Effect of Slurry Processing on the Properties of Catalytically Active Aerogel Material

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Abstract

We have developed a series of aerogel materials that show activity as three-way catalysts. These materials incorporate non-PGM metals such as nickel,[1] copper[2,3] and cerium[4] into a silica- or alumina-based aerogel backbone. To date, the catalytic performance of these materials has only been tested on aerogels in a dry granular form. To be a viable alternative to existing PGM-based washcoats, the aerogels need to withstand a slurrying process to enable coating onto a substrate. In this study, we slurried copper-alumina aerogel samples by adding aerogel powder to an acidic (pH 4) aqueous solution under mechanical stirring. The solution was then dried at 60 C under ambient pressure. The slurried powder samples were catalytically tested and are still catalytically active - they showed no significant loss in catalytic performance compared to the non-slurried samples.

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 Fig 1) using the patented Union College rapid supercritical extraction (RSCE) method.[5-7]

Some potential advantages of an aerogel-based catalyst include:

- **High Surface Area**: More active sites, improved gas/solid interaction
- **High Thermal Stability**: TWC close coupling, reduced active site diffusion/sintering
- **Chemically Tailorable**: PGM reduction or elimination
- **Low Thermal Inertia:** Reduced time to light-off temperature

Several open questions exist about the use of aerogel-based materials in TWC applications:

1. How are these catalytic aerogel materials affected by the **slurrying process**?
2. How are the materials affected by **water vapor** in the exhaust gas?
3. Can aerogel-based catalysts be implemented into the **existing manufacturing process** for catalytic converters?
4. What are the optimal metals, metal mixes and loadings (i.e. **formulations**) for aerogel-based catalysts?

The work presented here is aimed at addressing question 1.

***Figure 1**. Images of various catalytic aerogels fabricated via the RSCE method.*

References and Acknowledgements

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Methods

Sample Preparation: Copper alumina wet-gels were prepared via an impregnation method[2,3] and then processed in a metal mold using the Union RSCE method.[5-7] The precursor recipe employed in this study yields aerogel materials that contain 290 (± 40) mg Cu/g aerogel as prepared, and 450 (±70) mg Cu/g aerogel following heat treatment.[3] A schematic of the method is presented in Fig 2.

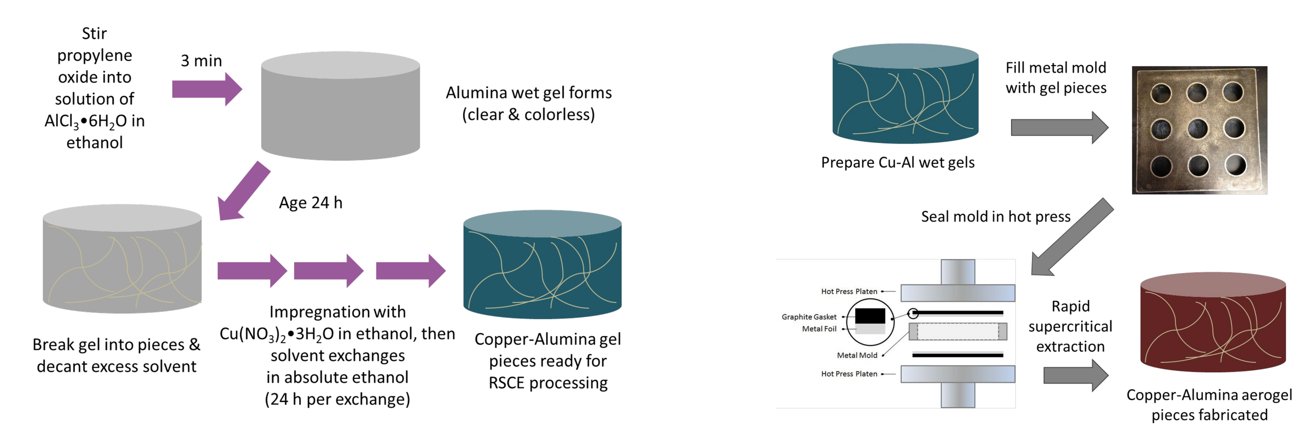

***Figure 2.** Catalytic aerogel synthesis method. Chemical processing (left) and RSCE (right).*

After RSCE processing, samples were heat treated in air at 800 C for 20-24 h. To slurry the samples, they were added to a beaker containing an acid (~pH 4) solution prepared from nitric acid and DI water. The beaker was covered with paraffin film and placed on a mechanical stirrer. After 1.5 h (when the solution of aerogel and water was well mixed) the film was loosened and the solution was heated to 60 C for 1-4 h and then allowed to dry under ambient condition.

