

# Evaluation of Low Temperature CO Removal Catalysts

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**CO removal from spacecraft gas streams was evaluated for three commercial, low temperature oxidation catalysts: Carulite 300, Sofnocat 423, and Hamilton Sundstrand Pt1. The catalysts were challenged with CO concentrations (1-100 ppm) under dry and wet (50% humidity) conditions using 2-3 % O<sub>2</sub>. CO removal and CO<sub>2</sub> concentration were measured at constant feed composition using a FTIR. Water vapor affected the CO conversion of each catalyst differently. An initial screening found that Caulite 300 could not operate in humid conditions. The presence of water vapor affected CO conversion of Sofnocat 423 for challenge concentrations below 40 ppm. The conversion of CO by Sofnocat 423 was 80% at CO concentrations greater than 40 ppm under both dry and moist conditions. The HS Pt1 catalyst exhibited CO conversion levels of 100% under both dry and moist conditions.**

## Nomenclature

<i>ATCO</i>	= Ambient Temperature Catalytic Oxidizer
<i>HS</i>	= Hamilton Sundstrand
<i>HTCO</i>	= high temperature catalytic oxidizer
<i>ISS</i>	= International Space Station
<i>TCCS</i>	= trace contaminant control system
<i>RVCS</i>	= Regenerable VOC Control System

## I. Introduction

Carbon monoxide is colorless, odorless, tasteless gas that is very difficult for people to detect. It is harmful to humans and symptoms of mild acute poisoning include light-headedness, confusion, headaches, vertigo, and flu-like effects; larger exposures can lead to significant toxicity of the central nervous system and heart, and even death. The NASA 7-day SMAC is set at 55 ppm and the 30-day and 180-day SMACs are set at 15 ppm.

In Shuttle, carbon monoxide was removed from cabin air using the Ambient Temperature Catalytic Oxidizer (ATCO) catalyst (2% platinum on carbon)<sup>3,4</sup>. The on-board trace contaminant control system (TCCS) for the International Space Station (ISS) U.S. On-orbit Segment consists of a granular activated carbon bed for the removal of high molecular weight contaminants and ammonia followed by a heated catalytic bed for low molecular weight hydrocarbons. The high temperature catalytic oxidizer (HTCO) of the TCCS removes low molecular weight compounds such as carbon monoxide (CO), formaldehyde (CH<sub>2</sub>O), and methane (CH<sub>4</sub>) operates at 400°C, requiring significant energy input<sup>1, 2</sup>. Heating the HTCO represents a considerable amount of power, which could be reduced if low temperature CO removal catalysts were identified.

In this study, three low temperature oxidation catalysts for removal of CO from spacecraft gas streams were evaluated for operation at 40% humidity. These catalysts have been previously studied for CO removal, however, experiments varied greatly for [CO], flow rates, and humidity levels making comparisons of the technology difficult. Low temperature oxidation catalysts may result in power savings to the TCCS, and may also be used in with post-fire cleanup of cabin air<sup>3</sup>.

## II. Materials and Methods

Three candidate low temperature CO removal catalysts were used in this study:

- **Carulite® 300**, developed by Carus Corporation; it is a dark brown/black manganese dioxide/copper oxide catalyst with a bulk density of 0.8-0.9 g ml<sup>-1</sup> and surface area of approximately 200 m<sup>2</sup> g<sup>-1</sup>. General applications include destruction of CO in compressed breathing air, respirators, escape masks, and in cryogenic gas purification.

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- **Sofnocat™ 423**, developed by Molecular Products, Inc. Sofnocat™ 423 is a platinum/palladium/tin oxide catalyst with a bulk density of 1.4-1.6 g ml<sup>-1</sup> and is claimed to have high water tolerance for applications including destruction of CO in breathing gas filters, removal of hydrogen within enclosed environments, abatement of volatile organic compounds (VOCs), and gas purification.
- **HS Pt1**, a CO oxidation catalyst developed by Hamilton Sundstrand.



Figure 1. Three low temperature oxidation catalysts for removal of CO from spacecraft gas streams were evaluated for operation at 40% humidity.

The candidate low temperature CO removal catalysts differed in their composition ( Table 1) and each catalyst had its own particle size distribution (Table 2). The size of the particles is important as it may affect the flow of CO molecules into the active catalytic sites within the catalyst particles. The catalysts were sieved using several sieves (3.35 mm, 2.36 mm, 2 mm, 1.4 mm, 1 mm, 0.47 mm, and a bin to collect the <0.47 mm fraction.

