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RARE-ISOTOPE AND KINETIC STUDIES OF Pt/SnO_2 CATALYSTS

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ABSTRACT

Closed-cycle pulsed CO_2 laser operation requires the use of an efficient CO-O_2 recombination catalyst for these dissociation products which otherwise would degrade the laser operation. The catalyst must not only operate at low temperatures but also must operate efficiently for long periods. In the case of the Laser Atmospheric Wind Sounder (LAWS) laser, an operational lifetime of 3 years is required. Additionally, in order to minimize atmospheric absorption and enhance aerosol scatter of laser radiation, the LAWS system will operate at 9.1 micrometers with an oxygen-18 isotope CO_2 lasing medium. Consequently, the catalyst must not only operate at low temperatures but must also preserve the isotopic integrity of the rare-isotope composition in the recombination mode.

Several years ago an investigation of commercially available and newly synthesized recombination catalysts for use in closed-cycle pulsed common and rare-isotope CO_2 lasers was implemented at the NASA Langley Research Center. Since that time, mechanistic efforts utilizing both common and rare oxygen isotopes have been implemented and continue. Rare-isotope studies utilizing commercially available platinum-tin oxide catalyst have demonstrated that the catalyst contributes oxygen-16 to the product carbon dioxide thus rendering it unusable for rare-isotope applications. A technique has been developed for modification of the surface of the common-isotope catalyst to render it usable. In this paper we report on results of kinetic and isotope label studies using plug flow, recycle plug flow, and closed internal recycle plug flow reactor configuration modes.

INTRODUCTION

A problem affecting the use of pulsed CO_2 lasers for applications involving atmospheric transmission is the attenuation of the intensity of the laser output due to absorption by atmospheric CO_2 which is present at about 330 ppm concentration. As this is predominantly the common isotope, $^{12}C^{16}O_2$, the use of a rare-isotope of CO_2 would enable the laser to emit at frequencies which would not be readily absorbed by the atmosphere.

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Among the available rare-isotope CO_2 compounds, $^{12}C^{18}O_2$ is the least expensive. Furthermore, in addition to providing enhanced atmospheric transmission, it has the added advantage of enhanced aerosol scattering due to its comparatively short wavelength of 9.1 micrometers which may be further enhanced by surface interactions with some aerosol species (ref. 3). Frequency-envelopes or "windows" which are favorable for atmospheric transmission are presented for various CO_2 isotopes in references 1 and 2.

A second problem associated with the operation of pulsed CO_2 lasers is that the electrical discharge normally used to excite such lasers inevitably decomposes some of the CO_2 to CO and O_2. This decomposition is harmful to long-life laser operation both because of the loss of CO_2 and because of the buildup of O_2. The loss of CO_2 results in a corresponding gradual loss of laser power; the buildup of even small concentrations (about 0.1 percent to 1.0 percent) of O_2 can cause rapid power loss and even complete laser failure. To obviate these problems with no wastage of costly rare-isotope gases the product CO and O_2 must be recombined with a suitable catalyst.

Rare-isotope $^{12}C^{18}O_2$ laser operation has been carried out at 300°C with a common-isotope Pt/Al_2O_3 catalyst at Los Alamos National Laboratory (ref. 4). In these studies, while the alumina was considered an inert substrate and not a participant in the catalytic recombination of $^{12}C^{18}O$ and $^{18}O_2$ to form CO_2, special attention and care were necessary to reduce the exchange or scrambling of the normal-isotope oxygen in $Al_2{}^{16}O_3$ with the $^{18}O_2$ and the $^{12}C^{18}O$ dissociation products of the laser medium. A platinum-tin oxide catalyst (Pt/SnO_2) has been shown to operate with a respectable recombinative efficiency at considerably lower temperatures than achieved in the Los Alamos study of platinum on alumina (ref. 5), but again the possibility of isotope exchange between a common-isotope catalyst and rare-isotope gases exists.

The primary goals of the present study were to measure isotopic exchange between the rare-isotope laser gases $^{12}C^{18}O_2$, $^{12}C^{18}O$, and $^{18}O_2$ and common-isotope Pt/SnO_2 catalyst material and to develop techniques to maximize isotopic integrity of the rare-isotope laser gases to maintain laser power at the desired frequency. A further goal was to utilize common and rare-isotope gases to determine mechanistic details of CO oxidation on the Pt/SnO_2 catalyst.

