Phase II Final Report

Escape Respirator for First Responders

By

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A. Executive Summary

The Phase II project started on 8/1/2009 and ended 7/31/2013

TDA Research, Inc. (TDA) and Mine Safety Appliances Company (MSA) are collaborating to develop a respirator filter canister for MSA's Response Escape Hood to protect the workforce in general, and first responders in particular, from Chemical, Biological, Radiological and Nuclear (CBRN) hazards and carbon monoxide (CO). MSA's escape hood (and all other escape hoods made by other manufacturers) currently use a filter cartridge filled with treated carbon that is effective against CBRN agents and other toxic substances, but this treated carbon does nothing to remove CO, which does not adsorb on activated carbon. The ability to remove CO is necessary for NIOSH certification. MSA has tested Hopcalite (a Cu-Mn oxide CO oxidation catalyst) but found that it is rapidly deactivated by moisture in the air, and consequently requires an upstream desiccant bed, which adds weight to the filter canister. Therefore, the goal of the project is for TDA is to develop an inexpensive, durable and active catalyst that destroys CO by oxidation to CO_2 that is insensitive to moisture, and to demonstrate its use in an MSA Response Escape Hood.

TDA has developed a catalyst that is active for CO oxidation at temperatures down to 0°C that is insensitive to moisture. TDA's low temperature CO oxidation catalyst contains gold nanocrystallites supported on iron oxide. Testing in Phase II by MSA demonstrated that TDA's catalyst is ideal for use in their Response Escape Hood. MSA found that when challenged according to the NIOSH certification standard for CO removal (64 liter/min of air at 0°C, 3600 ppm CO, for 30 min), TDA's catalyst far exceeded the NIOSH requirements; the CO concentration downstream of TDA's catalyst never exceeded 1 ppm (the NIOSH requirement is to never have a spike above 500 ppm).

TDA has successfully optimized the catalyst formulation, scaled up the catalyst synthesis to multi-kilogram quantities and demonstrated that the scaled up synthesis produces a catalyst that meets or exceeds the requirements for use in the CBRN filter canister. The current cost per filter for the catalyst is significantly less than the goal set by MSA at the beginning of the Phase II project of $25 per filter. TDA, MSA and Pressure Chemical Co.(our toll catalyst manufacturer) are planning to manufacture the catalyst during Phase III.

B. Key Personnel

The following key personnel performed the work during the Phase I effort.

Table 1. Research Staff

Name	Title	Dates of Service	Hours
Dr. Girish Srinivas	Principal Investigator	8/1/09 – 7/31/13	1250
Dr. Steven Gebhard	Senior Chemist	8/1/09 – 7/31/13	338
Ms. Rita Dubovik	Chemist	8/1/09 – 7/31/13	1035
Mr. Andrew Galloway	Senior Chemist	8/1/09 – 7/31/13	2580

Dr. Srinivas was the principal investigator who directed the research effort in addition to meeting with personal protective equipment manufacturers and first responders to determine industry needs.

Dr. Steven Gebhard helped with the design of the larger gold deposition reactor systems, in addition to performing the economic analysis and reporting.

Ms. Rita Dubovik is the chemist that developed the gold deposition process that was used to synthesize the CO oxidation catalyst.

Mr. Andrew Galloway was the engineer that performed the laboratory testing, designed and built the test apparatus, and developed the catalyst substrate.

C. Specific Aims

The National Institute for Occupational Safety and Health (NIOSH) announced on October 8, 2003 that it would use an expedited program to test and certify escape respirators for emergency preparedness in the workplace. Escape respirators, also called escape hoods, are designed to protect users from breathing harmful gases, vapors, fumes, and dusts for a limited amount of time so that the wearer can reach fresh air. Escape respirators that pass the full set of tests will be approved by NIOSH, allowing manufacturers to label the approved products as NIOSH certified against chemical, biological, radiological, and nuclear (CBRN) agents in workplace escape emergencies (NIOSH, 2003 a&b). Because of the serious health threat posed by carbon monoxide (CO, a product of incomplete combustion of organic materials) to personnel including first responders, NIOSH is requiring CO protection be added to the CBRN escape hood requirements for certification. It is not particularly difficult to develop an escape hood that meets the NIOSH standards if the CO requirement is ignored, but meeting the CO requirement is very difficult. As of December 2013, ten years after NIOSH promulgated the new standard, there are still no NIOSH approved escape plus CO hoods.

TDA Research, Inc. (TDA) and Mine Safety Appliances (MSA) are collaborating to design and develop an escape respirator (a.k.a. escape hood) that will protect the workforce in general, and first responders in particular, from CBRN agents and CO. MSA's carbon canister already removes CBRN threats; TDA's catalyst is used to oxidize CO into CO_2 at room temperature and lower and is insensitive to moisture, in contrast to Hopcalite which is rapidly deactivated by moisture. Our catalyst is iron oxide that has been promoted with 0.2 wt.% gold nanocrystallites (typically 4-5 nm across). The notation used throughout this report for this catalyst is $Au/\alpha\text{-}Fe_2O_3$. When tested at MSA, in Phase II using the NIOSH CBRN CO challenge of 64 liter/min of air at 0°C with 3600 ppm CO for 30 min, the performance of TDA's catalyst far exceeded the NIOSH requirements; the CO concentration downstream of TDA's catalyst never exceeded 1 ppm (the NIOSH requirement is to never have a spike above 500 ppm).

MSA is the largest company dedicated to producing a complete range of protective equipment and systems for workers. MSA is a $1 billion/year global company serving customers on five continents. Almost one quarter of their revenues ($250 million/year) are generated by sales of self-contained breathing apparatus (SCBA) and another quarter from the sale of air purifying respirators (APR). MSA serves a variety of industries which include firefighting, industrial manufacturing, industrial hygiene, chemical, pharmaceutical, steel, construction, hazardous materials, abatement operations, mining, oil refining, nuclear, utilities, shipbuilding, agriculture, pulp & paper, homeland security, and home improvement retailing.

MSA has developed their Response^{TM} Escape Hood as a practical solution for respiratory protection that permits escape from chemical, biological, riot-controlled agents, and fires. MSA currently uses a carbon-impregnated filter cartridge that contains about 30 grams of activated carbon to protect the user from CBRN agents. The carbon-impregnated filter cartridge used by MSA, while effective on CBRN agents, is incapable of removing carbon monoxide because CO does not adsorb on activated carbon. MSA had been testing catalysts for CO oxidation for use in their escape hood, with little success until now with the development of TDA's low temperature Au/α-Fe_2O_3 catalyst. The industry standard room temperature CO oxidation catalyst has been Hopcalite (Cu-Mn oxide). Developed between the two world wars, the formulation of Hopcalite has changed very little (Hoskins and Bray 1926). MSA tested Hopcalite and found that even though 87 years have passed since its invention, it is still rapidly deactivated by moisture in the air. Therefore a desiccant canister must be placed upstream of the Hopcalite to remove moisture and prevent deactivation. Unfortunately, this greatly increases the volume, weight, and cost of the canister. Meeting the NIOSH CO specifications using a Hopcalite catalyst requires almost150 grams of catalyst plus an additional 90 grams of desiccant, increasing the weight of material in the cartridge by almost a factor of ten over that of ordinary activated carbon. MSA is therefore interested in TDA's development of an active and stable catalyst that oxidizes CO to CO_2 that is unaffected by moisture. In MSA's design, TDA's CO oxidation catalyst would be placed behind the activated carbon cartridge. By placing the catalyst behind the activated carbon, the catalyst is protected against fouling and poisoning from chemical vapors or smoke. TDA's catalysts exhibit high activity and only 60 grams is required per respirator cartridge (far less than the 240 grams of additional weight when using the desiccant/Hopcalite combination). As a result, the required amount of TDA's catalyst is only 25% of the weight of a Hopcalite based CO oxidation catalyst.

D. Significance and Related R&D

D.1. Fire and Other Hazardous Situations

First responders are the men and women who are first on the scene immediately after a disaster. Fires, earthquakes, floods, hurricanes, tornados, chemical spills, car accidents, train derailments, and a host of other events can cause disasters where human lives and property are in danger. In additional to natural disasters and accidents, there are significant numbers of groups and individuals in the world intent on harming U.S. interests and its citizens. Terrorist attacks are becoming increasingly sophisticated, and there is considerable concern that chemical, biological, radiological or possibly even nuclear attacks may occur in the future. Although terrorist attacks are dramatic and serious, they are rare compared to fires; there were 1,375,000 fire incidents in the U.S. in 2012 which resulted in 2,885 deaths, 16,500 injuries and estimated monetary losses of almost $13 billion (NFPA 2013). Fires produce significant quantities of hazardous compounds including carbon monoxide (CO), a colorless, odorless poisonous gas that is the product of incomplete combustion of organic materials, HCN, HCl, NO_2 and other vapors (Table 2). HCN is produced when anything that contains both carbon and nitrogen burns, such as urethane, nylon, wool and leather. HCl is produced when vinyl (polyvinyl chloride) burns. Polystyrene and other plastics contain aromatic groups that can produce benzene during a fire. These products are produced by both pyrolysis and combustion. Typical concentrations of some of these toxic compounds are shown in Table 2 along with the concentrations that are considered to be immediately dangerous to life and health (IDLH).

