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Comparison of the Performance Characteristics of Pt/SnO$_x$ and Au/MnO$_x$ Catalysts for Low-Temperature CO Oxidation

STEVEN D. GARDNER,* GAR B. HOFLUND,* BILLY T. UPCHURCH,†
DAVID R. SCHRYER,† ERIK J. KIELIN,†,[1] AND JACQUELIN SCHRYER†

*Department of Chemical Engineering, University of Florida, Gainesville, Florida 32611; and †NASA Langley Research Center, Hampton, Virginia 23665

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Platinized tin oxide (Pt/SnO$_x$) and gold supported on manganese oxide (Au/MnO$_x$) catalysts have been shown to be good CO oxidation catalysts at low temperatures (30–100°C). The performance of these catalysts has been compared by reacting mixtures of CO and O$_2$ and He under similar conditions. The Au/MnO$_x$ catalyst is superior to Pt/SnO$_x$ catalysts with regard to both activity and decay characteristics under the conditions examined. As expected, Au/MnO$_x$ catalysts exhibit greater activity as the reaction gas mixture becomes more oxidizing.

INTRODUCTION

Long used as a research tool to study heterogeneous catalysis, the catalytic oxidation of CO is being utilized in an increasing number of practical applications. CO oxidation catalysts are often an integral component of pollution control devices designed to reduce industrial and automotive emissions. Air purification devices (for respiratory protection) (*1–4*) and CO gas sensors (*4–9*) commonly employ CO oxidation catalysis. Soon the catalytic oxidation of CO will be utilized in orbiting, closed-cycle CO$_2$ lasers (*10–14*) used for weather monitoring or in other remote sensing applications. Sealed CO$_2$ lasers must incorporate a CO oxidation catalyst to recombine stoichiometric concentrations of CO and O$_2$ which are produced during the lasing process because both CO$_2$ loss and O$_2$ build-up can degrade the performance of the laser.

Therefore, there is a growing demand for CO oxidation catalysts which are more effective and versatile. Research directed toward the development of long-life, sealed CO$_2$ lasers (*13, 14*) has produced several new materials which actively catalyze CO oxidation near ambient temperatures. In 1983 Stark and co-workers (*10, 11*) identified platinized tin oxide (Pt/SnO$_x$) as a good catalyst for this application. After screening numerous catalysts Gardner and co-workers (*15*) have suggested that gold supported on manganese oxide (Au/MnO$_x$) performs even better than Pt/SnO$_x$ with respect to activity and decay characteristics for oxidation of CO under stoichiometric conditions. The purpose of this study is to compare the long-term CO oxidation performance of several Pt/SnO$_x$ and Au/MnO$_x$ catalysts and evaluate their potential utility in the applications mentioned above.

EXPERIMENTAL

Details regarding sample preparation and the CO oxidation reactor have been described previously (*15–17*). The samples prepared for this study include 19.5 wt% Pt/SnO$_x$ (15.8 at.% Pt based on Pt and Sn content), 14.5 wt% Pt/SnO$_x$/SiO$_2$ (11.4 at.% Pt based on Pt and Sn content) and 10 at.% Au/MnO$_x$ (based on Au and Mn content). The SnO$_x$ support was prepared by dissolving Sn powder in nitric acid and heating to

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[1] Formerly David R. Brown.

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dryness at 150°C. For the sample containing SiO_2, this was done in the presence of deaerated SiO_2 particles. Pt deposition was accomplished by reducing tetraaminoplatinum (II) hydroxide with formic acid in the presence of the deaerated SnO_x and SnO_x/SiO_2 supports. The resulting slurry was dried in air at 150°C. The Au/MnO_x sample was prepared via coprecipitation from aqueous tetrachloroauric acid, manganese (II) nitrate, and sodium carbonate. The precipitate was washed with hot water, dried in air at 110°C, and calcined at 400°C for 4 h. Since the final Mn oxidation state is unknown at this point, the Au/MnO_x composition is based on the molar ratio of Au : Mn in the precursor solutions. A 2 wt% Pt/SnO_x (1.6 at.% Pt based on Pt and Sn content) catalyst was obtained from Engelhard Industries. The experiments were conducted at 35 or 55°C using 50–150 mg of catalyst in powdered form. Unless noted otherwise, the reactor feed contained 1 vol% CO, 0.5 vol% O_2, and 2 vol% Ne (for GC (gas chromatograph) calibration) in helium flowing at 10 sccm and 1 atm of total pressure. No CO_2 was present in the reactor feed.

