AMBIENT-TEMPERATURE CO-OXIDATION CATALYSTS

Billy T. Upchurch
NASA Langley Research Center
Hampton, VA 23665

David R. Schryer
NASA Langley Research Center
Hampton, VA 23665

Kenneth G. Brown
Old Dominion University
Norfolk, VA 23529

Erik J. Kielin
Old Dominion University
Norfolk, VA 23529

ABSTRACT

Oxidation catalysts which operate at ambient temperature have been developed for the recombination of carbon monoxide (CO) and oxygen (O₂) dissociation products which are formed during carbon dioxide (CO₂) laser operation. Recombination of these products to regenerate CO₂ allows continuous operation of CO₂ lasers in a closed-cycle mode. Development of these catalyst materials provides enabling technology for the operation of such lasers from space platforms or in ground-based facilities without constant gas consumption required for continuous open-cycle operation. Such catalysts also have other applications in various areas outside the laser community for removal of CO from other closed environments such as indoor air and as an ambient-temperature catalytic converter for control of auto emissions.

INTRODUCTION

The electrical discharge used to excite many pulsed CO₂ lasers generally causes some decomposition of CO₂ to CO and O₂. This decomposition can be detrimental to long-life laser operation due to both the loss of CO₂ and the buildup of O₂. CO₂ loss causes a corresponding gradual decrease in laser power, but the buildup of relatively small amounts of O₂ can cause rapid power loss and even complete failure in many lasers. In some commercial applications these problems are overcome by operating the lasers open-cycle with a continuous flow-through of fresh laser gas to effect removal of dissociation products. Such open-cycle operation is impractical for space-based applications or other applications involving weight or volume constraints. Consequently, closed-cycle operation with recycling of the laser gas is necessary.

Closed-cycle operation of CO₂ lasers requires a suitable CO-oxidation catalyst to recombine the dissociation products, CO and O₂, to regenerate CO₂. For effective closed-cycle laser operation, the catalyst used must have a high recombination efficiency at low concentrations of O₂ and ambient laser gas temperatures, typically between 25 °C and 75 °C, so additional energy is not required to heat the catalyst. Additionally, applications with rare isotope CO₂ for enhanced atmospheric transmission require utilization of a catalyst whose operation is compatible with the particular isotope chosen without contributing normal isotope impurities. The NASA Laser Atmospheric Wind Sounder (LAWS) will use such a laser requiring five years of continuous operation to measure global winds from orbit. For such long-term operation, this application requires a closed-cycle, pulsed C²O₂ laser and a C²O-oxidation catalyst which will operate under ambient temperature laser gas conditions without isotopic scrambling. Such CO-oxidation catalysts with high activity at ambient laser gas temperatures and low oxygen concentrations were nonexistent until fairly recently [2-4,11-23].
CO-oxidation catalysts which have been effective at low oxygen concentrations generally have been noble metals such as platinum (Pt) or palladium (Pd) on a support and have shown activity only at elevated temperatures. CO-oxidation catalysts with useful activity at ambient temperature generally require air or other gases which supply high concentrations of O_2 to be effective. The commercial catalyst Hopcalite which is a mixture of nonprecious metal oxides is such a catalyst.

Recently a new class of catalysts has been developed which consists of a noble metal on an active reducible-oxide support. Several of these noble-metal/reducible-oxide (NMRO) catalysts such as platinized tin-oxide (Pt/SnO_2) and gold/manganese dioxide (Au/MnO_2) have been shown to have high activity for CO oxidation at room temperature even with low and stoichiometric concentrations of CO and O_2. Consequently these catalysts are suitable for O_2 and CO removal through CO_2 regeneration in closed-cycle CO_2 lasers. Since the activity of these catalysts increases with increasing O_2 concentration they have very high ambient-temperature activity for CO oxidation in air and are thus potentially useful for air purification. They may also be useful as a catalyst component for internal combustion engine exhaust gas conversion as high gas temperatures are not required for effective operation of the catalyst.

