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NASA-LaRC RESEARCH ON

CATALYSTS FOR LONG-LIFE CLOSED-CYCLE CO₂ LASERS

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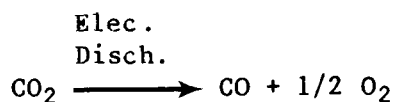
SUMMARY

Long-life, closed-cycle operation of pulsed CO₂ lasers requires catalytic CO - O₂ recombination both to remove O₂, which is formed by discharge-induced CO₂ decomposition, and to regenerate CO₂. Platinum metal on a tin (IV) oxide substrate (Pt/SnO₂) has been found to be an effective catalyst for such recombination in the desired temperature range of 25°C to 100°C. This paper presents a description of ongoing research at NASA-LaRC on Pt/SnO₂ catalyzed CO - O₂ recombination. Included are studies with rare-isotope gases since rare-isotope CO₂ is desirable as a laser gas for enhanced atmospheric transmission. Results presented include (1) achievement of 98% - 100% conversion of a stoichiometric mixture of CO and O₂ to CO₂ for 318 hours (> 1 x 10⁶ seconds), continuous, at a catalyst temperature of 60°C and (2) development of a technique, verified in a 30-hour test, to prevent isotopic scrambling when C¹⁸O and ¹⁸O₂ are reacted in the presence of a common-isotope Pt/Sn¹⁶O₂ catalyst.

INTRODUCTION

Pulsed CO₂ lasers have several potential remote sensing applications, both military and non-military, which require long-life operation with high conversion-efficiency and good power-stability. However, two problems are associated with such applications.

One problem is that the electrical discharge normally used to excite pulsed CO₂ lasers inevitably decomposes some of the CO₂:



This decomposition is harmful to long-life laser operation both because of the loss of CO₂ and because of the buildup of O₂. The loss of CO₂ results in a corresponding gradual loss of laser power. The buildup of even relatively small concentrations (0.1% - 1.0%) of O₂ molecules can cause rapid power loss and even complete laser failure.

The second problem has nothing to do with CO₂ lasers themselves; it is caused by the fact that the atmosphere contains a significant concentration, about 300 ppm, of common-isotope CO₂ (¹²C¹⁶O₂). If common-isotope CO₂ is used in a CO₂ laser intended for atmospheric transmission, the emission frequencies available to the laser will correspond to the absorption frequencies of the atmospheric CO₂ and poor transmission will result.

The solutions to these two problems are superficially quite simple: (1) continuously remove O₂ as it is formed and replenish CO₂ and (2) use some form of rare-isotope CO₂ (such as ¹²C¹⁸O₂, ¹³C¹⁶O₂, or ¹³C¹⁸O₂) in all lasers intended for applications involving atmospheric transmission so that the emission frequencies of such lasers will differ from the absorption frequencies of atmospheric ¹²C¹⁶O₂. Actual implementation of these two solutions, however, is far from simple.

Removal of O₂ and replenishment of CO₂ can be achieved in certain applications simply by operating the laser open-cycle with a continuous flow-through of fresh laser gas and the consequent removal of dissociation products. However for space-based applications or other applications involving weight and/or volume constraints, the amount of gas required for open-cycle operation would be unacceptable and, instead, closed-cycle laser operation with recycling of the laser gases would be imperative. Closed-cycle operation would also be highly desirable for any applications where rare-isotope CO₂ is used for enhanced atmospheric transmission because of the expense of the large volumes of rare-isotope gas which would be required for flow-through operation.

Closed-cycle CO₂ laser operation with removal of O₂ and regeneration of CO₂ can be achieved, in principle, simply by accomplishing CO-O₂ recombination.



