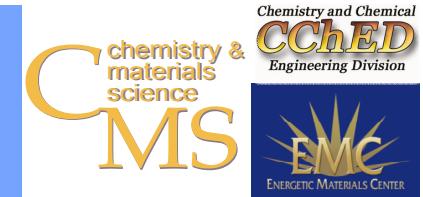




2003 CMS Post Doctoral Symposium



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

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Materials Center, Lawrence Livermore National Laboratory

UCRL-PRES-154135

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Energy by the University of California Lawrence Livermore National
Laboratory under contract No. W-7405-Eng-48.



Energetic Nanocomposites: Thermite Reactions

Idealized energetic reactions :

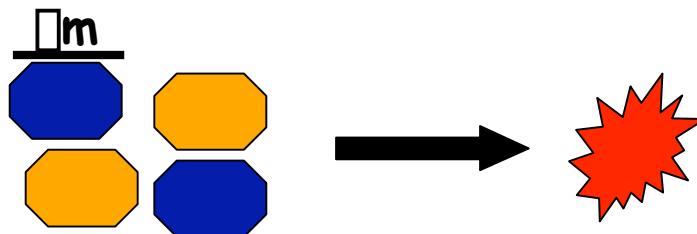
Thermite :



Thermite with gas generator :

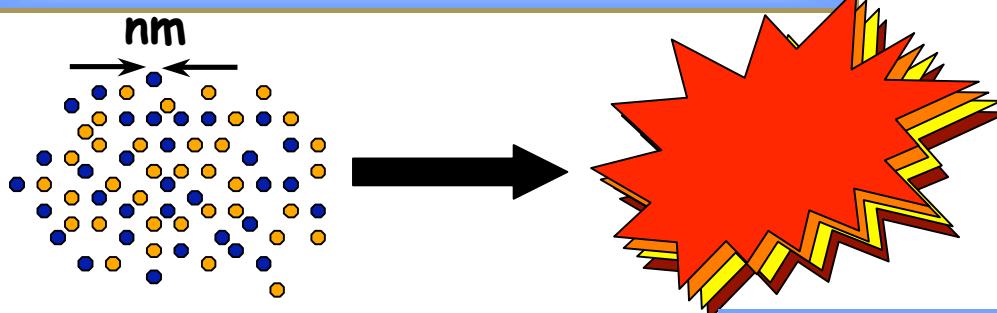


Conventional ($\square\text{m}$ -sized particles):



- 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



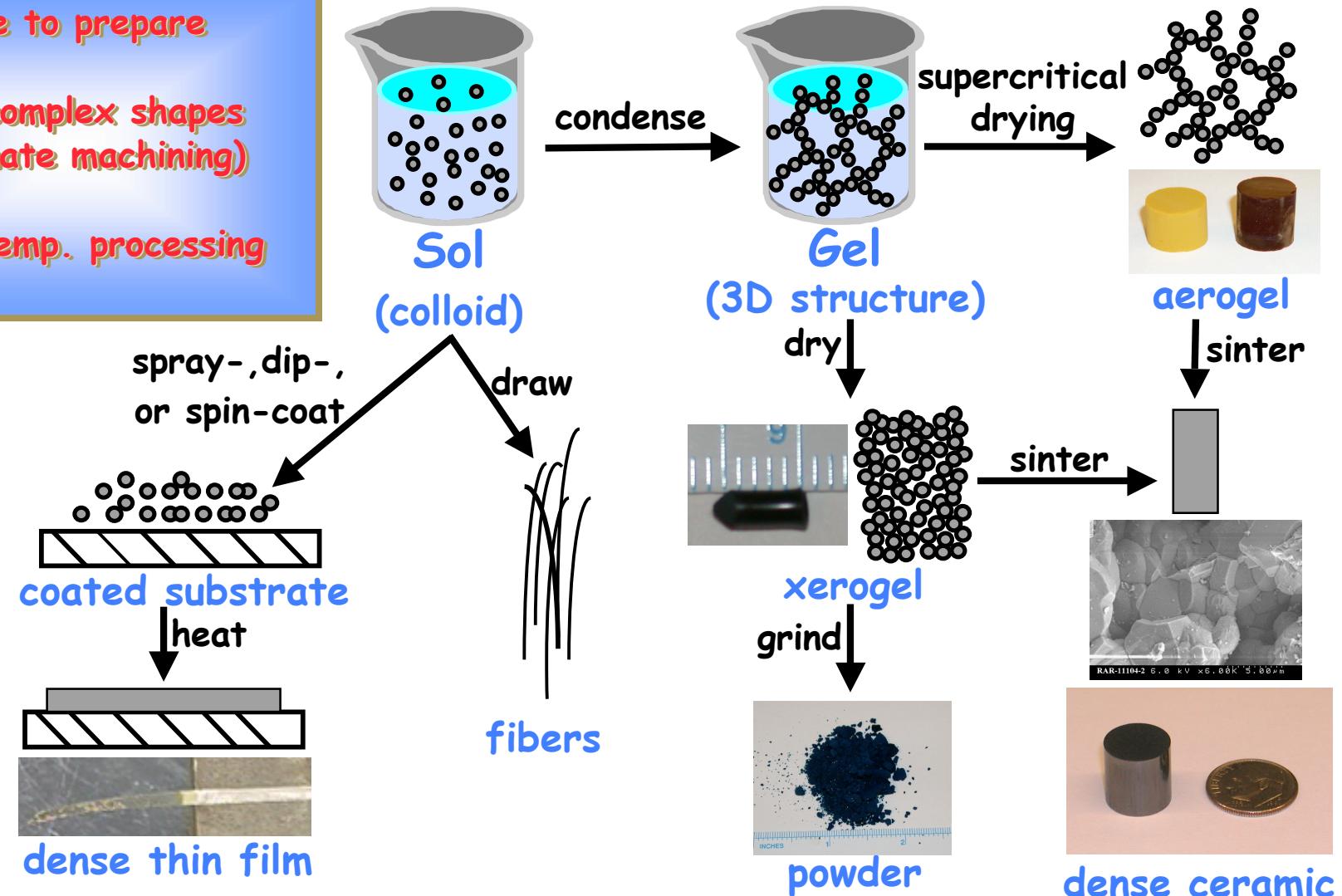
The Sol-gel Methodology: Inherently "Nano"