Table 2. Typical contaminant levels in fire smoke (Savolainen and Kirchner, 1998)

Contaminant	Typical Conc (ppm)	Max Conc (ppm)	IDLH (ppm)
Acrolein	1.9	98	5
Benzene	4.7-56	250	3000
CO	246-1450	27000	1500
HCl	0.8-1.3	280	100
HCN	0.14-5.0	75	50
NO_2	0.04-0.7	9.5	50
SO_2	2.3	42	100
Particulates (mg/m^3)	232	15000	n.a.

D.2. Carbon Monoxide Hazard

Carbon monoxide is a toxic, colorless, odorless gas that is produced by the incomplete combustion of carbon containing materials. When CO is inhaled, it bonds to iron in hemoglobin in the blood to form carboxyhemoglobin (COHb). Each molecule of hemoglobin that is bonded to a CO molecule is unavailable to transport oxygen from the lungs. At high enough concentrations organ failure, unconsciousness, and death occur. Carbon monoxide concentrations high enough to cause rapid fatality ([CO] > 2000 ppm) are routinely formed during fires (Fierro, et al. 2001).

D.3. Escape Respirators

When working in extremely hazardous environments firefighters and other first responders use a self-contained breathing apparatus (SCBA) which typically contains a 30 min supply of air in a high pressure gas bottle that is worn like a backpack. A hose from the regulator on the air tank is attached to a full face mask to supply fresh air until the tank is almost empty. Various alarms are incorporated into the SCBA to alert the user when it is time to leave the scene and get a fresh tank. For short term protection, typically just for egress, there are small, lightweight escape respirators. These devices are made to be relatively inexpensive, small, lightweight, and easy for untrained people to don in case they need to escape from a burning building or some other emergency situation.

There are two main types of escape respirators, both are designed to give a person time to safely get out of a hazardous environment and to be easily donned. The first type uses a hood with an airtight neckpiece and a small cylinder of compressed air similar to a SCBA (5 min escape pack). The hood provides a barrier against contaminated outside air, and the user breathes clean bottled air. The other type uses a canister filter mounted in the hood and is called an air purifying escape respirator. The user breathes outside air through the canister, which removes harmful contaminants.

Backpack type SCBA units are expensive ($2,000 - $3,000), heavy (up to about 30 lbs) and require specialized training to be able to use (e.g. firefighters). Escape hoods that use a small bottle of air are somewhat heavy (about 5-10 lbs), relatively expensive (ca. $600) and only last about 5 min. In contrast, a filter cartridge type respirator escape hood sells for about $230, weighs only a few pounds, and is certified to last for 15 min.

MSA has developed a filter cartridge hood called the Response Escape Hood (Figure 1) that can be used to escape from chemical, biological or riot-control agents in the event of a respiratory threat emergency. The hood covers the head and neck and is made of a laminate material that is easy to don. Inhaled air flows directly into the faceplate through a canister filter that contains activated carbon. Exhaled air exits through a separate valve. The carbon canister contains about 50% more activated carbon than is used in U.S. armed forces gas masks. The MSA Response Escape Hood has been tested for use in CBRN applications by MSA and the mask effectively protects against a variety of chemical warfare agents, toxic organic chemicals, acid gases and pepper spray. The ultrafine filter located upstream of the activated carbon bed removes dust and pathogens. Currently, the hood does not protect the user from carbon monoxide exposure.

Figure 1. MSA Response Escape Hood.

Current CBRN escape respirators are sold without NIOSH endorsement for protection against CO. Ten years ago NIOSH finalized a set of standards for testing CBRN escape hoods (NIOSH 2003a,b). On November 6, 2003, NIOSH began accepting applications to test and evaluate air-purifying respirators for use against CBRN agents. In its most recent standards, NIOSH requires that respirators be able to protect the user from carbon monoxide. Since carbon-based sorbents do not adsorb CO, none of the current respirators on the market can pass the CO requirement. To make respirators capable of removing CO at room and lower temperatures, CO must be catalytically oxidized into CO_2. A catalyst is necessary because there are no known solid CO sorbents that work in air (because air is an oxidizing environment).

We are aware that both 3M Corporation and Dräger Safety have been trying to develop escape respirators that meet the NIOSH test criteria. Dräger Safety currently offers a Parat-C Escape Respirator that claims to remove CO. However, the test conditions specified are: testing performed at 30 LPM, constant flow at 73°F and 70% relative humidity. These conditions are not nearly as severe as those prescribed by NIOSH and therefore do not meet the NIOSH criteria. First, the 73°F operating temperature is much higher than the NIOSH test temperature of 32°F. Second, the volumetric flow rate of air through the test cartridges for the Dräger Safety product is less than half that of the NIOSH specified test (which is 64 L/min). We have already shown that both temperature and space velocity (a measure of air flow rate through the catalyst bed in the cartridge) are very important in determining the performance of the CO oxidation catalyst. To the best of our knowledge, our catalyst and canister configuration are the only ones that will pass the demanding NIOSH-specified tests.

TDA has developed a CO oxidation catalyst that is very active at low temperatures and that is not adversely affected by moisture (in contrast to Hopcalite). TDA's catalyst is ideally suited for use with the activated charcoal filters in MSA's respiratory protection products. We have focused on catalytically removing CO because MSA's activated carbons do a perfectly good job of protecting the user against other toxic gases encountered in fires, in addition to toxic chemical releases and CBRN agents (Table 2).

D.4. Carbon Monoxide Removal

While activated carbon can remove a wide variety of chemical vapors and fumes, it has essentially no affinity for carbon monoxide. The ideal way to remove CO is to catalytically oxidize it to CO_2. Fortunately, CO can be oxidized given the appropriate catalyst. Also, for practical purposes CO_2 is essentially nontoxic. For example, the OSHA TWA (time weighted average for 8 hours of exposure limit) for CO is 50 ppm (the NIOSH PEL is 35 ppm). In contrast, the TWA PEL for CO_2 is 5,000 ppm (0.5%) and the ACGIH STEL (short term exposure limit for 15 minutes) for CO_2 is 30,000 ppm (3%). Even a rapidly fatal level of CO is innocuous when it is converted to CO_2.

D.5. Hopcalite Catalyst for CO Oxidation

Current designs for escape hoods that remove CO require almost 150 grams of Hopcalite, a catalyst that is approximately $CuMn_2O_3$, along with 90 grams of desiccant located upstream of the catalyst because moisture deactivates Hopcalite. The sensitivity of Hopcalite to moisture makes its use impractical in high relative humidity environments. While adding about 1% silver oxide (Ag_2O) to Hopcalite reduces its sensitivity to water, a desiccant bed is still required. Hopcalite was first invented for use in gas masks in World War I and is still used for some applications (Mantell 1951). It has a long track record, but its sensitivity to water is a major drawback. Any oxidation catalyst that is used in an escape hood or gas mask must work at room temperature and colder (NIOSH requires tests at 25°C and 0°C) and function in high humidity environments (the NIOSH test is done at 90% RH). TDA's catalyst is not deactivated by moisture.

D.6. Metal and Metal Oxide Catalysts for CO Oxidation

Many transition and precious metals and their oxides catalysts will oxidize CO to CO_2, including Hopcalite, $(CuMn_2O_3)$, Co_3O_4, Fe_2O_3 and platinum. All of these catalysts work extremely well as long as the temperature is high enough (Figure 2), and in the case of Hopcalite, the gas is also dry. For example, cobalt oxide supported on alumina does not exhibit high CO conversions until the temperature is near 300°C. Iron oxide on alumina is slightly worse. In contrast, when Au nanoparticles (nanocrystallites) are added to these same oxides, their activity at low temperatures is increased enormously (Figure 2). As a result, transition metal oxide catalysts that have been promoted with gold nanoparticles (nanocrystallites) are ideally suited for use in escape respirators.

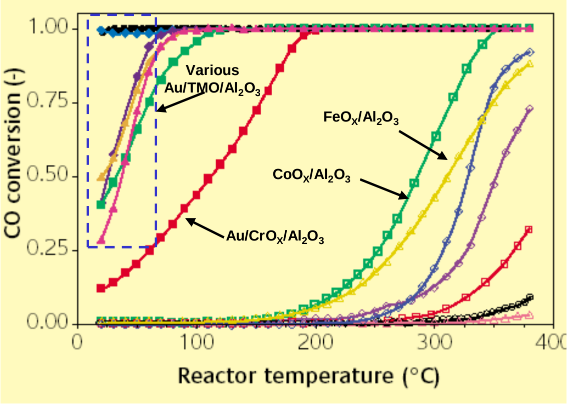

Figure 2. CO oxidation over Au/TMO catalysts (Grisel, et al. 2002).

D.7. Catalysis by Gold and Low Temperature CO Oxidation

Until the 1970s, gold was not very interesting to the catalysis community because of its apparent inertness. Bulk gold is essentially inert because of its high atomic number (79) and poor shielding by the 14 electrons in the seven 4f orbitals that fill from La to Lu. Thus, the effective nuclear charge on the 6s electrons in Au is "abnormally large" which causes the 6s orbital to contract; this is the well-known lanthanide contraction. Both electrostatic and relativistic effects contribute to the contraction. In large gold agglomerates this manifests itself as both the 6s and 5d levels being well below the Fermi level (E_F) and therefore unavailable for chemical bonding at ordinary temperatures (Bond et al. 2006).

