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NOTES

Effects of Pretreatment Conditions on a Pt/SnO_2 Catalyst for the Oxidation of CO in CO_2 Lasers

CO oxidation catalysts are important for long-life closed-cycle operation of CO_2 lasers (*1*). The electrical discharges frequently used to excite such lasers decompose some CO_2 to CO and O_2 but many of their applications, including remote sensing from space vehicles, prohibit addition of makeup gas or removal of decomposition products because of volume and weight constraints.

These lasers thus represent a new and important application for low-temperature CO oxidation catalysts, since for space applications, no catalyst heating is allowed to minimize power consumption. The most promising catalysts whose performance has been verified by actual laser operation consist of Pt and/or Pd on tin(IV) oxide (*2, 3*). This paper presents results of a study of various pretreatment techniques on the activity of a commercially available Pt/SnO_2 catalyst.

The catalyst used in this investigation was 2% (by weight) Pt/SnO_2 powder obtained from Engelhard Industries. This catalyst had an average particle size of 1 μm and a BET surface area of 6.9 m^2/g.

Tests were performed in two plug-flow reactor systems previously described by Batten *et al.* (*4*). Although a variety of test conditions were run, one reactor was run predominantly at 85°C and 5 SCCM (Figs. 1 and 4) and the other at 75°C and 10 SCCM (Figs. 2 and 3).

The protocol for all experiments was as follows. A weighed catalyst sample packed between quartz-wool plugs in a reactor tube was brought to the desired initial temperature under a flow of pure He. In most cases the catalyst was then exposed to a flow of one of the following pretreatment gases: pure He, 5.00% CO in He, 5.00% H_2 in He, or 5.00% O_2 in He. For all gas mixtures 2.00% Ne was also present as an internal calibration standard. After pretreatment the gas flow was switched to pure He and the reactor-oven temperature was lowered to the desired test temperature. The gas flow was then switched to a stoichiometric mixture of 1.00% CO and 0.50% O_2 (plus 2.00% Ne) in He. The product gases were analyzed periodically with a gas chromatograph for CO, CO_2, and O_2 concentrations to determine the conversion efficiency for the particular experimental conditions. In a few cases control samples were not pretreated prior to exposure to the reaction-gas mixture. In other experiments the catalyst samples were exposed to H_2O vapor in He following pretreatment or the reaction gas mixture was humidified.

Figure 1 presents the percentage yield of CO_2 as a function of time for the four pretreatment gas compositions. For simplicity the percentages loss of CO and O_2, although measured, are not plotted in Fig. 1 and subsequent figures; in each case stoichiometry was observed within experimental error. Pretreatment with the reducing gases, CO and H_2, produces approximately equal steady-state CO_2 yields which are significantly higher than those for the other pretreatment gases, although the steady-state is more rapidly attained with the H_2 pretreatment. Pretreatment with O_2 in He results in only slightly greater CO_2 yield than pretreatment with He alone. An initial dip in activity is observed in all cases. Clearly, a reductive pretreatment of the catalyst results in significantly greater CO_2

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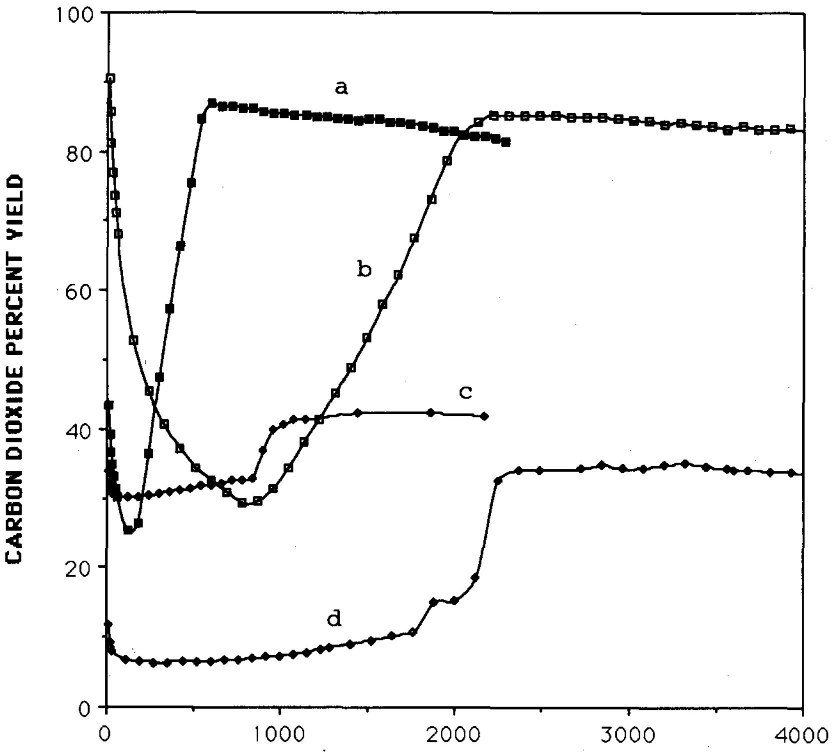