NMRO catalysts, particularly those based on Pt/SnO_2, have been extensively studied at the NASA Langley Research Center (LaRC) over the past several years. While the principle impetus for this research has been CO_2 laser applications related to NASA's LAWS laser instrument development program, research involving application of NMRO catalysts in air purification has been initiated as well. Results of these efforts will be presented and discussed.

EXPERIMENTAL

The Au/MnO_2 and Pt/SnO_2 catalysts were tested in plug-flow or recycle reactors, the details of which have been reported earlier [1-3]. Briefly, the plug flow reactor is designed to simulate laser dissociation conditions by flowing a test gas containing low partial pressures of CO and O_2 in an inert matrix gas over a catalyst sample in a temperature controlled quartz tube and then measuring the resulting conversion to CO_2. Quantitative analysis of the gas composition is accomplished either gas chromatographically or mass spectrometrically in the case of isotopic studies.

Unless otherwise indicated, the catalyst sample sizes were 0.050 grams for monolith supported samples. This value is exclusive of support. The test gases used were one or more of the following: (1) stoichiometric 1.0% CO, 0.50% O_2; (2) stoichiometric with 16% CO_2; (3) twice the stoichiometric amount of CO: 2.0% CO, 0.5% O_2; (4) twice the stoichiometric amount of O_2: 1.0% CO, 1.0% O_2; and (5) 500 ppm CO in air for air purification studies. All test gases except the air purification test gas mixture were in a high purity He matrix with 2 percent Ne added as an internal calibration standard. Conversion efficiencies were measured at 35°C and 55°C unless otherwise specified.

The Au/MnO_2 catalysts in powder form were prepared by Gar Hoflund at the University of Florida using standard coprecipitation techniques. All Pt/SnO_2 samples and Au/MnO_2-coated monolith samples were made at NASA LaRC. Syntheses of Pt/SnO_2 catalysts has been reported earlier [4]. The Hopcalite was 8 mesh commercially available material. Monolith coating techniques are proprietary at present.

DISCUSSION

The first catalyst to show significant near ambient temperature CO-oxidation activity was platinized tin-oxide (Pt/SnO_2), a noble-metal/reducible-oxide (NMRO) catalyst. Platinized tin oxide has been extensively researched to optimize formulation, synthesis, and pretreatment conditions resulting in a significantly improved catalyst [1-12]. Unfortunately, this catalyst loses about half of its initial activity within a few days and then exhibits a slower decay with a half-life of several months. Research into the cause of decay indicates that the initial decay is due to CO_2 retention, possibly forming bicarbonate or carbonate, whereas the long-term decay appears to be associated with changes in surface morphology.
Since the discovery of the synergistic effect of combining Pt and SnO\textsubscript{2} for the enhanced catalytic oxidation of CO by O\textsubscript{2} at near-ambient temperatures, several improvements have been made, not only in Pt/SnO\textsubscript{2} but also in other noble-metal/reducible-oxide (NMRO) catalysts. The research efforts at NASA Langley Research Center in the development of CO-oxidation catalysts have been reported extensively in other articles [1-13]. Improvements over commercially available catalysts resulting from these research efforts include: (1) development of an inherently clean method of preparing catalysts, eliminating chloride contaminants and allowing formerly unprecedented loadings of up to 46% Pt/SnO\textsubscript{2}; (2) determination of the optimum ratios of Pt/SnO\textsubscript{2} and Pd/Pt/SnO\textsubscript{2} for best activity (17% Pt and 5% Pd by weight); (3) development of a method of coating Pt/SnO\textsubscript{2} onto a high-surface-area, silica gel support providing enhanced activity with minimal humidification of the laser gas; and (4) determination of the optimum reductive pretreatment conditions of time (1.0 hour), temperature (125 °C), and gas (5% CO in He) for best catalyst activity [11].

