Catalytically Active Aerogel Material for Automotive Exhaust Mitigation Applications

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Abstract

Aerogels are high surface area, low density, low thermal mass, nanoporous materials that are stable at high temperatures. Due to this unique combination of properties, aerogels have potential applications in a range of areas including sensing, insulation, comet dust collection, and catalysis. We have developed a series of catalytically active aerogels which show activity as three-way catalysts. These materials are fabricated using a rapid supercritical extraction method [1]. It is relatively easy to incorporate a variety of metals, including non-PGM metals such as nickel [2], copper [3] and cerium [4] into a silica- or alumina-based backbone. Through use of the Union Catalytic Aerogel Testbed, UCAT, an in-house designed catalytic test system [5], we have demonstrated that these materials have three-way catalytic ability. UCAT tests catalytic material performance for conversion of NO, UHCs and CO over a range of temperatures from 200-700 C using customizable simulated exhaust gas mixtures.

Background

Aerogels can be readily tailored for catalytic activity by combining a catalytically active metal species with an aerogel support matrix.

- The aerogel structure consists of nanoscale-sized spherical clusters linked together in chains, ultimately forming an amorphous spatial grid with air-filled pores on the order of tens of nanometers.
- This nanostructure can be tailored to fit a specific activity through control of synthesis and processing conditions.
- We have developed methods for making a variety of catalytic aerogels (see Figs 1-3) using the patented Union College rapid supercritical extraction (RSCE) method.

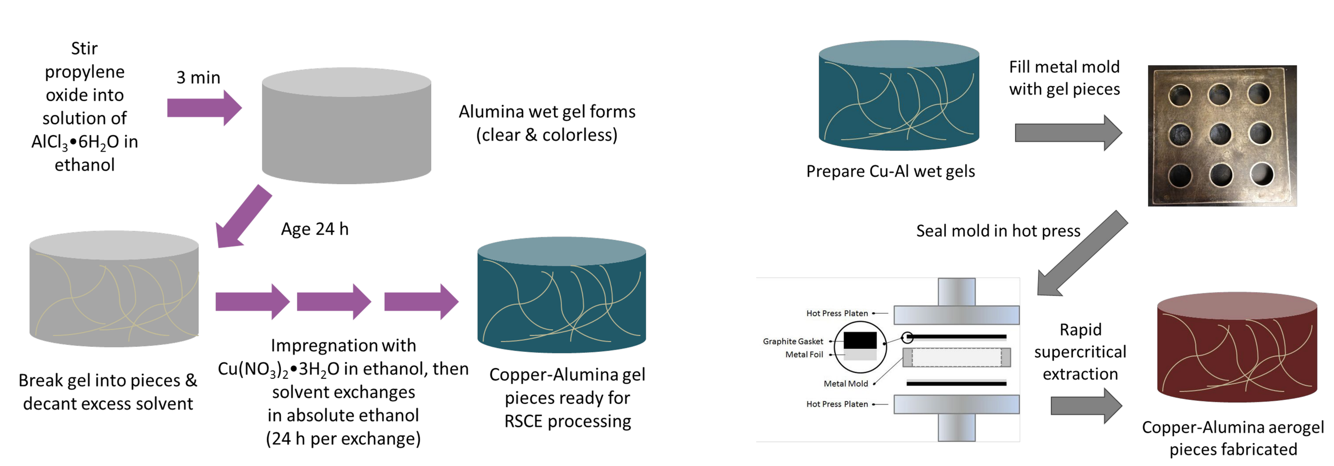

Figure 1. Catalytic aerogel synthesis method. Chemical processing (left) and RSCE (right).

Cu-Al | Cu-Si | Cu-Si (NP) | Ce-Cu-Al | Ce-Al

Figure 2. Images of various catalytic aerogels fabricated through RSCE.

