

THE EFFECT OF H₂O AND PRETREATMENT ON THE ACTIVITY OF A Pt/SnO₂ CATALYST

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ABSTRACT

CO oxidation catalysts with high activity at 25°C to 100°C are important for long-life, closed-cycle operation of pulsed CO₂ lasers. A reductive pretreatment with either CO or H₂ has been shown to significantly enhance the activity of a commercially available platinum on tin (IV) oxide (Pt/SnO₂) catalyst relative to an oxidative or inert pretreatment or no pretreatment. Pretreatment at temperatures of 175°C and above causes an initial dip in the observed CO₂ yield before the steady-state yield is attained. This dip has been found to be caused by dehydration of the catalyst during pretreatment and is readily eliminated by humidifying the catalyst or the reaction gas mixture. It is hypothesized that the effect of humidification is to increase the concentration of OH groups on the catalyst surface which play a role in the reaction mechanism.

INTRODUCTION

CO oxidation catalysts are important for long-life closed-cycle operation of CO₂ lasers which are excited by pulsed electrical discharges since such discharges decompose some of the CO₂ to CO and O₂ (Ref. 1). The gradual loss of CO₂ results in a corresponding gradual loss of laser power. However, the buildup of even small concentrations of O₂ molecules can cause discharge instabilities, which result in severe power loss, and even complete laser failure. Although CO₂ lasers differ somewhat in their O₂ tolerance, it is generally desirable to keep the O₂ concentration below a few tenths of 1 mole-percent. CO has no significant deleterious effect on CO₂ laser performance at moderate concentrations.

Many of the potential applications of pulsed CO₂ lasers, including remote sensing from satellites and other space vehicles, require that they operate in a closed-cycle mode with no addition of make-up gas or removal of decomposition products because of volume and weight constraints. To achieve such operation the CO and O₂ produced by the electrical discharge must be recombined continuously to regenerate CO₂. Thus, these lasers represent a new and important application for CO oxidation catalysts. Candidate catalysts must have high efficiency at average 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. For space applications no heating of the catalyst is allowed in order to minimize power consumption.

The catalytic oxidation of CO to CO₂ has been extensively studied for a number of catalysts over a wide range of conditions (Refs. 2 and 3). However, few catalysts have the desired efficiency at the low average temperatures and low oxygen partial-pressures characteristic of typical repetitively 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). The present paper presents results of studies of various pretreatment techniques on the activity of a commercially available platinum on tin (IV) oxide (Pt/SnO₂) catalyst.

EXPERIMENTAL

The catalyst used in this investigation was 2% (by weight) Pt/SnO₂ powder obtained from Engelhard Industries. This catalyst had an average particle size of 1 μm and a BET surface area of 6.9 m²/g. Tests were performed in a plug-flow reactor previously described by Batten et al. (Ref. 6). Gravimetric-grade premixed gas-mixtures which were commercially obtained were used for all experiments. All gas mixtures contained 2.00% Ne as an internal standard in addition to their other constituents. The carrier gas was dry, high-purity He. Gas mixtures were analyzed prior to use in each experiment. All gas analyses were obtained using commercial gas chromatographs (GCs). Sampling and analysis were automated for unattended, continuous operation. The chromatographic column was a coaxial-type with a silica gel/molecular sieve combination to allow concurrent analysis for CO, CO₂, N₂, O₂, and H₂O using a Ne internal standard. The GCs were calibrated frequently with a gravimetric-grade calibration mixture consisting of 1.00% CO, 1.00% CO₂, 1.00% O₂, and 2.00% Ne in dry, high-purity He.

The protocol for all experiments was as follows. A weighed catalyst sample packed between quartz-wool plugs in a reactor tube was inserted into the flow system in the reactor oven and brought to the desired initial temperature. In most cases the catalyst was then exposed for some time to a flow of one of the following pretreatment gases: pure He, 5.00% CO in He, 5.00% H₂ in He, or 5.00% O₂ in He. After pretreatment the gas flow over the sample was temporarily switched to pure He and the reactor-oven temperature was lowered to the desired test temperature. When the test temperature was reached, the gas flow was switched to a stoichiometric mixture of 1.00% CO and 0.50% O₂. The product gases which exited the reactor were then analyzed periodically for CO, CO₂, and O₂ concentrations to determine the conversion efficiency for the particular experimental conditions. The N₂ concentration was also monitored to determine if any air leaks developed in the gas lines or the reactor itself.