Experiments described in this paper demonstrate that, while some oxygen exchange between the gaseous oxygen and carbon monoxide species and the Pt/SnO_2 substrate does indeed occur even at low reaction temperatures, isotopic scrambling may be eliminated by an inexpensive isotope-exchange surface-labeling technique developed at Langley Research Center (ref. 6). Also, evidence is presented for the formation of a carbonate species on the catalyst when the conversion of CO and CO_2 occurs.

EXPERIMENTAL

The experimental apparatus for isotope measurements consisted of a test gas cylinder connected through a gas-drying chamber, flow controller, and a temperature-controlled catalyst reactor-chamber to a mass spectrometer gas-sampling inlet. The drying chamber was charged with anhydrous magnesium perchlorate. A Hastings mass-flow controller was placed upstream from the catalyst chamber. Excess gas flow not passing into the mass spectrometer was diverted through a Hastings mass-flow meter to the outside atmosphere. The mass spectrometer was a DuPont CEC Model 21-104 magnetic-sector unit. The catalyst reactor-chamber was built from components and maintained temperature control within 0.5°C. The catalyst of 1 percent Pt/SnO_2 was obtained from Englehard Industries. All catalyst charges were placed in the chamber enclosed within a 6.35 mm internal diameter by an approximately 40 cm long quartz tube. The catalyst was held in place by quartz wool plugs on each end of the charge. All rare-isotope gas compositions were obtained from Cambridge Isotope Laboratories with stated isotopic purities of better than 98 atomic-percent and were analyzed mass spectrometrically in our laboratory prior to use. All other gases were from Scott Specialty Gases. Chemisorption measurements were carried out using a Shimadzu thermal-conductivity-detector gas-chromatograph. All test-gas flow rates were 5 standard cubic centimeters per minute. All CO concentrations were 2 percent by volume in neon. All O_2 concentrations were 1 percent by volume in neon. All stoichiometric mixtures of CO and O_2 were 2 percent and 1 percent, respectively, with a 2 percent neon spike (as an internal standard) and the balance helium. Hydrogen was 7.5 percent by volume in helium.

For kinetic studies a recycle plug-flow reactor was operated in a recirculatins volume of approximately 200 ml with a recirculating flow rate of 200 ml/min. Samples were contained in a temperature-controlled quartz reactor tube as in the isotope measurement experiment. The recycle plug-flow reactor was evacuated and filled with test gas and operated in a closed recycle configuration for all kinetic studies. Internal recycle flow rates were nominally 200 ml/min for all kinetic experiments. Catalyst test specimens were 0.050 g in order to lower conversion rates enough to allow sufficient gas chromatographic analyses to follow the reaction through several half-lives. During tests to determine the kinetic order for oxygen in the catalytic reaction the CO concentration was nominally held constant at 50 percent. Initial oxygen concentrations were nominally 2 percent. Repetitive tests were carried over a temperature range of 0-125°C using a NASA prepared platinum oxide/silica gel catalyst (refs. 7, 8, 9).

RESULTS AND DISCUSSION

During carbon monixide chemisorption studies, it was found that some CO chemisorbed onto the Pt/SnO_2 catalyst at room temperature while other CO was oxidized and immediately evolved as CO_2 with the consequent reduction of the catalyst surface by removal of some oxide. A room-temperature CO chemisorption titration of a 1.0 gram sample of 1 percent Pt/SnO_2 catalyst was found to bind 42 microliters of CO in some form. Thermal desorption yielded 42 microliters of CO_2 as measured mass spectrometrically. To determine whether or not the CO was converted to CO_2 by the heat involved in the thermal desorption another sample of catalyst with chemisorbed CO was treated with gaseous HCl. It evolved CO_2 at room temperature, which indicated that oxidation of the CO had already occurred, possibly as a carbonate-like species. Subsequently, chemisorption of $^{12}C^{18}O$ upon a normal isotope Pt/SnO_2 catalyst substrate followed by thermal desorption of CO_2 yielded an approximately 4:4:1 ratio of $^{12}C^{16}O^{18}O$:$^{12}C^{18}O_2$:$^{12}C^{16}O_2$ as would be expected from a carbonate species, thus lending further support to the existence of such an intermediate species in the recombinative mechanism.

Since the primary goal of this research was to develop a catalytic $CO\text{-}O_2$ recombination system for the operation of a rare-isotope closed-cycle pulsed CO_2 laser system, isotope-exchange studies were subsequently carried out to thoroughly investigate the Pt/SnO_2 catalyst system with regard to isotopic interactions with all laser gas species as shown in table I.