**Table 1: Catalyst Characteristics**

Catalyst	Manufacturer	Active Metal	Support
<b>Carulite® 300</b>	Carus Corporation.	MnO <sub>2</sub> /CuO	Al <sub>2</sub> O <sub>3</sub>
<b>Sofnocat™ 423</b>	Molecular Products, Inc.	Pt, Pd	SnO <sub>2</sub>
<b>HSPT</b>	Hamilton Sundstrand	Pt	NA

Particle size distribution was measured by sieving the catalysts. The particles were sieved using several sieves (3.35 mm, 2.36 mm, 2 mm, 1.4 mm, 1 mm, 0.47 mm, and a bin to collect the <0.47 mm fraction.

**Table 2: Catalyst Particle Size Distributions**

	HS Pt	Sofnocat 423	Carulite 300
3.35 mm		21.6 %	
2.36 mm		67.4 %	18.5 %
2 mm		4.8 %	50.5 %
1.4 mm	1.3 %	5.2 %	35.1 %
1 mm	78.7 %	1.3 %	0.36 %
0.47 mm	20.1 %		
< 0.47 mm	0.35 %		

The CO catalysts were challenged in single pass mode with moist gas streams produced by blending 400 ppm of CO into a gas stream of breathing air, which could be humidified or not. The gas stream passed through the CO catalyst and was analyzed using a Gasmeter DX-3030 FTIR (Fig 2).

The apparatus used received close scrutiny by safety personnel. The tests were conducted only after the following CO Hazard Mitigation scheme was implemented:

- Perform a system leak test prior to use
- Contain CO within a cage vented via a snorkel
- Deploy a calibrated CO meter with an alarm
- Only utilize dilute concentrations of CO
- Use the buddy system during the tests.

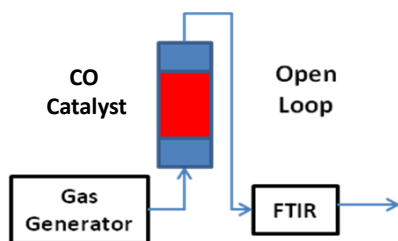


Figure 2. Apparatus to measure CO removal

### ***Oxidation Catalyst Comparison***

The catalysts (~2-4g) were loaded onto a ½ inch-diameter sorbent bed of the Regenerable VOC Control System (RVCS) testbed. CO gas streams were mixed using a tank of 400 ppm CO with balance N<sub>2</sub>, and breathing to provide O<sub>2</sub>. This approach provided ~2-3 % O<sub>2</sub> to the gas stream. The challenge gas stream was passed through the bed in a single pass mode and the CO concentration of the post-chamber air was analyzed using a Gasmeter FTIR. CO concentration s from 100ppm down to < 1 ppm were used. The catalyst were evaluated using: Relative Humidity: 0%, 40-50%, Temperature: 23 °C, Flow rate of gas stream (L/min): 1500 - 1600 mL min<sup>-1</sup>.

The oxygen excess with respect to the amount of oxygen required for the oxidation of CO to CO<sub>2</sub> is commonly characterized by the process parameter,  $\lambda$  (Kalich et al, 1997):

$$\lambda = 2[\text{O}_2]/[\text{CO}] = 2P_{\text{O}_2}/P_{\text{CO}} \quad (1)$$

where,  $\lambda = 1$  is sufficient to provide for the complete oxidation of CO to CO<sub>2</sub> in the absence of an oxygen-consuming side reactions. The conditions used in this study ensured that  $\lambda$  ranged from 200 to 8000.

The conversion of CO was defined as follows:

$$X_{\text{CO}} (\%) = 100 * ( [\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}} ) / [\text{CO}]_{\text{in}} \quad (2)$$

### **III. Results and Discussion**

An initial assessment of the performance of these three catalysts was conducted. This initial comparison of CO removal was conducted using 25 ppm CO and 40% relative humidity. The results of this effort identified that both Sofnocat and HS Pt performed well under humid conditions, but Carulite 300 did not (Fig 3).

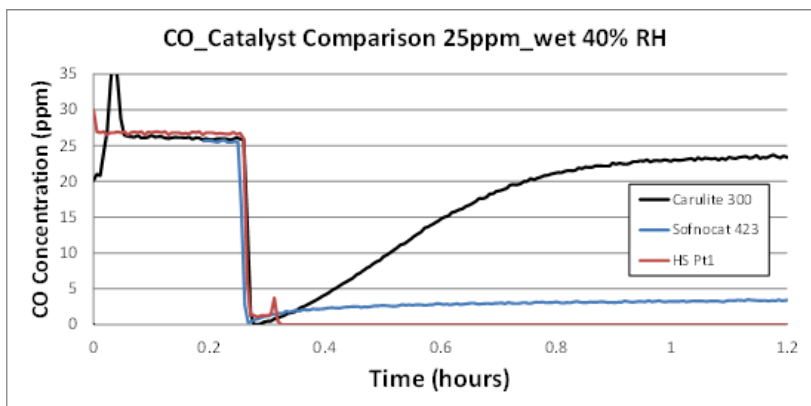
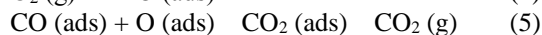


Figure 3. Initial comparison of CO removal from moist gas stream by the 3 candidate catalysts. Sofnocat 423 removed 80% and HS Pt1 removed 100%, but CO removal of Carulite 300 was only temporary.