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EMC
ENERGETIC MATERIALS CENTER

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

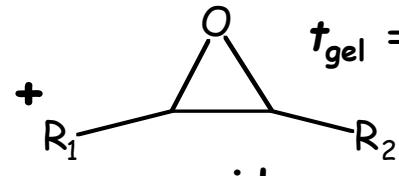
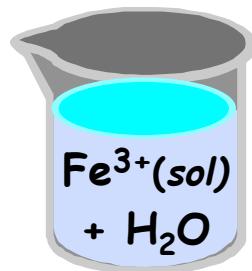


Brinker, C.G.; Scherer, G.W. *Sol-Gel Science*, Academic Press; New York, 1990.



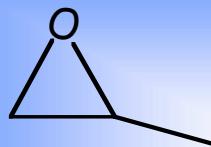
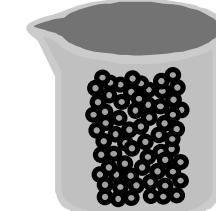
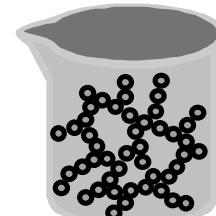
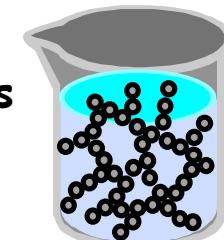
New Approach Uses Epoxide Addition for Synthesis of Gels

Does not use alkoxides as starting material

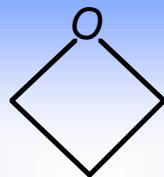


(Proton scavenger)

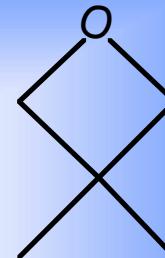
$t_{\text{gel}} = \text{minutes/hours/days}$



propylene oxide
(PO)



trimethylene oxide
(TMO)



dimethyloxetane
(DMO)

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

Chemistry and Chemical
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chemistry &
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1 H Hydrogen 1.00794	
3 Li Lithium 6.941	4 Be Beryllium 9.012182
11 Na Sodium 22.989770	12 Mg Magnesium 24.3050
19 K Potassium 39.0983	20 Ca Calcium 40.078
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62
55 Cs Cesium 132.90545	56 Ba Barium 137.327
87 Fr Francium (223)	88 Ra Radium (226)



sol-gel methodology



sol-gel/epoxide addition

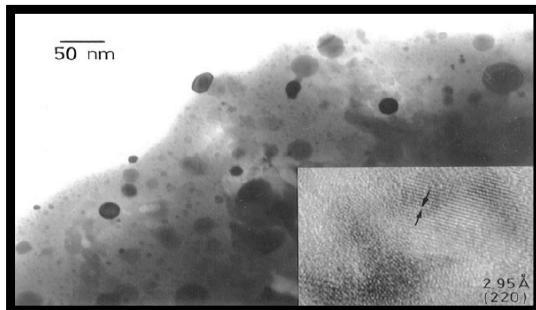
5 B Boron 10.81	6 C Carbon 12.01	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	2 He Helium 4.003
15 P Phosphorus 30.973761	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948		
33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80		
48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.70	52 Te Tellurium 127.60	53 I Iodine 126.90447	
81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98038	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)

58 Ce Cerium 140.116	59 Pr Praseodymium 141.000	60 Nd Neodymium 144.242	61 Pm Promethium (145)	62 Sm Samarium 150.400	63 Eu Europium 152.000	64 Gd Gadolinium 157.000	65 Tb Terbium 158.900	66 Dy Dysprosium 162.000	67 Ho Holmium 164.900	68 Er Erbium 167.200	69 Tm Thulium 168.900	70 Yb Ytterbium 173.000	71 Lu Lutetium 174.900
90 Th Thorium 232.0381	91 Pa Protactinium 231.03588	92 U Uranium 238.0289	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (258)	101 Md Mendelevium (259)	102 No Nobelium (259)	103 Lr Lawrencium (262)

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



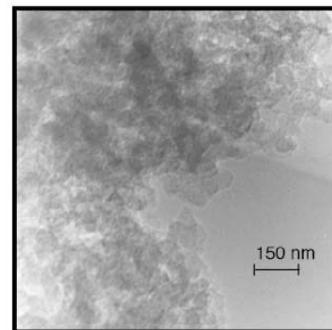
Fe-Si Mixed Oxide Composites



Morales et. al. - Instituto Ciencia de Materiales Madrid

Sol-gel synthesis using TEOS and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ results in materials of $\text{Fe/Si} = 0.2 - 0.4$. Further heat treatment ($200 - 400^\circ\text{C}$) results in the formation of $\square\text{-Fe}_2\text{O}_3$ and $\square\text{-Fe}_2\text{O}_3$ domains.