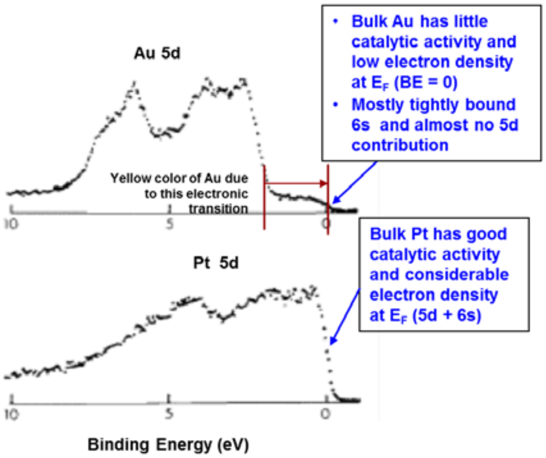

Figure 3. Comparison of valence band XPS spectra showing the electron densities at E_F for bulk Au and Pt (Briggs and Seah 1983).

While large gold agglomerates are catalytically inert, nanometer sized Au crystallites are quite active (Figure 4). Experimental evidence indicates that as the size of Au crystallites decreases to a few nanometers, a transition from metallic to nonmetallic character occurs, and Au begins to exhibit catalytic activity (Bond et al. 2006). It is currently thought that the activity of nanocrystalline Au is due to the existence of a large number of coordinatively unsaturated Au atoms associated with the corners edges and defects of nanocrystallites. Haruta and co-workers were the first to discover that nanometer sized gold crystallites on transition metal oxides (TMO) could catalyst CO oxidation at temperatures as low as -70°C (e.g. Haruta et al. 1996, 1997, 1983, 1987, 1988; Iizuka et al. 1999), and at the time catalytic activity at such low temperatures was unprecedented (if not shocking); however, the results have been verified many times in other laboratories (including TDA's). While there are not many applications for CO oxidation at -70°C, Au/TMO catalysts have now been shown to be active for room temperature CO oxidation, propylene epoxidation, gas phase synthesis of hydrogen peroxide (H_2O_2) from H_2 and O_2, cyclohexane oxidation to cyclohexanone and a wide variety of other industrially useful partial oxidations (Bond et al 2006; Corti et al. 2005). It is the ability of these types of catalysts to oxidize CO at 0°C (32°F) that interested us in using them for removing CO from air in escape hood respirators.

The fact that the catalytic activity of Au/TMO catalysts is very sensitive to the preparation method has been demonstrated many times. This is because the preparation method determines the sizes of the gold nanocrystallites. Fortunately, once a method for preparing an active catalyst has been developed, the reproducibility of the synthesis is usually quite good. We have found this to be true in TDA's laboratories as well. Traditional (and rather straight forward) techniques such as wet impregnation of the bulk support with soluble gold salts (e.g. $HAuCl_4$) generally result in micron-sized Au crystallites, which exhibit little catalytic activity. The highest-activity catalysts are obtained using the so-called deposition-precipitation (DP) method and the optimum Au particle size appears to be about 5 nanometers or smaller. DP also uses $HAuCl_4$ as a starting material, but in DP, $Au(OH)_3$ precipitates <u>on</u> the TMO particles as fast as it is formed and the rate of nucleation exceeds the rate of agglomeration. In our earlier work with Au catalysts, we spent considerable time optimizing the DP synthesis method at the small scale (ca. 50 grams of catalyst) and all of our catalysts to date have been made using DP.

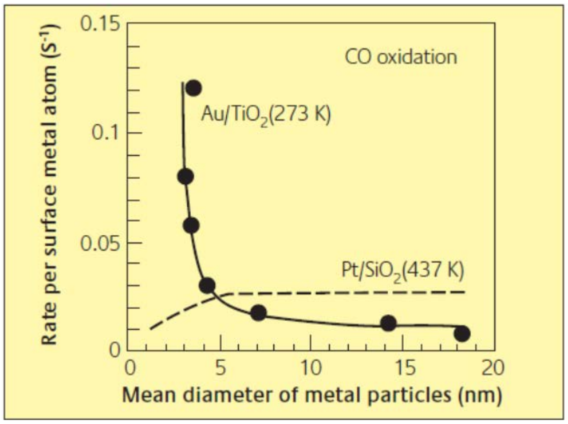

Figure 4. Turnover frequency for CO oxidation for Pt/SiO_2 and nano-Au/TiO_2 (Haruta 2004).

Two key factors that appear to be necessary in gold catalysis are: 1) the Au crystallites must be smaller than about 5 nm, and 2) catalysts that use reducible oxides (e.g. iron, cobalt, nickel, titanium, etc.) give more active catalysts than non-reducible supports such as Al_2O_3 and SiO_2. As a result, the best supports for gold catalysts are oxides such as Fe_2O_3, Co_3O_4 and TiO_2. Unfortunately, there is still no consensus on why certain transition metal oxides are better than others, let alone agreement on the reaction mechanism for CO oxidation on these nanocrystalline gold catalysts (Bond et al. 2006; Meyer et al. 2004). There is some evidence that O_2 dissociates on low coordination number Au atoms present on nanocrystallites; however O_2 also adsorbs on transition metal oxides and the mechanistic role of O_2 remains unresolved. The general consensus seems to be that CO adsorbs on the Au (Figure 5). Nevertheless, certain combinations (e.g. our Au/α-Fe_2O_3 catalyst) are highly active and long lived under the conditions necessary to oxidize CO to CO_2 for use in escape respirator applications.

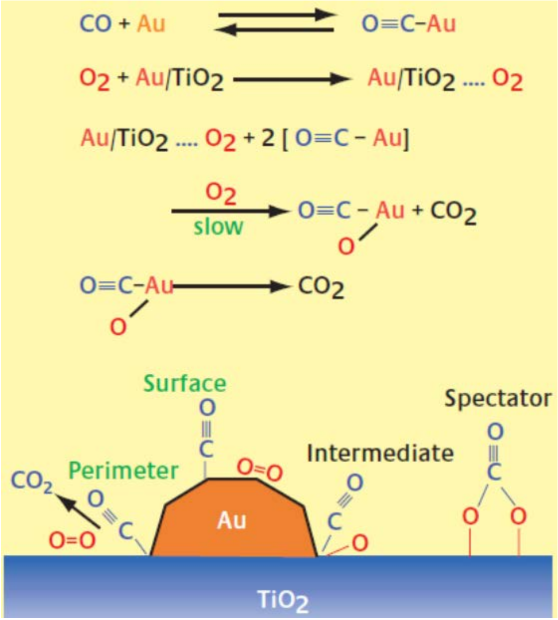

Figure 5. Proposes mechanism for CO oxidation on an Au/TiO_2 catalyst (Haruta 2004).

In heterogeneous catalysis, catalytically active metals are frequently supported as microscopic crystallites on various oxides in order to increase the amount of metal surface area available for reaction (dispersion) and in the case of expensive metals such as Pt, Rh, Au, etc., to reduce the amount of metal required. In the case of Au nanoparticles, the Au atoms nearest the surface are thought to form bonds with the underlying support that are partly ionic in nature (Figure 6) (Bond and Thompson 2000, Bond et al. 2006). Thus, the Au nanoparticles are chemically bonded to the surface and cannot be inhaled when using the escape hood respirator. Also, it should be pointed out that the term "nanoparticles" as commonly used in the catalytic community is somewhat misleading; "nanocrystallites" is more technically accurate. The gold "nanoparticles" precipitate on and are chemically bonded to the surface of the transition metal oxide (TMO) in crystalline form and have dimensions of several to tens of nanometers. In fact, there is evidence that the gold atoms closest to the oxide surface are at least somewhat ionized ($Au^{\delta+}$) forming ionic bonds with the support (Figure 6).

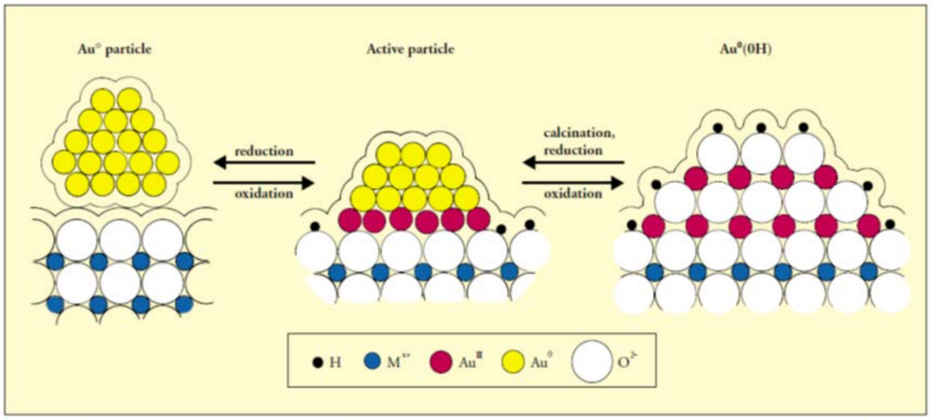

Figure 6. Gold ions are suggested to be what bonds the Au nanoparticles to the underlying transition metal oxide (TMO) support (Bond and Thompson 2000).