The experimental procedures varied depending upon whether the catalysts were pretreated prior to the onset of reaction. The unpretreated samples were exposed to 10 sccm of helium for 1 h as the reactor temperature stabilized. Pretreated samples were subjected to the following sequence of events: (1) heating to the desired pretreatment temperature in 10 sccm of helium for 1 h, (2) exposure to the pretreatment gas mixture (10 sccm) for 2 h, and (3) cooling to the reaction temperature in 10 sccm of helium for 1 h. In each case the helium flow was subsequently replaced with the reaction gas mixture and product sampling was initiated. At predetermined time intervals an automated sampling valve directed a 1-mm portion of the reaction products to a gas chromatograph for quantitative analysis of moles of CO_2 formed (referenced to 0°C and 1 atm) per second per gram of catalyst (moles CO_2/s/g). The results were plotted versus time to yield the CO oxidation activity curves for each catalyst.

RESULTS AND DISCUSSION

Air purification and CO detection commonly involve the oxidation of small concentrations of CO in air (excess oxygen) which may contain substantial amounts of water and/or other pollutants. Operating temperatures range from nearly ambient for respiratory aids to above 150°C for CO gas sensors (*6*). CO oxidation in CO_2 lasers is characterized by small, stoichiometric concentrations of CO and O_2 with a large partial pressure of CO_2 at temperatures near 50°C. Such diverse environments can have a dramatic effect on the performance of low-temperature CO oxidation catalysts. For example, an Au/Fe_2O_3 catalyst has recently been shown to exhibit excellent CO oxidation activity in air (both wet and dry) near ambient temperature (*18, 19*). However, experiments by Gardner and co-workers (*15*) indicate that its performance is unacceptable in a CO_2 laser environment. Apparently, CO oxidation proceeds much more rapidly on these supported catalysts when excess oxygen is available.

The CO oxidation activities of the 10% Au/MnO_x, 19.5% Pt/SnO_x, and 2% Pt/SnO_x samples are shown in Fig. 1 as a function of time for unpretreated surfaces (open circles, squares, and triangles) and surfaces pretreated with a 5 vol% CO/He mixture at 50°C (solid circles, squares, and triangles). The unpretreated Pt/SnO_x catalysts exhibit similar overall reaction profiles which are maximum at the onset of reaction but readily decay with time. The data are consistent with results of previous experiments which indicate that maximum Pt/SnO_x activity occurs near 15 to 20 wt% Pt under similar reaction conditions (*17*). The unpretreated Au/MnO_x catalyst exhibits remarkable CO oxidation activity which is approximately an order of magnitude greater than that of the 19.5% Pt/SnO_x sample after 6000 min of reaction. The fact that Au/MnO_x exhibits

