J. Non-Cryst. Solids, May 2003.

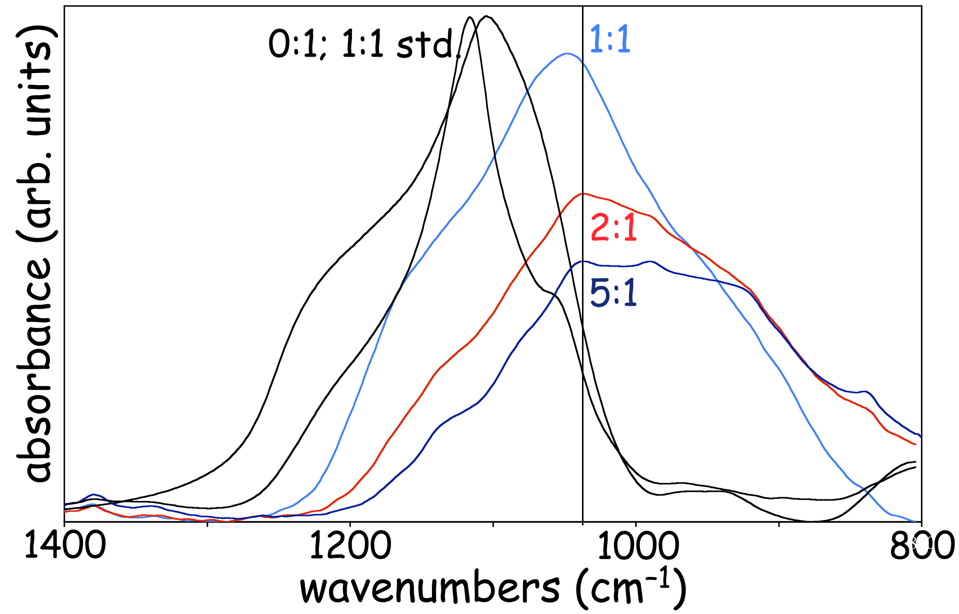
Dispersion of Fe and Si Oxides: ^{29}Si MAS-NMR & FTIR

^{29}Si MAS-NMR Fe/Si=1



* PDMS (reference) spinning side bands

ν_{as}(Si-O-Si) Fe:Si (mol:mol)

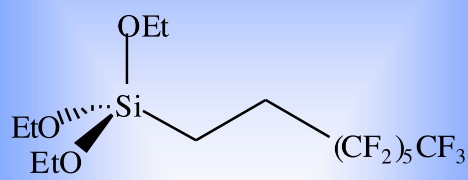


- ^{29}Si MAS-NMR
  - Loss of ^{29}Si signal indicates good dispersion of Si with paramagnetic Fe(III)
- FTIR
  - ν_{as}(Si-O-Si) shift (ΔE = -12 cm^{-1}) suggests a small degree of Si-O-Fe bonding

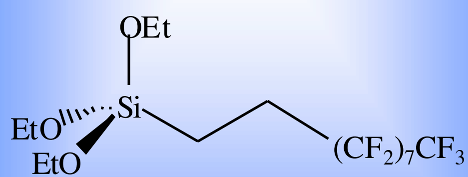
Clapsaddle, B. J. *et. al.;* Submitted to J. Non-Cryst. Solids, May 2003.

