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Pt/SnO₂-BASED CO-OXIDATION CATALYSTS FOR LONG-LIFE CLOSED-CYCLE CO₂ LASERS

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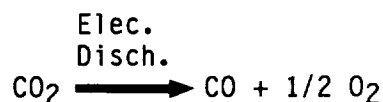
ABSTRACT

Noble-metal/tin-oxide based catalysts such as Pt/SnO₂ have been shown to be good catalysts for the efficient oxidation of CO at or near room temperature. These catalysts require a reductive pretreatment and traces of hydrogen or water to exhibit their full activity. Addition of Palladium enhances the activity of these catalysts with about 15 to 20 percent Pt, 5 percent Pd, and the balance SnO₂ being an optimum composition. Unfortunately, these catalysts presently exhibit significant decay due in part to CO₂ retention, probably as a bicarbonate. Research on minimizing the decay in activity of these catalysts is currently in progress. A proposed mechanism of CO oxidation on Pt/SnO₂-based catalysts has been developed and is discussed in this paper.

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 potentially associated with such applications.

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



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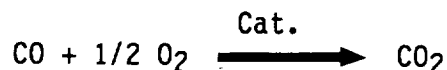
This decomposition is harmful to long-life laser operation both because of the loss of CO₂ and because of the buildup of O₂. The loss of CO₂ results in a corresponding gradual loss of laser power. The buildup of even relatively small concentrations of O₂ molecules can cause rapid power loss and even complete laser failure. Although CO₂ lasers differ somewhat in their tolerance of O₂, it is generally desirable to keep the O₂ concentration below a few tenths of 1 mole-percent. CO has no significant deleterious effect on laser performance at moderate concentrations.

The second problem is 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 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.

Achievement of closed-cycle operation of pulsed CO₂ lasers requires catalytic recombination of the decomposition products, CO and O₂, to regenerate CO₂.



Candidate catalysts must have high efficiency at steady-state laser conditions which are, generally, 25°C to 100°C and about one atmosphere of total pressure with low partial-pressures of CO and O₂. Some excess CO may be added to the laser-gas mixture but generally it is not. It is desirable that little or no heating of the catalyst be required in order to minimize power consumption.

The catalytic oxidation of CO to CO₂ has been extensively studied at various conditions for a number of catalysts. These include the noble metals and various metal oxides (refs. 1 and 2) and the commercial catalyst, Hopcalite (ref. 3), which is a mixture of CuO and MnO₂ plus small quantities of other oxides. However, few catalysts have sufficiently high activity to allow operation at the low steady-state temperatures and low oxygen partial pressures characteristic of typical pulsed CO₂ lasers.

The most promising catalysts studied to date, whose performance has been verified by actual closed-cycle laser operation, consist of Pt and/or Pd on tin (IV) oxide (refs. 4 and 5). A systematic study of (Pt, Pd)/SnO₂ catalysts for use with closed-cycle pulsed CO₂ lasers, including the preparation and testing of improved catalyst formations, has been in progress at the Langley Research Center of NASA (LaRC) for the past several years (refs. 5-16). This study has been expanded by joint research with investigators at Old Dominion University, the University of Florida, the University of California, San Diego, and Science and Technology Corporation (refs. 1, 5-11, 13, 15-21).

TEST FACILITIES

Catalyst research at LaRC is carried out both in laboratory reactors and in a commercial CO₂ TEA laser.

Laboratory Reactors

Laboratory reactors are used for catalyst study under controlled conditions. Several laboratory reactors are presently operational, most of which are flow-through (plug-flow) 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 enters and 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. For many tests the test-gas mixtures used are purchased premixed in a high-purity He carrier, typically 1.00 percent CO and 0.50 percent O₂ plus 2.00 percent Ne (as an internal calibration standard for gas analysis). For some tests the gas mixtures are blended in the laboratory using high-purity component gases and calibrated flow controllers.

All except one of the 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 continuously around-the-clock. One 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, pretreatment conditions, 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 an automated-GC reactor) 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 and a pulsed reactor are also available. In the recirculating reactor a gas mixture is continuously recirculated through a temperature-controlled reactor tube containing a sample of catalyst, and the conversion of CO and O₂ to CO₂ is monitored as a function of time. Gas analysis is performed with a GC. This reactor is used to study the kinetics and mechanism of catalysis for selected catalyst compositions.