Other noteworthy discoveries reported earlier are that (1) appropriate pretreatment temperature, moisture, and Pt loading eliminate the initial dip in catalytic activity; (2) bicarbonate and/or carbonate build up contribute to catalyst decay [11,13]; (3) isotopic scrambling of common-isotope 16\textsubscript{O} from the catalyst surface in the C\textsuperscript{18}O-oxidation process can be eliminated by replacing reactive surface oxygen in Pt/SnO\textsubscript{2} with 18\textsubscript{O} [4,11]; (4) the reaction between O\textsubscript{2} and CO is first order in O\textsubscript{2} and apparent first order for the overall reaction [2,11]. Extensive surface studies of Pt/SnO\textsubscript{2} indicate that a Pt/Sn alloy having surface hydroxyls forms when Pt/SnO\textsubscript{2} is reductively pretreated. Both the alloy and the surface hydroxyls are believed to contribute to the catalytic activity. [14-23].

Recent advances made in CO\textsubscript{2} laser catalysts to be discussed herein include comparisons of the activity of Au/MnO\textsubscript{2} to Pt/SnO\textsubscript{2} catalysts with possible explanations for observed differences. The catalysts were compared for the effect of test gas composition, pretreatment temperature, long term activity, effects of added promoter compounds, and surface labeling for isotopic laser gas compatibility, and applicability for use as ambient temperature air purification catalysts.

As shown in Figure 1 the activity of the Au/MnO\textsubscript{2} catalyst decreases significantly when the O\textsubscript{2} is less than stoichiometric and increases dramatically under O\textsubscript{2}-rich conditions. Pt/SnO\textsubscript{2} behaved similarly. The activity enhancement from O\textsubscript{2} is expected as the reaction is first order in O\textsubscript{2}. The catalysts do not exhibit a simple reaction order with respect to CO. The apparent CO order is zero at high excesses of O\textsubscript{2} and at stoichiometric levels. It is probable that CO adsorption competes with O\textsubscript{2} for active sites thus giving the observed reduced activity [13]. Thus, in air these catalysts could function in air purification applications.

In the absence of CO\textsubscript{2}, Au/MnO\textsubscript{2} possesses both higher activity and lower decay than Pt/SnO\textsubscript{2}. As shown in Figure 2, however, when CO\textsubscript{2} is present at high concentrations in the test gas, the activity of the Pt/SnO\textsubscript{2} remains relatively unaffected while that of the Au/MnO\textsubscript{2} falls below that of the Pt/SnO\textsubscript{2}. These results indicate that while the Au/MnO\textsubscript{2} would not be a viable candidate for CO\textsubscript{2} laser applications, both catalysts could function in gas purification applications in which the CO\textsubscript{2} concentration is low.

A promoter compound has recently been found which significantly enhances the catalytic activity of Pt/SnO\textsubscript{2} when incorporated into its formulation. Methods for depositing both promoted and unpromoted Pt/SnO\textsubscript{2} and Au/MnO\textsubscript{2} onto Cordierite monoliths have been developed. At the present time both the promoted catalyst composition and the monolith coating technology are proprietary. As shown in Figure 3, the activity of the Pt/SnO\textsubscript{2} is significantly enhanced by the addition of the promoter compound to the extent that catalytic activities at 35 °C are greater than the activities observed for the unpromoted cases at 55 °C. Additionally, the presence of high concentrations of CO\textsubscript{2} in the test gas has no deleterious effect on the activity, thus demonstrating that the promoted catalyst material should function in a laser gas environment. The promoted monolithic catalyst has already been successfully tested for one million pulses in a closed-cycle CO\textsubscript{2} laser. Initial tests on the Cordierite supported Au/MnO\textsubscript{2} showed a reduced activity when compared with its unsupported counterpart. It is believed that the activity was reduced by chloride contamination from HAuCl\textsubscript{4}, the starting material used for gold impregnation. Alternatives to this contaminating material are under investigation.
Isotopic integrity studies were carried out on both Au/MnO₂ and promoted and unpromoted Pt/SnO₂. The catalysts were prerduced with H₂ and then reoxidized with O₂. Upon subsequent exposure to a stoichiometric test gas containing C₉ and O₂ (Au/MnO₂ for 3 days and Pt/SnO₂ for 5 days), the isotopic composition of the CO produced indicated no isotopic scrambling. The rare-isotope test gas mixture was also tested on the unlabeled Au/MnO₂ for 10 days and little isotopic scrambling was observed toward the end of the test indicating that surface labeling had occurred during the 10 day test. As shown in Figure 4, the isotope labeling process has little affect on the activity of the catalyst.