Organic Functionalized Fe-Si Mixed Oxide Nanocomposite

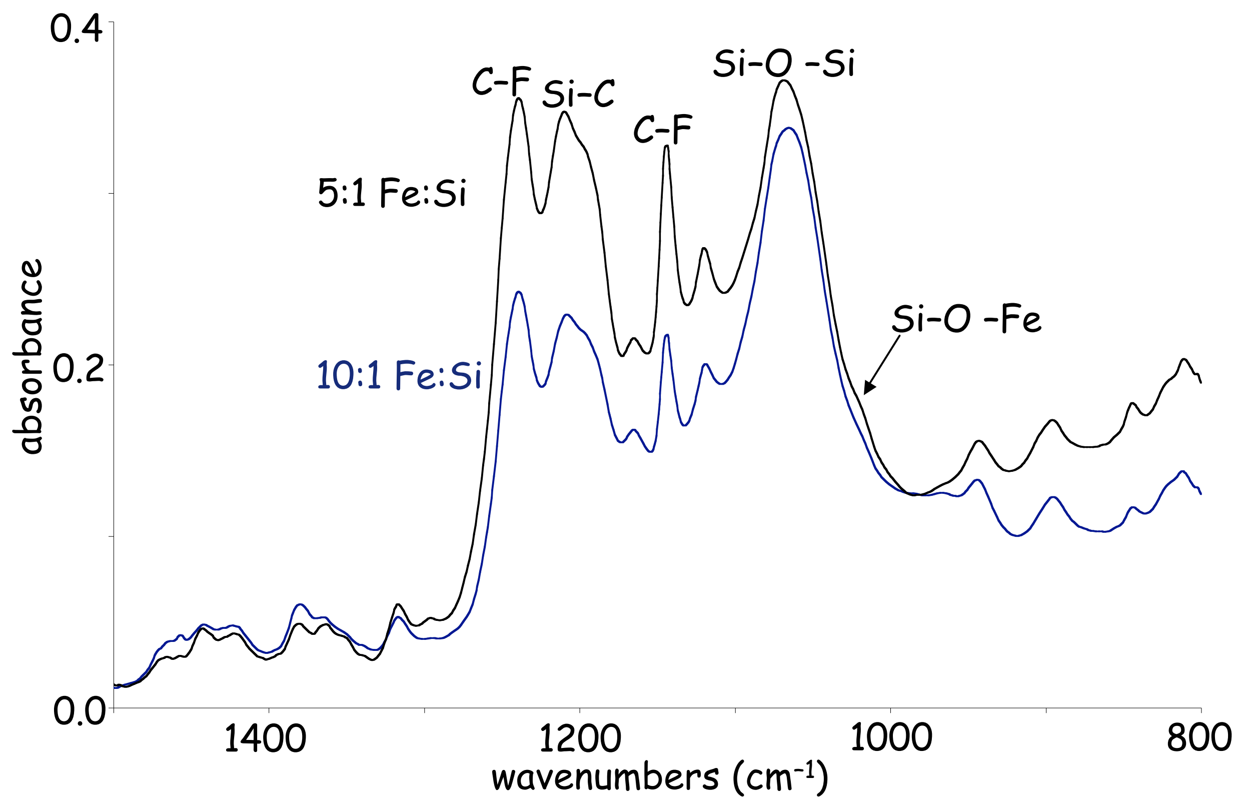
Fluorinated Silsesquioxane Si-oxide precursors



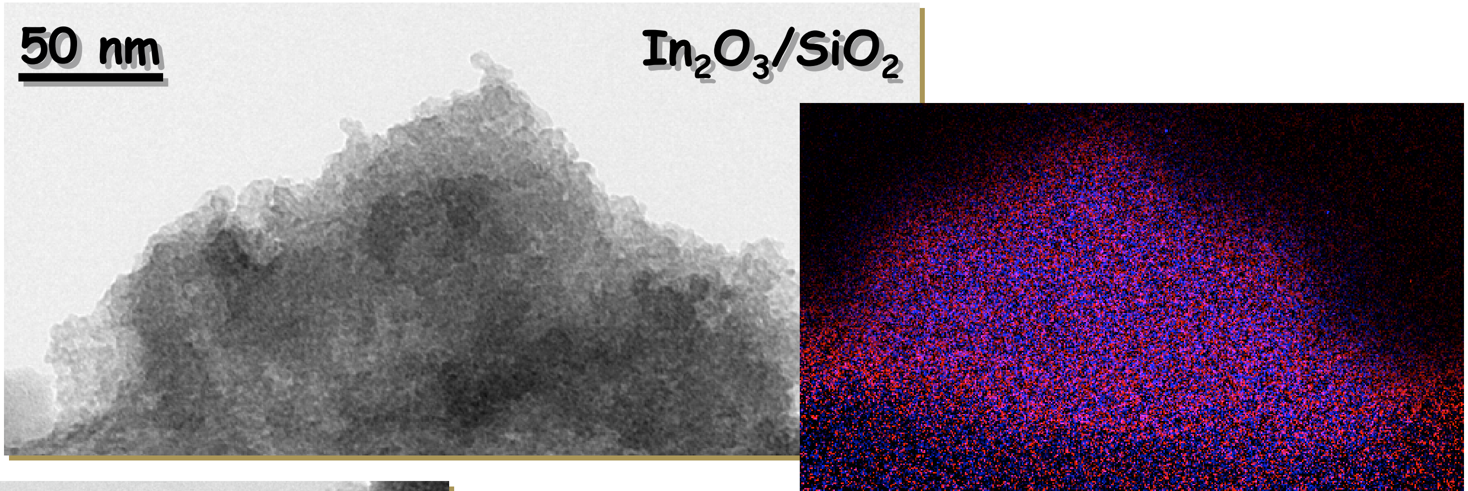
(tridecafluoro-1,1,2,2-tetrahydrooctyl)-triethoxysilane (TDFTES)



