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

(Running Title: Effects of Pretreatment)

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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 CO_2 lasers. A reductive pretreatment with either CO or H_2 has been shown to significantly enhance the activity of a commercially-available platinum on tin (IV) oxide (Pt/SnO_2) 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 CO_2 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 CO_2 lasers which are excited by pulsed electrical discharges (1). Such discharges decompose some of the CO_2 to CO and O_2. The gradual loss of CO_2 results in a corresponding gradual loss of laser power. However, the buildup of even small concentrations of O_2 molecules can cause discharge instabilities, which result in severe power loss, and even complete laser failure. Although CO_2 lasers differ somewhat in their O_2 tolerance, it is generally desirable to keep the O_2 concentration below a few tenths of 1 mole-percent. CO has no significant deleterious effect on CO_2 laser performance at moderate concentrations.

Many of the potential applications of pulsed CO_2 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 contraints. To achieve such operation the CO and O_2 produced by the electrical discharge must be recombined continuously to regenerate CO_2. 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 O_2. 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 CO_2 has been extensively studied for a number of catalysts over a wide range of conditions (2, 3). However, few catalysts have the desired efficiency at the low average temperatures and low oxygen partial-pressures characteristic of typical repetitively-pulsed CO_2 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 (4, 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/SnO_2) catalyst.

Methods

All data reported in this investigation were obtained using 2% (by weight) Pt/SnO_2 obtained from Engelhard Industries. This catalyst had the following properties: average particle size- 1 µm, bulk density- 1.934 g/cm^3, SnO_2 density- 7.0 g/cm^3, BET area- 6.9 m^2/g, and specific void volume- 0.374 cm^3/g.

Samples of the 2% Pt/SnO_2 catalyst were placed in a quartz reactor tube of approximately 6.4 mm inner diameter with quartz wool plugs on each side to hold them in place. Sample masses were between 0.12 g and 1.50 g depending upon the test conditions and the information sought. The quartz reactor tubes were mounted vertically in a reactor oven which was controlled to within ± 1°C. No effort was made to directly measure the temperature of the catalyst plug. A schematic of the experimental setup and a photograph of the quartz reactor tube have been presented previously (6).

Commercially-obtained premixed gas-mixtures were used for all experiments. All gas mixtures were Master Gas Gravimetric grade from Scott Specialty Gases and contained 2.00% Ne as an internal standard in addition to any other constituents. The carrier gas was dry, high-purity He. Gas mixtures were analyzed prior to use in each experiment. Gas flow rates were measured with digital flowmeters manufactured by Hastings-Raydist which were frequently calibrated.

All gas analyses were obtained using Shimazdu gas chromatographs (GCs) with Shimadzu data processors to acquire data, control the experiment, and perform the calculations. Sampling and analysis were automated for unattended, continuous operation. The chromatographic column was an Alltech CTR I which is a coaxial-type column with a silica gel/molecular seive combination to allow concurrent analysis for CO, CO_2, N_2, O_2, and H_2O using a Ne internal standard. The column flow in the gas chromatograph was 40 standard cm^3/minute (SCCM) of He. The GCs were calibrated frequently with a gravimetric-grade calibration mixture consisting of 1.00% CO, 1.00% CO_2, 1.00% O_2, and 2.00% Ne in dry, high-purity He to insure analytical accuracy and precision.

The protocol for all experiments was as follows. A weighed catalyst sample was packed between quartz-wool plugs in the reactor tube which 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% H_2 in He, or 5.00% O_2 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% O_2. The product gases which exited the reactor were then analyzed periodically for CO, CO_2, and O_2

concentrations to determine the conversion efficiency for the particular experimental conditions. The N_2 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 H_2O vapor following pretreatment or the reaction gas mixture was humidified.

Measurement precision was checked by performing 50 consecutive analyses of the reaction-gas mixture which was passed through a bypass reactor which was situated in parallel with the catalyst reactor in the reactor oven. As noted above, this mixture was nominally 1.00% CO and 0.50% O_2. The average of 50 measurements of CO concentration gave a value of 0.995 mole percent with a standard deviation of 0.003 while the O_2 concentration was determined to be 0.508 mole percent with a standard deviation of 0.002. These values are well within the accuracy of the gas mixtures obtained.