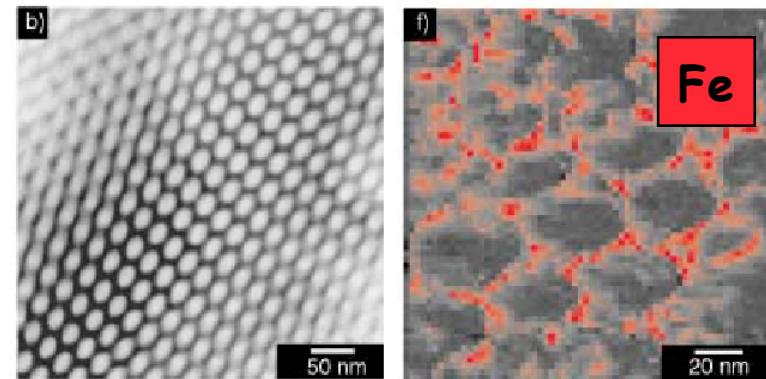
Langmuir, 1997, 13, 3627 - 3634.



Baiker et. al. - Swiss Federal Institute of Technology

Sol-gel synthesis using TMOS/TEOS and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ results in materials of $\text{Fe/Si} \approx 0.1$. Dispersion and crystalline phase of Fe(III) oxide depends on heat treatment ($200 - 900^\circ\text{C}$).

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



Wiesner et. al., Cornell University

Polymeric structure directing agent results in $\square\text{-Fe}_2\text{O}_3$ doped, $\text{Fe/Si}=0.3-1$, 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

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CChED
Engineering Division

chemistry &
materials
CMS
science

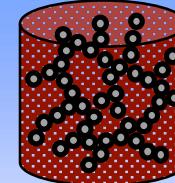
EMC
Energetic Materials Center



Epoxide (PO, TMO)
(Proton scavenger)

R = ethyl (TEOS)
or methyl (TMOS)

t_{gel} = min./hrs./days

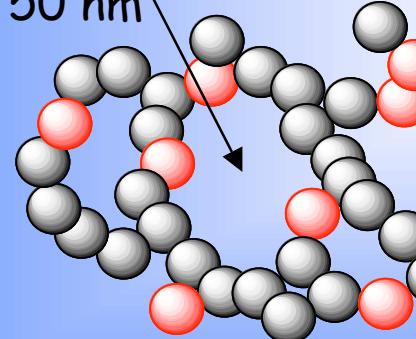


Fe(III)-Si
mixed oxide
composite

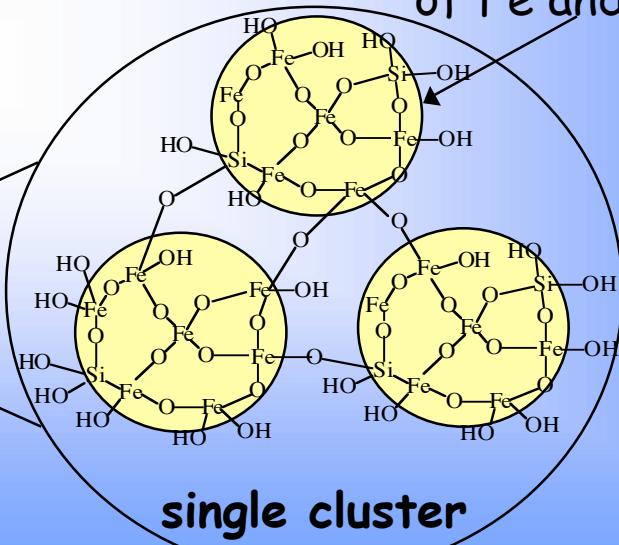
Microstructure of Sol-gel Fe-Si Oxide Nanocomposites:

clusters with
microporosity:
 $d \leq 2 \text{ nm}$

mesoporosity:
 $2 \leq d \leq 50 \text{ nm}$



nanoscale mixing of
Fe and Si oxide clusters

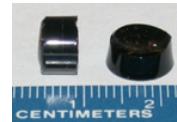


primary particles:
molecular mixing
of Fe and Si oxides



Fe-Si Mixed Oxide Composites: Epoxide Addition

Fe/Si = 1 nanocomposites



xerogel



aerogel

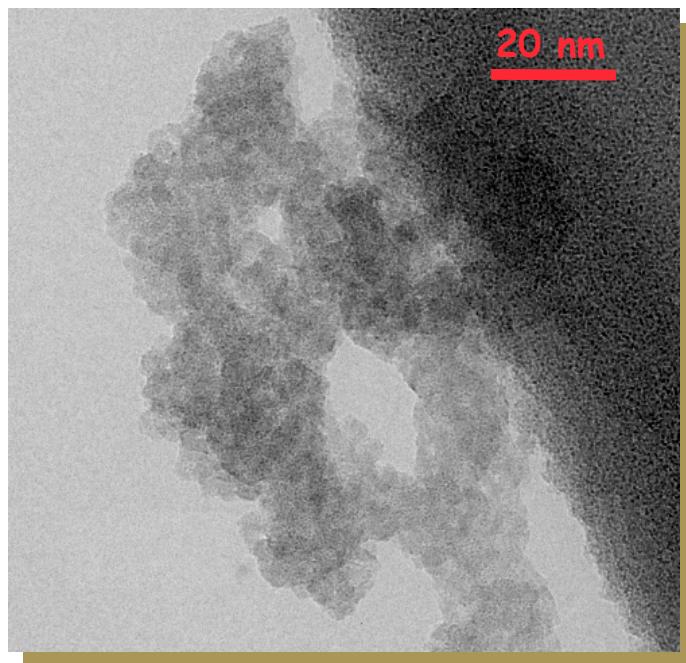
calc. Fe/Si (mol/mol)	silica precursor	epoxide	t_{gel} (hr)	actual Fe/Si (mol/mol)	surf. area (BET; m^2/g)	pore vol. (mL/g)	avg. pore diam. (nm)
5	TMOS	PO	0.5	5.3	401	4.10	29
2	TMOS	PO	0.6	2.0	432	3.74	28
1	TMOS	PO	9	1.0	389	1.63	18
5	TEOS	PO	0.8	5.3	359	4.82	30
2	TEOS	PO	0.8	2.3	395	3.26	27
1	TEOS	PO	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.

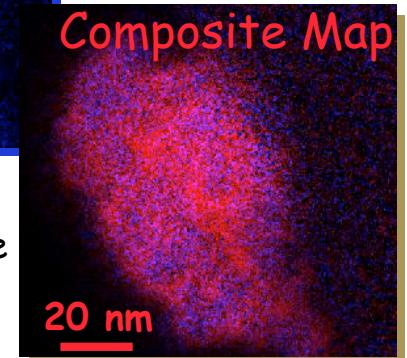
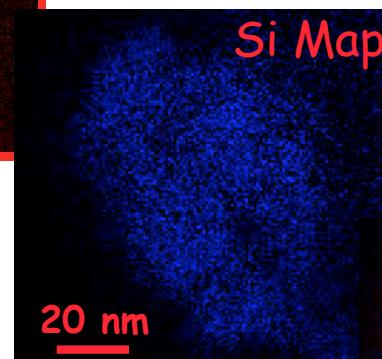
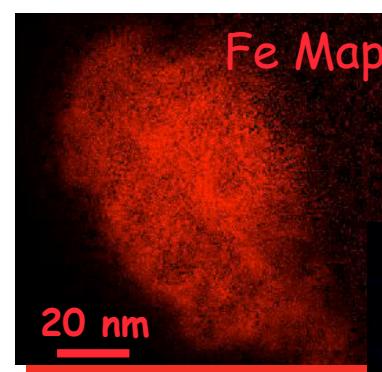


Dispersion of Fe and Si Oxides: TEM & EFTEM

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



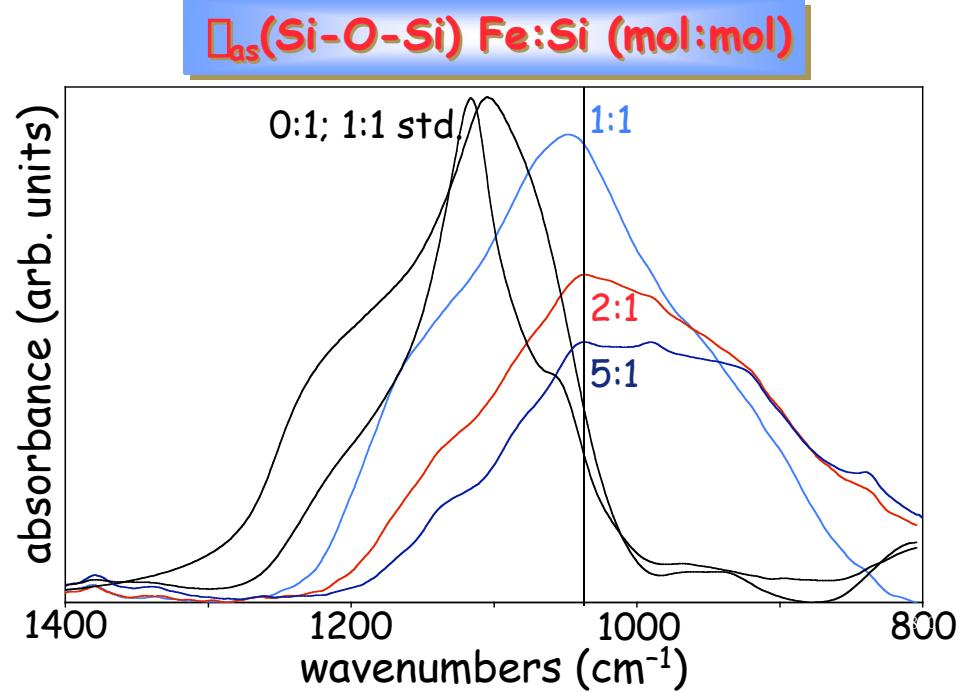
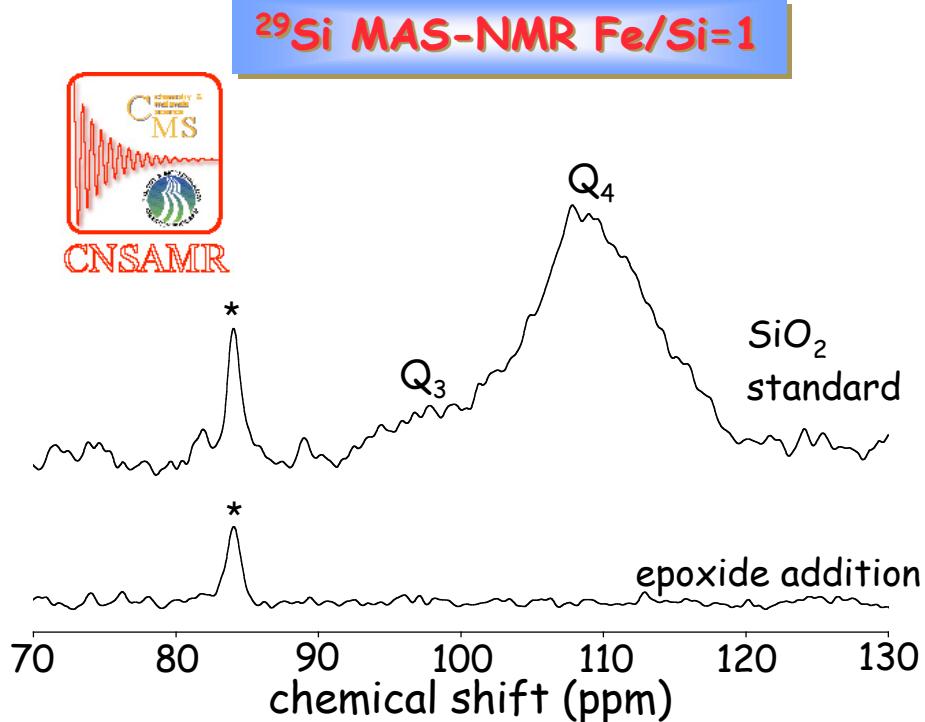
Energy Filtered Transmission Electron Micrographs:
Elemental maps show good mixing of the Fe and Si oxide phases on the nanoscale.