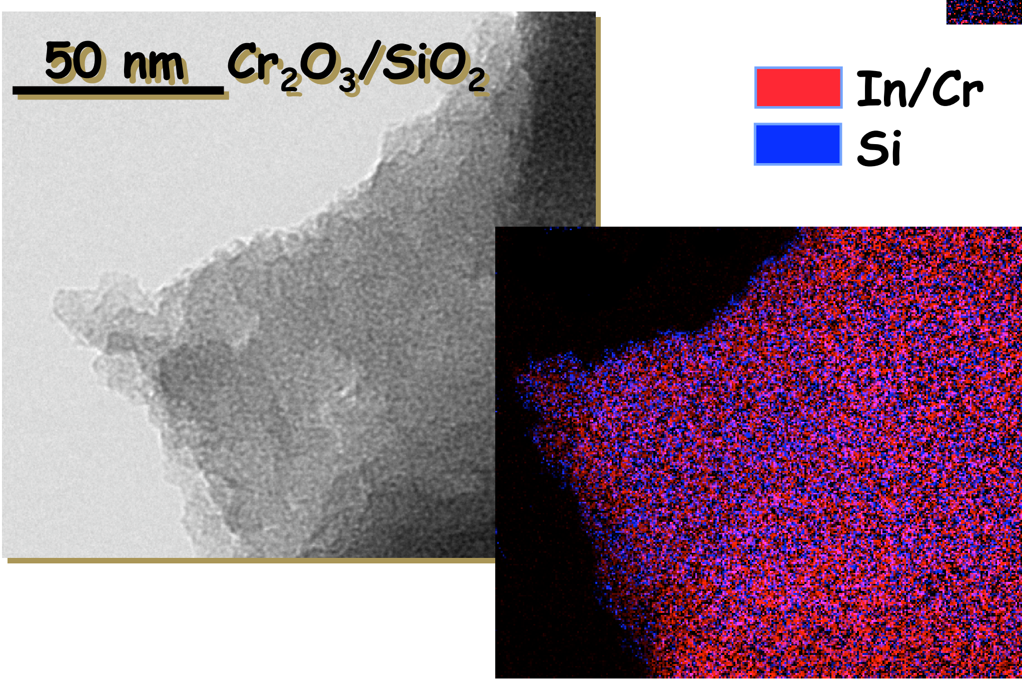
(heptadecafluoro-1,1,2,2-tetrahydrooctyl)-triethoxysilane (HDFTES)