FIG. 1. Effect of different pretreatment gases on the activity of a Pt/SnO_2 catalyst. (a) 5% H_2, 2% Ne, balance He; (b) 5% CO, 2% Ne, balance He; (c) 5% O_2, 2% Ne, balance He; (d) He with 2% Ne. In each case, the sample size was 0.12 g, and the pretreatment was for 2 h at 225°C with a 5 SCCM flow. The test gas was 1% CO, 0.5% O_2, 2% Ne in He. The test temperature was 85°C with a flow of 5 SCCM.

yields than does either oxidative or inert pretreatment. Therefore, CO pretreatment was employed for all subsequent tests.

Figure 2 compares the percentage CO_2 yield for a non-pretreated catalyst sample with that for a sample pretreated with CO for 1 h and for another sample pretreated for 20 h. Both pretreatments enhance the CO_2 yield but the 20-h pretreatment is less effective than that for 1 h.

Figure 3 compares the percentage yield of CO_2 for a non-pretreated catalyst sample to that for equal-mass samples pretreated at four temperatures. All of the pretreated samples exhibit greater CO_2 yields than the unpretreated sample. No difference in CO_2 yield is observed for pretreatment temperatures of 125 through 225°C, but the 100°C pretreatment results in a somewhat lower yield.

It is apparent that a fairly mild prereduction of these catalysts is sufficient to produce significant activity and that more severe pretreatment (e.g., 20 h or so) produces less than optimum results. Analysis of the exit gas during each pretreatment showed that conversion of CO to CO_2, and thus reduction of the catalyst surface, was essentially complete in less than 1 h under the conditions utilized.

In Figs. 2 and 3 no dip occurs in the CO_2 yield for the non-pretreated catalyst samples. However, a dip is present for the samples in Fig. 2 which were pretreated for 1 h and 20 h at 225°C. In Fig. 3, no dip is present for the samples which were pre-