Iron(III) oxide
Silica



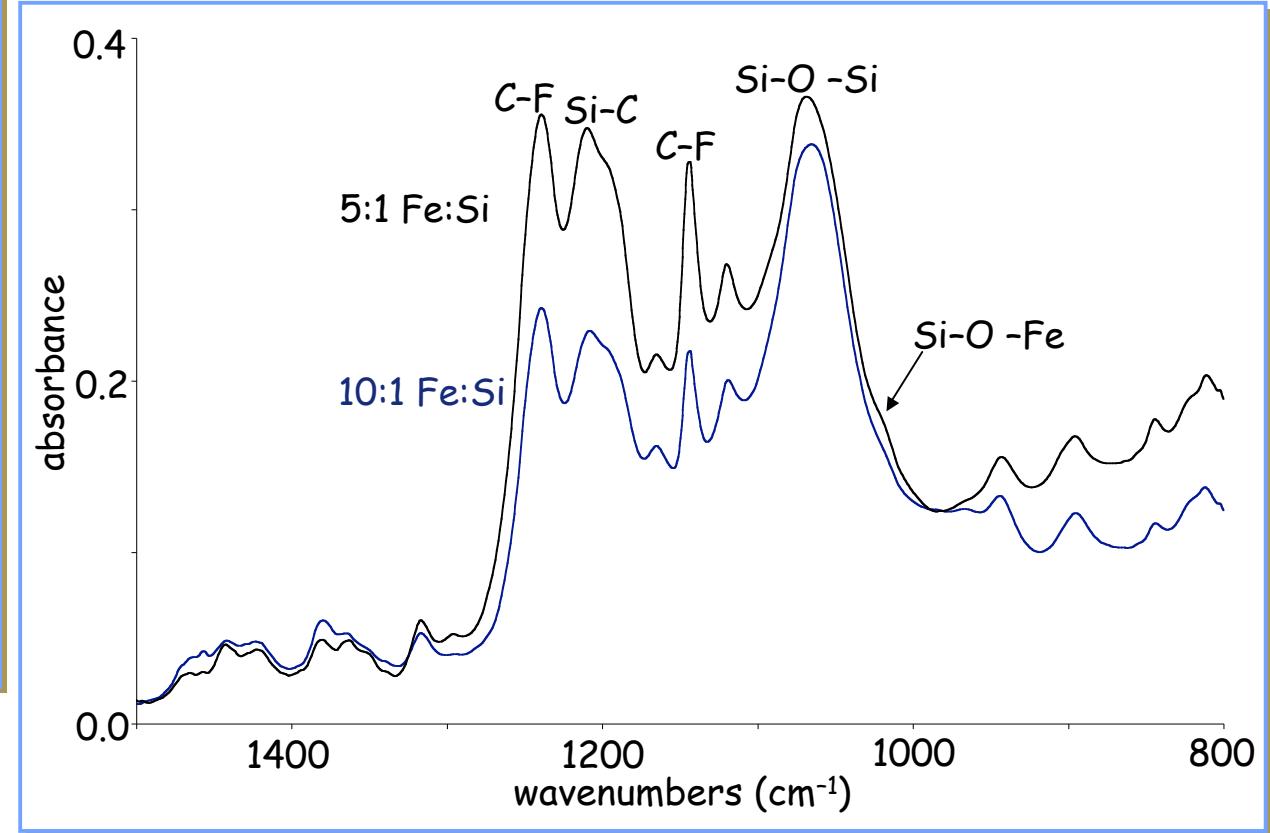
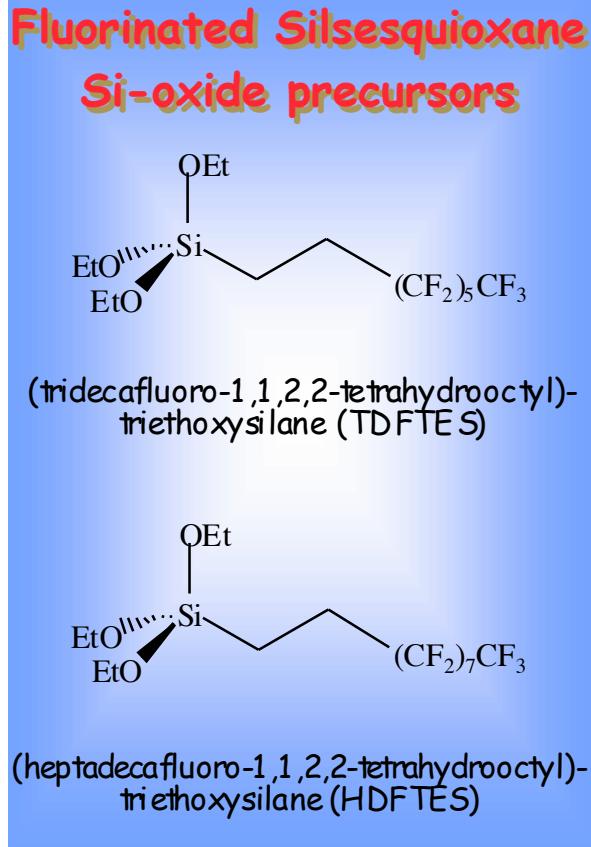
Dispersion of Fe and Si Oxides: ^{29}Si MAS-NMR & FTIR