E. Phase II Results

E.1. Objectives of the Phase II Project

The overall goal of the project was for TDA to develop, and test catalysts that destroy CO at low temperatures and could be incorporated into MSA's CBRN respiratory protection filter canister.

All of the goals of the Phase II project were successfully met, they were:

- Optimize the catalyst composition
- Thoroughly characterize the catalyst to establish the relationships between composition, structure and activity.
- Scale up the catalyst synthesis to multi-kilogram quantities
- Test the scaled up catalyst at TDA
- Perform NIOSH challenge testing at TDA
- Perform NIOSH challenge testing with our commercial partner.

E.2. Modification to the Phase II work plan

Task 3 in the Phase II proposal's work plan was to optimize the functioning of a lithium chloride (LiCl) CO oxidation catalyst preheating layer. The task existed because, at the time of the Phase II proposal's funding, our best CO oxidation catalysts weren't fully active at temperatures below 0°C. This poor low temperature performance meant that the first carbon monoxide the catalyst encountered was able to slip through the catalyst bed without being oxidized. As a consequence of the CO slippage, mask users would have to endure a spike of CO when they encountered cold, CO contaminated air. As the work began on Task 1, we started to experiment with combinations of Co-TiO_2 /iron oxide to reduce the cost of the catalyst support. Over time, the catalyst support formulation moved entirely to mixtures of iron oxides. The iron oxide only formulation was not only less expensive, but it also produced CO oxidation catalysts that were far more active at low temperatures than the old Au/Co-TiO_2 catalysts, which made the LiCl bed unnecessary and therefore its uses was abandoned.

E.3. Summary of the Phase II Results

Figure 7 shows the 0°C testing results from Phase I. Taking those results as a starting point, we had to remedy the known issue of poor low temperature performance at the beginning of the test (to meet the NIOSH standard of no CO spikes above 500ppm). The Phase I results shown in Figure 7 also offered an opportunity to optimize the particle size distribution of the CO oxidation catalyst.

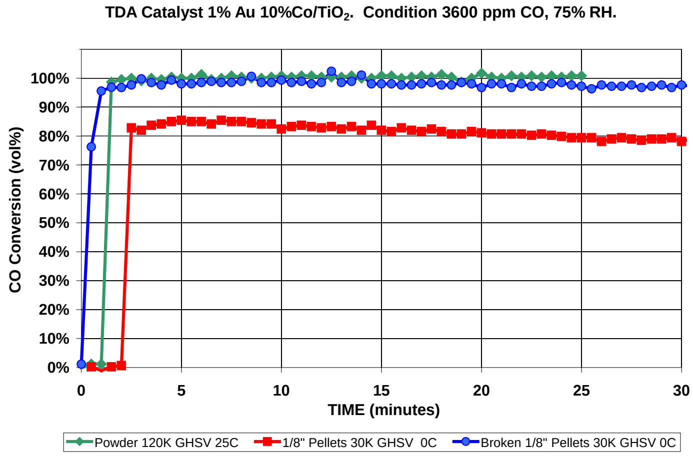

Figure 7. Results from 0°C testing at the end of the Phase I project.

Early in 2009, we began to have success overcoming the poor low temperature performance with the iron oxide based catalysts. By crushing and sieving the new, highly active catalysts to -20/+40 mesh, we were able to create catalyst beds that exhibited very low pressure drop, had essentially no channeling, and gave us very high conversion of CO to CO_2. The final, critical improvement to the catalyst was fine tuning of the size distribution of gold nanocrystallites to reduce the total amount of gold required in the catalyst.

By early 2012 we were able to reproducibly make 1 kg batches of 0.2 wt% Au/α-Fe_2O_3. Figure 8 shows the performance typically observed when testing one of the large catalyst batches. Note that in contrast to the performance of the older catalysts that exhibited an induction time of a few minutes before the CO conversion started to increase (Figure 7) the new Au/α-Fe_2O_3 catalysts respond more or less immediately, and even after 15 min, the concentration of CO is below 20 ppm; therefore, the current Au/α-Fe_2O_3 catalyst would easily pass the NIOSH CBRN-CO requirements for certification.

In an effort to reduce the cost of the Au/α-Fe_2O_3 catalyst, we measured the activity of several catalysts made with successively lower Au loadings. In fact, we have observed good activity from catalysts containing as little as 0.075 wt.% Au (about 1/3 of the original loading). The synthesis of the 0.075 wt% Au/α-Fe_2O_3 catalyst is very reproducible in small batches and we are currently developing the large batch procedure. The current cost of materials and labor to produce catalyst for the CBRN cartridge is $13.50 using 0.2 wt% Au, and we estimate that if we reduce the amount of Au to 0.1 wt%, the price per cartridge would be $6.85.

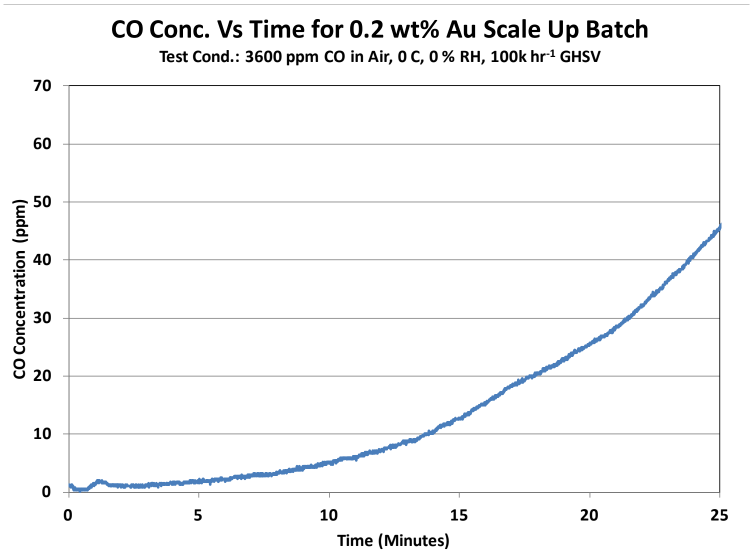

Figure 8. Results from a 2 kg batch produced late in the Phase II project that are representative of the performance of multi kilogram batches of TDA's CO oxidation catalyst. Particle size is +20/-40 mesh.

E.4. Results for Task 1: Optimizing CO Oxidation Catalyst Composition

The catalyst for use in the CBRN CO canister is sized to -20/+40 (0.400 to 0.841 mm), which is about the same size as MSA’s activated carbon granules and can be handled in MSA’s manufacturing equipment. Since gold is expensive, it is important to ensure that as much as possible of the catalytically active phase (i.e. Au nanocrystallites) is located on the outer surface of the support where it is accessible to the passing air. While we initially developed our Au/α-Fe_2O_3 catalyst in Phase I using powdered Fe_2O_3, making the catalyst in this manner and then forming the powders into granules would waste gold since some would be buried in the bulk material and not available for catalysis at the surface. Therefore, we had to develop methods to deposit Au nanoparticles on the surfaces of preformed -20/+40 mesh α-Fe_2O_3 granules.

To produce our iron oxide catalyst substrate for making the preformed granules, we mix iron oxide powder with 18 to 21 percent wt.% deionized water and mixed until the water is evenly distributed throughout the powder. The wet mixture is then run through an extruder to produce 0.125 inch extrudates. The extrudates are dried at 100°C and then crushed and sieved to -20/+30 mesh. The particles are then sintered at 600°C to increase the substrate's crush strength.

Following the sintering process the iron oxide is screened again to remove particles smaller than +40 mesh (0.4 mm). There is usually less than 3 wt.% loss during this last screening step. Losses during this step are not returned to the substrate production process due to their thermal history and are discarded.

The catalyst is prepared by treating the iron oxide granules with a solution that contains urea $[(NH_2)_2CO]$ and $HAuCl_4$. The amount of $HAuCl_4$ depends on the desired loading. The iron oxide particles are added to the $HAuCl_4$/urea solution at room temperature and the temperature is gradually increased to about 90°C. As the temperature increases aqueous urea decomposes into CO_2 and NH_3, which slowly increases the solution pH. As the pH increases $Au(OH)_3$ forms and nucleates on the iron oxide surface as nanoparticles. The catalyst is then washed, dried and calcined in air which converts the $Au(OH)_3$ into Au.

In deposition-precipitation, not all of the Au in solution is deposited on the iron oxide surface. Therefore, after each deposition-precipitation catalyst synthesis, we reclaim the Au remaining in solution for subsequent use. To a first approximation, the weight of gold on the catalyst can be calculated by subtracting the weight of the reclaimed gold from the weight of the gold that was used to make the initial Au solution. This method of calculating gold content is surprisingly accurate and agrees well with the results of Au analysis (done by ICP-AES) done by Huffman Laboratories in Golden, CO. This suggests that for the weight difference method is sufficiently accurate for determining the Au loading on our catalysts.