Results and Discussion

Figure 1 is a typical plot of percent loss of CO and O_2 relative to their initial concentrations and of percent yield of CO_2 relative to the initial concentration of CO. The test was preceded by pretreatment of the sample with 5% CO in He at 5 SCCM and 225°C for 2 hours. The test temperature was 85°C and test-gas flow rate was 5 SCCM.

The values of the 3 parameters can be seen to be essentially equal at all times, which indicates that the reaction is stoichiometric as expected. For simplicity, only the percent yield of CO_2 is plotted in subsequent figures even though the percent loss of CO and O_2 were determined and stoichiometry was observed in all cases.

In figure 1 note the initial dip in the percent yield of CO_2 before the steady-state value is attained. Investigation of the cause of this dip yields important insight into the behavior of Pt/SnO_2 catalysts, as discussed below.

Pretreatment Gas Composition

Figure 2 presents the percent conversion of CO to CO_2 for four different pretreatment gas compositions: (1) pure He, (2) 5% O_2 in He, (3) 5% CO in He, and (4) 5% H_2 in He. The pretreatment was carried out for 2 hours at 225°C and 5 SCCM, and the reaction conditions were 85°C and 5 SCCM in each case.

It can be seen that pretreatment with the two reducing gases, CO and H_2, produce approximately equal steady-state CO_2 yields which are higher than those for the other pretreatment gases. However, the steady-state yield is more rapidly attained with the H_2 pretreatment. Pretreatment with O_2 in He results in no greater CO_2 yield than pretreatment with He alone. The initial dip in activity is observed in all cases. It is clear from figure 2 that a reductive pretreatment of the catalyst results in greater CO_2 yields than does either an oxidative or inert pretreatment. Therefore, a CO pretreatment was employed for all subsequent tests.

Time and Temperature Effects

Figure 3 compares the percent CO_2 yield for an unpretreated catalyst sample with that for an equal-mass catalyst sample pretreated with CO for 1 hour and for another sample pretreated for 20 hours. The pretreatment temperature was 225°C and the reaction temperature was 75°C. The gas flow rate for both pretreatment and reaction was 10 SCCM. Clearly, pretreatment with CO enhances the CO_2 yield but the 20 hour-pretreatment is less effective than that for 1 hour.

Figure 4 compares the percent yield of CO_2 for an unpretreated catalyst sample to that for equal-mass samples pretreated at various temperatures. The flow rate in all cases was 10 SCCM and the reaction temperature was 75°C. All of the pretreated samples exhibited greater CO_2 yields than the unpretreated sample. No difference in CO_2 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 gas which exited the reactor tube during each pretreatment in this study showed that conversion of CO to CO_2, 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.

Cause and Elimination of Dip in CO_2 Yield

The initial dip in CO_2 yield which is frequently encountered 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 CO_2 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 CO_2 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 CO_2 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 somwhere 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 H_2O 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 H_2O content is sufficient. Figure 9 reproduces the CO_2 yield which was originally presented in figure 2 and which clearly exhibits an initial dip. The other curve is the CO_2 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 $CaCl_2{\bullet}2H_2O$. The resultant H_2O content of the reactant gas was about 0.2 mole-percent. No dip occurs. Furthermore, a higher yield of CO_2 was attained with the humidified reaction-gas than with the dry reaction-gas. Croft and Fuller (7) 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 that OH groups on the surface of the tin-oxide phase serve as oxidants for CO chemisorbed on the Pt. Hoflund and coworkers (8-10) have observed OH groups on tin-oxide surfaces using electron-stimulated desorption (ESD), secondary-ion mass-spectrometry (SIMS) and electron energy-loss spectroscopy (ELS). It is postulated that 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 concentration of OH resulting in the observed decline in catalyst activity. Migration of H_2O (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 the OH concentration at the catalyst surface is restored by humidification of the catalyst or the reaction gas, no dip is observed. If the OH concentration at the catalyst surface is increased by humidification, the activity of the catalyst is enhanced as shown in figure 9. This hypothesis, although tentative, is consistent with all of the observations presented in this paper.

Conclusions

The pretreatment conditions of Pt/SnO_2 catalysts are important in determining their activity for the oxidation of CO to CO_2. Reductive pretreatment with either CO or H_2 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 CO_2 yield before the steady-state yield is attained. This dip is caused by 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.

