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RARE ISOTOPE STUDIES INVOLVING CATALYTIC OXIDATION OF CO OVER PLATINUM-TIN OXIDE

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SUMMARY

In this report results of studies utilizing normal and rare oxygen isotopes in the catalytic oxidation of carbon monoxide over a platinum-tin oxide catalyst substrate are presented. Chemisorption of labeled carbon monoxide on the catalyst followed by thermal desorption yielded a carbon dioxide product with an oxygen-18 composition consistent with the formation of a carbonate-like intermediate in the chemisorption process. The efficacy of a method developed for the oxygen-18 labeling of the platinum-tin oxide catalyst surface for use in closed cycle pulsed rare isotope carbon dioxide lasers is demonstrated for the equivalent of 10^6 pulses at 10 pulses per second.

INTRODUCTION

A primary problem limiting the use of pulsed CO_2 lasers for applications involving atmospheric transmission is due to the attenuation of the intensity of the laser frequency via absorption by the atmospheric carbon dioxide present at the level of about 330 ppm concentration. As this is almost exclusively the common isotope $^{12}C^{16}O_2$, the use of the rare isotope CO_2, where the carbon and the oxygen are in the forms of carbon-12 and oxygen-18, would enable the laser to pulse at frequencies which would not be absorbed by the atmosphere. These frequency envelopes or "windows" have been determined (refs. 1 and 2). Among the available rare isotope CO_2 compounds, $C^{18}O_2$ not only contains the cheaper of the two oxygen rare isotopes, but it also provides a laser frequency at 9.1 micrometers with improved atmospheric transmission along with the added potential for an enhanced aerosol scattering coefficient (ref. 3). Other lasing frequencies are available for other possible applications.

Rare isotope $C^{18}O_2$ laser operation has been carried out at 300°C with a 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 $C^{18}O$ 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 $C^{18}O$ dissociation products of the laser medium. A platinum-tin oxide catalyst has been shown to operate with a respectable recombinative efficiency at considerably lower temperatures than the Los Alamos study of platinum on alumina (ref. 5).

The primary goals of this effort were to measure isotopic exchange between rare-isotope laser gases (CO_2, CO, O_2) and common isotope Pt/SnO_2 catalyst material and to develop techniques to maximize isotopic integrity of rare isotope laser gases to maintain laser power at the desired frequency. A further goal was to utilize these rare isotope gases to determine mechanistic details of CO oxidation on the Pt/SnO_2 catalyst.

Experiments described in this paper demonstrate that, while oxygen exchange between the gaseous oxygen and carbon monoxide species and the Pt/SnO_2 substrate does indeed occur at low reaction temperatures, the isotopic scrambling may be eliminated by an inexpensive isotope exchange surface labeling technique developed at Langley Research Center (ref. 6).

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 $0.5^{o}C$. The catalyst of $1\%Pt/SnO_2$ was obtained from Englehard Industries. All catalyst charges were placed in the chamber enclosed within a 6.35 mm internal diameter by approximately 40 cm 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 purities of better than 98 atom 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 and the balance helium. Hydrogen was 7.5 percent by volume in helium.

RESULTS AND DISCUSSION

During carbon monoxide chemisorption studies, it was found that some CO chemisorbed onto the Pt/SnO_2 catalyst at room temperature while some CO simultaneously oxidized and evolved as CO_2 with the subsequent reduction of the catalyst surface by removal of some oxide. A room temperature CO chemisorption titration of a 1.0 gram sample of 1% Pt/SnO_2 catalyst was found to bind 42 microliters of CO. Thermal desorption yielded 42 microliters of CO_2 as measured mass spectrometrically. Another sample after CO chemisorption followed by chemical displacement by gaseous hydrogen chloride evolved CO_2 as detected with the mass spectrometer. Subsequently, chemisorption of $C^{18}O$ upon a normal isotope Pt/SnO_2 catalyst substrate followed by thermal desorption of CO_2 yielded an approximately 4:4:1 ratio of $C^{16}O_2:C^{16}O^{18}O:C^{18}O_2$ as would be expected from a carbonate species thus lending further support for the existence of such an intermediate species in the recombinative redox mechanism.

Since our primary goal was to develop a catalytic regeneration 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 1.

As is noted in table I, $C^{18}O$ was found to readily extract oxygen-16 from the unlabeled Pt/SnO_2 at temperatures from room temperature upwards. Thus, the isotopically unlabeled catalyst cannot be used 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/SnO_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 normal isotope Pt/SnO_2 catalyst at 100°C, 85 percent and 15 percent $C^{18}O_2$ and $C^{16}O^{18}O$, respectively, were initially formed (row 5, table I). These yields gradually changed to 90 percent and 10 percent after 8 hours or more of operation. Evidently, there are two possible recombinative mechanisms occurring, one of which is perhaps at the surface, and one which is interactive with the SnO_2 surface. In addition, the SnO_2 surface must slowly become isotopically labeled with oxygen-18 via the interactive exchange mechanism. Complete surface labeling by this technique would require an inordinately long time for sufficient isotope labeling to be attained even if diffusion from the bulk were inoperative.

With the foregoing data in hand, it was decided that an attempt would be made to label the surface of the $Pt/Sn^{16}O_2$ catalyst with oxygen-18 by first chemically reducing the SnO_2 surface to elemental tin followed by reoxidation of the tin surface to $Sn^{18}O_2$ with $^{18}O_2$. Should all of the active normal-isotope oxygen at the surface 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 does not occur.

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_2O 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% $^{18}O_2$ until the $^{18}O_2$ concentration exiting the catalyst chamber had attained and remained at the 1 percent concentration level for at least one 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 partly the basis for our patent application (ref. 6).

The 1% $Pt/Sn^{18}O_2$ 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 for a period of 30 hours of operation before shutting down the reactor voluntarily. 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. While the efficacy of the surface labeled catalyst has been demonstrated during continuous operation for 30 hours at the elevated temperature, as well as other periods at lower temperatures, longer term evaluative tests are needed and will be performed during 1987.

CONCLUDING REMARKS

To summarize our accomplishments and ongoing efforts involving oxygen isotope labels we have demonstrated supportive evidence for the existence of a carbonate-like intermediate species involving the catalyst and chemisorbed CO for the redox mechanism. We have discovered an economical method for preparing a catalyst for use in a closed cycle rare isotope pulsed carbon dioxide laser and have demonstrated its efficacy in our surrogate test facility over test periods which would be comparable with 10^6 pulses at 10 pps. However, studies of longer duration are needed and the ultimate test should, of course, be carried out in a rare isotope pulsed carbon dioxide laser. We are also currently considering developing our own normal and rare isotope Pt/SnO_2 catalyst coatings on high surface-area-to-weight ratio inert support spheres.

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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	$C^{18}O_2$