With the pulsed reactor, the single-gas or gas-mixture to be studied (in a He carrier) is exposed to the catalyst sample in a series of discrete pulses. The pulses are spaced in time such that the gas exiting the reactor after each pulse can be analyzed by GC. The cumulative gain or loss of each species as a function of time can thus be more finely resolved than with the continuous flow-through and recirculating reactors. The pulsed reactor is used for both reaction and chemisorption studies.

Laser Reactor

A Lumonics model TEA-820 pulsed CO₂ laser (7 Watt, 1-50 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

The following results have been obtained in studies performed to date.

Common-Isotope Laboratory Studies

- (1) Pt on SnO₂ (Pt/SnO₂) has significantly higher catalytic activity for CO oxidation than either Pt or SnO₂ alone (ref. 5). The effect is clearly synergistic and apparently involves separate but complementary roles for the Pt and SnO₂ phases.
- (2) The efficiency of Pt/SnO₂-catalyzed oxidation of CO to CO₂ is approximately proportional to catalyst mass until complete conversion is achieved (ref. 5).
- (3) The catalyst mass required to achieve complete oxidation of a given concentration of CO is roughly proportional to the flow rate of the gas through the catalyst (ref. 7). This makes possible the extrapolation of results obtained with laboratory reactors to CO₂ lasers.
- (4) A technique for achieving much higher Pt loadings than are commercially available has been developed (ref. 16). Platinum loadings as high as 46 percent have been achieved. All metal loadings given in this paper are percentages by weight.
- (5) The activity for CO oxidation of Pt/SnO₂ catalysts increases with Pt loading until a maximum activity is reached at about 17 percent Pt (Ref. 14). Since Pt loadings between 11 percent and 17 percent and between 17 percent and 24 percent were not tested, the precise optimum loading is somewhat uncertain but it is believed to lie in the range of 15 to 20 percent.
- (6) Addition of a small quantity of Pd to a Pt/SnO₂ catalyst can enhance its activity. For example, a catalyst consisting of 1 percent Pt and 1 percent Pd (with the balance SnO₂) has been found to be more active than a catalyst with 2 percent Pt and no Pd. For a catalyst with 15 to 20 percent Pt, the optimum Pd loading is about 5 percent.

(7) A reductive pretreatment enhances the activity of Pt/SnO₂ catalyts relative to no pretreatment or to pretreatment with O₂ or an inert gas (Ref. 15). Pretreatment consists of a flow of the pretreatment gas (in a helium carrier, for safety and convenience) over the catalyst sample at an elevated temperature prior to exposure of the catalyst to the reaction gas mixture at the selected reaction temperature. Both CO and H₂ are suitable gases for reductive pretreatment (Ref. 15); in this study they were used at a concentration of 5 percent in He.

(8) The temperature at which a Pt/SnO₂ catalyst is pretreated can affect its subsequent activity (Ref. 15). Pretreatment temperatures of 125°C, 175°C, and 225°C resulted in equal catalytic activity, for the catalyst tested, but pretreatment at 100°C yielded somewhat lower activity.

(9) Duration of the pretreatment also affects subsequent catalyst activity (Ref. 15). Catalyst activity after a 20-hour CO pretreatment was found to be lower than after a 1-hour pretreatment. Too short a pretreatment also diminishes catalyst activity. For optimum results the effluent gases from the pretreatment should be analyzed and the pretreatment terminated when no significant yield of oxidation product (CO₂ or H₂O) is detected.

(10) Pretreatment of a Pt/SnO₂ catalyst sample at elevated temperatures--above about 125°C--results in an initial dip in catalyst activity before the steady-state activity is achieved for studies in the flow-through reactors (Ref. 15). No dip occurs if the catalyst is pretreated at lower temperatures. If the catalyst is exposed to moisture following pretreatment but prior to exposure to the reaction gas mixture, or if the reaction gas mixture is humidified, no dip occurs (Ref. 15).

(11) In many cases moisture not only eliminates the initial dip in catalyst activity, it also enhances the activity of the catalyst (Ref. 15). In fact, addition of moisture has been shown to increase the activity even of an unpretreated catalyst. As discussed in the following section, this is believed to be due to conversion of surface oxides to more-active surface hydroxyls.

(12) No initial dip in catalyst activity has been observed in flow-through reactor studies when the Pt loading exceeded 24 percent even at pretreatment temperatures of 225°C. No dip has been observed in studies in the recirculating reactor at any Pt loading or pretreatment temperature.