In a few cases catalyst samples which served as controls were not pretreated prior to exposure to the reaction-gas mixture. In other experiments the catalyst samples were exposed to H₂O vapor following pretreatment or the reaction gas mixture was humidified.

RESULTS

Figure 1 is a typical plot of percent loss of CO and O₂ relative to their initial concentrations and of percent yield of CO₂ relative to the initial concentration of CO. The pretreatment and test conditions are given on this and subsequent figures. The values of the 3 parameters can be seen to be essentially equal at all times, which indicates that the reaction is stoichiometric. For simplicity, only the percent yield of CO₂ is plotted in subsequent figures even though the percent loss of CO and O₂ were determined and stoichiometry was observed in all cases.

In figure 1 note the initial dip in the percent yield of CO₂ before the steady-state value is attained. Investigation of the cause of this dip yields important insight into the behavior of Pt/SnO₂ catalysts, as discussed below.

Figure 2 presents the percent conversion of CO to CO₂ for four different pretreatment gas compositions: (1) pure He, (2) 5% O₂ in He, (3) 5% CO in He, and (4) 5% H₂ in He. Pretreatment with the reducing gases, CO and H₂, produces approximately equal steady-state CO₂ yields which are significantly higher than those for the other pretreatment gases, although the steady-state yield is more rapidly attained with the H₂ pretreatment. Pretreatment with O₂ in He results in only slightly greater CO₂ 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 CO₂ yields than does either oxidative or inert pretreatment. Therefore, CO pretreatment was employed for all subsequent tests.

Figure 3 compares the percent CO₂ yield for an unpretreated catalyst sample with that for an equal-mass sample pretreated with CO for 1 hour and for another sample pretreated for 20 hours. Both pretreatments enhance the CO₂ yield but the 20 hour-pretreatment is less effective than that for 1 hour.

Figure 4 compares the percent yield of CO₂ for an unpretreated catalyst sample to that for equal-mass samples pretreated at various temperatures. All of the pretreated samples exhibited greater CO₂ yields than the unpretreated sample. No difference in CO₂ yield is observed for pretreatment temperatures of 125°C through 225°C, but the 100°C pretreatment results in a somewhat lower yield.

It is apparent from figures 3 and 4 that a fairly mild pre-reduction of these catalysts is sufficient to produce significant activity and that more severe pretreatment (e.g., 20 hours or so) produces less than optimum results. Analysis of the exit gas during each pretreatment showed that conversion of CO to CO₂, and thus reduction of the catalyst surface, was

complete in less than 1 hour for the conditions utilized. It is recommended that such an analysis be performed each time a catalyst sample is pretreated and that pretreatment be terminated when no further reduction of the sample is observed.

DISCUSSION

The initial dip in CO₂ yield which is frequently encountered following catalyst pretreatment is more than an experimental inconvenience. Figure 5 shows the results of a 27-day test of a 1.50 g catalyst sample which was pretreated with pure He for 20 hours at 225°C and 10 SCCM prior to testing at 85°C and 10 SCCM. This test produced a dip that lasted for about 25,000 minutes or 17 days. Clearly such a dip is unacceptable for virtually all practical applications. The long duration of the dip in this case appears to have been caused by the long pretreatment time and relatively large sample mass. Nevertheless, a dip lasting even a day or two is not only inconvenient but can cause erroneous results if its existence is not known and a test is terminated at or near the trough of the dip. Thus, it is important to determine the cause of the dip and to eliminate it if possible. In order to achieve these goals, a review of the conditions under which the dip occurs is in order.

In figures 3 and 4 it can be seen that no dip occurs in the CO₂ yield for the unpretreated catalyst samples. However, a dip is clearly present for the samples in figure 3 which were pretreated for 1 hour and 20 hours at 225°C. In figure 4, no dip is present for the samples which were pretreated at 100°C and 125°C, but a dip occurs for the samples pretreated at 175°C and 225°C, although this is somewhat difficult to see in this figure. Figure 6 is an expansion of the first 800 minutes of figure 4 with only the 125°C and 175°C pretreatment data shown. In figure 6 a dip can clearly be seen for the 175°C pretreatment but not for the 125°C pretreatment.