References

1. Schryer, D. R. et al., in "Closed-Cycle, Frequency-Stable CO_2 Laser Technology" (Batten, C. E., et al., Eds.), p. 113, NASA CP-2456, 1987.

2. Herz, R. K. in "Closed-Cycle, Frequency Stable CO_2 Laser Technology" (Batten, C.E., et al., Eds.), p. 103, NASA CP-2456, 1987.

3. Engel, T. and Ertl, G., in "The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis" (King, P. A. and Woodruff, D. P., Eds.), p. 73, Elsevier, New York, 1982.

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

5. Brown, K. G., et al., SPIE Proc. 663, 136, (1986).

6. Batten, C. E., et al., in "Closed-Cycle, Frequency-Stable CO_2 Laser Technology" (Batten, C. E., et al., Eds.), p. 113, NASA CP-2456, 1987.

7. Croft, G. and Fuller, M. J., Nature 269, 585, (1977).

8. Hoflund, G. B., et al., Appl. Surf. Sci. 14, 281, (1982-3).

9. Cox, D. F., Hoflund, G. B., and Laitenen, Appl. Surf. Sci. 20, 30, (1984).

10. Hoflund, G. B., et al., Thin Solid Films (in press).

Figure Captions

Figure 1. Typical test of Pt/SnO_2 catalyst.

Figure 2. Effect of several pretreatment gases on activity of Pt/SnO_2 catalyst.

Figure 3. Effect of pretreatment duration on activity of Pt/SnO_2 catalyst.

Figure 4. Effect of pretreatment temperature on activity of Pt/SnO_2 catalyst.

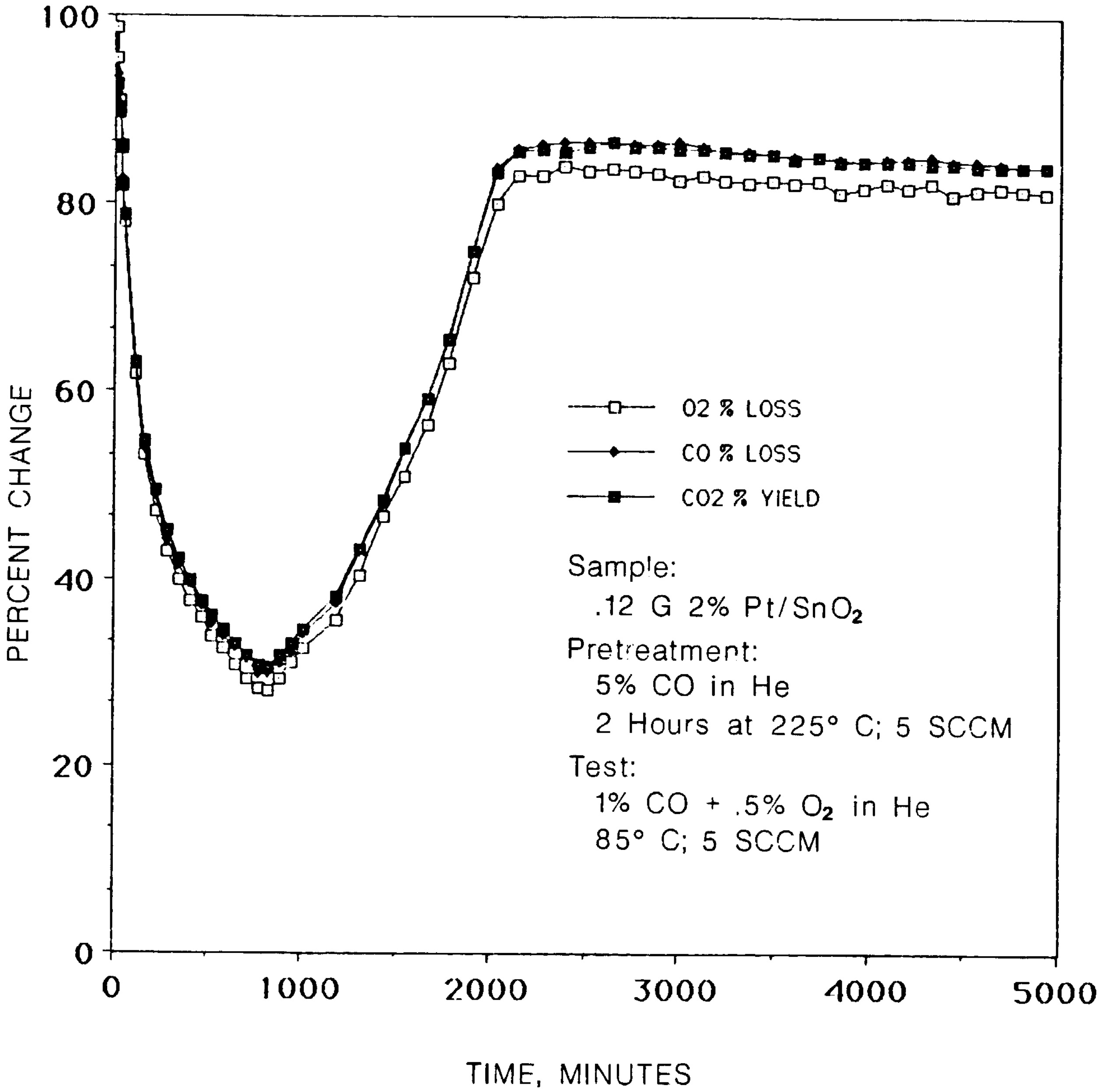
Figure 5. 28-day test of 1.5 grams of Pt/SnO_2 catalyst following extended pretreatment.