Figure 5 shows the evolution of the laser catalyst development effort at LaRC. As can be seen, the CO conversion rate (or pumping speed efficiency) increased from near zero standard milliliters CO per gram (sccm CO/g) of catalyst with the commercial catalyst tested at 35 °C in 1985 to approximately 3.5 sccm CO/g for the promoted monolith catalyst developed at LaRC in 1991.

Air purification studies have been initiated at LaRC for application of the most promising catalyst materials for removal of CO in purification of air. Figure 6 shows the results of comparative testing of 8-mesh Hopcalite granules, Au/MnO₂ powder, and promoted and unpromoted Pt/SnO₂ powders with a test gas of 500 parts-per-million by volume (ppm) CO in air. The benchmark material for CO removal has been Hopcalite for several decades. At both 35 °C and 24 °C the LaRC catalyst materials clearly were more efficient than Hopcalite for CO removal. At both temperatures the promoted and unpromoted Pt/SnO₂ powders completely removed CO from the gas stream. While the LaRC Cordierite monolith supported catalysts are yet to be tested for CO removal in an air medium, it is predicted that their performance will be considerably more efficient than their corresponding powder forms.

CONCLUSIONS

It is concluded from this effort that the promoted Pt/SnO₂ on a monolithic support functions well as both a CO-oxidation catalyst for use in closed-cycle CO₂ lasers at ambient laser gas temperatures and as a very effective means for quantitative removal of CO for application in the purification of air under ambient temperature conditions. Furthermore, the Au/MnO₂ catalyst, while limited in applications in which high concentrations of CO₂ are present, also functions well as a catalyst for the ambient temperature removal of CO in air. The Pt/SnO₂ catalysts could also be applicable in removal of CO and other incompletely combusted exhaust gas constituents in internal combustion engine exhausts during the cooler temperature exhaust gas condition which occurs during and shortly after cranking of a cold engine before exhaust gases heat up the catalytic converter to make it functional.

REFERENCES

Figure 1. Effect of test gas on the activity of Au/MnOx.

Figure 2. Effect of CO2 rich test gas on the activity of Au/MnOx and Pt/SnO2 catalysts.
Promoted Pt/SnO2 on Cordierite at 35°C

Catalyst Data:
50 mg (support exclusive)

Pretreatment:
5% CO in He at 10 sccm for 60 min at 125°C

Test Conditions:
1% CO and 0.5% O2 in He at 10 sccm (NO CO2)

Figure 3. Effect of CO2 in test on the activity of promoted and unpromoted Pt/SnO2.
Figure 4. Effect of O-18 labeling on the activity of promoted Pt/SnO2 on Cordierite.

Catalyst Data:
50 mg (support exclusive)
Promoted Pt/SnO2
Pretreatment:
5% CO in He at 10 sccm for 60 min at 125°C
Test Conditions:
8% CO2, 1% CO and 0.5% O2 in He at 10 sccm and 35°C

Figure 5. Catalyst efficiencies in laser test gas.

Promoted Pt/SnO2
Monolith
LaRC, 35°C
Engelhard
LaRC 35°C
Pt/SnO2/Silica Gel
LaRC 35°C
Au/MnOx
UF/LaRC 35°C

Figure 6. Daily average comparison of CO-oxidation catalysts in air.