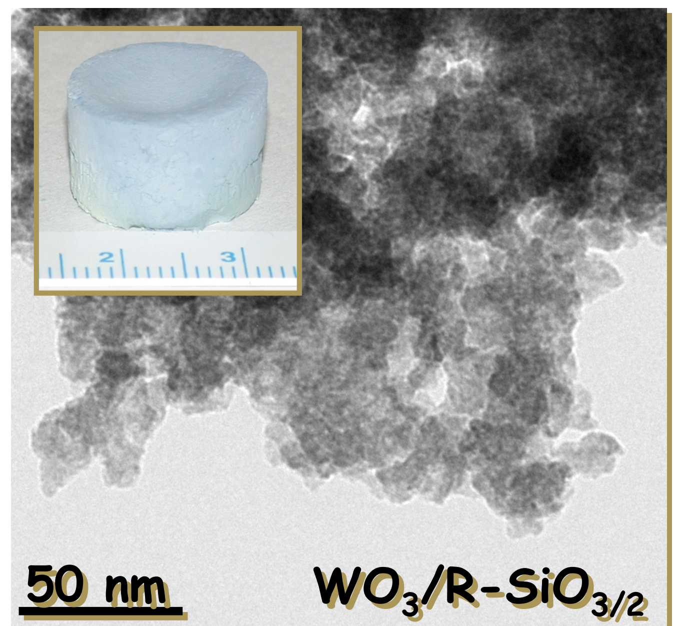


Other M-Si Mixed Oxide Nanocomposites

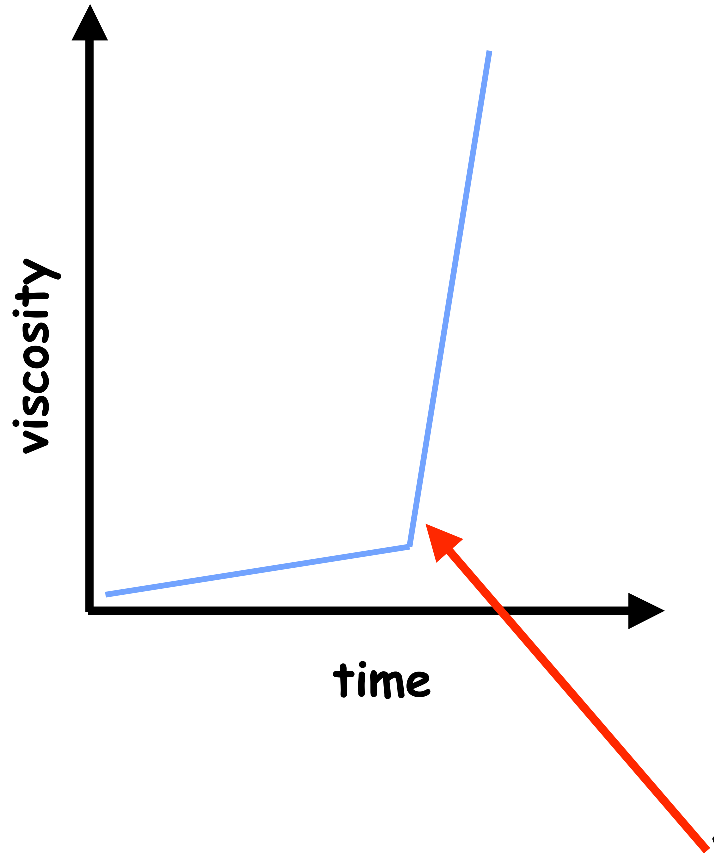


In/Cr
Si





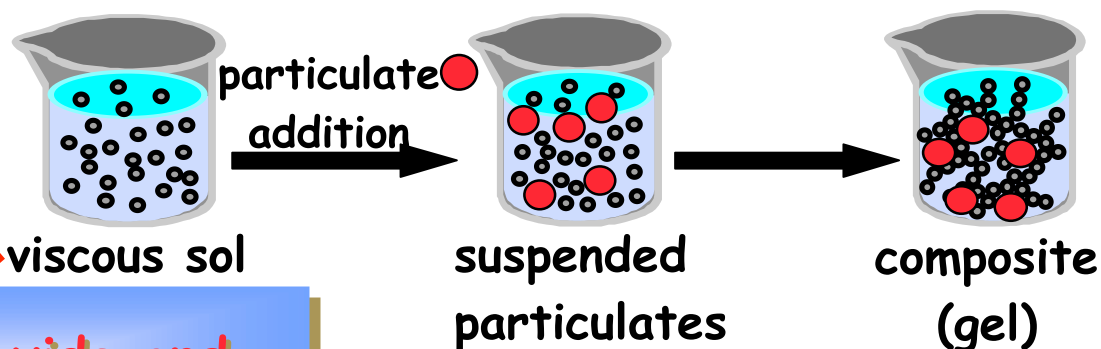
Viscous Sol Method for Particle Addition