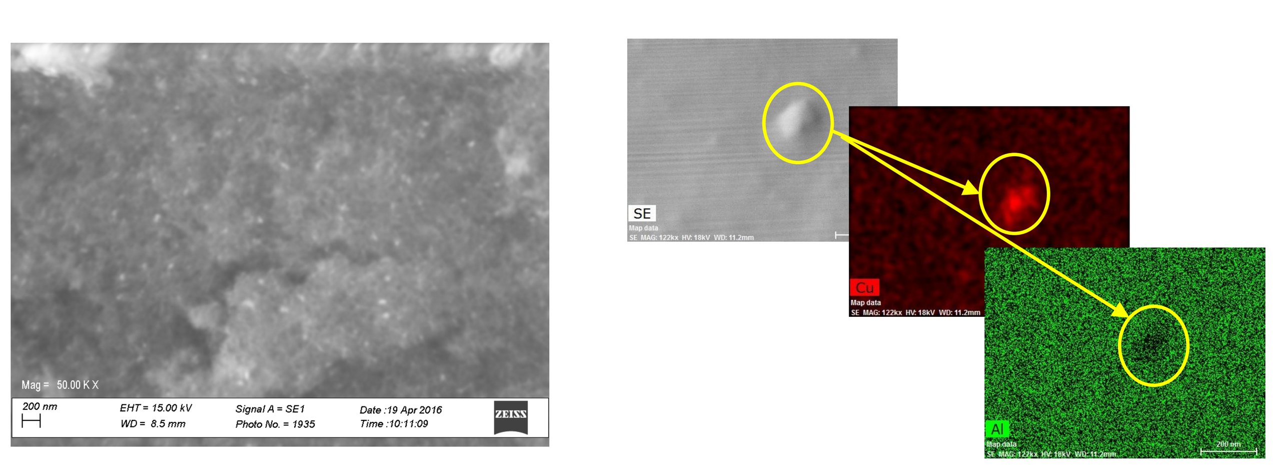

Figure 3. SEM (left) and EDX (right) micrographs of Cu-Al aerogels show evidence of formation of copper-containing nanoparticles.

Potential Aerogel Advantages

High Surface Area:
- More active sites
- Improved gas/solid interaction

High Thermal Stability:
- Close coupling
- Reduced active site diffusion/sintering