- **^{29}Si MAS-NMR**
 - Loss of ^{29}Si signal indicates good dispersion of Si with paramagnetic Fe(III)
- **FTIR**
 - $\square_{as}(\text{Si-O-Si})$ shift ($\square E = -12 \text{ cm}^{-1}$) suggests a small degree of Si-O-Fe bonding



Organic Functionalized Fe-Si Mixed Oxide Nanocomposite





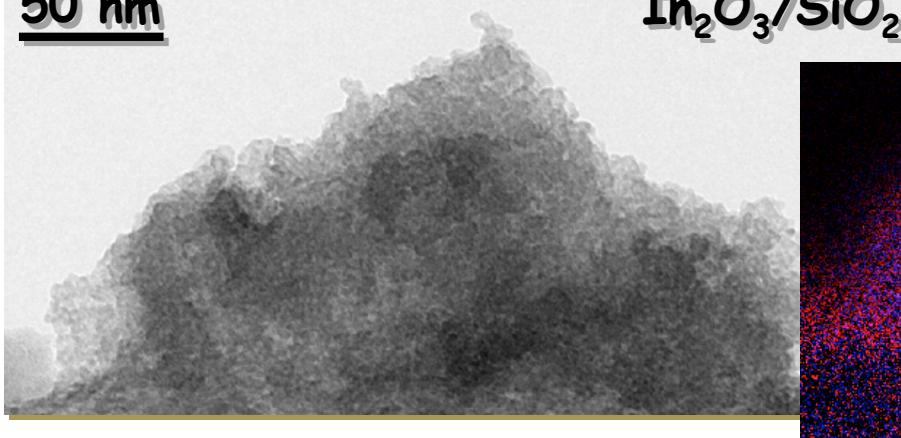
Other M-Si Mixed Oxide Nanocomposites

Chemistry and Chemical
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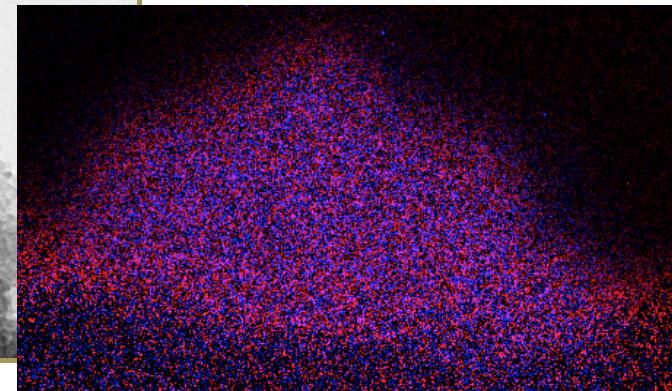
chemistry &
materials
science
CMS