Figure 7 presents the CO₂ yield for a sample that underwent a vacuum pretreatment for 2 hours at a catalyst temperature of 225°C prior to its exposure to the reaction gas mixture at 85°C and 5 SCCM. A pronounced initial dip can be seen.

It is apparent from the foregoing observations that the initial dip in CO₂ yield occurs only when the catalyst samples have been exposed to an elevated temperature during pretreatment. Based on the data presented in Figure 6, the critical temperature for the onset of the dip lies somewhere between 125°C and 175°C. All samples which were exposed during pretreatment to a temperature of 175°C or higher exhibit the dip, but the dip is not exhibited by any sample that was pretreated at 125°C or less or not pretreated at all.

This observation suggests that the dip may somehow be associated with dehydration of the catalyst during pretreatment at elevated temperatures. This hypothesis is confirmed by the data presented in figure 8. The two equal-mass catalyst samples represented in this figure were both pretreated with CO in He for 2 hours at 225°C and then exposed to the reaction gas mixture at 85°C and 10 SCCM. However, one sample was

humidified following pretreatment and before reaction by exposure for 20 minutes to a 5 SCCM flow of He that had been bubbled through water. The H₂O content of the He was about 2 mole-percent. The unhumidified sample exhibited the initial dip; the humidified sample did not.

Alternatively, humidification of the catalyst can be achieved simply by humidifying the reaction gas mixture. Furthermore, a relatively low H₂O content is sufficient. Figure 9 reproduces the CO₂ yield which was originally presented in figure 2 and which clearly exhibits an initial dip. The other curve is the CO₂ yield from an equal-mass catalyst sample which underwent identical pretreatment but for which the reaction-gas mixture was humidified by passing it through a container of CaCl₂•2H₂O. The resultant H₂O content of the reactant gas was about 0.2 mole-percent. No dip occurs. Furthermore, a higher yield of CO₂ was attained with the humidified reaction-gas than with the dry reaction-gas. Croft and Fuller (ref. 7) have previously reported an enhancement of CO₂ yield for a Pd/SnO₂ 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 serve as oxidants for CO chemisorbed on adjacent Pt sites. Hoflund et al., (ref. 8) have observed OH groups as a significant constituent of tin-oxide surfaces. Reductive pretreatment of the catalyst enhances chemisorption of O₂ on the tin-oxide surface. Chemisorbed O₂ is converted to OH by reaction with surface H₂O or H. Pretreatment of the catalyst at elevated temperatures dehydrates its surface and thereby significantly 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 OH and partially reoxidizes the surface resulting in the observed decline in catalyst activity. Migration of H₂O (or possibly OH or H) from the catalyst bulk eventually increases the surface concentration of OH and restores the catalyst activity. The sequential decline and increase in catalyst activity results 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 H₂O 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 figures 8 and 9 and as observed by Croft and Fuller (ref. 13).

CONCLUSIONS

The pretreatment conditions of Pt/SnO₂ catalysts are important in determining their activity for the oxidation of CO to CO₂. Reductive pretreatment with either CO or H₂ is superior to oxidative or inert pretreatment. The pretreatment conditions can be relatively mild with the temperature as low as 125°C and the duration only long enough to reduce the catalyst surface. Pretreatment at elevated temperatures results in an initial dip in the observed CO₂ yield before the steady-state yield is attained. This dip is associated with dehydration of the catalyst and can

readily be eliminated by humidifying the catalyst or the reaction-gas mixture. Such humidification can result in an enhancement of catalyst activity, possibly by increasing the concentration of OH groups on the catalyst surface.