Figure 6. Expansion of selected data from Figure 4.

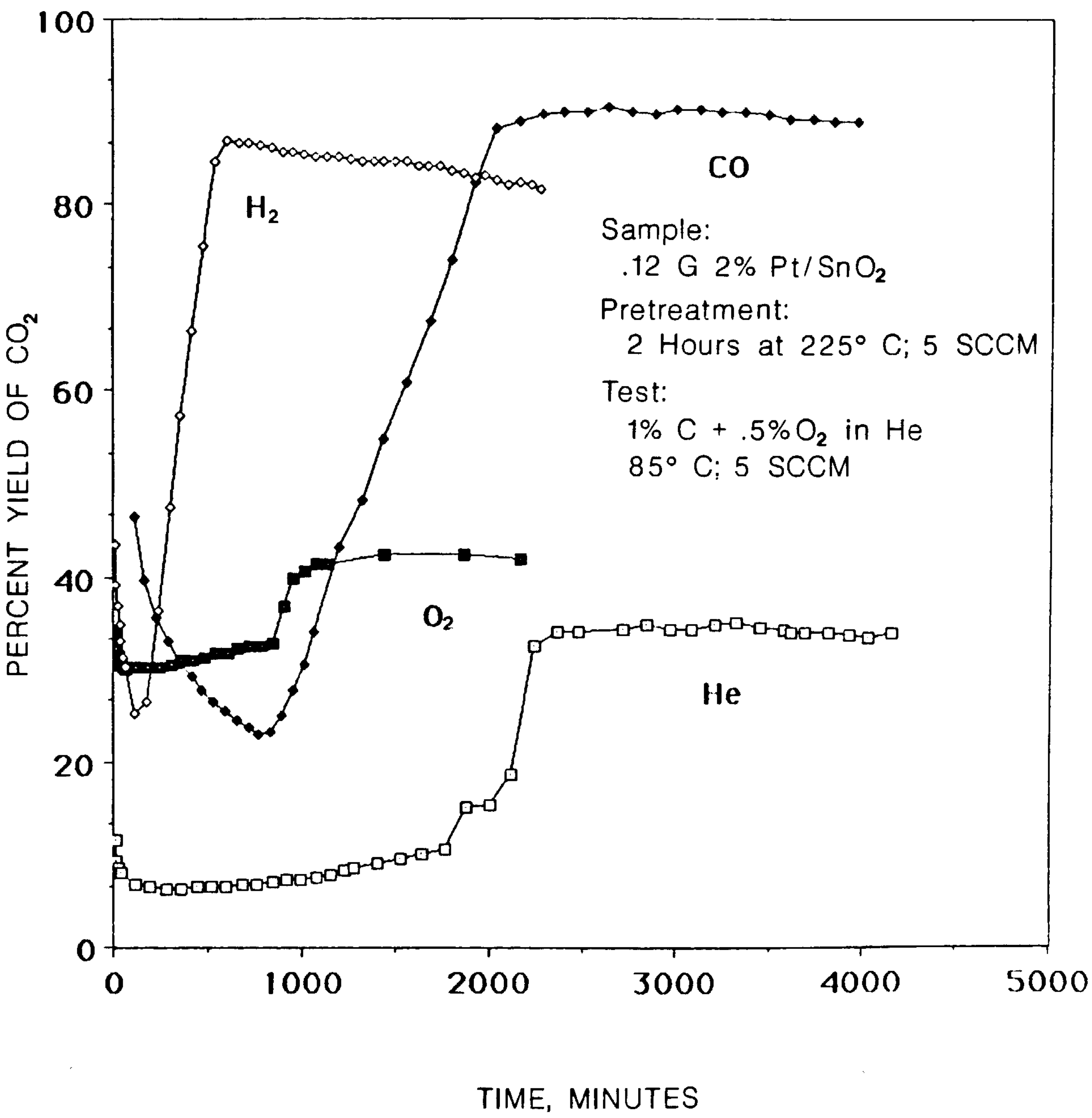
Figure 7. Effect of vacuum pretreatment on behavior of Pt/SnO_2 catalyst.