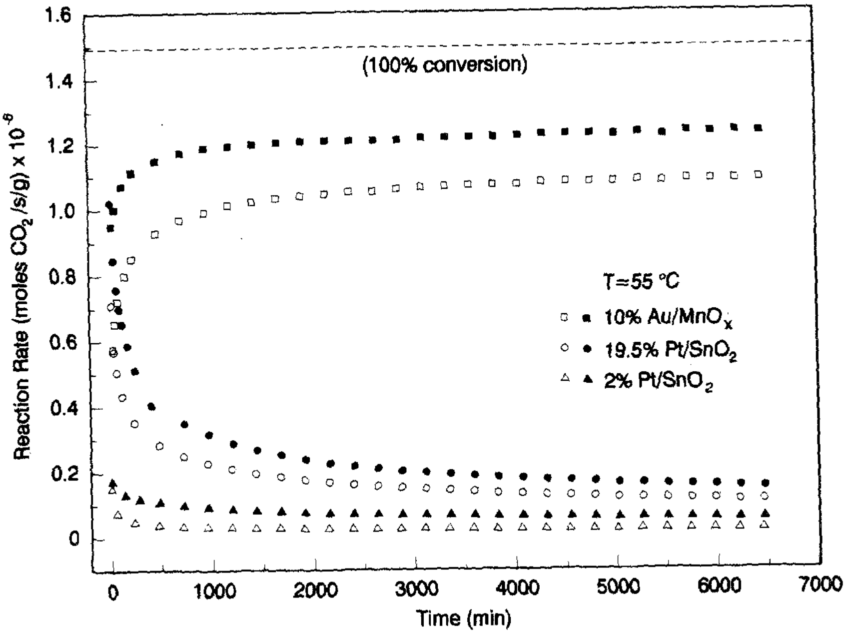

FIG. 1. The CO oxidation activity of 10 at.% Au/MnO$_x$, 19.5 wt% Pt/SnO$_x$, and 2 wt% Pt/SnO$_x$ at 55°C without pretreatment (open symbols) and pretreatment in 5 vol% CO/He at 50°C (solid symbols).

superior CO oxidation activity without the need for pretreatment is critical in many applications including respiratory protection.

It has previously been shown that CO pretreatments enhance the activity of Pt/SnO$_x$ surfaces toward low-temperature CO oxidation (*20*). This fact is clearly illustrated by the data in Fig. 1. Furthermore, a CO pretreatment at 50°C significantly enhances the activity of Au/MnO$_x$ as well, and the effect is most dramatic for Au/MnO$_x$, where the CO conversion increases by approximately 10%. It is interesting to note that while the activity of each sample is enhanced as a result of the CO pretreatment, the overall character of the activity profiles remains unaffected.

As shown by the data in Fig. 2, increasing the CO pretreatment temperature from 50°C (open) to 125°C (solid) further enhances the long-term activity of these catalysts. The activity profile of the 19.5% Pt/SnO$_x$ catalyst is affected most by the increased pretreatment temperature. However, characteristics of an induction phenomenon (initial steep decline in activity followed by an increase and then a slow decline) soon become apparent in the activity profiles of both 2% Pt/SnO$_x$ and 19.5% Pt/SnO$_x$. Although similar induction phenomena have been observed in a previous study of Pt/SnO$_x$ catalysts (*20*), identical CO pretreatments at 125°C do not result in any significant induction period during reaction at 75 or 85°C. The fact that an induction period ensues during reaction at 55°C is consistent with the hypothesis that the induction results from temporary surface dehydration caused by the reductive pretreatment (*20*) because replenishment of catalyst surface moisture via bulk diffusion would be less facile at 55°C relative to 75 or 85°C. Although the induction period exhibited by 19.5% Pt/SnO$_x$ is the least severe, it spans a much greater time period (approximately 5300 min) relative to the 2% Pt/SnO$_x$ sample. Nevertheless, beyond the induction period the CO oxidation activity of both Pt/SnO$_x$ samples steadily