Physical Characterization: All sample densities were estimated via mass and volume measurement after RSCE processing, after heat treatment and after slurrying. Pore size distributions and surface area were measured on select samples using an ASAP 2020 Gas Adsorption system. A Rigaku Smartlab SE XRD with a Cu K source was used to assess the crystalline structure of the as-prepared, heat-treated, slurried and catalytically tested samples.

Catalytic Performance: The Union Catalytic Aerogel Testbed (UCAT, Fig 3) was used to assess the catalytic performance of the slurried aerogels.[8]

- Twelve slurried samples were combined to make two separate 20-mL samples which were placed in the UCAT test cells.
- The oven was set to test temperatures between 200 and 500 C with flow rate adjustment at each temperature to provide a space velocity through the sample of 61,200 h^{-1}.
- Pollutant concentrations are measured with a five-gas analyzer, first with the emissions blend bypassing the sample, then with the emissions blend flowing through the sample.

The UCAT test conditions (see Table 1) were based on US Drive Recommendations[9] for testing at λ = 0.97 (low air) and λ = 1.02 (high air) conditions with a couple of notable modifications:

- Pure propene was used as the HC to avoid complexities due to the five-gas analyzer's differential response to different hydrocarbons.
- H_2O was not included as a component for this initial round of testing due to concerns that condensation between test runs could negatively affect the aerogel samples.

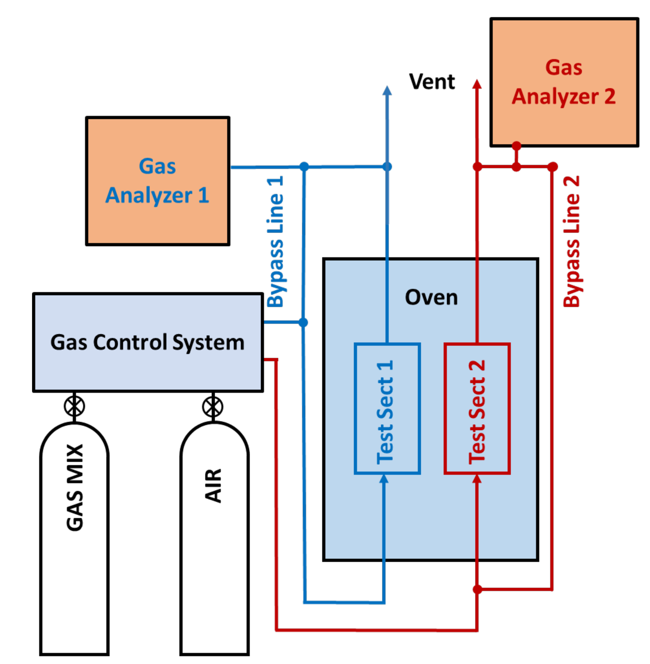

***Figure 3:** Schematic of Catalytic Test Bed*

***Table 1**. US Drive recommended emissions blend, Modified (dry) emissions blend used in UCAT tests.*

Component	NO (ppm)	UHC (ppm)	CO (%)	H_2 (%)	CO_2 (%)	H_2O (%)	O_2 (%)
US Drive, Recommended[9]	1000	Ethene: 525 Propene:500 Propane:150	0.5	0.17	13	13	0.12-1.15
Modified DRY/Propene (High Air)	1126	Propene: 1126	0.56	0.19	14.6	0	1.15
Modified DRY/Propene (Low Air)	1184	Propene: 1184	0.59	0.2	15.4	0	0.12