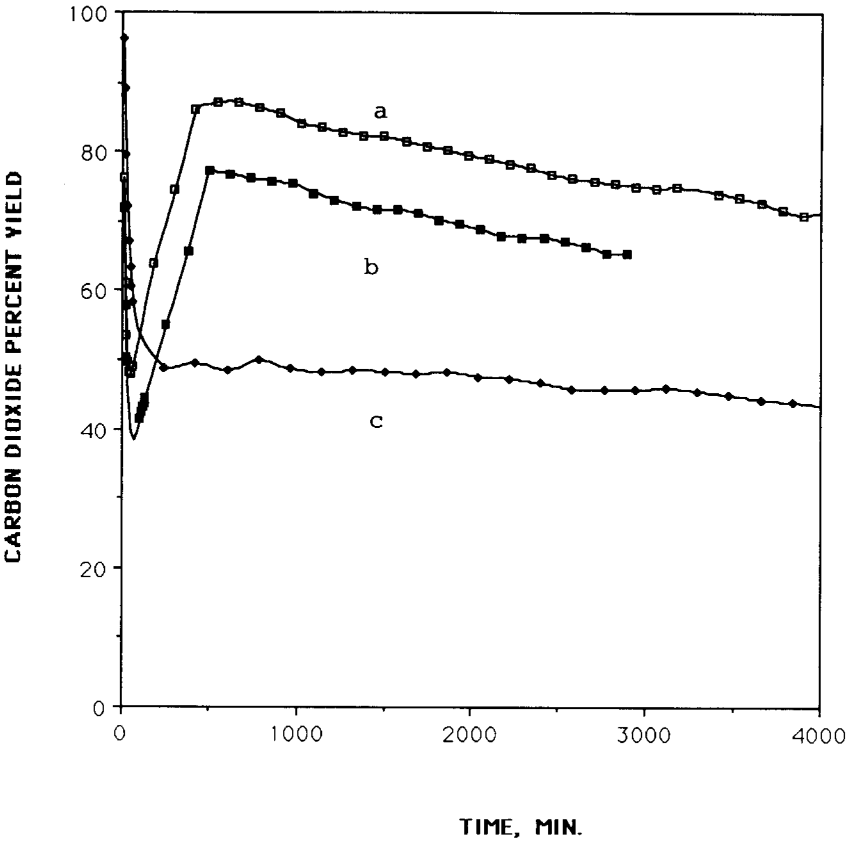

FIG. 2. Effect of the duration of pretreatment of a 0.15 g Pt/SnO_2 catalyst with the 5% CO gas mixture at a temperature of 225°C and a flow of 10 SCCM. (a) 1 h; (b) 20 h; (c) no pretreatment. The test gas was the same as in Fig. 1. The test temperature was 75°C and the flow was 10 SCCM.

treated at 100 and 125°C, but a dip occurs for the samples pretreated at 175 and 225°C, although this is somewhat difficult to see in this figure. Thus, the initial dip in CO_2 yield occurs when the catalyst samples have been exposed to an elevated temperature during pretreatment. It appears that the critical temperature for the onset of the dip lies somewhere between 125 and 175°C.

It is proposed that the dip is associated with dehydration of the catalyst during pretreatment at elevated temperatures. This hypothesis is confirmed by the data presented in Fig. 4. The two equal-mass catalyst samples represented in this figure were both pretreated with CO in He for 2 h at 225°C. However, one sample was humidified following pretreatment and before reaction by exposure to a flow of He that had been bubbled through water. The unhumidified sample exhibited the initial dip; the humidified sample did not. Humidification of the reaction gas mixture has been found to be equally effective. Croft and Fuller (*5*) have previously reported an enhancement of CO_2 yield for a Pd/SnO_2 catalyst when the reaction gas was humidified. They did not, however, address the problem of the pretreatment-induced activity dip dealt with in this paper.

A possible explanation of the phenomena reported herein is as follows. It is postulated that OH groups on the surface of the tin oxide phase participate in the oxidation