### ***Oxidation of CO on Pt catalysts***

The CO oxidation reaction is generally believed to be described by a Langmuir-Hinshelwood mechanism of the following type for conditions where CO is the primary surface species:



The reaction depends on the adsorption of CO and oxygen onto the surface of the catalyst. The reaction of adsorbed CO occurs with adsorbed O and release of produced CO<sub>2</sub> is a fast reaction. Langmuir has described the reaction kinetics as first-order in O<sub>2</sub> pressure and negative-first-order with respect to the CO pressure. The rate of the reaction is governed by desorption of CO or the lifetime of CO on the surface, depending on the reaction temperature, whereas the pressure dependence simply reflects the competition for adsorption sites between O<sub>2</sub> and CO.

### ***HS Pt1 Catalyst***

The low temperature CO oxidation capacity of the HS Pt1 catalyst was evaluated using several CO concentrations ranging between 0.5 to 140 ppm under both dry and moist (50% relative humidity) conditions. In each experiment, CO conversion (X<sub>CO</sub>) was measured at constant feed composition. The conversion of CO by HS PT1 was 100% under both dry and moist conditions (Fig 4).

CO<sub>2</sub> production occurs as soon as the CO stream surrounds the catalyst (Fig 5). A spike in CO<sub>2</sub> concentration, much larger than would be expected from kinetics of CO oxidation, is observed the 1st time the catalyst is used. The second time the catalyst is exposed to CO, a smaller spike in CO<sub>2</sub> concentration is observed and no spikes are observed in subsequent runs. This suggests that the spike occurs as CO<sub>2</sub> adsorbed on the surface of the catalyst during storage is displaced by CO and becomes adsorbed (Equation 3). The CO<sub>2</sub> produced by the oxidation of CO persists until CO is removed from the catalyst. The amount of CO<sub>2</sub> produced during CO oxidation increases in linear fashion as the inlet CO concentration increases (Fig 6).

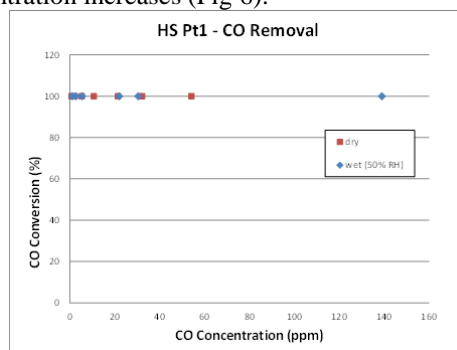


Figure 4. The HS Pt1 catalyst exhibited CO conversion levels of 100% under both dry and moist (50% relative humidity) conditions.

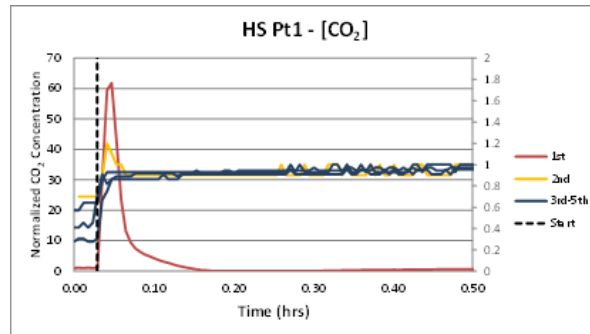


Figure 5. The CO<sub>2</sub> concentration rises as soon as CO surrounds the catalyst. The initial spike in CO<sub>2</sub> concentration upon 1st exposure is probably caused by CO displacing CO<sub>2</sub> already adsorbed on the catalyst surface.

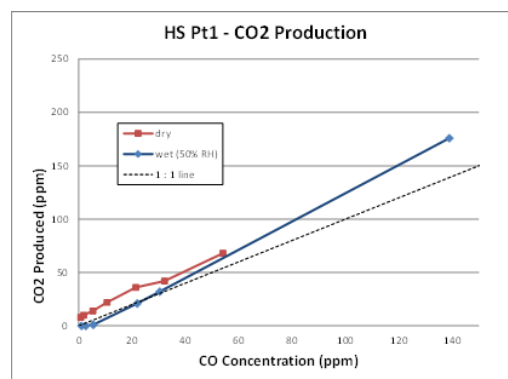


Figure 6. The amount of CO<sub>2</sub> produced during the oxidation of CO rises linearly as the inlet CO concentration increases. The amount of CO<sub>2</sub> is greater than the 1:1 line, probably due to the release of previously adsorbed CO<sub>2</sub> from the surface of the catalyst.