E.5. Results for Task 2: Catalyst Characterization

E.5.1. X-Ray Diffraction

Catalyst characterization is important because heterogeneous catalysts frequently have multiple phases and a wide variety of catalytically active sites present, and knowing which catalysts perform better than others, it is possible to correlate chemical and physical structure of the catalysts with their performance, and ultimately improve them. The major techniques we used were x-ray diffraction, BET surface area measurements, transmission electron microscopy (TEM) and crush strength (important for physical durability during use).

Figure 9 shows the x-ray diffraction pattern obtained from one of our typical Au/α-Fe_2O_3 catalysts. The data indicate the presence of magnetite (Fe_3O_4), hematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3It may be that the crush strength of the particles is enhanced when the surface of Fe_3O_4 that is converted into γ-Fe_2O_3 and is now in registry with the previously separate γ-Fe_2O_3 particles allows them to fuse together.

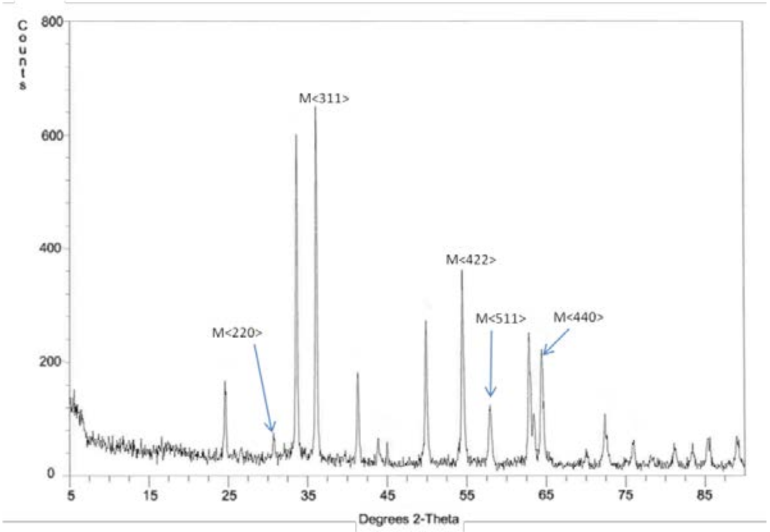

Figure 9. XRD trace from the mixed iron oxide catalyst support after sintering but before gold deposition.

E.5.2. Transmission Electron Microscopy (TEM)

In TEM, the catalyst sample is placed on a carbon grid and illuminated with a high energy electron beam (generally around 100 keV). As the beam passes through the material, the electrons are scattered producing shaded regions on the fluorescent screen below the sample.

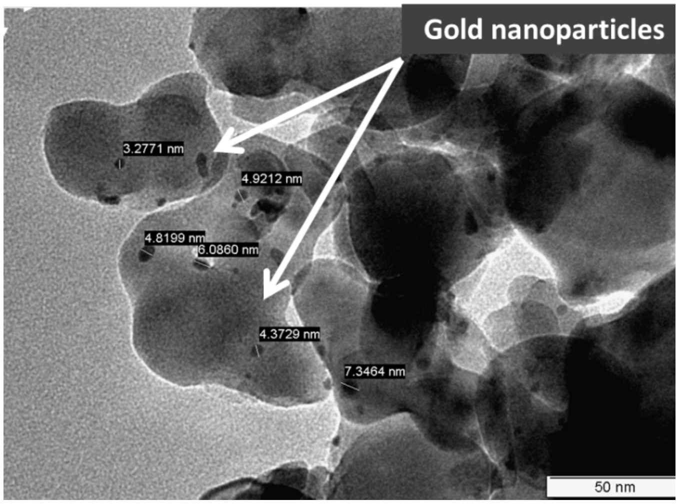

Figure 10. TEM of Au/α-Fe_2O_3 catalyst showing Au nanoparticles (dark spots).

In a classical picture, when the electron beam passes through materials with a high atomic number, (large numbers of electrons like Au) more of them are absorbed and those regions appear dark against a lighter background; this mode of operation is termed bright field. In addition, the electron beam is diffracted by crystals via Bragg scattering, and as a result crystallographic information such as plane spacing, faceting etc., can be determined. The TEM images were obtained at the Colorado School of Mines using with a 100 keV beam energy.

Figure 10 shows a TEM image of one of our active Au/α-Fe_2O_3 catalysts. The Au nanoparticles show up as small dark spots between about 3 and 7 nanometers along their largest dimension. This is consistent with the high activity of these catalysts for CO oxidation because it is well established that Au nanoparticles must be in this size range to be active. The large dark areas are where the catalyst particles were too large for the 100 keV electron beam to penetrate; grinding the catalyst can damage the Au nanoparticles, so our images were taken at the edges of the catalyst particles where the electron beam was able to penetrate.

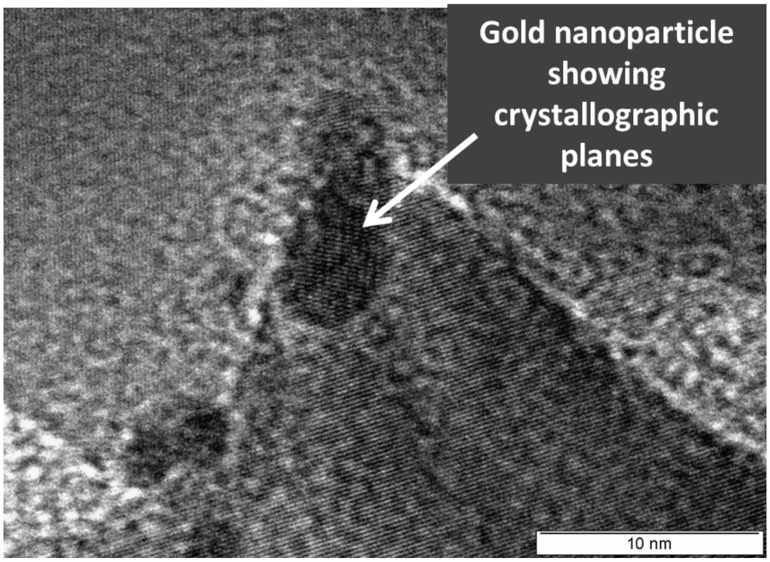

Figure 11. Lattice imaging of a ~5x10 nm Au particle.

Figure 11 is a lattice image of one of a Au nanoparticle on our Au/α-Fe_2O_3 catalyst. The magnification is quite a bit higher than in Figure 10 so the image is fuzzier. Nevertheless, the dark spots are clearly crystalline and the lattice spacing is consistent with those expected from gold. Again, the structure and size of the Au nanoparticles is consistent with that expected for a very active CO oxidation catalyst.

E.5.3. Surface Area Measurements

Surface area measurements are one way (in addition to XRD) that we can rapidly determine if we have successfully reproduced one of our highly active CO oxidation catalysts. Higher specific surface area (m^2/g) has been correlated to higher CO oxidation activity, apparently because higher surface area is an indirect measure of the number of nucleation sites for growing the gold nanoparticles. A larger concentration of gold nanoparticles leads to increased catalytic activity. Careful control of the iron oxide substrate's sintering temperature (600°C) helps us balance the competing requirements for the crush strength, attrition resistance and surface area. Figure 12 shows how the surface area varies as a function of sintering time at 500°C and 600°C. The slope of the 600°C line agrees with the slope predicted for a surface diffusion mechanism. The surface areas were measured using the BET method in house.

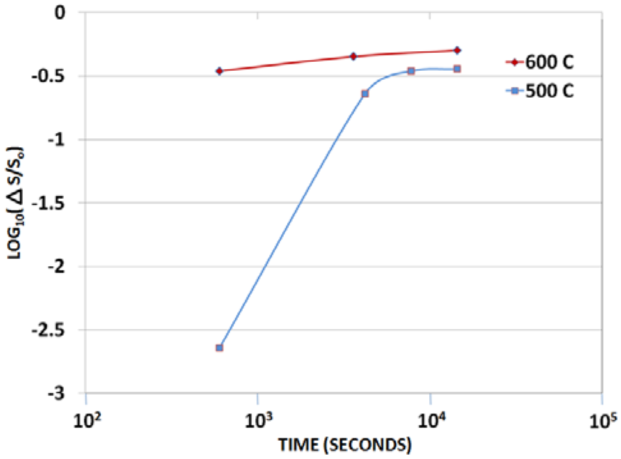

Figure 12. Reduction in specific surface area when sintering in air at 500°C and 600°C.

E.5.4. Crush Strength Measurements

One measure of the mechanical strength of substrate catalyst pellets is crush strength. In this test, a cylindrical pellet is placed horizontally in a MecMesin press (Figure 13) so that it is cross loaded with the plunger The motor pushes the plunger down until the pellet breaks, and the instrument records the force when the pellet broke. The catalyst crush strength is given as the load (lb) divided by the pellet diameter in millimeters. Our extruded substrate pellets had average crush strengths of 42 lb/mm. By tolerating a 50% reduction in surface area, we were able to increase the crush strength by 350% (to 42 lb/mm).