EMC
Energetic Materials Center

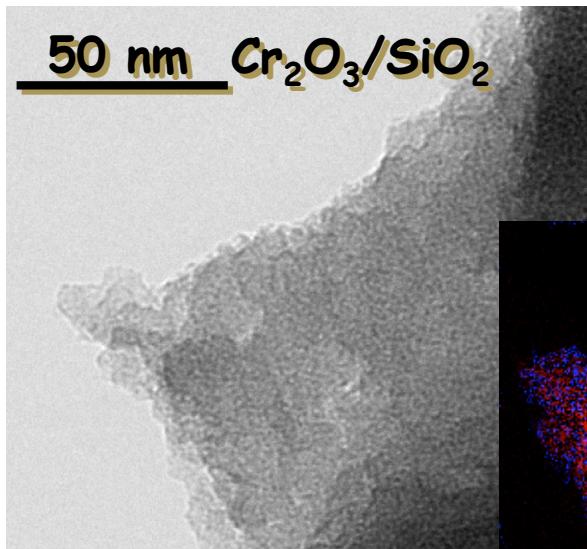
50 nm



$\text{In}_2\text{O}_3/\text{SiO}_2$

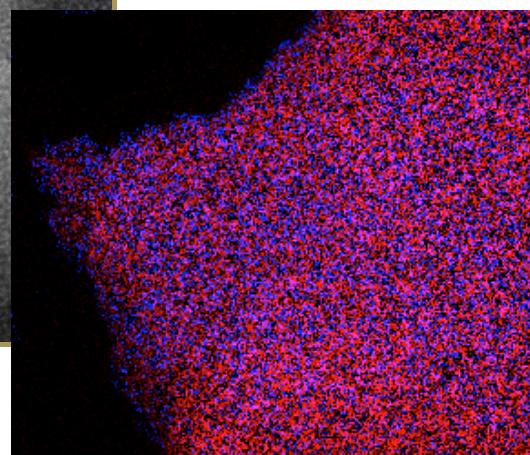


50 nm



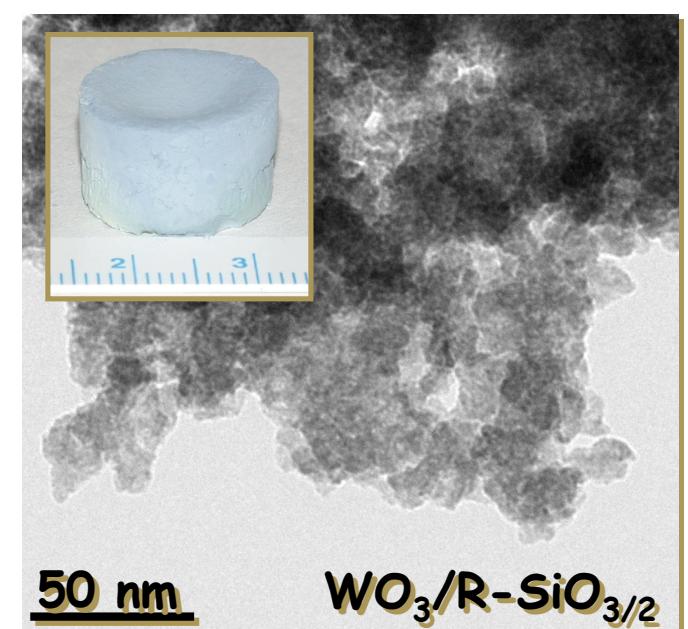
$\text{Cr}_2\text{O}_3/\text{SiO}_2$

In/Cr
 Si



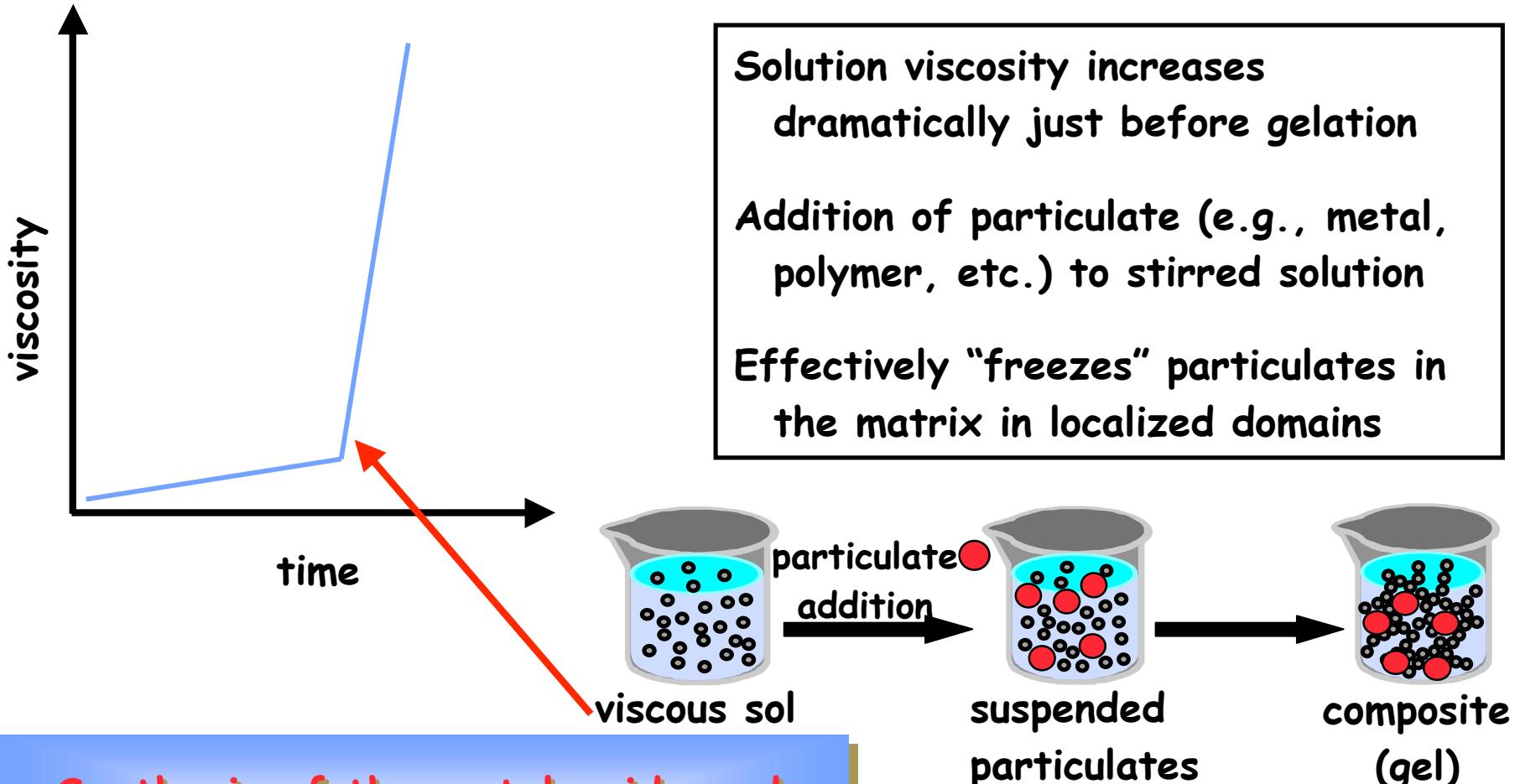
50 nm

$\text{WO}_3/\text{R}-\text{SiO}_{3/2}$