### ***Sofnocat 423***

The low temperature CO oxidation capacity of the Sofnocat 423 catalyst was evaluated using several CO concentrations ranging between 0.5 to 130 ppm under both dry and moist (50% relative humidity) conditions. In each experiment, CO conversion ( $X_{CO}$ ) was measured at constant feed composition. The conversion of CO by Sofnocat 423 was 80% at CO concentrations greater than 40 ppm under both dry and moist conditions (Fig 7). The CO conversion of dry Sofnocat 423 decreased from 100% down to 80% as CO concentration was increased and it illustrates the negative-first-order kinetics with respect to CO pressure. The oxygen and carbon monoxide molecules in the surrounding gas compete with each other in reaching vacant spaces on the surface of the catalyst. If a space becomes filled with an oxygen molecule, this molecule (or each of the resulting oxygen atoms) can react with the carbon monoxide molecules which strike it and thus form carbon dioxide, which will be held by weaker chemical forces and be released rapidly. This process leaves the space still vacant so that another oxygen molecule can be adsorbed and a carbon dioxide molecule formed. This action continues until the space becomes filled by a carbon monoxide molecule. Under these conditions, the velocity of the reaction will be proportional to the pressure of oxygen and inversely proportional to that of the carbon monoxide.

The effect of water vapor in reducing the rate of catalytic oxidation of CO may be accounted for in either of two ways: by assuming that the water vapor reduces the activity of the catalyst or that, by reversible adsorption, water molecules occupy active sites on the surface of the catalyst. It appears that the effect of water vapor at low CO concentrations is to compete with CO and O<sub>2</sub> for active sites on the catalyst surface (Fig 7), but that this effect diminishes above 40 ppm CO.

The concentration of CO<sub>2</sub> produced during CO oxidation increased linearly as CO concentration increased (Fig 8). However, the concentration of CO<sub>2</sub> produced at low CO concentrations falls below the 1:1 line thereby reflects the reduction in CO oxidation caused by water vapor.

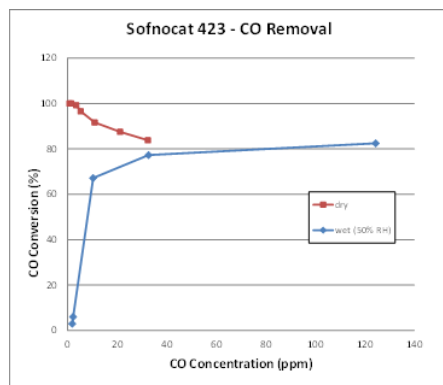


Figure 7. In dry Sofnocat 423, CO oxidation is reduced as CO outcompetes oxygen for sites on the catalyst surface. In humid Sofnocat 423, the water vapor may outcompete CO at low CO. The effect of water vapor is diminished above 40 ppm CO.

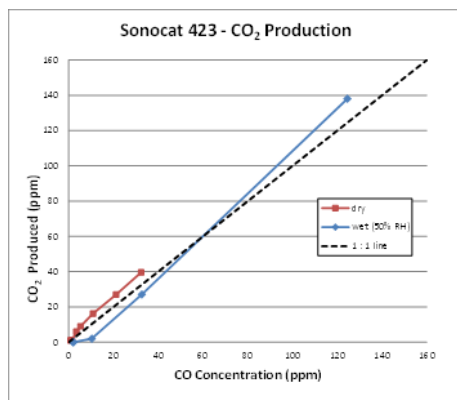


Figure 8. The CO<sub>2</sub> concentration produced increased linearly as CO concentration increased in dry Sofnocat 423. In wet conditions, the CO<sub>2</sub> produced fell below the 1:1 line indicating that water vapor may be responsible for reducing the rates of CO oxidation at CO concentrations below 40 ppm.

### Future Work

The CO oxidation of Sofnocat 423 should be compared at a smaller particle size. Nearly 67% of the Sofnocat 423 used in this study was composed of particles >23.6 μm. In contrast, the 70% of the HS Pt1 catalyst was composed of 1 μm particles. The Sofnocat 423 capacity should be evaluated after grinding it down to 1 μm particles to see if the 20% lower CO conversion of Sofnocat 423 vs HS Pt1 is caused by mass transfer limitations due to its larger particle size.

### Acknowledgments

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<sup>5</sup>Carus Corporation Carulite 300 Information Page. <http://www.caruscorporation.com/content.cfm/carulite-300> (April 15, 2013).

<sup>6</sup>Sofnocat 423 Technical Datasheet. <http://www.molecularproducts.com/pdf/Sofnocat%20423%20UK%20DS.pdf> (May 1, 2013),