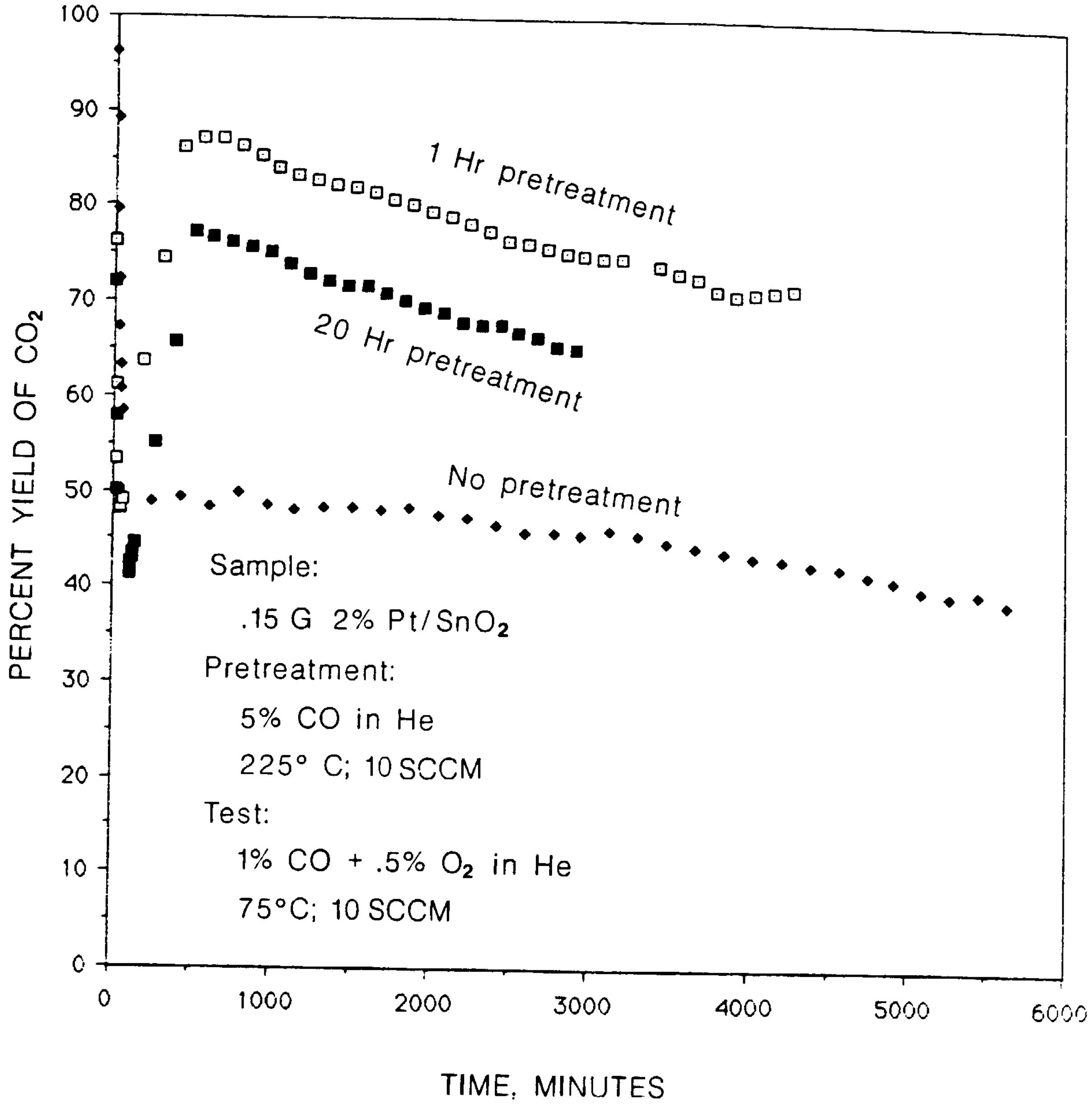
Figure 8. Effect of water addition following pretreatment on behavior of Pt/SnO_2 catalyst.