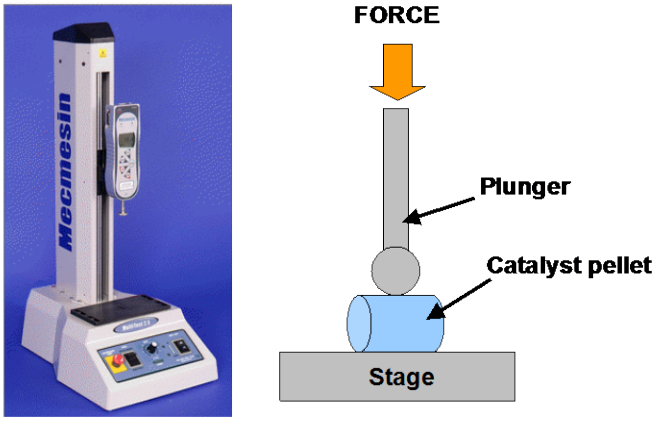

Figure 13. MecMesin test stand.

Figure 14 shows the increase in crush strength achieved during sintering at 500°C and 600°C. The samples used to produce the data shown in Figure 14 were sintered at the same time as those discussed in Figure 12 so that the results could be compared directly. The reduction in surface area, while substantial in each case, increased the crush strength but did not adversely affect the catalytic activity for CO oxidation. The catalyst is sufficiently strong for use in the CBRN CO escape hood canisters because it is located behind the activated carbon in a compressed packed bed.

E.6. Results for Task 3: Scale Up of CO Oxidation Catalyst Synthesis

Initial laboratory scale syntheses of the CO oxidation catalysts were performed by agitating catalyst support in round bottomed flasks filled with a solution of $HAuCl_4$ and urea $[(NH_2)_2CO]$ at 91°F, and the gold solution to catalyst support was 7:1 (by weight). Having a fixed ratio of solution to support created physical limitations during catalyst synthesis scale up because simply using larger glassware introduces mixing difficulties that diminish the quality of the final catalyst. Therefore, we designed a continuous Au deposition system where the $HAuCl_4$ + urea solution is circulated through a fluidized bed of catalyst particles. With the fluid pumped up from the bottom, the catalyst particles are fluidized, resulting in excellent mixing.

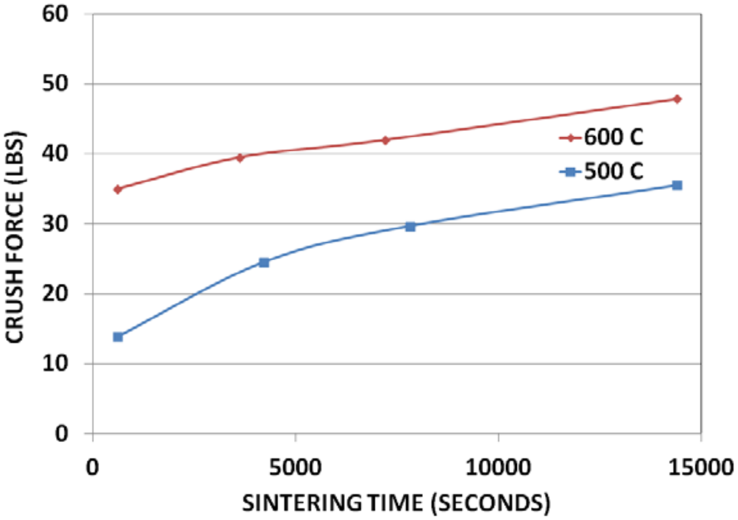

Figure 14. Increase in crush strength of the catalyst substrate vs sintering time for two temperatures.

Figure 15 is a photograph of our fluidized bed gold deposition reactor. The process is easily scalable and very simple to control. Catalyst support is loaded into the reactor, and gold solution is loaded into a heated reservoir. The solution is then pumped into the bottom of the bed where it fluidizes the catalyst particles and gradually deposits the gold. Solution exiting the top of the reactor flows back to the reservoir. Once the system is circulating, the process heaters are turned on and the system temperature gradually increases to 91°C where it is maintained for a prescribed time. Gold deposition times ranged from 15 minutes to 4 hours, with 1 hour found to give the best catalysts; too short and not enough gold deposits, too long and the Au particle size starts to increase. In addition, at times greater than about 1 hour, catalyst attrition becomes detrimental.

Figure 15. The 2.5 kilogram-of-substrate fluidized bed gold deposition reactor.

The time required for gold deposition period is determined primarily by the growth rate of the gold nanoparticles. It is not clear if gold nanoparticles are formed at nucleation sites on the catalyst support (iron oxide) or in solution and are then precipitated; however, most of the literature suggests that nucleation occurs on the catalyst support. The quality of each catalyst batch was determined by its performance in the NIOSH low temperature CO oxidation test.

The pump used to circulate the gold solution from the reservoir, through the catalyst bed, and back was sized to provide sufficient velocity to fluidize the bed of iron oxide catalyst support particles. We used twice the minimum fluidization velocity calculated using the methods described in Kunii and Levenspiel, 1991. At a fluid velocity of ~2 cm/sec, circulation of the entire fluid volume occurred 8-10 times per minute.

While the iron oxide catalyst support particles are significantly hardened during the calcining step in their preparation, there is still some loss due to attrition. Attrition occurs in fluidized beds because the particles are constantly abrading against one another. As a result, we typically lose 2-3% of the catalyst weight during a gold deposition. While a down flow reactor design would eliminate attrition, this would be at the expense of good mixing and uniform deposition of gold.

E.7. Results for Task 4: Design and Build a Pellet Catalyst Test Apparatus at TDA

Meeting MSA's particle size requirements required us to design and build a test apparatus that realistically approximated how our Au/α-Fe_2O_3 CO oxidation catalyst would function in real life. The result was the temperature controlled chamber shown in Figure 17.

We knew that the mask testing chamber (MTC) should have the ability to control the temperature of the challenge gas as well as the temperature of the chamber walls. The MTC would ideally have a shape that would eliminate dead spots in the circulatory pattern. We chose an oval shape to eliminate corners from the flow path and consequently the oval shape made it an easy task to wrap the MTC's inner wall with the 1/2 inch tubing that carries the challenge gas. Incorporating the challenge gas cooling system into the cooling system for the chamber addressed both of our cooling needs in one unit. We can use the MTC for all of our mask cartridge testing because it operates in the range from 50°C to -5°C.

The reusable mask cartridge (RMC) is a heavy, metal assembly of brass and stainless steel plates, rings, and a body (Figure 16). The brass collar screws onto the cartridge body (fine thread) that allows the pressure applied to the catalyst and carbon beds to be gentle and uniform. Due to the reusable mask cartridge's large thermal mass it must be given time to equilibrate at 0°C before testing. To do this, we pre-chill the RMC for about 1 hour, load the new test sample of catalyst, reinstall the RMC, and allow for another 15 minutes for the temperature to equilibrate before starting the test. The bed diameter (both carbon followed by catalyst) is 4 inches (12.6 in^2). There are some flow occlusions of the top layer of the upstream carbon bed that are created by the clamping plate's thick cell walls (third component from the top in Figure 16); however, calculations and empirical data have shown that the gas flows is uniform across the frontal area of the catalyst bed (the carbon bed acts as a flow distributor). The RMC has made testing the pelletized catalyst samples under small amounts of compaction simple and repeatable.

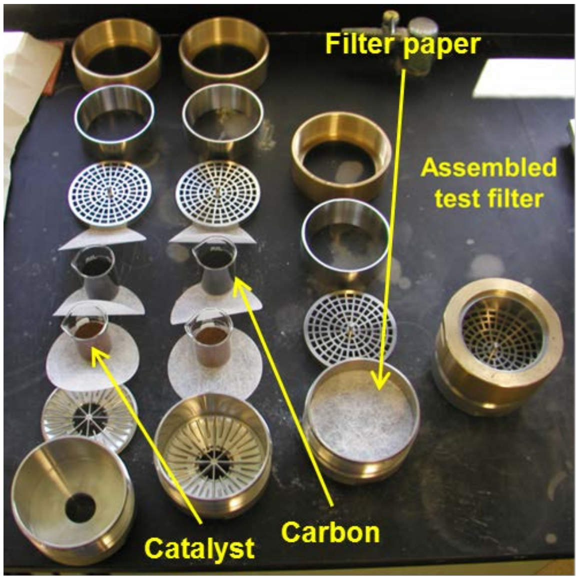

Figure 16. Components of the RMC.

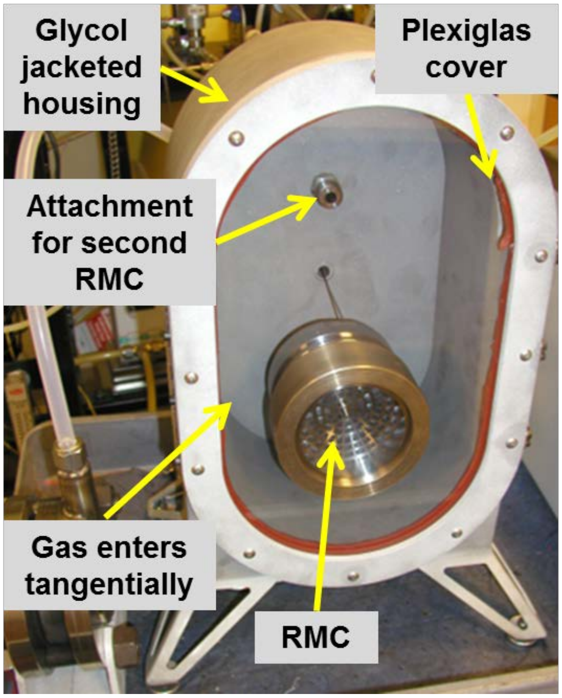

Figure 17. Mask testing chamber (MTC) for CO oxidation catalyst testing under NIOSH conditions.