Solution viscosity increases dramatically just before gelation

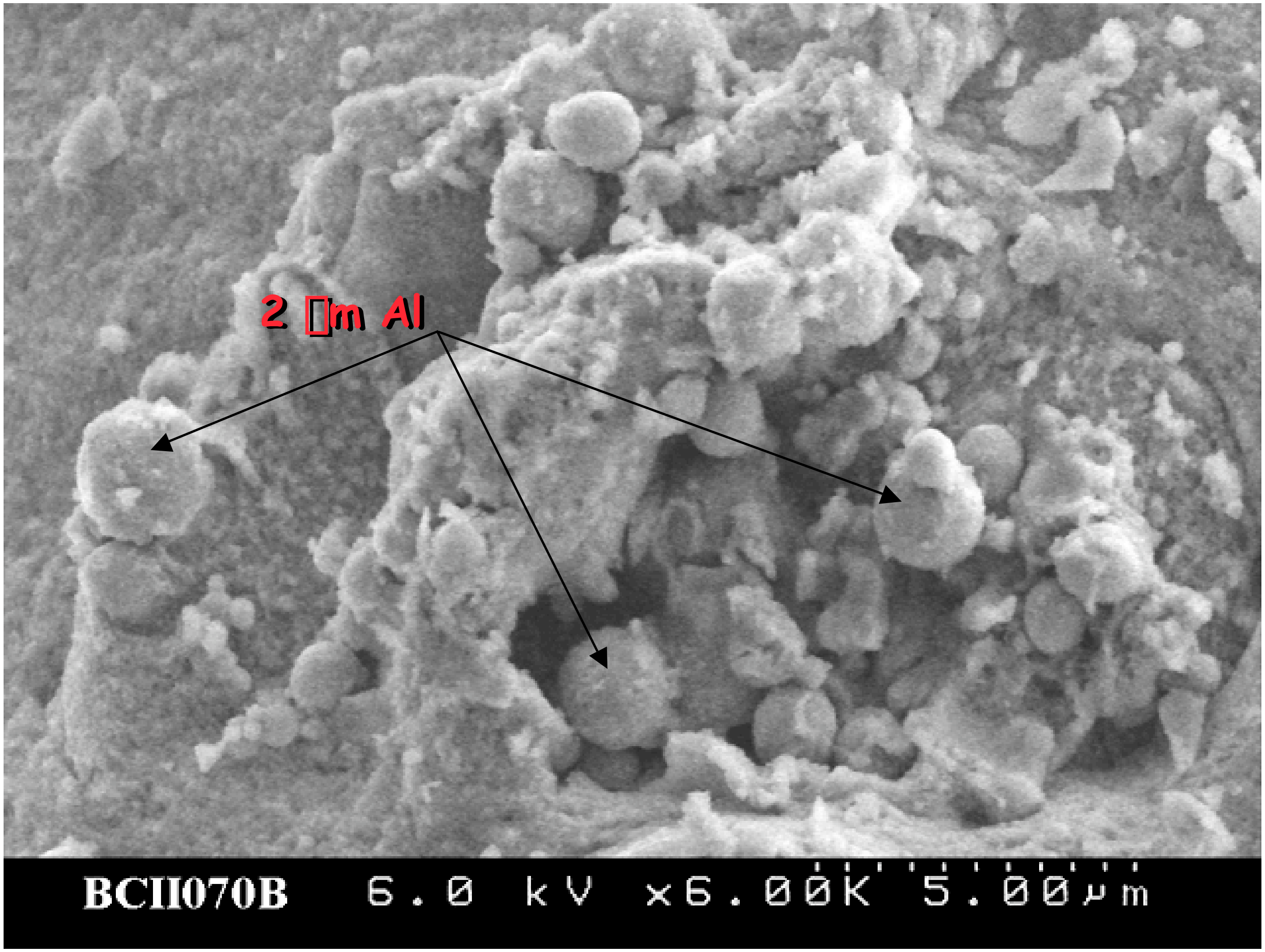
Addition of particulate (e.g., metal, polymer, etc.) to stirred solution