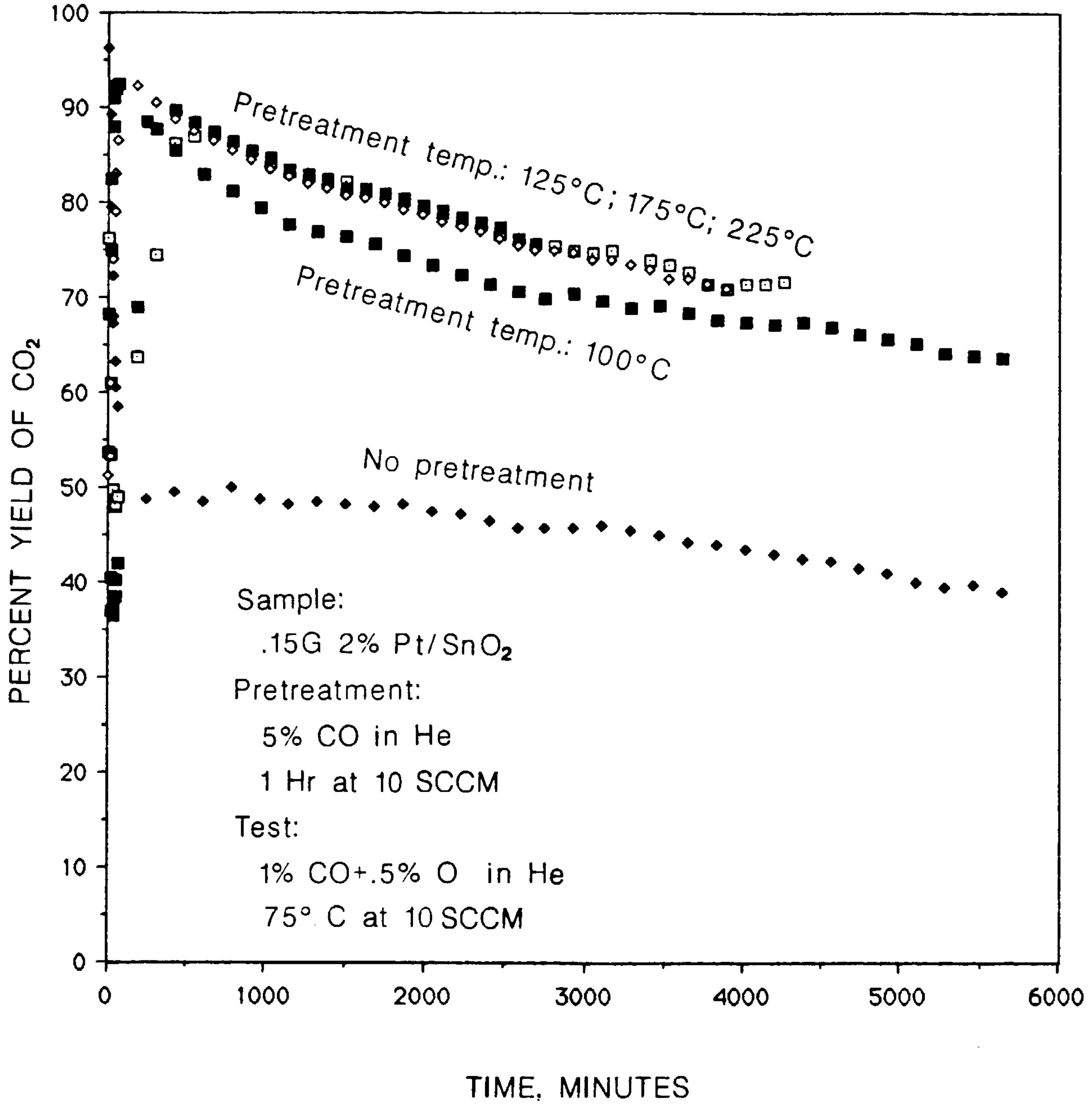
Figure 9. Effect of adding water to test gas on behavior of Pt/SnO_2 catalyst.