(13) The activities of Pt/SnO₂ catalysts exhibit some decay with time. Initial activity can be readily restored by outgassing the catalyst either by heating it or by exposing it to an inert gas for about 2 hours. In either case, restoration of activity has been found to be associated with outgassing of CO₂ from the catalyst but decay in activity occurs again when CO oxidation is resumed. An additional long-term decay which is not associated with CO₂ retention has also been observed. This decay is reversible by reduction of the catalyst.

(14) The yield of CO₂ for a given catalyst sample and set of reaction conditions is increased by addition of O₂ to a stoichiometric mixture of CO and O₂ and decreased by addition of CO to such a mixture (Ref. 22). The reaction has been found to be approximately first order with respect to O₂ concentration. Determination of the reaction order with respect to CO concentration is currently in progress. The true rate equation appears to be somewhat complex.

Rare-Isotope Catalyst Studies

- (1) Reaction of $C^{18}O$ and $^{18}O_2$ on a common-isotope $Pt/Sn^{16}O_2$ catalyst yields about 85 percent $C^{18}O_2$ and 15 percent $C^{18}O^{16}O$ (Ref. 10). This concentration of the mixed-isotope species $C^{18}O^{16}O$ is unacceptable.
- (2) A technique has been developed for modifying the surface of common-isotope Pt/SnO_2 so that all reactive surface oxygens are ^{18}O (ref. 10). Reaction of $C^{18}O$ and $^{18}O_2$ over this modified catalyst yielded only $C^{18}O_2$, within experimental error, in a test of 17 days (Ref. 23).
- (3) Rare-isotope studies have indicated that some sort of carbonate or bicarbonate species is formed when CO is oxidized on Pt/SnO_2 catalysts (ref. 10).

Surface Characterization Studies

Extensive surface characterization studies have been performed by Hoflund and coworkers at the University of Florida. These studies utilized an ultrahigh vacuum system containing multiple surface techniques including ion scattering spectroscopy (ISS), electron spectroscopy for chemical analysis (ESCA), Auger electron spectroscopy (AES), and electron stimulated desorption (ESD) with pretreatment capabilities at elevated pressures and temperatures. The following results have been obtained:

- (1) The surface hydrogen present at a polycrystalline tin oxide film has been studied using ESD before and after annealing the film at $500^\circ C$ (Ref. 17). Annealing reduces the concentration of surface hydrogen by a factor of 8, and energy analysis of the desorbing ions indicates that at least 3 chemical bonding states of H are present at the surface. Further research is necessary to elucidate the nature of these states.
- (2) The reduction by vacuum annealing from 200 to $350^\circ C$ of a platinized tin oxide film has been examined using ISS, ESCA and AES (Ref. 18). The data show that tin is reduced to metallic form which alloys with the supported platinum.
- (3) Since Pt/Sn alloys form in reduced Pt/Sn systems, it is important to characterize the behavior of Pt/Sn alloys. As part of a continuing study of Pt/Sn alloy surfaces, the reduction in H_2 of an air-exposed Pt/Sn alloy surface has been examined using ISS, ESCA and angle-resolved AES (Ref. 19). Initially, a tin-depleted Pt-rich region is covered by a 30\AA thick uniform layer of tin oxide. During reduction, oxygen is removed from the surface forming metallic tin and platinum migrates to the surface through vacancies left by the oxygen to alloy with the metallic tin.
- (4) An unsupported commercial 2 percent Pt/SnO_2 catalyst has been examined using ISS, AES, and ESCA as a function of pretreatment temperature (air exposed, 75, 100, 125, and $175^\circ C$) at 4 and 40 Torr of CO (Ref. 24). During the reduction the O/Sn ratio is decreased, the Pt is reduced from platinum oxides to $Pt(OH)_2$, the surface hydroxyl group concentration is reduced, and a Pt/Sn alloy forms. This is the same catalyst whose activity as a function of reductive-pretreatment temperature is discussed in item (8) of the section on common-isotope studies.

(5) A silica-supported Pt/Sn catalyst developed at NASA has been characterized before and after pretreatment at 125 and 225°C in CO (Ref. 20). The 125°C reduction, which yields a highly catalytically active surface, converts the Pt oxides primarily to Pt(OH)₂. Reduction at 225°C produces a surface which is much less active catalytically. The surface studies show that this is due to coverage of the surface Pt by contaminant species, including silica, and reduction of the Pt(OH)₂ to metallic Pt.

Laser Studies

(1) The Lumonics Model TEA-820 laser has been operated closed-cycle with a catalyst bed of 150 g of 2 percent Pt/SnO₂ at 100°C (Refs. 5 and 8). The laser achieved 96.5 percent (± 3.5 percent) of steady-state open-cycle power for 28 hours (1 x 10⁶ pulses at 10 pulses/second). Both the laser and catalyst were fully operational at the conclusion of the test. Additional laser tests are in progress.