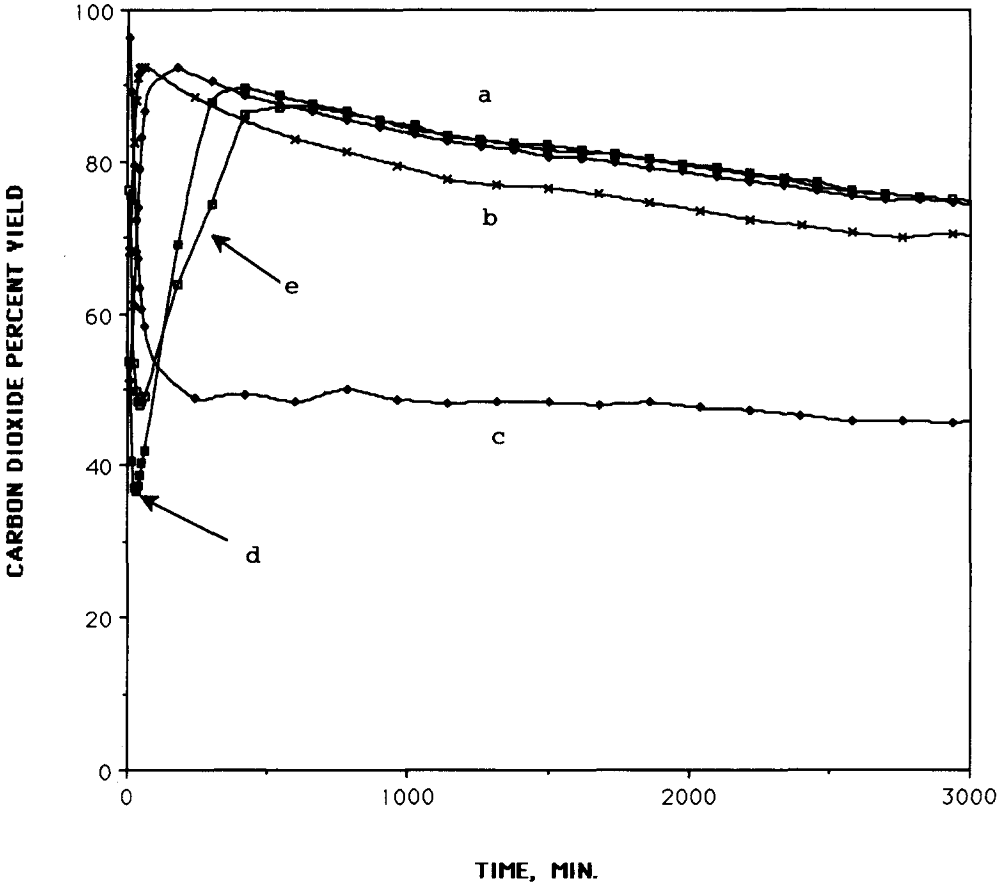

FIG. 3. Effect of pretreatment temperature on the activity of a Pt/SnO_2 catalyst. (a) 125°C; (b) 100°C; (c) no pretreatment; (d) 175°C; (e) 225°C. The test conditions were identical to those in Fig. 2.

of CO chemisorbed on adjacent Pt sites. Hoflund *et al.* (*6*) have observed OH groups as a significant constituent of tin oxide surfaces. Pretreatment of the catalyst at elevated temperatures partially dehydrates it and thereby significantly depletes the available OH. The initial reaction which occurs when the catalyst is exposed to the test gas mixture further depletes the surface OH and partially reoxidizes the surface, resulting in the observed decline in catalyst activity. Restoration of surface OH by migration of hydrogen and/or H_2O from the catalyst bulk eventually restores the catalyst activity. The sequential decline and increase in catalyst activity result in the observed dip. If, after pretreatment, the OH concentration at the catalyst surface is restored by humidification of the catalyst or the reaction gas, no dip is observed. Also, if the pretreatment temperature is low enough that surface OH and H_2O are substantially retained, no dip is observed. If the OH concentration at the catalyst surface is increased by humidification, the activity of the catalyst is somewhat enhanced as shown in Fig. 4 and as observed by Croft and Fuller (*5*).

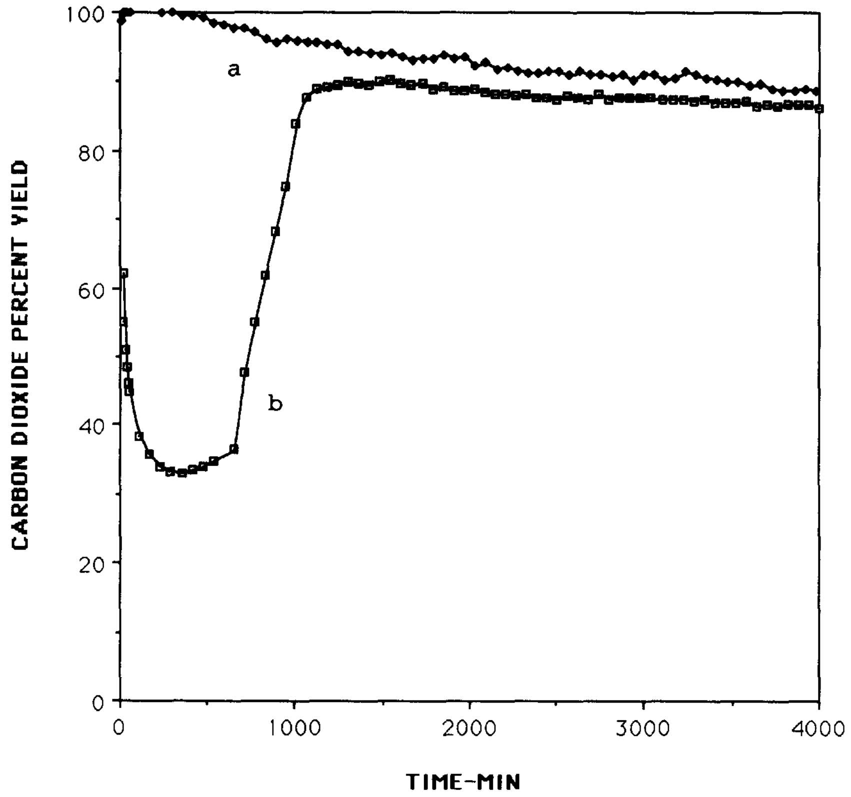

FIG. 4. Effect of exposure to water vapor, following pretreatment, on the behavior of a Pt/SnO_2 catalyst. (a) Sample humidified; (b) CO pretreatment only. Test conditions were the same as those in Fig. 1.

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