However, this recombination is negligibly slow at steady-state temperatures (about 50°C to 100°C) achieved by the gas mixture in a typical CO₂ laser. Thus, although some recombination can occur in the region of the electric discharge where effective temperatures are quite high, no significant recombination can occur in the main body of the laser gas unless a catalyst is used. Several materials have been found to catalyze CO-O₂ recombination under various conditions. Most such catalysts utilize noble metals (especially Pt and/or Pd), metal oxides, or both. Catalysts consisting of Pt or Pd on a tin (IV) oxide substrate (Pt/SnO₂, Pd/SnO₂) have been shown to be much more efficient than Pt, Pd, or SnO₂ alone at moderate temperatures (Refs. 1 and 2).

At the NASA Langley Research Center (NASA-LaRC) we have investigated several catalysts for potential use with long-life, closed-cycle CO₂ lasers including Pt/SnO₂, Pt/SiO₂, unsupported Pt, Pd/C, and Cu/Cu₂O/CuO (Refs. 2 and 3). The most promising of these catalysts has been found to be Pt/SnO₂ and so a detailed investigation of this catalyst has been undertaken and is currently in progress. Studies of this and other catalysts are being carried out in several laboratory reactors as well as in a pulsed CO₂ laser.

TEST FACILITIES

Laboratory Reactors

Laboratory reactors are used for catalyst study under controlled conditions. Three laboratory reactors are presently operational, all of which are flow-through reactors. In these reactors a test-gas mixture flows through a reactor tube containing a catalyst sample which is situated in a temperature-controlled oven. The gas which exits the reactor tube is quantitatively analyzed with either a gas chromatograph (GC) or mass spectrometer (MS) and from this analysis the amount of CO and O₂ converted to CO₂ by the catalyst sample is determined. The test-gas mixtures used are purchased premixed in a high-purity He carrier, typically 1.00% CO and 0.50% O₂ plus 2.00% Ne (as an internal calibration standard for gas analysis).

Two of the flow-through reactors are used with common-isotope gases and use GC's for gas analysis. These GC's are fully automated so that tests with common-isotope gases can be conducted in the flow-through reactors around-the-clock without an operator present. The third flow-through reactor is used with rare-isotope gases and uses an MS for gas analysis.

Studies performed in the flow-through reactors are (1) parametric studies to determine the effect of such parameters as catalyst mass, temperature, reactor residence-time, etc., on the performance of a given catalyst material, (2) comparison of different catalyst compositions (such as Pt/SnO₂, Pd/SnO₂, and Pt + Pd/SnO₂) and concentrations to determine the optimum catalyst formulation, (3) long-term performance tests (using the automated-GC reactors) to determine how a catalyst performs with long-term exposure to the test gases, and (4) isotopic studies (using the MS reactor) to determine the interaction of a given catalyst with rare-isotope gases.

A recirculating reactor is presently being assembled and should be operational shortly. In this reactor a gas mixture will be continuously recirculated through a temperature-controlled reactor tube containing a sample of catalyst, and the conversion of CO and O₂ to CO₂ monitored as a function of time. Gas analysis will be performed with a GC. This reactor will be used to determine the rate of CO-O₂ recombination using various catalyst materials and also to study the mechanism of catalysis. Knowledge of these factors is important for optimization of catalyst performance.

Also to be assembled shortly will be a system to quantitatively measure chemisorption of gases on a catalyst surface when some of the chemisorbed species undergo desorption as a product gas.

Laser Reactor

A Lumonics model TEA-820 pulsed CO₂ laser (.7Joule/pulse, 1-20 pulses/second) is available for catalyst testing under actual laser operating conditions. The laser is operated closed-cycle with an external catalyst bed (in a temperature-controlled oven) and the results are compared with the open-cycle performance of the laser at the same flow rate. It is intended that ultimately the

laser will be operated with no heating of the catalyst other than by the laser gas. Gas analysis is performed with a GC in current common-isotope tests. An MS will be used when the laser is operated with rare-isotope CO₂.

RESULTS AND ON-GOING RESEARCH

This section presents a summary of results obtained to date using the currently operational reactors described in the previous section as well as a synopsis of work currently in progress or planned.