The RMC is tested in the mask testing chamber which has an oval, jacketed, one-inch-thick outer wall through which coolant (glycol) is circulated with a chiller. The CO contaminated air flows through 10 wraps of 1/2 inch stainless steel tubing inside the cooling jacket before entering the testing chamber. For 0°C testing we set the temperature controlled glycol chiller to a set point of -5°C. The set point is 5°C lower to compensate for cooling the 64 L/min, challenge gas stream (CO contaminated air) and a small amount of heating by ambient air in the laboratory. The chiller setting maintains the temperature at 0°C for the 30 minute CBRN NIOSH test. To ensure that the CO contaminated feed air is uniformly mixed in the test chamber, the air enters the MTC tangentially, which creates turbulence that mixes the gas and maintains it at a uniform temperature. The MTC has the capacity to test dual cartridge configurations in the event that our commercial partners choose a dual filter design (Figure 17).

Gases are metered into the mask test chamber (MTC) using electronic mass flow controllers. Breathing quality air (from a “six-pack” of cylinders) is humidified by passing it through a Perma Pure humidifier. Perma Pure gas humidifiers are tube-in-shell moisture exchangers that transfer water vapor from liquid water to the gas stream using a large number of pervaporation membrane tubes. One of their main uses is humidification of PEM fuel cells. The airstream is then cooled to the desired test temperature by passing it through a tube-in-tube coil heat exchanger.

The entire apparatus is controlled by a desktop PC running the process control program Control EG. The program uses proportional-integral-derivative (PID) logic to control all of the temperatures and flow rates in the system. Control EG also monitors these variables and shuts down the apparatus in the event that any of these parameters are out of specification. Data from the tests are output from Control EG to a spreadsheet compatible format for further analysis. The testing procedure can be programmed to run and collect data without operator attention, which permits 24/7 operation if desired. Because of the toxicity of CO, there is an electronic CO monitor in the laboratory located next to the apparatus that is attached to the process control computer. If the CO monitor is tripped (it is set to alarm at the OSHA TWA-PEL of 50 ppm) an audible alarm sounds and the computer receives a signal that starts a controlled shutdown of the entire apparatus. This stops the gas flows and powers down the system. Finally, gas exiting the test chamber is analyzed using an online infrared CO/CO_2 analyzer, its signal is recorded by the process control computer, followed by venting into the laboratory fume hood system. Ultra-high purity gases are used when calibrating the IR analyzer.

E.8. Results for Task 5: NIOSH Challenge Testing and Selection of Best Catalyst

E.8.1. CO Testing Procedure

The standard tests were performed at TDA using a gas hourly space velocity (GHSV) of 100,000 $cm^3_{air}/cm^3_{catalyst}$/hour (which corresponds to 64 slpm) with a CO concentration of 3,600 ppm and room temperature (25°C) and 0°C. After the air passes through the mask where the CO is oxidized to CO_2, it flows into a California Instruments online infrared analyzer that measures the concentrations of both CO and CO_2. The CO and CO_2 concentrations are recorded every 0.5 seconds (2 Hz sampling rate). The analyzer concentration ranges are 0-2.5% for CO and 0-20% for CO_2. The analyzer is zeroed with ultrahigh purity nitrogen. The span is calibrated with flowing 1% CO in N_2. The response of the instrument is linear. There is also a bypass around the test chamber that allows us to verify that the feed air contains 3600 ppm of CO. Gas exiting the analyzer is sent to the laboratory ventilation system using nylon tubing.

E.8.2. NIOSH Test Results

Once we were able to reproducibly make large batches of catalyst that passed NIOSH's CBRN-CO test, our focus turned to cost reduction. Gold is the most expensive component of the catalyst, and therefore, we made and tested several batches of catalyst that had reduced gold content. The result shown in Figure 18 was very common for catalysts synthesized in 2010 and 2011. Catalysts that contain 0.35 wt.% Au or more are too expensive to be viable. Therefore, in the last two years, considerable effort was expended in optimizing the large scale catalyst synthesis procedure to produce catalysts that were active but contained the lowest possible amount of gold.

Figure 19 shows the results from our 0.2 wt% $Au/\alpha\text{-}Fe_2O_3$ catalyst. This catalyst is the optimized compromise between good activity and minimum amount of gold. This catalyst is the least expensive ($13.50/cartridge, at a gold cost of $50 per gram) that passes the NIOSH CBRN-CO certification test with a substantial margin of safety.

NIOSH's carbon monoxide penetration limits for escape respirators use a calculated figure of merit called Concentration-Time (Ct) that has units of ppm-minutes. NIOSH's limits for CO inhalation average 402 ppm/minute. TDA awards a passing grade to catalysts that average less than 130 ppm/minute over a 30 minute test to insure that catalysts that may have lost efficacy due to handling or aging will still protect the user to at least the NIOSH recommended level.

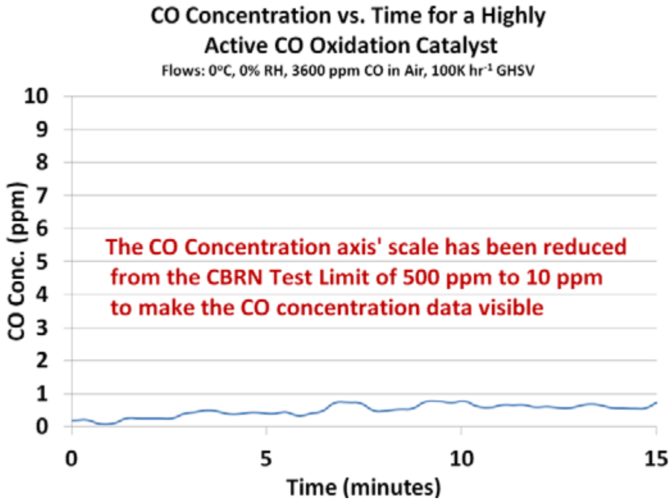

Figure 18. 0°C test results for a catalyst containing 0.6wt.% Gold.

In conclusion, TDA has developed a low temperature 0.2 wt% $Au/\alpha\text{-}Fe_2O_3$ catalyst that contains $13.50 of catalyst per mask that will protect the user from long term exposure (30 minutes) to CO concentration that maintains the CO concentration at or below 0.5% CO at temperatures above -5°C.

E.9. Results for Task 6: NIOSH Challenge Field Testing of Best Catalyst

In addition to having our best catalyst tested by our partner MSA, we have also submitted samples to Scott Health and Safety, Avon Protection and 3M. Tests are ongoing at MSA, Scott and Avon, and the results of the testing at 3M are given in Figure 20.

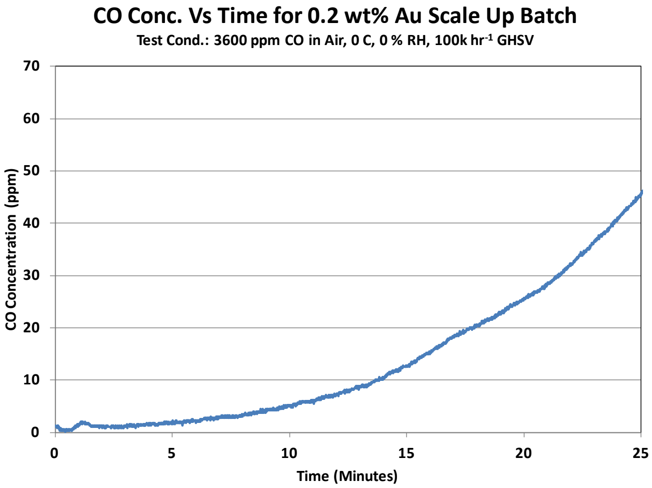

Figure 19. CO oxidation results for TDA's best catalyst that contains 0.2 wt% Au nanoparticles (same as Figure 8).

Figure 20 shows catalyst tests done by Dr. Larry Brey at 3M. The tests performed at 3M were: Test #1: 1200 ppm CO followed by a jump to 10,000 ppm CO to examine the catalyst's response to changing CO concentrations. (Figure 20, upper left); Test #2: was identical to Test #1, using the same sample #3M-1as in Test #1 but with a different detector (a fast responding MIRAN) covering the time period from several minutes before the concentration jump to several minutes after. Test #2 included the result for 3M 12X20 mesh catalyst (Figure 20, upper right) in order to display the fast response of 3M's best catalyst in this test. Test #3 was a 100 ppm CO test with RH cycled up and down to judge effect of capillary condensation on catalyst efficiency (low CO so insignificant thermal effects)(Figure 20, lower left); Test #4 shows the effect on CO catalyst of wet storage at 50°C for 3 days(Figure 20, lower right).

