

# Chemistry Seminar Abstracts for Spring 2017

<b>Ring Fusion Aromatization: A Key Step Toward Pyrolytic Carbonization of Phenolic Resin Type of Aerogels .....</b>	<b>2</b>
By Hojat Majedi Far, Dept. of Chem., MS&T	
<b>Mining Water for the Production of Spacecraft Fuels and Propellants .....</b>	<b>3</b>
By Leslie S. Gertsch, Rock Mechanics & Explosives Research Center, Dept. of Geological Sciences & Engineering, MS&T	
<b>Shape-Memory Polyisocyanurate Aerogels and Porous Metal Aerogels as Energetic Materials .....</b>	<b>3</b>
By Suraj Donthula, Dept. of Chem., MS&T	
<b>Part A: Design, Synthesis, and Reactivity Studies of Novel AGE-Inhibitors and AGE Breakers. Part B: Novel Synthetic Methods for Monofluorination and gem-Difluorination .....</b>	<b>4</b>
By Jatin Mehta, Dept. of Chem., MS&T	
<b>Low-Coordination Numbers, Unusual Bonding, and Dispersion Force Effects in Molecules .....</b>	<b>5</b>
By Philip P. Power, Dept. of Chem., University of California, Davis	

# Ring Fusion Aromatization: A Key Step Toward Pyrolytic Carbonization of Phenolic Resin Type of Aerogels

Hojat Majedi Far, Dept. of Chem., MS&T

**Abstract:** Part A: Synthesis and Oxidative Aromatization of Phenolic Resin Aerogels

We describe how polymer backbone oxidation can get involved in the pyrolytic carbonization of phenolic-resin aerogels. Using as our conceptual point of departure the need for oxidative stabilization (240 °C/air) during pyrolysis of polyacrylonitrile (PAN) and polybenzoxazine (PBO), we study the effect of oxidation on the polymeric backbone of four classical phenolic resins: resorcinol-formaldehyde (RF), terephthalaldehyde-phloroglucinol (TPOL), phloroglucinol-formaldehyde (FPOL), and phenol-formaldehyde (PF). Use of those resins in aerogel form is beneficial because it allows air circulation through their bulk, thus facilitating oxidation. Solid-state <sup>13</sup>C NMR, FTIR, CHN and XPS showed that curing at 240 °C / air oxidizes the -CH or -CH<sub>2</sub> groups and forces ring-fusion along the polymer backbone and formation of six-membered heteroaromatic systems (pyrylium cations).

Part B: Ultra-high Surface Area Carbons via Oxidative Aromatization of Phenolic-Resins: Applications as Energy Storage Materials and Adsorbents

We discovered that by introducing oxidative ring-fusion aromatization (240 °C/air) along pyrolysis of phenolic-resin aerogels (RF, TPOL, FPOL, and PF) we increased the surface areas of the resulting carbon aerogels substantially. For comparison, phenolic aerogels were also carbonized at 800 °C/Ar without prior oxidation at 240 °C/air and the resulting carbons were analyzed in terms of their chemical composition and their nano- and microscopic structures. Spectroscopic results (<sup>13</sup>C NMR, FTIR, XPS) and CHN analysis showed that irrespective of the pyrolytic route (i.e., with or without oxidation), all phenolic-resin-derived carbons chemically converged. However, 240 °C/air-treated carbons exhibited higher surface areas and microporosity when compared to non-treated carbons. For example, the surface area of 240 °C/air-treated carbons could be as high as 792 m<sup>2</sup> g<sup>-1</sup>, versus 678 m<sup>2</sup> g<sup>-1</sup> of untreated carbons. These findings are attributed to the early rigidity imposed on the polymeric backbone by the oxidative curing process. Encouraged by those findings, surface areas were further increased using reactive etching (at 1000 °C under flowing CO<sub>2</sub>). The latter process increased microporosity dramatically and yielded extremely high surface areas (up to 2521 m<sup>2</sup> g<sup>-1</sup>, by N<sub>2</sub> sorption). Apart from potential uses as electrodes in supercapacitors, fuel cells and batteries, those materials are explored as adsorbents for CO<sub>2</sub> and CH<sub>4</sub> capture and separation.

## Mining Water for the Production of Spacecraft Fuels and Propellants

Leslie S. Gertsch, Rock Mechanics & Explosives Research Center, Dept. of Geological Sciences & Engineering, MS&T

**Abstract:** A range of materials representative of carbonaceous near-Earth asteroids have been subjected to stepwise heating in a vacuum to investigate volatiles release and capture behavior in space. Results show that most of the mass lost during heating is predictable by well-known reactions: dehydroxylation, de-hydration, and pyrolysis. Cryotrapping has been shown to effectively capture the volatiles produced. These findings form a base for additional investigations, so that the trade space of potential processes for extracting volatile compounds from carbonaceous solar system bodies can be explored effectively.