Laboratory Reactor Studies

Common-Isotope Gases

(1) Conversion of 1% CO and .5% O₂ to CO₂ at an efficiency of 98%-100% has been achieved in a laboratory reactor with 1.5 grams of 2% Pt/SnO₂ at 60°C and 10 std. mL/minute flow rate. This efficiency was maintained for 318 hours (> 10⁶ seconds or 13 days). The test was terminated because of a GC failure not because of a loss of catalyst efficiency. Tests at lower temperatures are in progress. Scheduled are laser tests to verify this result in actual laser operation, and laboratory-reactor tests involving non-stoichiometric gas mixtures (both CO and O₂ rich).

(2) At a given catalyst temperature, catalyst surface-area-to-mass ratio, and gas flow rate, the conversion of CO and O₂ to CO₂ over a Pt/SnO₂ catalyst appears to be an approximately linear function of catalyst mass until 100% efficiency is achieved. (See Figure 1)

(3) The conversion efficiency per unit mass of Pt/SnO₂ has been approximately doubled (or the catalyst mass halved) by pretreating the catalyst with flowing 1% CO in He for one hour at 225°C relative to pretreatment for the same time and temperature with He alone. The conversion efficiency per unit mass of Pt/SnO₂ has been more than doubled (or the mass more than halved) by pretreating the catalyst with flowing He at 225°C for twenty hours relative to pretreatment with He at the same temperature for only one hour. Tests are scheduled to determine the optimum pretreatment time and temperature to achieve maximum catalyst efficiency. Also to be investigated is whether combination of extended He pretreatment with CO pretreatment will further increase catalyst efficiency.

(4) The catalytic efficiency of 2% Pt/SnO₂ at 100°C has been found to be nearly twice that of 1% Pt/SnO₂ of equal sample mass and surface area. The optimum loading of noble metal to SnO₂ will be determined in future tests.

(5) Initial tests comparing 2% Pt/SnO₂ with 2% Pd/SnO₂ and 1% Pt + 1% Pd/SnO₂ have been performed at 75°C. More than twice the conversion efficiency was achieved with 2% Pt/SnO₂ than was achieved with 2% Pd/SnO₂. A slightly higher conversion efficiency was achieved with 1% Pt + 1% Pd/SnO₂ than was achieved with 2% Pt/SnO₂. Comparison of various catalyst materials will continue including both comparison of Pt/SnO₂ with other catalysts and comparison of Pt/SnO₂ prepared at this laboratory and by Prof. Gar Hoflund at the University of Florida with the commercially available products used in our studies to date.

Rare-Isotope Gases

(1) Exposure of common-isotope Pt/Sn¹⁶O₂ to 1% C¹⁸O and .5% ¹⁸O₂ at 100°C yields about 85%-90% C¹⁸O₂ and 10%-15% of the mixed-isotope species, C¹⁶O¹⁸O. This result tends to imply that two competing reactions occur when CO and O₂ are oxidized with a Pt/SnO₂ catalyst. The reaction which yields C¹⁸O₂ appears to involve reaction of C¹⁸O and ¹⁸O₂ on the catalyst surface but no reaction of these species with the surface. The reaction which yields C¹⁶O¹⁸O implies oxidation of C¹⁸O by ¹⁶O atoms in the surface lattice and then, presumably, reoxidation of the surface by ¹⁸O₂. Further isotopic studies will be performed to verify the occurrence of two competing reactions and to determine their mechanisms in detail.

(2) A technique has been developed to prevent formation of the mixed isotope species C¹⁶O¹⁸O when C¹⁸O and ¹⁸O₂ are recombined using a Pt/Sn¹⁶O₂ catalyst (as in the preceding item). The technique involves reducing the catalyst surface with a measured quantity of H₂ to remove all reactive ¹⁶O atoms and then reoxidizing the surface with ¹⁸O₂. The net effect is to replace all reactive ¹⁶O atoms on the catalyst surface with ¹⁸O atoms so that any exchange of oxygen atoms between the gaseous species and the catalyst surface does not result in isotopic scrambling of the gases. This technique (for which a Patent Application has been filed) has been validated in a 30-hour test.