As is noted in table I, $^{12}C^{18}O$ was found to readily extract some oxygen-16 from common-isotope Pt/SnO_2 at temperatures from room temperature upwards. Thus, the common-isotope catalyst cannot be used, in unmodified form, for regeneration of the dissociation products which would be encountered in a closed-cycle rare-isotope CO_2 laser. Rows 2, 3, and 4 in table I show that there was no exchange or scrambling reaction observed between $^{18}O_2$ (alone or in combination with $^{16}O_2$) and the $Pt/Sn^{16}O_2$ catalyst substrate until temperatures substantially greater than the expected operating temperatures of the laser catalyst bed were attained.

When a stoichiometric mixture of the oxygen-18 labeled carbon monoxide and oxygen was passed over the common-isotope Pt/SnO_2 catalyst at 100°C, 85 percent $^{12}C^{18}O_2$ and 15 percent $^{12}C^{16}O^{18}O$ were initially formed (row 5, table I). These yields gradually changed to 90 percent and 10 percent, respectively, after 8 hours or more of operation. Evidently, there are two reactive mechanisms occurring. The dominant reaction appears to involve CO and O_2 adsorbed on the catalyst surface, while the lesser reaction involves oxidation of CO by the SnO_2 surface. In addition, the SnO_2 surface then slowly become isotopically labeled with oxygen-18 via the interactive exchange mechanism. Complete surface labeling by this technique would, however, require an inordinately long time even if diffusion from the bulk were inoperative.

With the foregoing data in hand, it was decided to deliberately label the surface of the $Pt/Sn^{16}O_2$ catalyst with oxygen-18 by first removing all readily reactive oxygen-16 by hydrogen reduction followed by reoxidation of the reduced surface to $Sn^{18}O_2$. If all of the active normal-isotope oxygen at the surface could be exchanged in this way, then the catalyst would be suitable for use in a rare-isotope closed-cycle CO_2 laser if diffusion of the bulk matrix oxygen-16 to the surface is negligable.

The chemical reduction of the Pt/SnO_2 catalyst was accomplished by exposing it to a flowing stream of 7.5 percent H_2 in helium at 225°C. The active surface-oxygen removal was judged complete after the mass spectrometrically monitored $H_2{}^{16}O$ concentration in the stream had dropped to the instrument background level. The reduced substrate surface was then reoxidized at 225°C with a gas stream containing 1 percent $^{18}O_2$ until the $^{18}O_2$ concentration exiting the catalyst chamber had attained and remained at the 1 percent concentration level for at least 1 hour as measured on the mass spectrometer. The temperature was then reduced to ambient under neon flow. The preceding isotope-exchange labeling of the metal-oxide catalyst was accomplished in about 5 hours and is covered in a patent (ref. 6).

The 1 percent Pt/$1sn^{18}O_2$ surface-labeled catalyst was then evaluated under conditions listed in row 6 of table I and was found to maintain the isotopic integrity of the rare-isotope gas composition in a test of 17 days duration. The subsurface normal oxygen-16 isotope in the bulk of the catalyst material obviously does not diffuse to the surface at or below the test temperature of 100°C during the test duration.

Kinetic studies were undertaken for the Pt/tin oxide/silica gel catalyst using the recycle reactor in the internal recycle mode. The graphical results of these studies were consistent with a rate law showing first order oxygen dependency over the temperature range of 0-125°C. In earlier studies, we and others reported that the overall reaction took place with an overall first order rate law (refs. 10, 11). Activation energies over the above temperature interval are tabulated in table II for the CO oxidation reaction. The activation energy for the reaction was found to be 36 kJ/mol over the 0-75°C interval with an abrupt decrease to 17 kJ/mol over the 75-125°C interval. The former value is somewhat lower than that reported by Stark and Harris for unsupported platinum on tin oxide catalyst (ref. 10). The decrease in the activation energy at 75°C has mechanistic implications which have not thus far been explained. Furthermore, if the overall reaction is first order then the obvious conclusion is that the reaction must be zero order in CO. Preliminary studies indicate that such is indeed the case under excess oxygen conditions. However, under excess CO conditions the reaction seems to be inhibited, thus indicating otherwise. As is noted in table II, the activation energy for the stoichiometric condition does not show a change at 75°C as was observed in the excess CO experimental condition. Kinetic studies are continuing.

CONCLUDING REMARKS

Rare-isotope studies have demonstrated that when CO and O_2 are reacted on a Pt/SnO_2 catalyst the dominant reaction mechanism involves these adsorbed species and only a minor amount of oxidation of the CO by oxygen from the SnO_2 occurs. Furthermore, we have developed a simple, economical surface-labelling technique, validated in a 17-day test, to prevent isotopic scrambling from this minor reaction between rare-isotope CO and common-isotope Pt/SnO_2. Additionally, we have obtained supportive evidence for the formation of some carbonate-like intermediate species when CO is oxidized on Pt/SnO_2.