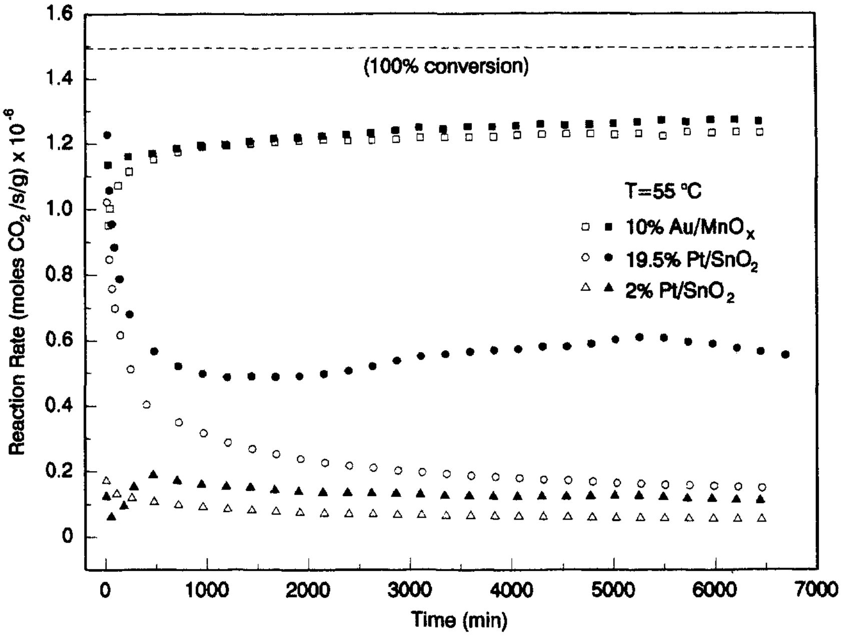

FIG. 2. The CO oxidation activity of 10 at.% Au/MnO$_x$, 19.5 wt% Pt/SnO$_x$, and 2 wt% Pt/SnO$_x$ at 55°C after pretreatment in 5 vol% CO/He at 50°C (open symbols) and 125°C (solid symbols).

decays with time. On the other hand, subsequent to CO pretreatment at 125°C, the Au/MnO$_x$ catalyst continues to exhibit its characteristic reaction profile with negligible activity decay. While reductive pretreatments are beneficial with regard to the low-temperature CO oxidation activity of Au/MnO$_x$, they have been shown to be detrimental to the CO oxidation performance of Pt/MnO$_x$ under similar conditions (*15*).

In addition to reductive pretreatments, pretreatments in an oxidizing atmosphere were also investigated. As shown in Fig. 3, a pretreatment in 5 vol% O$_2$/He at 50°C (solid) decreases the CO oxidation activity of all the samples relative to no pretreatment (open). The effects of oxygen pretreatment on Au/MnO$_x$ are the most significant, but the shape of the overall activity profile is retained and activity decay remains negligible. The results for 2% Pt/SnO$_x$ are once again consistent with a previous study which was performed using considerably different experimental conditions (*20*). However, the relative degree of activity decline is much less under the conditions of this study. The effects of the oxygen pretreatment are noticeable only during the first 500 min of reaction after which the unpretreated and pretreated curves essentially coincide. Similar behavior is also evident for 19.5% Pt/SnO$_x$, where the majority of the activity decrease occurs during the initial stages of reaction. After running the reaction for 6500 min, the effect of the oxygen pretreatment is much less apparent.

Although the performance criteria of low-temperature CO oxidation catalysts may vary considerably for different applications, there is a common need for catalysts which maintain high activity over extended time periods without experiencing a significant decay in performance. The operational lifetime of catalysts utilized in respiratory aids is of course a critical factor to be considered. Catalysts for CO$_2$ lasers are expected to perform well for at least 3 years (*13, 14*). In CO gas sensor applications, low-temperature operation is desirable without the need for periodic flash heating in order to restore cat-