Laser Studies

The Lumonics Model TEA-820 laser has been operated closed-cycle with a catalyst bed of 150 g of 2% Pt/SnO₂ at 100°C. The laser achieved 96.5% (± 2.5%) of steady-state open-cycle power for 28 hours (1 x 10⁶ pulses at 10 pulses/second). (See Figure 2) A test of 10⁷ pulses at a catalyst temperature <100°C is planned for 1987.

CONCLUDING REMARKS

Pt/SnO₂ has been shown to be an effective CO - O₂ recombination catalyst at steady-state temperatures achieved by the gas mixture in pulsed CO₂ lasers. Its catalytic efficiency can be enhanced by suitable pretreatment techniques and optimum metal loading. Even though the substrate SnO₂ contains predominantly common-isotope oxygen, it appears that reduction of the catalyst surface with H₂ and reoxidation with ¹⁸O₂ renders the catalyst compatible with rare-isotope C¹⁸O₂ and its rare-isotope dissociation products. A systematic research project, described in this report, is in progress at NASA-LaRC to further evaluate and enhance the catalytic properties of Pt/SnO₂ and other catalysts for use in long-life, closed-cycle CO₂ lasers.

REFERENCES

1. Bond, Geoffrey C.; Moloy, Leslie R.; and Fuller, Martin J.: Oxidation of Carbon Monoxide over Palladium-Tin (VI) Oxide Catalyst: An Example of Spillover Catalysis. *Journal of the Chem. Soc. Chem Comm.*, 1975, pp. 796-797.
2. Brown, K. G.; Sidney, B. D.; Schryer, D. R.; Upchurch, B. T.; Miller, I. M.; Wood, G. M.; Hess, R. V.; Batten, C.; Burney, L. G.; Paulin, P. A.; Hoyt, R.; and Schryer, J.: Catalytic Recombination of Dissociation Products with Pt/SnO₂ for Rare and Common Isotope Long-Life, Closed-Cycle CO₂ Lasers. *Laser Radar Technology and Applications, Proceedings of SPIE, Vol. 663, 1986*, pp. 136-144.
3. Rogowski, R. S.; Miller, I. M.; Wood, G.; Schryer, D. R.; Hess, R. V.; and Upchurch, B. T.: Evaluation of Catalyst for Closed Cycle Operation of High Energy Pulsed CO₂ Lasers. *Coherent Infrared Radar Systems and Applications II, Proceedings of SPIE, Vol. 415, 1983*, pp. 112-117.