The most important result from the testing at 3M was that the CO penetration through our catalyst bed never exceeded 500 ppm during the 4 tests. We certainly could have sent catalysts that would have outperformed 3M's VPC-10 catalyst. However, we opted to send the catalyst with the lowest cost that would still pass the NIOSH testing easily.

The top graphs are replicates of the jump from 1200 ppm to 10,000 ppm test. They show the excellent result that even when exposed to 1% CO, our catalyst never permits more than 120 ppm CO penetration. 3M's catalyst heats much more quickly due to its very low thermal mass. Our iron oxide substrate may take longer to reach its terminal temperature but this behavior does not impact the catalyst's ability to pass the test.

The lower two graphs show the catalysts' ability to handle moisture saturated situations. Once again our two catalysts passed the tests. It is worth noting that TDA's sample 3M-1 was chosen for the high moisture aging test, and while it was the less efficient of the two catalysts, it passed the aging test easily.

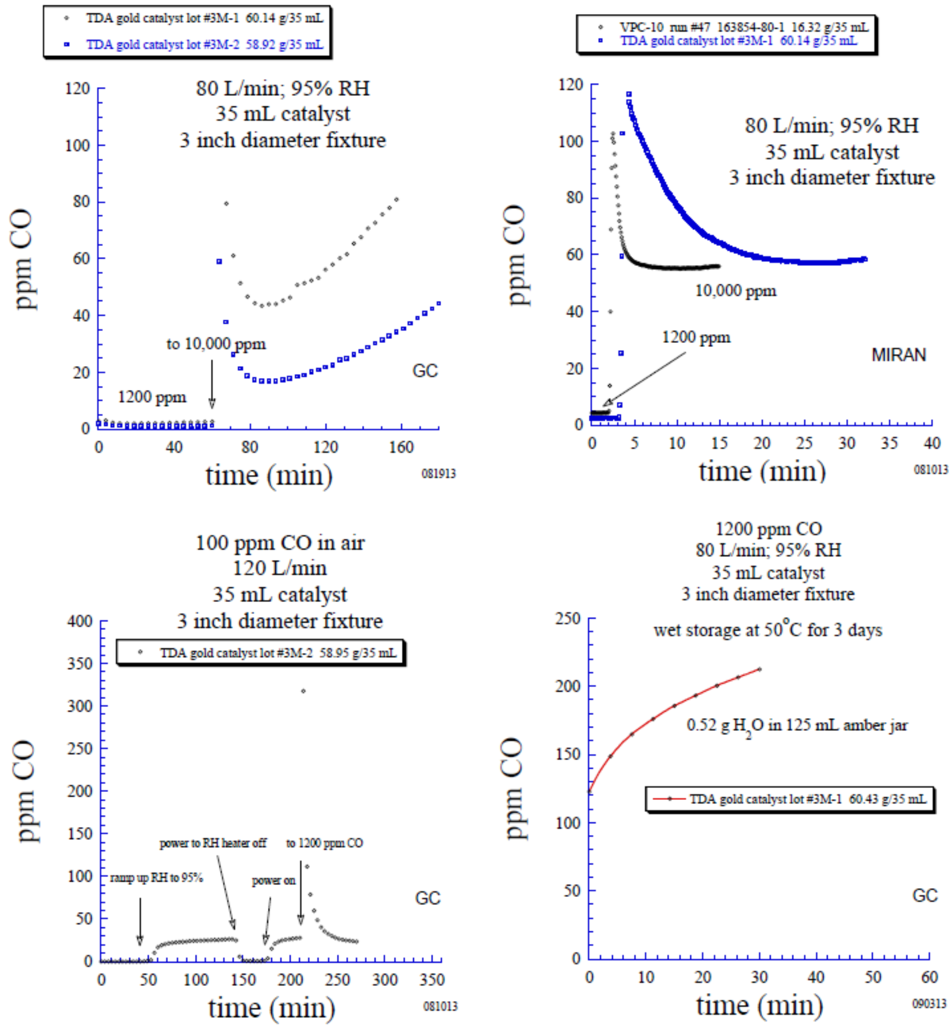

Figure 20. 3M's field testing results for TDA's CO Oxidation Catalyst.

F. Phase II Summary and Conclusions

TDA has developed a catalyst that is active for CO oxidation at temperatures down to 0°C that is insensitive to moisture and passes the NIOSH test for CO protection certification for CBRN air purifying respirators (APR). TDA's low temperature CO oxidation catalyst contains gold nanocrystallites supported on mixed iron oxide phases. Testing in Phase II by TDA and 3M demonstrated that TDA's catalyst is ideal for use in Response Escape Hoods. When challenged according to the NIOSH certification standard for CO removal (64 liter/min of air at 0°C, 3600 ppm CO, for 30 min), TDA's catalyst far exceeded the NIOSH requirements; the CO concentration downstream of TDA's catalyst never exceeded 1 ppm (the NIOSH requirement is to never have a spike above 500 ppm).

TDA has successfully optimized the catalyst formulation, scaled up the catalyst synthesis to multi-kilogram quantities, and demonstrated that the scaled up synthesis is reproducible and produces a catalyst that exceeds the requirements for use in a CBRN filter canister. The current cost per filter is approximately $13.50 (at a gold price of $50 per gram), which is significantly less than the goal set by MSA at the beginning of the Phase II project of $25 per filter. TDA, MSA and Pressure Chemical Co.(toll catalyst manufacturer) will manufacture the catalyst for use in CBRN APR cartridges during Phase III.

G. Publications from Phase II Effort

There have been no publications or public disclosure about the composition of methods of manufacturing TDA's low temperature CO oxidation catalyst. The use of the catalyst for CO protection in CBRN applications has been discussed several in oral and poster presentations and performance data have been shown (Srinivas et al. 1996, Srinivas et al., 2010a&b, Srinivas 2011, Srinivas et al, 2012).

H. Patents, Copyrights, Trademarks, Invention Reports

No public disclosure of the composition of matter or method of manufacturing the catalyst has been disclosed. An invention report is being prepared. We are currently discussing whether we should apply for a patent on the manufacturing method or protect the method via trade secret.

I. Current Status of the Technology Developed from this SBIR

TDA Research has developed its catalyst for CO oxidation that exceeds the NIOSH requirements for certification for CO protection when incorporated into CBRN air purifying respirators. While continued optimization and reduction in gold content (if possible) would reduce the catalyst cost, it is currently economically viable to incorporate into CBRN APRs at a cost of $13.50/cartridge, which is well below MSA's estimated upper limit of $25/ctg.

J. Benefit to TDA

MSA has informed TDA that catalyst costs below about $25 per hood are acceptable; this is based on charging a $40/unit premium for CO protection. Based on MSA's estimate of respirator market capture, MSA's incremental revenue would be $20 million per year with a projected margin (revenue minus catalyst cost) of $12.5 million annually (based on selling 500,000 cartridges per year). TDA and MSA have tentatively negotiated a royalty of $1/cartridge that TDA would derive from the sales of the escape respirator that incorporates our catalyst. Thus, TDA would derive $500,000/year for the first few years after commercialization (between 7 and 4% of the margins that MSA would derive). MSA estimates that canister sales could double to 1,000,000 units/yr in three years and in that the case, TDA would derive $1,000,000/yr from royalties. A summary of the analysis is shown in Table 3.

Since 2010, TDA Research has been able to manufacture approximately 600 lbs per working shift of a different catalyst that uses production techniques that are similar to those used to make our low temperature Au/α-Fe_2O_3 CO oxidation catalyst. A 600 lbs/shift catalyst production rate is 132,000 lbs/year, or twice as much production as is forecasted to be needed in the first year.

Table 3. Summary of projected sales and royalties to TDA.

Parameter	Value	Units
Projected initial respirator sales per year with CO protection in the U.S. and Europe	500,000	cartridges
Current retail price of escape respirator	$230	per cartridge
Premium that MSA can charge per respirator for CO protection	$40	per cartridge
Incremental revenue for MSA (initially)	$20,000,000	per year
Projected use of catalyst per respirator cartridge	60	grams
Current catalyst cost per cartridge from Pressure Chemical Inc.	$25	per cartridge
Projected catalyst cost per cartridge produced by TDA	$8	per cartridge
Projected catalyst need per year based on 500,000 cartridges (in lbs)	66,000	lbs.
Current expected margin per year for MSA	$7,333,333	per year
Projected margin per year for MSA	$16,070,000	per year
Expected royalties per cartridge for TDA	$1	per cartridge
Expected royalties per year for TDA	$500,000	per year
Current expected percentage of margins that are paid towards royalties	6.82%	
Projected percentage of margins that are paid towards royalties	3.11%	
Projected sales per year of respirators after 3 years of commercialization	1,000,000	cartridges
Current Expected margin per year for MSA	$14,666,667	per year
Projected margin per year for MSA	$32,140,000	per year
Expected royalties per year for TDA (after 3 years)	$1,000,000	per year
Current expected percentage of margins that are paid towards royalties	6.82%	
Projected percentage of margins that are paid towards royalties	3.11%	

K. Other Information

No human or animal subjects were used in this Phase I project. No protocol or software were generated.

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