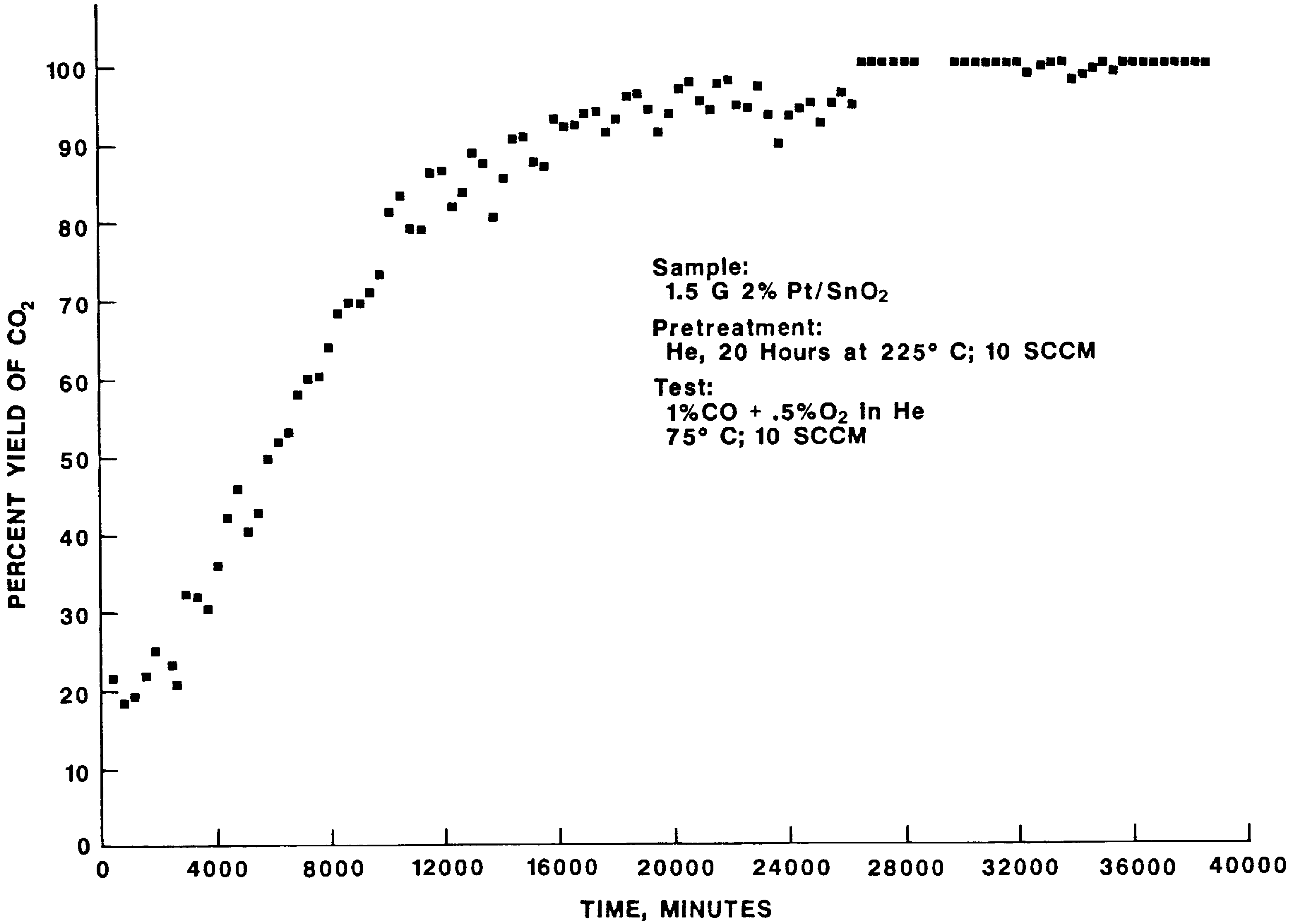