(2) Herz and coworkers at the University of California, San Diego, (ref. 21) have developed a computer program which can be used to design catalyst monoliths for specific laser applications. The critical information a user needs to supply is the first-order-overall rate constant and activation energy for the catalyst formulation of interest. After the user supplies other information such as gas composition, gas flow rate and monolith dimensions, the program computes the conversion of oxygen and pressure drop as a function of monolith length. By varying input parameters, the user can investigate various design alternatives. One conclusion of a design study performed with the program is that standard off-the-shelf monoliths are not optimal for use in CO₂ laser applications. This is because standard monoliths have been designed for combustion or emission control applications where reactions occur very fast at high temperature and high gas flow-rates. Gas flow-rates in lasers are relatively low and reactions occur at low temperatures and thus, are relatively slow. Monoliths optimized for laser applications to provide for minimum monolith size will have thicker layers of active catalyst material than monoliths used for combustion and emission control. The computer program is available through NASA's COSMIC office.

PROPOSED MECHANISM

One result of the study described in the foregoing sections of this paper is that several features of the mechanism of Pt/SnO₂-catalyzed CO oxidation have begun to emerge. Primary among these is the role of surface hydroxyl groups in the oxidation of CO chemisorbed on Pt sites. Although much is still, at best, uncertain or ambiguous and much else is simply unknown, it is now possible to put forth, in some detail, a tentative mechanism which is consistent with a broad range of experimental observations. This proposed mechanism, including detailed reaction equations is presented in this section.

The experimental observations reported in the previous section suggest the postulate that surface OH groups participate in the oxidation of CO chemisorbed on Pt sites. Hoflund and coworkers have observed OH groups on both tin-oxide and platinized tin-oxide surfaces (refs. 17 and 24). Reductive pretreatment of

the catalyst enhances its activity but pretreatment at elevated temperatures also dehydrates the catalyst surface and thereby depletes the surface concentration of OH. The initial reaction which occurs when the catalyst is exposed to the test-gas mixture further depletes the surface concentration of OH and partially re-oxidizes the surface. This results in the observed decline in catalyst activity. Rehydroxylation of the surface, probably by migration of H (or H⁺) from the catalyst bulk, eventually restores the catalyst activity. The sequential decline and increase in catalyst activity results in the observed dip. If the OH concentration at the catalyst surface is restored by humidification of either the catalyst or the reaction gas no dip is observed. Humidification of the catalyst surface may increase the OH concentration above the initial value and the activity of the catalyst may then be enhanced as reported in Reference 15.

Most of the CO₂ formed immediately desorbs from the Pt phase, but a fraction of the CO₂ molecules interact with surface OH sites and are retained, probably as bicarbonate. This bicarbonate eventually undergoes decomposition, but until such decomposition occurs, the chemisorbed-CO₂/bicarbonate species ties up OH sites and, thus, contributes to the observed decay in catalyst activity. Outgassing of the chemisorbed CO₂ restores the catalyst activity, as observed.

An equation set which represents the foregoing proposed mechanism is

Pretreatment



The surface of the "tin-oxide" and "platinum" phases of platinized tin-oxide consists of complex hydroxy oxides which are represented here as HOSnO_x and HOPtO_y, respectively; following reduction some Pt and Sn are formed which are present predominantly as a PtSn alloy with some surface hydroxyl groups (refs. 18-20).

Chemisorption



Rate Determining Step

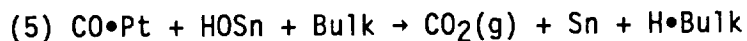


Fast

CO chemisorbs readily on Pt but does not chemisorb significantly on Sn, whereas O₂ chemisorbs on both Pt and Sn (ref. 25). It is assumed herein that these chemisorption properties hold for the Pt and Sn atoms of the PtSn alloy as well as for the individual metals. Although O₂ can chemisorb on Pt, it is not normally significantly present on room-temperature Pt surfaces when CO is also present; this is because of the relatively low sticking coefficient of O₂ on Pt as well as the fact that each O₂ molecule requires a pair of adjacent vacant surface sites whereas CO molecules require only individual vacant sites (ref. 1). We suggest that the presence of Sn atoms in the PtSn alloy component of prerduced platinized tin-oxide significantly alters this situation. Because each Pt atom of

the PtSn alloy is surrounded by Sn atoms which can chemisorb O₂ but not CO, O₂ molecules can compete with CO molecules for chemisorption on vacant Pt atoms with adjacent Sn atoms providing the necessary second sites. However, because of the higher sticking coefficient of CO on Pt, surface coverage by CO will still exceed that by O₂ for CO:O₂ ratios anywhere near stoichiometry. In fact, chemisorption of O₂ probably is the rate limiting step of this reaction set.