Results & Discussion

Physical Characterization Results: The as-prepared materials have low density (0.13 g/mL), high surface area (333 m^2/g) and high pore volume (3.5 cm^3/g) as shown in Table 2. After heat treatment, the pore volume and surface area decrease, likely due to pore collapse via sintering, and the density increases. After slurrying, the density further increases, there is no change to surface area but the pore volume increases. Fig 4 shows pore distributions for several different samples. The as-prepared materials show a broad peak in the 20-80 nm range, centered at 40 nm. These pores disappear after heat treatment, but surprisingly, some return after slurrying with a smaller peak in the 20-50 nm range. Fig 5 plots XRD patterns showing no change after slurrying. The patterns for the heat-treated CuAl aerogels match well to a copper-alumina spinel. Sidewings centered at the peak at 37° for the UCAT-tested sample are consistent with previous work and match to CuO peaks.[2]

***Table 2**. Effect of heat treatment and slurrying on physical properties. The values presented are the average of 3-4 measurements with ± 1 standard deviation.*

	Density (g/mL)	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)
As-Prepared	0.13 ± 0.01	333 ± 17	3.5 ± 0.1
Heat Treated	0.27 ± 0.02	70 ± 3	0.100 ± 0.004
HT & Slurried	0.6 ± 0.1	70 ± 3	0.50 ± 0.01

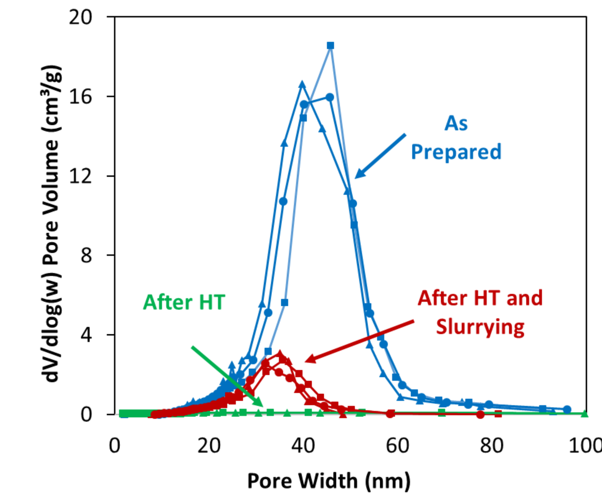

***Figure 4** . Desorption-based pore distributions for as prepared, heat treated (HT) and slurried materials for three distinct samples.*

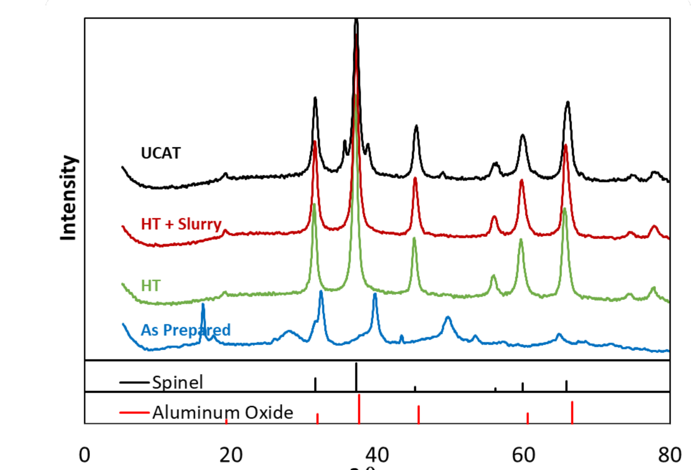

***Figure 5.** XRD patterns for as prepared, heat treated (HT), slurried and UCAT-tested materials. Patterns are offset for clarity.*

Catalytic Performance Results: Fig 6 shows the catalytic performance for the slurried (left column) and un-slurried samples (right column). The results show that the slurried samples remain catalytically effective. The conversion of CO and HC is about the same, however the NO conversion is somewhat diminished.