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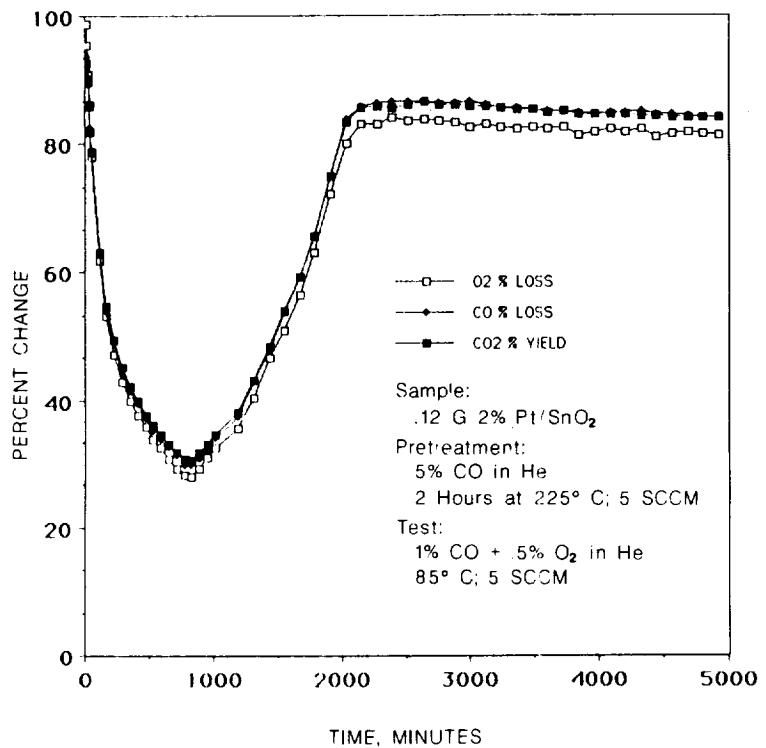


Figure 1. Typical test of Pt/SnO₂ catalyst.

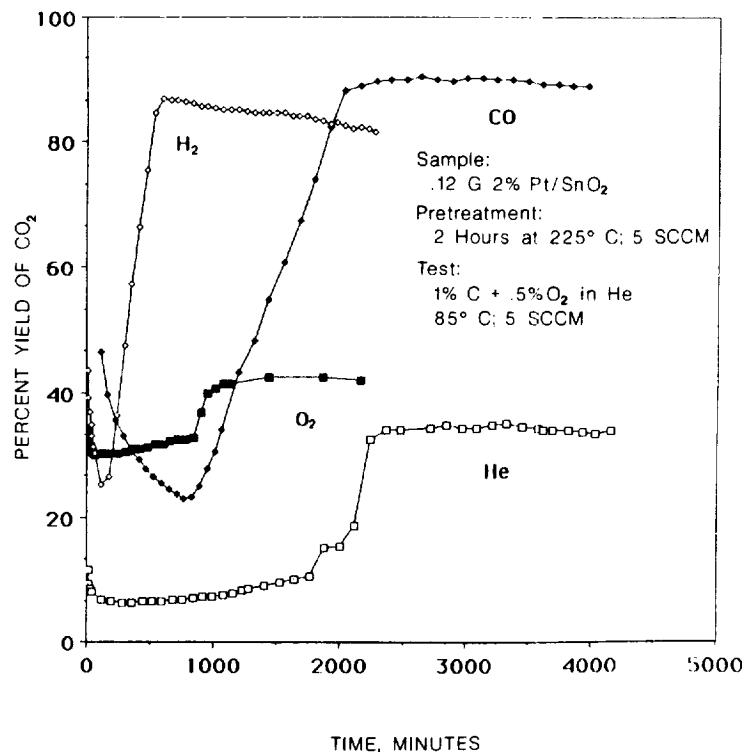


Figure 2. Effect of several pretreatment gases on activity of Pt/SnO₂ catalyst.

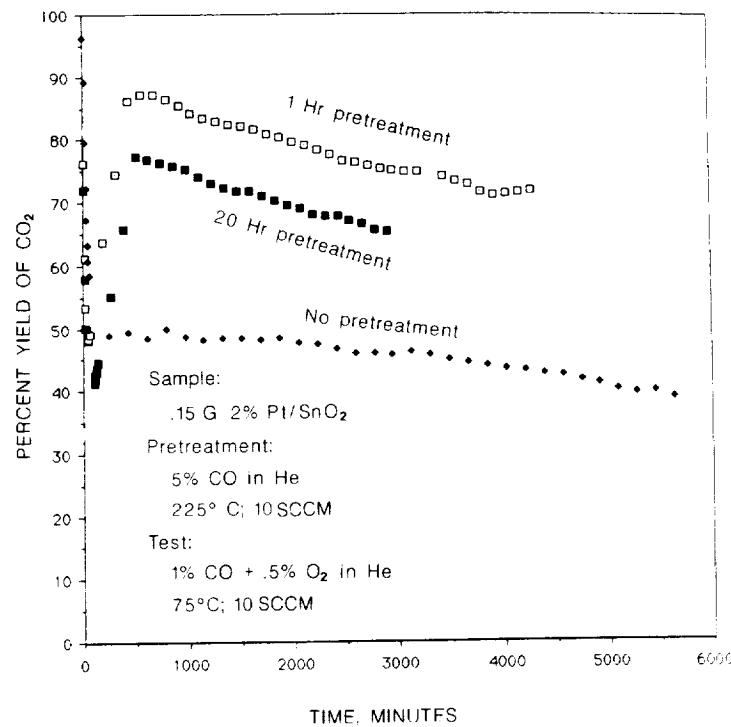


Figure 3. Effect of pretreatment duration on activity of Pt/SnO₂ catalyst.