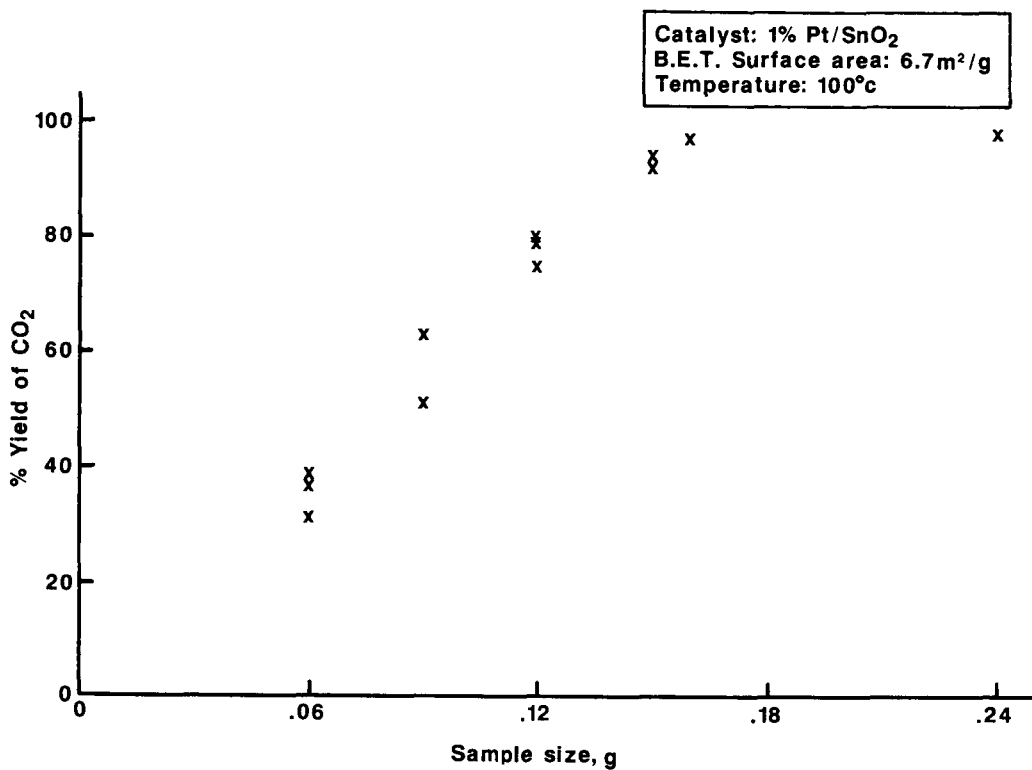


Figure 1. Conversion efficiency of catalyst versus sample weight.

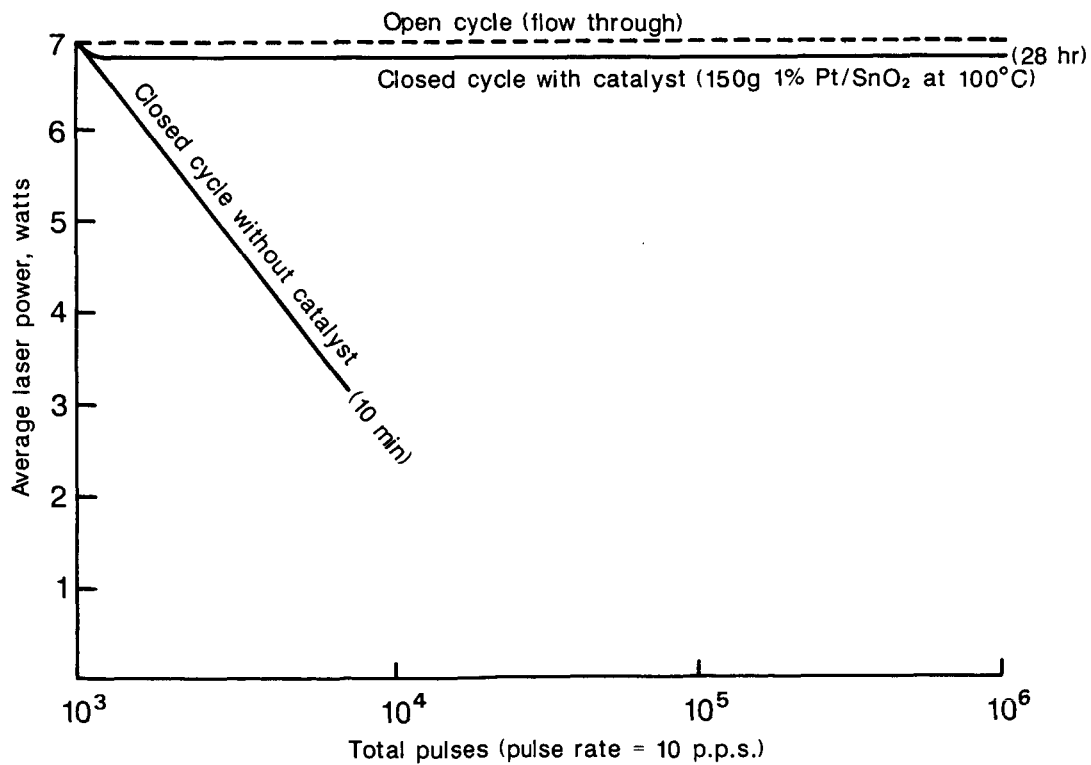


Figure 2. Performance of pulsed CO₂ layer with and without recombination catalyst.