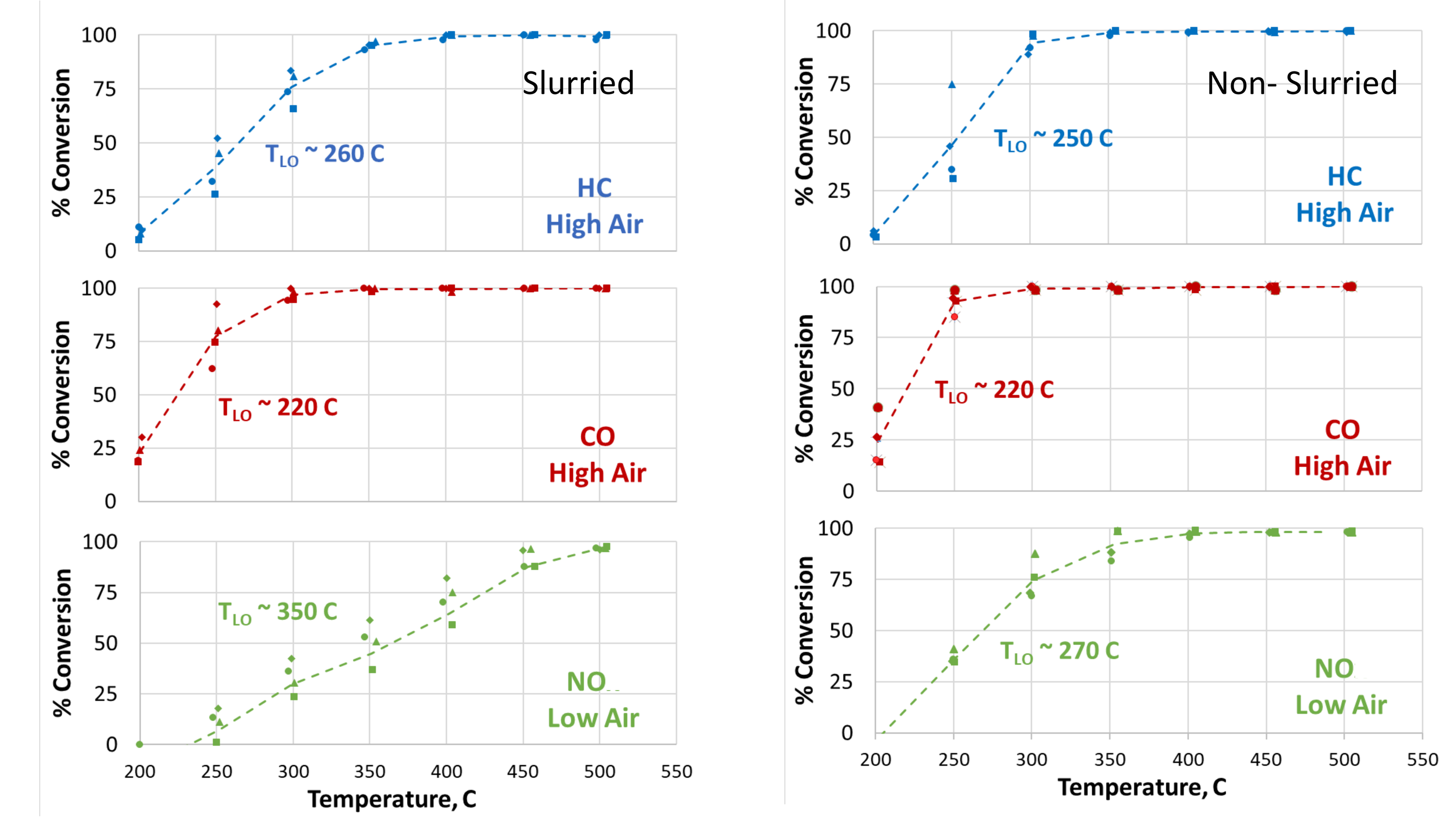

***Figure 6**. Catalytic test results for slurried (left) and unslurried (right) samples. T_{LO} indicates the approximate light-off temperature. Data points represent the results of a single test, the dashed line is the average of four tests. HC and CO results are presented for high-air conditions, NO results are for low-air conditions.*

Conclusion & Future Directions

Our primary finding is that CuAl aerogel can undergo a water-based slurrying process and retain catalytic performance. The similar pre- and post-slurrying XRD results provide further evidence that the slurrying process does not adversely affect the aerogel catalyst. The fact that catalytic aerogels are resilient to slurrying opens valuable avenues for their application so further R&D is warranted. Future work will address the effect of water vapor on performance.