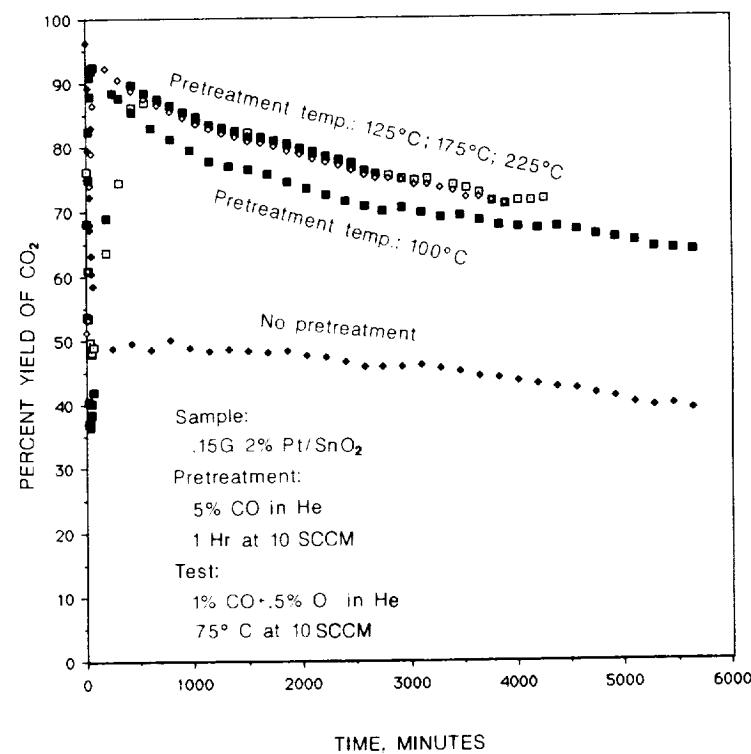


Figure 4. Effect of pretreatment temperature on activity of Pt/SnO₂ catalyst.