CO Oxidation



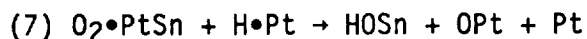
We propose that chemisorbed CO is oxidized predominately by surface hydroxyls rather than by oxygen atoms. This is analogous to the situation in the gas-phase oxidation of CO (ref. 1) and is consistent with the results presented in the previous section.

Hydrogen Exchange



It is assumed that hydrogen (possibly as H⁺) is relatively plentiful in the prerduced catalyst and that it exchanges readily between the bulk and the surface, preferentially at Pt sites.

Surface Rehydroxylation



Although the oxidizing species, HOSn, is regenerated by equation (6), the surface is also reoxidized--and, thus, deactivated--by this step. This is probably the cause of the downward portion of the initial dip in activity when the catalyst has been dehydrated during pretreatment. It is possible that surface reoxidation can be partially undone by



However, the experimental data suggest that conversion of surface oxide to surface hydroxyl is most readily accomplished by reaction with water:



or

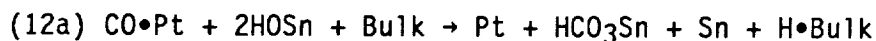


Although water may conceivably migrate from the catalyst bulk to the surface to allow the catalyst to come out of the initial dip in activity via equation (10a), it is more likely that the migrating species is H (or H⁺) yielding surface H₂O via



Of course, if water is supplied continuously by humidifying the reaction gas mixture, OH groups are continuously regenerated by equation (10b) and no dip in activity occurs; in fact the activity may be enhanced somewhat, as observed (Ref. 15).

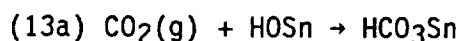
Bicarbonate Formation and Decomposition



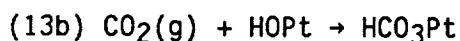
or



Although the oxidation of chemisorbed CO normally proceeds with the immediate release of $\text{CO}_2(\text{g})$, as in equation (5), bicarbonate formation can occur as in equation (12a) or (12b) when two HOSn groups are adjacent to a chemisorbed CO. It is not known whether the bicarbonate group is on a Pt on an Sn site; either would effectively deactivate the catalyst. It is possible that bicarbonate formation can occur by reaction of surface hydroxyl with gas phase CO_2 :



or



However, experimental data indicate that CO_2 retention by the catalyst is relatively insensitive to the gas phase concentration of CO_2 in most cases. It is not yet known whether bicarbonate decomposition is thermal or caused by reaction with surface hydrogen. Nevertheless, it is clear that a steady-state eventually is attained in which bicarbonate is formed at the same rate at which it is decomposed. This steady-state then limits the effective activity of the catalyst to a value about half of its activity if no bicarbonate buildup occurred. In addition to the fairly rapid loss of activity due to bicarbonate buildup, some sort of slow morphological change further deactivates the catalyst with a half-life of several months.

The foregoing mechanism admittedly is speculative in many ways. It is likely that it will require modification in some (perhaps many) details. Nevertheless, it is consistent with all experimental data currently available and it offers a point of departure for future studies of Pt/SnO₂-based catalysts. It is presented for consideration in this context.

CONCLUDING REMARKS

Noble-metal/tin-oxide based catalysts such as Pt/SnO₂ have been shown to be good catalysts for the efficient oxidation of CO at or near room temperature. They are the most promising catalysts for use in closed-cycle pulsed CO_2 lasers whose performance has actually been verified by tests in such lasers. The catalysts require a reductive pretreatment and traces of hydrogen or water to exhibit their full activity. Addition of

Palladium enhances the activity of these catalysts with about 15 to 20 percent Pt, 5 percent Pd, and the balance SnO₂ being an optimum composition. Unfortunately, these catalysts presently exhibit significant decay due in part to CO₂ retention, probably as a bicarbonate. Research on minimizing the decay in activity of these catalysts is currently in progress. A proposed mechanism of CO oxidation on Pt/SnO₂-based catalysts has been developed and is discussed in this paper. The mechanism, although somewhat speculative, is consistent with experimental results obtained to date.

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SECTION II

CATALYST DEVELOPMENT