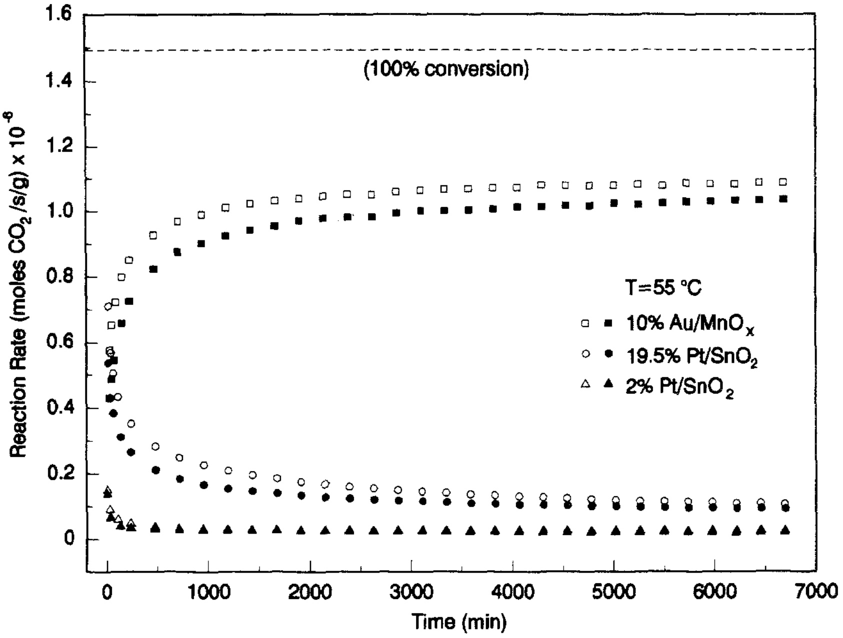

FIG. 3. The CO oxidation activity of 10 at.% Au/MnO_x, 19.5 wt% Pt/SnO_x, and 2 wt% Pt/SnO_x at 55°C without pretreatment (open symbols) and pretreatment in 5 vol% O_2/He at 50°C (solid symbols).

alyst activity (*6*). Considering these important performance criteria, the data in Fig. 4 indicate that Au/MnO_x is a promising candidate for all of these applications. Even after 70 days near ambient temperature, Au/MnO_x continues to exhibit excellent CO oxidation performance with negligible activity decay. The optimized 14.5% Pt/SnO_x/SiO_2 catalyst does not perform nearly so well. It experiences a significant induction period which lasts approximately 1 week followed by considerable activity decay which precludes its use in long-term applications.

Further understanding of the performance characteristics of the Au/MnO_x catalyst has been gained by varying the CO/O_2 concentration ratio in the reaction gas mixture. As shown by the data in Fig. 5, the composition of the test gas has a marked effect on the activity profile of Au/MnO_x. Overall performance is significantly enhanced in an oxygen-rich atmosphere whereas activity in a CO-rich reaction mixture is diminished considerably. Similar results have been found for Pt/SnO_x catalysts as well (*17*). The data in Fig. 5 are important with regard to understanding the variations in catalyst performance with respect to compositional variations and indicate that excess CO should be avoided if possible. However, in the majority of low-temperature CO oxidation applications oxygen is present in at least stoichiometric concentrations relative to CO so Au/MnO_x should perform well in many applications. The mechanism responsible for the activity decay in a CO-rich reaction mixture is not fully understood at this time. During CO pretreatment of these catalysts, GC analysis suggests that the surfaces are progressively reduced with corresponding CO_2 formation. It is possible that excess CO in the reaction gas acts to further reduce the surface resulting in the subsequent loss of CO oxidation activity.

Under similar experimental conditions the performance data obtained in this study compare favorably with activity data for other low-temperature CO oxidation catalysts. All of the Pt/SnO_x catalysts prepared for this study have previously been shown