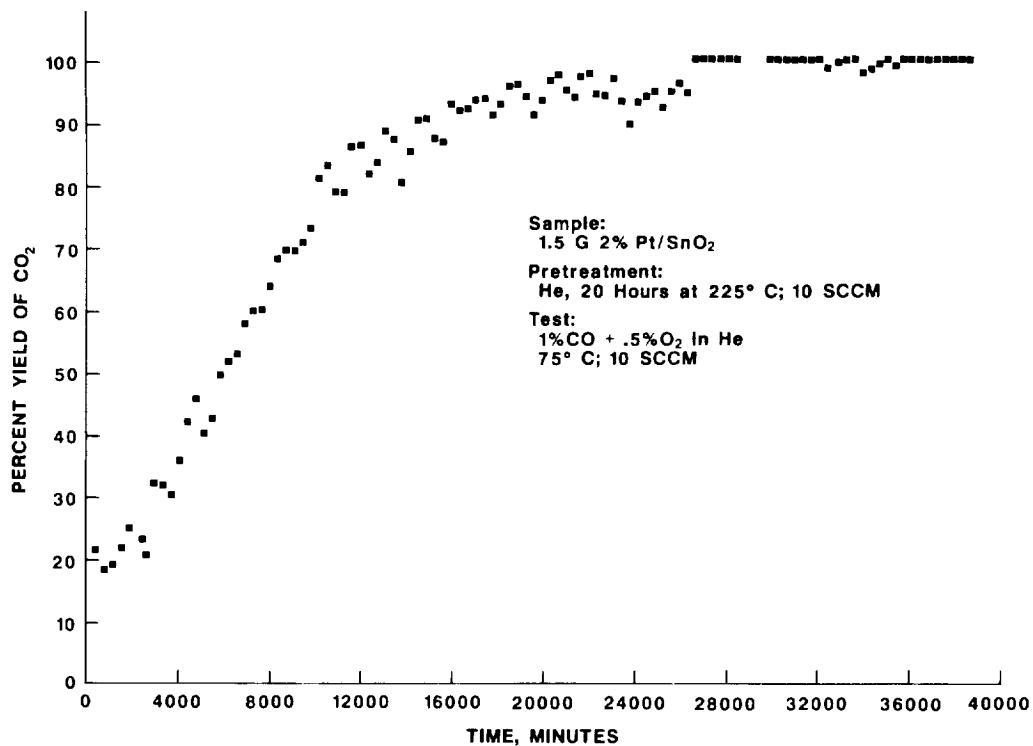


Figure 5. 28-day test of 1.5 grams of Pt/SnO₂ catalyst following extended pretreatment.

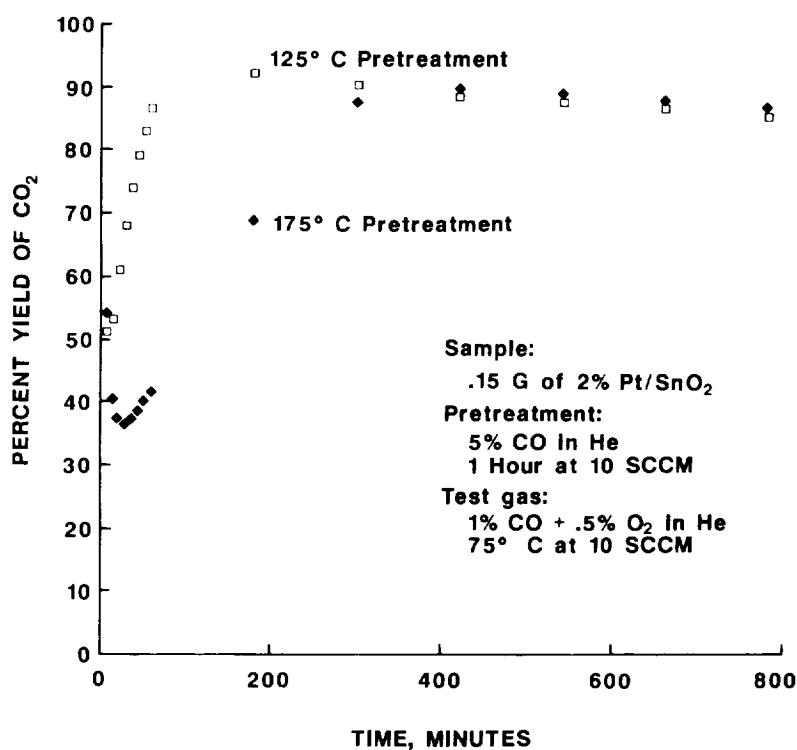


Figure 6. Expansion of selected data from Figure 4.

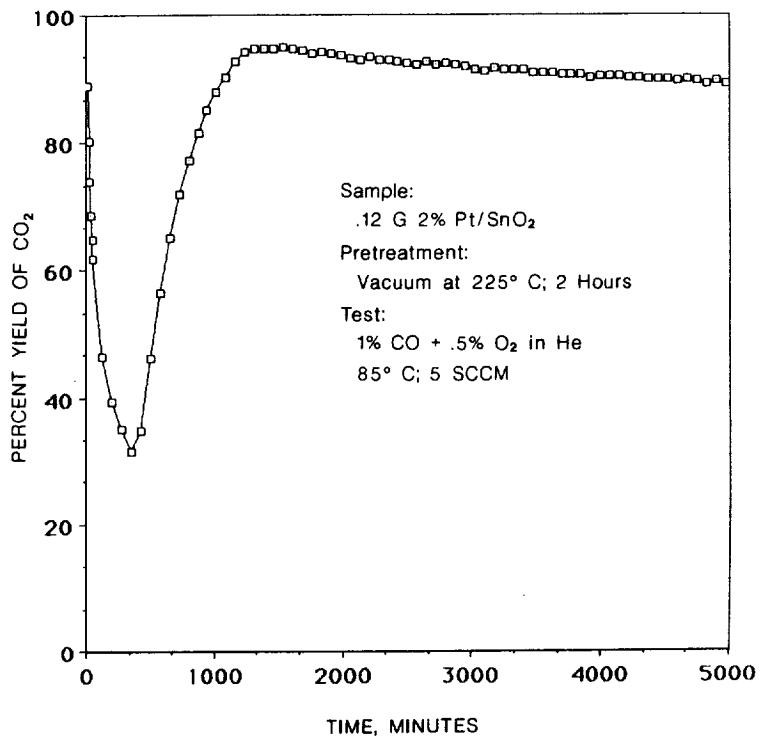


Figure 7. Effect of vacuum pretreatment on behavior of Pt/SnO₂ catalyst.