Chemically Tailorable:
- PGM reduction or elimination

Low Thermal Inertia:
- Reduced time to light-off temperature

Union Catalytic Aerogel Testbed

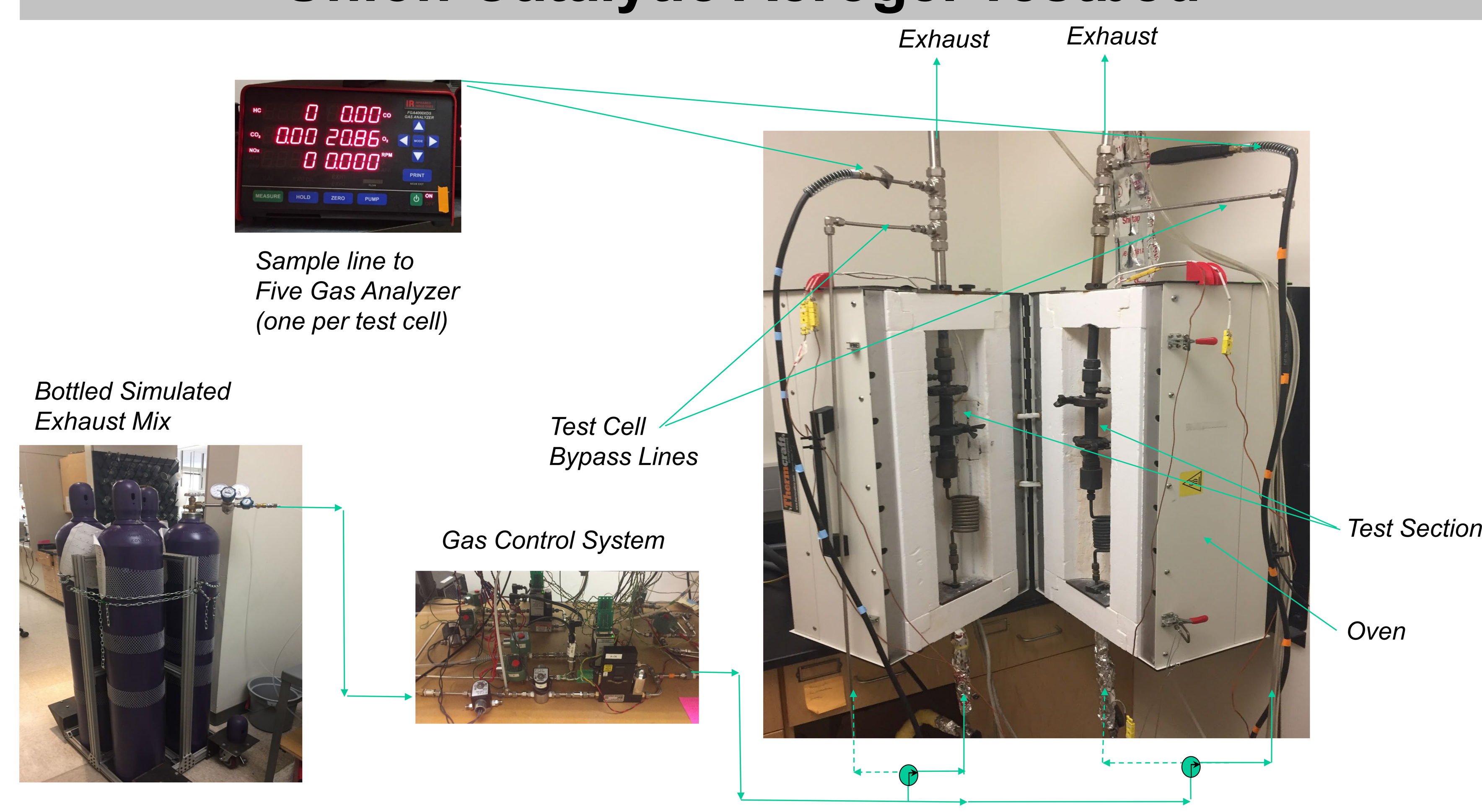

Figure 4: Flow chart depicting the relations between the numerous subsystems that comprise the UCAT.

The Union Catalytic Aerogel Testbed (UCAT, shown in in Figure 4) is designed to test the potential of catalytic aerogels to act as three-way catalysts [5]. UCAT is designed to work with small (15 - 25 mL), easily manufactured quantities of candidate aerogels. Aerogel catalyst performance (i.e. pollutant conversion efficiency) can be measured over a range of temperatures (150°C - 800°C), bulk space velocities (15 - 35 1/s) and exhaust chemistries (i.e. rich / lean, dry / humidified, various initial concentrations of NO, CO, CO_2, H_2, O_2, and UHC simulant (e.g. propane, propene, etc.). The primary analytical capability of the UCAT is provided by conventional five-gas analyzers (one per test cell, Infrared Industries FGA-4000XDS). It has two test cells to increase experimental throughput.

Typical UCAT testing protocol: A measured volume and mass of aerogel catalyst is placed into a UCAT test cell, typically as a packed bed of aerogel monolith "chunks" (see Figure 2). The oven is set to a desired test temperature and a flow rate is selected to provide the desired bulk space velocity through the sample. Shop air is passed over the sample until steady state temperature conditions are reached, at which point the warm up air is stopped and the selected simulated emissions mix flow is started. Recipes for these blends are provided in Table 1. Pollutant concentrations are measured with the five-gas analyzer, first with the emission blend bypassing the sample, next with the emissions blend flowing through the sample, and then again with the blend bypassing the sample. In all cases care is taken to ensure that sufficient time is provided for the five-gas analyzer readings to reach steady state.

Table 1. Simulated emissions blend used in UCAT Testing.

	Legacy California BAR 97 Low Based Mixes		New US Drive Based Mixes	
Component	BAR 97L	BAR 97L + O_2	US Drive Recommended [6]	US Drive HC Modified
NO (ppm)	300	295	1000	1000
UHC (ppm)	Propane, 200	Propane, 197	Ethene, 525 Propene, 500 Propane, 150	Propene, 1000
CO (%)	0.5	0.49	0.5	0.5
H_2 (%)	0	0	0.17	0.17
CO_2 (%)	6%	5.9%	13	13
H_2O (%)	0	0	13	13
O_2 (%)	0	3.6%	0.12-1.15	0.12-1.15

Results and Discussion

To date several candidate catalytic aerogels have undergone performance screening tests in UCAT. These include: cobalt-alumina aerogels (Figure 5), nickel-alumina aerogels [2], several types of coper- silica and copper-alumina aerogels [3] (e.g. Figure 6), ceria-alumina and ceria-silica aerogels [4] as well as "neat" alumina and silica aerogels (which are largely inert).