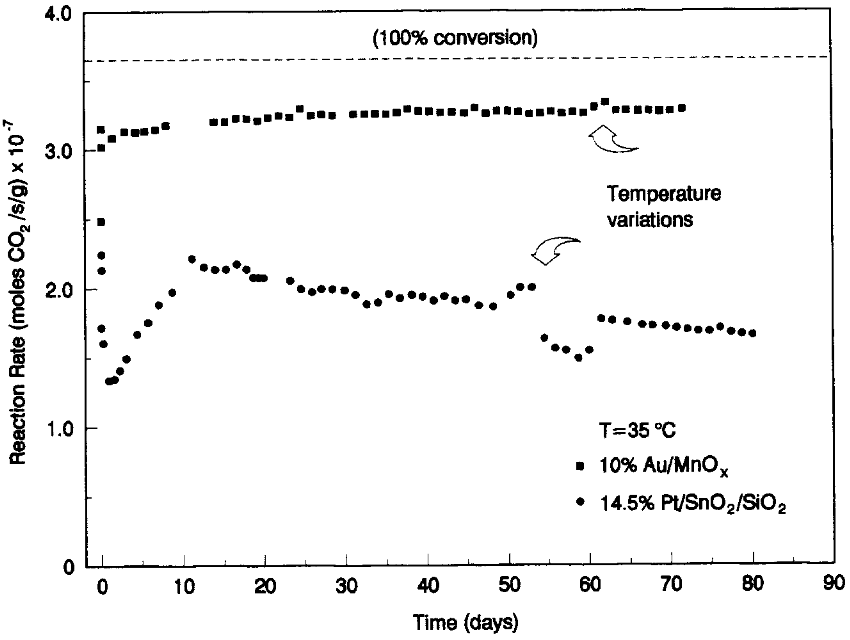

FIG. 4. The CO oxidation activity of 10 at.% Au/MnO$_x$ (unpretreated) and 14.5 wt% Pt/SnO$_x$/SiO$_2$ (pretreated in 5 vol% CO/He at 125°C) at 35°C.

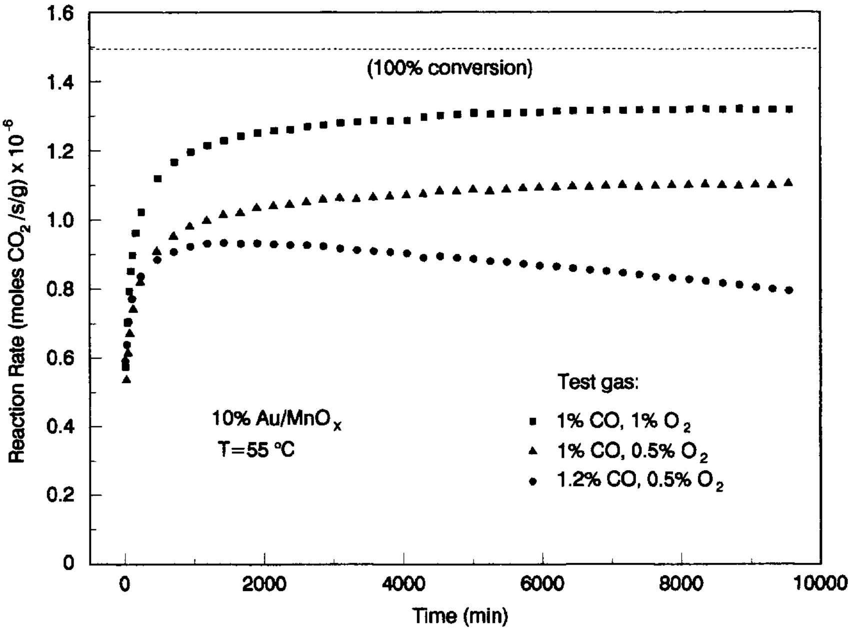

FIG. 5. The CO oxidation activity of 10 at.% Au/MnO$_x$ (unpretreated) and 55°C as a function of test gas composition (balance He).

to be superior to proprietary catalysts manufactured by General Motors and Teledyne (*17*). Furthermore, the activity of 19.5 wt% Pt/SnO_x and 14.5 wt% Pt/SiO_x/SiO_2 appears to be comparable to numerous other Pt/SnO_x, Pd/SnO_x, and Pt–Pd/SnO_x catalysts for similar reaction times (*17, 21, 22*). However, long-term activity decay continues to be a problem for all of the SnO_x-based materials. Consequently, Au/MnO_x appears to be the optimum catalyst under the test conditions used in this study.

REFERENCES

1. R. B. Jagow, R. A. Lamparter, T. Katan, and C. D. Ray, *Am. Soc. Mech. Eng. Pap.* **77-ENAs-28** (1977).

2. M. F. Collins, *in* "Closed-Cycle, Frequency-Stable CO_2 Laser Technology" (C. E. Batten, I. M. Miller, G. M. Wood, Jr., and D. V. Willetts, Eds.), pp. 153–163. NASA Conference Publication No. 2456, 1986.