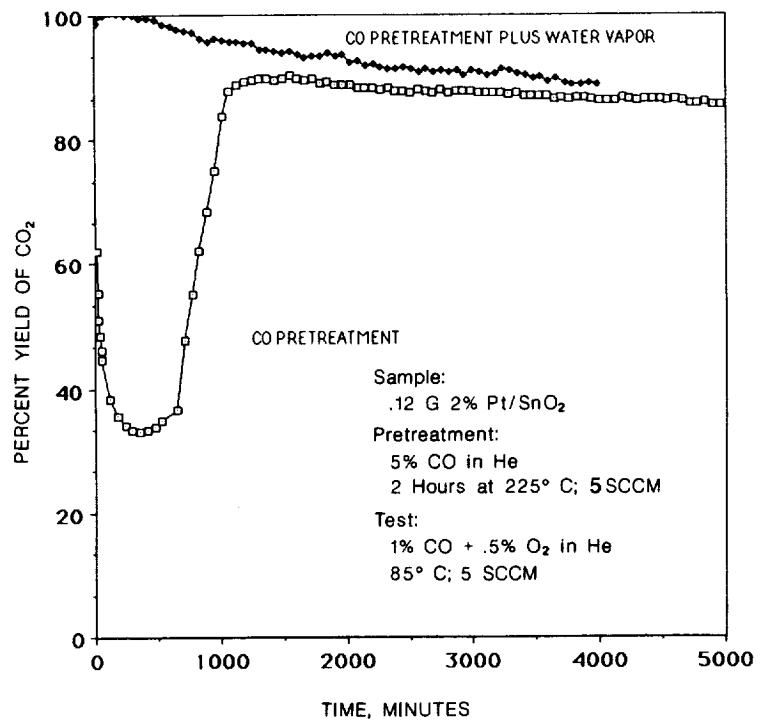


Figure 8. Effect of water addition following pretreatment on behavior of Pt/SnO₂ catalyst.

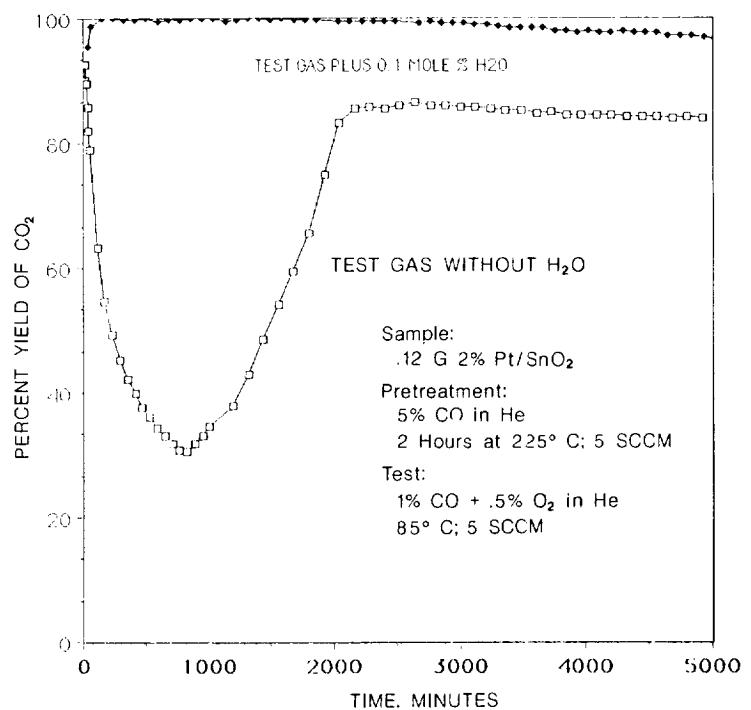


Figure 9. Effect of adding water to test gas on behavior of Pt/SnO₂ catalyst.