Results of kinetic studies on NASA prepared Pt/SnO_2/silica gel cataysts have demonstrated a first order dependence of O_2 for the CO oxidation reaction over the temperature range of 0-125°C with an abrupt decrease in activation energy at 75°C. Investigations are continuing with mechanistic and other studies for improving the performance of CO oxidation catalysts and to better predict a successful outcome for their application in long-life closed-cycle CO_2 lasers.

REFERENCES

1. Freed, C.; Ross, C.; and O'Donnell, R. C., J. Mol. Spec., 49, 439-453, (1974).
2. Freed, L. E.; Freed, C.; and O'Donnell, R. G., IEEE J. Quant. Elect., QE-18, 1229-1239, (1982).
3. Hess, R. V.; Brockman, P.; Schryer, D. R.; Miller, I. M.; Bair, C. H.; Sidney, B. D.; Wood, G. M.; Upchurch, B. T.; and Brown, K. G., NASA TM-86415, (1985).
4. Sorem, M. S. and Faulkner, A., Rev. Sci. Instrum., 52, 1193-1196, (1981).
5. Brown, K. G.; Sidney, B. D.; Schryer, D. R.; Upchurch, B. T.; Miller, I. M.; Wood, G. M.; Hess, R. V.; Burney, L. G.; Paulin, P. A.; Hoyt, R. F.; and Schryer, J., SPIE Proceedings, 663, 136-144, (1986).
6. Hess, R. V.; Upchurch, B. T.; Brown, K. G.; Miller, I, M.; Schryer, D. R.; Sidney, B. D.; Wood, G. M.; and Hoyt, R. F., Isotope Exchange in Oxide Containing Catalyst. U.S. Patent No. 4,839,330, June 13, 1989.
7. Upchurch, B. T.; Schryer, D. R.; Wood, G. M.; and Hess, R. V., SPIE Proceedings, 1062, (1989).
8. Upchurch, B. T.; Miller, I. M.; Brown, D. R.; Davis, P. P.; Schryer, D. R.; Brown, K. G.; and Van Norman, J. D., Catalyst for Carbon Monoxide Oxidation. U.S. Patent No. 4,912,082, March 27, 1990.
9. Upchurch, B. T.; Miller, I. M.; and Davis, P. P., Process for Making a Noble Metal on Tin Oxide Catalyst. U.S. Patent No. 4,855,274, August 8, 1989.
10. Stark, D. S., and Harris, M. R., J. Phys. E.: Sci. Instrum., 16, 492-496, (1983).
11. Miller, I. M.; Batten, C. E.; and Wood, G. M., NASA CP 2456, (1987).

TABLE I - OXYGEN ISOTOPE LABEL STUDIES

Reactants	Catalyst	T, °C	Product Yields
$C^{18}O$	$Pt/Sn^{16}O_2$	24-150	$C^{16}O^{18}O$
$^{18}O_2$	$Pt/Sn^{16}O_2$	25-225	No Reaction
$^{18}O_2 + {}^{16}O_2$	$Pt/Sn^{16}O_2$	25-225	No Reaction
$^{18}O_2 + {}^{16}O_2$	$Pt/Sn^{16}O_2$	> 350	$^{16}O^{18}O$
$C^{18}O + 1/2\,^{18}O_2$	$Pt/Sn^{16}O_2$	100	85-90% $C^{18}O_2$ 15-10% $C^{16}O^{18}O$
$C^{18}O + 1/2\,^{18}O_2$	$Pt/Sn^{18}O_2$	100	$C^{18}O_2$

TABLE II. O_2 ACTIVATION ENERGY VALUES FOR $Pt/SnO_2/SiO_2/H_2O$ CATALYST (CO EXCESS)

Run Number	E, kJ/mol	Temp Range, °C
184	36.1	0 - 35
185	36.8	0 - 35
174	36.9	33 - 57
175	35.7	35 - 57
176	28.6*	35 - 52
177	34.5	41 - 57
178	44.6*	35 - 62
179	35.2	35 - 73
181	16.5	75 - 100
182	15.7	75 - 125
183	17.8	75 - 126
This Work	E = 35.9 kJ/mol	0 - 73
This Work	E = 16.7 kJ/mol	75 - 125
Stark and Harris	E = 41.4 kJ/mol	21 - 60
This Work	E = 35.0 kJ/mol	35 - 100†

*Excluded Value

† Stoichiometric Gas Mix