3. E. Noordally and J. R. Richmond, *in* "Low-Temperature CO Oxidation Catalysts for Long-Life CO_2 Lasers" (D. R. Schryer and G. B. Hoflund, Eds.), pp. 387–402. NASA Conference Publication No. 3076, 1989.

4. E. J.Poziomek, *in* "Low-Temperature CO Oxidation Catalysts for Long-Life CO2 Lasers" (D. R. Schryer and G. B. Hoflund, Eds.), pp. 403–409. NASA Conference Publication No. 3076, 1989.

5. T. Kobayashi, M. Haruta, H. Sano, and M. Nakane, *in* "Sensors and Actuators," Soc. Auto. Engineers, Vol. 13, p. 339, 1988.

6. T. Kobayashi, M. Haruta, and H. Sano, *Chem. Express* **4**(4), 217 (1989).

7. C. Xu, J. Tamaki, N. Miura, and N. Yamazoe, *Chem. Lett.*, *441* (1990).

8. P. G. Harrison and M. J. Willett, *Nature* **332,** 337 (1988).

9. T. B. Fryberger and S. Semancik, *in* "Low-Temperature CO Oxidation Catalysts for Long-Life CO_2 Lasers" (D. R. Schryer and G. B. Hoflund, Eds.), pp. 277–289. NASA Conference Publication No. 3076, 1989.

10. D. S. Stark, A. Crocker, and G. J. Steward, *J. Phys. E: Sci. Instrum.* **16,** 158 (1983).

11. D. S. Stark and M. R. Harris, *J. Phys. E: Sci Instrum.* **16,** 492 (1983).

12. D. S. Stark and M. R. Harris, *J. Phys. E: Sci. Instrum.* **21,** 715 (1988).

13. C. E. Batten, I. M. Miller, G. M. Wood, Jr., and D. V. Willetts, Eds., "Closed-Cycle, Frequency-Stable CO_2 Laser Technology," Proceedings of a workshop held at NASA Langley Research Center, Hampton, VA, NASA Conference Publication No. 2456, 1986.

14. D. R. Schryer and G. B. Hoflund, Eds., "Low-Temperature CO Oxidation Catalysts for Long-Life CO_2 Lasers," Proceedings of a workshop held at NASA Langley Research Center, Hampton, VA, NASA Conference Publication No. 3076, 1989.

15. S. D. Gardner, G. B. Hoflund, D. R. Schryer, J. Schryer, B. T. Upchurch, and D. R. Brown, *Langmuir,* in press.

16. C. E. Batten, I. M. Miller, P. A. Paulin, and J. Schryer, *in* "Closed-Cycle, Frequency-Stable CO_2 Laser Technology" (C. E. Batten, I. M. Miller, G. M. Wood, Jr., and D. V. Willetts, Eds.), pp. 199–209. NASA Conference Publication No. 2456, 1986.

17. B. T. Upchurch, E. J. Kielin, and I. M. Miller, *in* "Low-Temperature CO Oxidation Catalysts for Long-Life CO_2 Lasers" (D. R. Schryer and G. B. Hoflund, Eds.), pp. 69–90. NASA Conference Publication No. 3076, 1989.

18. M. Haruta, T. Kobayashi, H. Sano, and N. Yamada, *Chem. Lett.,* 405 (1987).

19. M. Haruta, N. Yamada, T. Kobayashi, and S. Iijima, *J. Catal.* **115,** 301 (1989).

20. D. R. Schryer, B. T. Upchurch, J. D. Van Norman, K. G. Brown, and J. Schryer, *J. Catal.* **122,** 193 (1990).

21. C. F. Sampson and N. Jorgensen, *in* "Low-Temperature CO Oxidation Catalysts for Long-Life CO_2 Lasers" (D. R. Schryer and G. B. Hoflund, Eds.), pp. 57–68. NASA Conference Publication No. 3076, 1989.

22. "Catalysts for Long Range CO_2 Laser System," progress report from catalyst development program, GEC Avionics, UK Atomic Energy Authority Harwell and UOP Ltd., Royal Signals and Radar Establishment, Contract No. SDIO 84-87-C-0046, 1988.