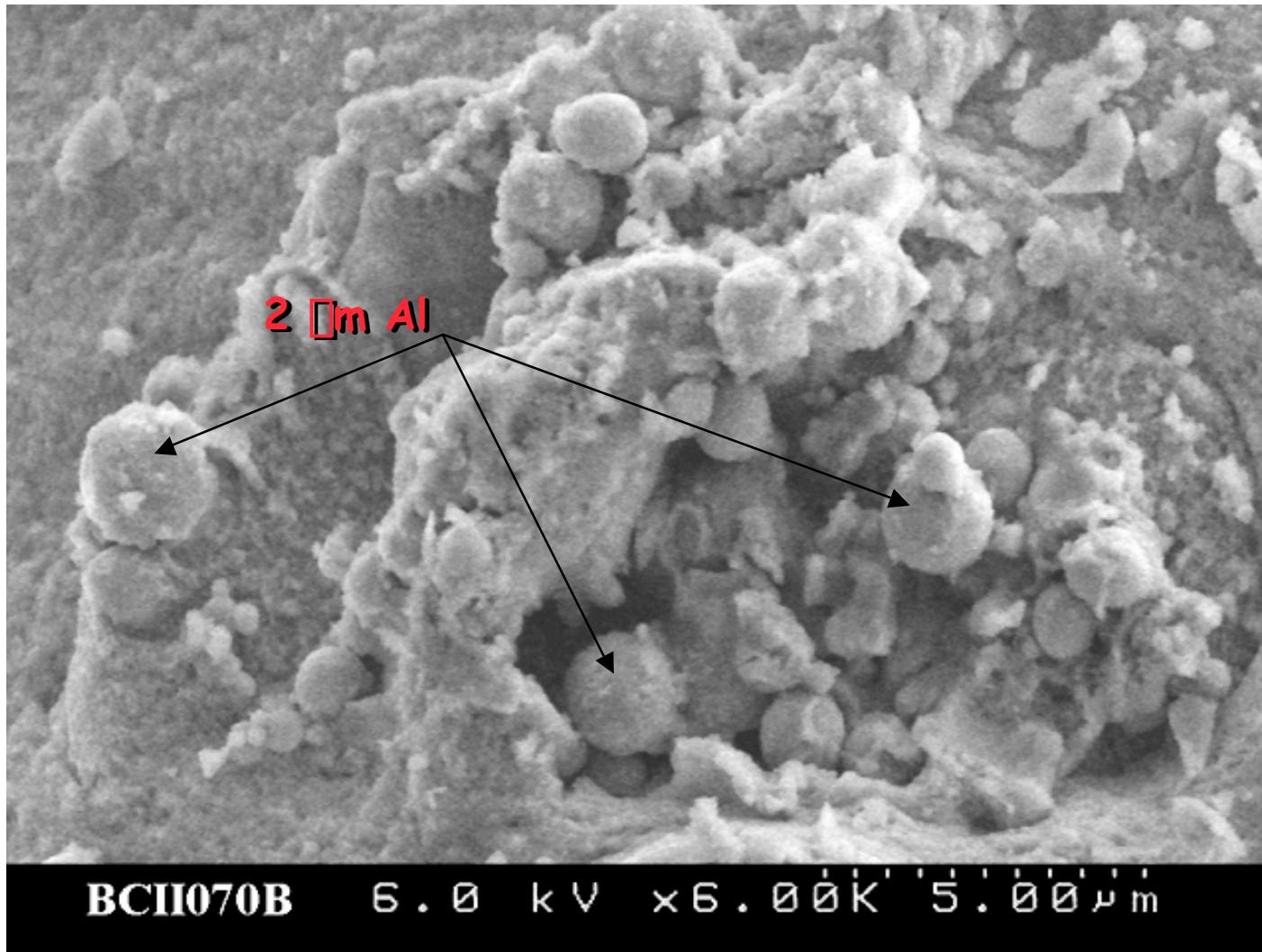
Viscous Sol Method for Particle Addition



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

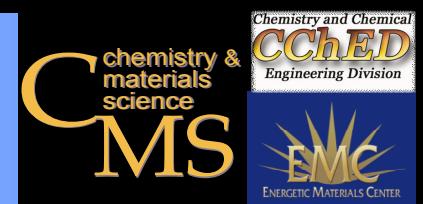


Viscous Sol Method for Particle Addition





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



Idealized energetic reaction:





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