Effectively "freezes" particulates in the matrix in localized domains



Synthesis of the metal oxide and mixing of the oxide/fuel is done in ONE step !!

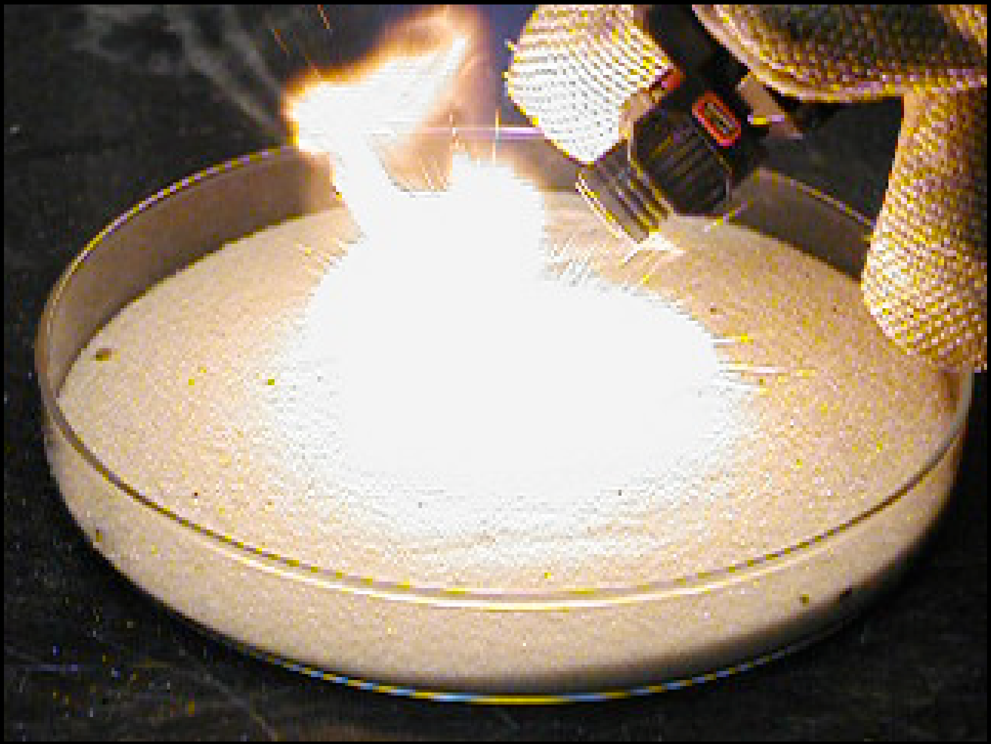
Viscous Sol Method for Particle Addition



Energetic Fe/Si-R Inorganic, Organic Nanocomposite (Fe/Si=5)

Idealized energetic reaction:

$$2Al + Fe_2O_3 + 3CF_2 \longrightarrow 2AlF_3 + 2Fe + 3CO + \Delta H$$



Future Work

- Optimize Composition of Energetic Materials
- Characterize Energetic properties
  - burn rates, temperatures
  - reaction products
- Other thermite systems
  - WO_3/Al
- Nanometer Al

Acknowledgements

- TEM/EFTEM - Jennifer S. Harper
- SEM - Jim Ferreira
- ^{29}Si MAS-NMR
  - Dr. Sarah Chinn, Dr. Julie Herberg, Dr. Bob Maxwell