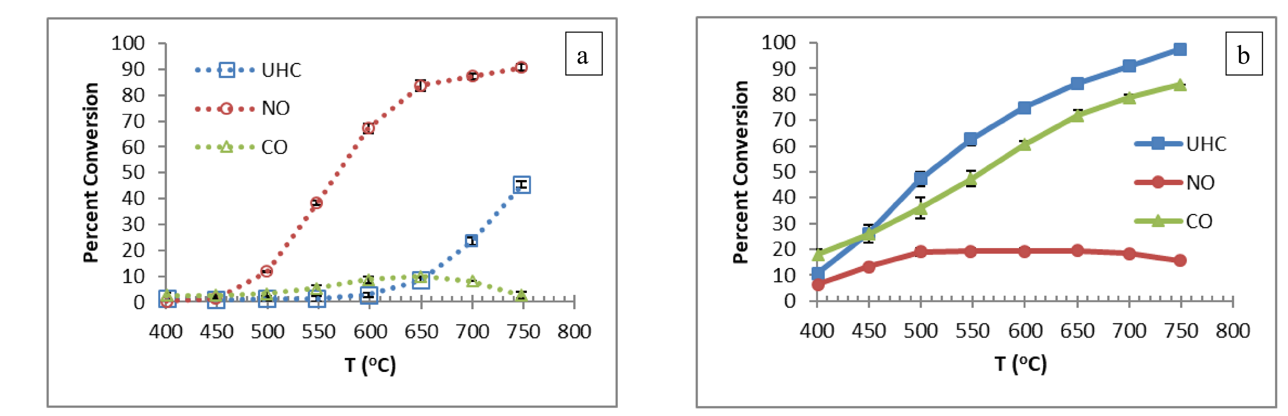

Figure 5: Cobalt-alumina aerogel (~3 mol%) steady-state UHC, NO, and CO conversion versus temperature when exposed to: a) BAR 97 exhaust blend without oxygen, b) BAR 97 exhaust blend with oxygen. Data points represent the average of three runs with error bars representing ±1 standard deviation. (reprinted from SAE 2016-01 0920)

Figure 6 illustrates that higher copper loading in copper-alumina (Cu-Al) aerogels decreases the light-off temperature. The 8g, 4g, and 2g samples were manufactured via a copper impregnation method [3] where 8g, 4g and 2g refer to the amount of copper salt used in the first solvent exchange which affects how much copper is impregnated into the aerogel, but the response is not linear. Analysis determined that actual Cu concentrations in the 4g and 8g aerogels are similar, but higher than the 2g aerogels. This explains why the 4g and 8g Cu-Al aerogels have comparable performance and both are more efficient than the 2g Cu-Al aerogel. As expected, all the Cu-Al aerogels perform betters than an inert silica aerogel.

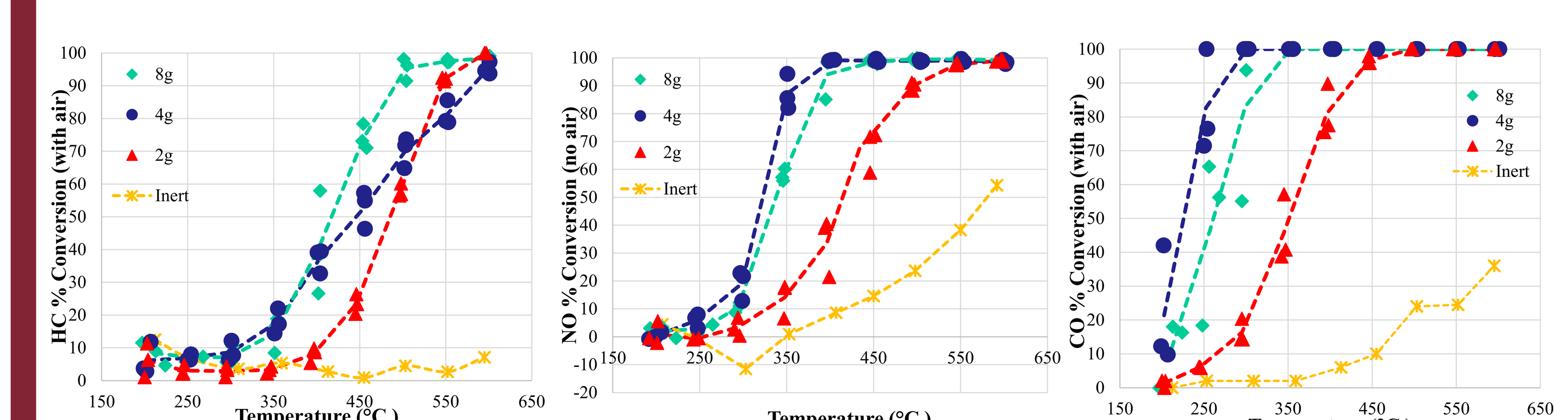

Figure 6: Average percent conversion for copper-alumina aerogels, with varying amounts of copper impregnated in the aerogel. The mass refers to the amount of copper salt in the first solvent exchange. Inert refers to a silica aerogel that has no copper in it. The graphs illustrate that aerogels with higher copper levels are better three-way catalysts. All tests conducted with BAR 97 based exhaust blends.

Future Work

Future studies will focus on development and testing of higher performance catalytic aerogels with the goal of replacing traditional TWC catalysts. Candidate aerogels will be fabricated containing different catalyst species, using nanoparticle metal species, and with combinations of several metal species. Additionally, an improved exhaust blend based on US Drive recommendations [6] will be utilized in future tests.

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