## Shape-Memory Polyisocyanurate Aerogels and Porous Metal Aerogels as Energetic Materials

Suraj Donthula, Dept. of Chem., MS&T

**Abstract:** Part 1: Shape Memory Polyisocyanurate Aerogels for Deployable Panels and Biomimetic Applications

Shape memory polymers (SMPs) remember and return to an original shape when triggered by a suitable stimulus, typically a change in temperature. They are pursued as cost-effective, low-density, higher-strain-tolerant alternatives to shape memory alloys. The ultimate refinement in terms of density reduction will be accomplished with porous SMP, and in that regard shape memory polymeric aerogels (SMPAs) offer the most viable approach which is implemented with rigid trifunctional isocyanurate nodes between flexible urethane tethers based on four short oligomeric derivatives of ethylene glycol:  $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$  ( $1 \leq n \leq 4$ ). Formation of self-supporting 3D networks of particles was varied with specific combinations of monomer concentration, chemical identity of the diol and composition of the solvent (CH<sub>3</sub>CN/acetone mixtures) using statistical design-of-experiments methods. SMPAs showed a robust shape memory effect (SME), the quality of which was evaluated with four figures of merit (strain fixity, strain recovery, strain recovery rate and the fill factor). The robust shape memory effect of the SMPAs of this study was demonstrated with deployable panels and bionic hands capable of mimicking coordinated muscle function.

Part 2: Explosives and Thermites with Iron(0) Aerogels Infiltrated with Perchlorates

Monolithic nanoporous iron was prepared via carbothermal reduction of interpenetrating networks of polybenzoxazine and iron oxide nanoparticles (PBO-FeOx). Excess carbon was burned off at 600 oC in air, and oxides produced from partial oxidation of the Fe(0) network

were reduced back to Fe(0) with H<sub>2</sub> at different temperatures (temp), ranging from 300 oC to 1300 oC. Fe-temp monoliths were infiltrated with perchlorates, dried exhaustively and were ignited with a flame in open air. Most experimentation was conducted with LiClO<sub>4</sub>. Depending on temp, monoliths fizzled out ( $\leq 400$  oC), exploded violently (500 oC to 900 oC), or behaved as thermites ( $\geq 950$  oC). The evolution from explosive to thermite behavior was rationalized with SEM, particle size determination via N<sub>2</sub> sorption, electrical conductivity measurements and mechanical strength data under quasi-static compression.

## **Part A: Design, Synthesis, and Reactivity Studies of Novel AGE-Inhibitors and AGE Breakers. Part B: Novel Synthetic Methods for Monofluorination and gem-Difluorination**

Jatin Mehta, Dept. of Chem., MS&T

**Abstract:** The formation of the toxic Advanced Glycation End-Products (AGEs) as a result of the non-enzymatic reaction (Maillard reaction) between reducing sugars and amino groups in proteins, lipids, and nucleic acids is associated with diabetic complications, atherosclerosis, and Alzheimer's disease. Reactive 1,2-dicarbonyl compounds are important intermediates of the Maillard reaction as they would lead to the formation of AGEs. Dehydroascorbic acid (DHAA), oxidized form of ascorbic acid (ASA), is a reactive 1,2-dicarbonyl compound that rapidly reacts with lens a $\alpha$ -crystallin and other long-lived proteins to form cross-linked aggregates that would eventually result in the cataract formation. Toward the goal of developing effective therapeutics, we have now synthesized the thiazolium and imidazolium-based novel AGE-inhibitors and AGE-breakers that would reverse the protein-crosslinking, and studied their reactivity towards the AGE-precursor DHAA, using <sup>13</sup>CNMR spectroscopy. In this presentation, we demonstrate for the first time that these AGE-inhibitors trap DHAA in vitro to form their corresponding adducts. Further studies are in progress for their in vivo effects.

Organofluorine compounds have important role as pharmaceuticals, agrochemicals, and in materials science due to their properties of enhanced lipophilicity and thereby bioavailability. Recent trend in the area of fluorination is toward developing <sup>18</sup>F-based positron-emission tomography (PET) agents for diagnostic imaging. We have developed convenient synthetic methods based on the Photoredox chemistry and the readily available fluorine-containing precursors, such as Selectfluor. In this presentation, we will outline our progress in this area of monofluorination and difluorination of organic compounds, and novel photoredox-catalyzed gem-difluorination of 1,3-dithiolanes..

## **Low-Coordination Numbers, Unusual Bonding, and Dispersion Force Effects in Molecules**

Philip P. Power, Dept. of Chem., University of California, Davis

**Abstract:** The theme of the lecture concerns the often subtle effects of London dispersion forces on the stability and structures of compound classes as diverse as two-coordinate transition metal complexes (including quintuply-bonded species), high valent transition metal alkyls, multiple bonded main group compounds, persistent main group radicals, and the Lewis acid/base properties of boranes. The main conclusion is that the consideration of dispersion forces is necessary in discussions of the structure and reactivity of all compounds substituted by bulky organic groups. The increased understanding of such forces should allow their effects to be deliberately used to enhance stability and allow access to hitherto unknown types of compounds.