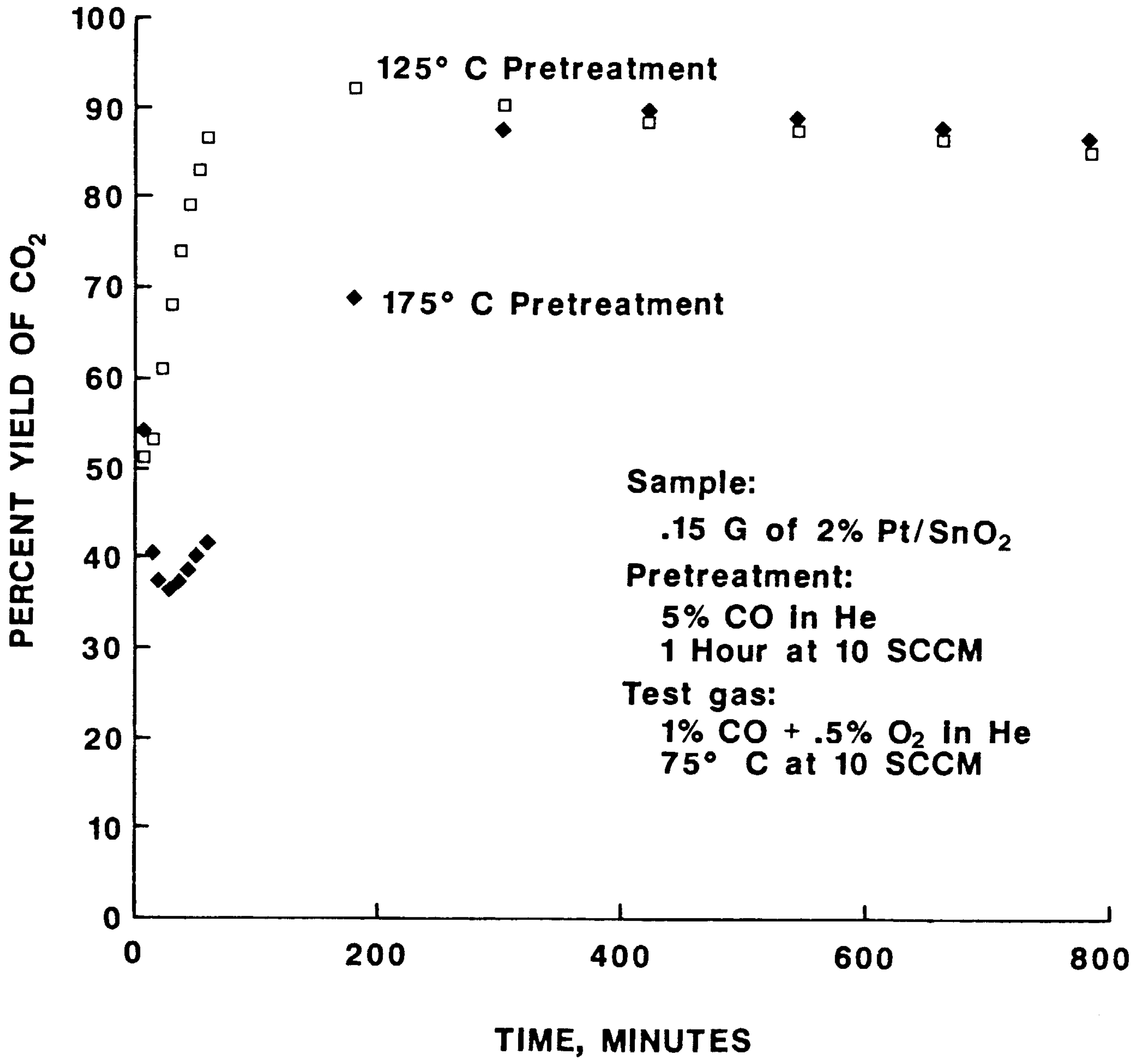
100
80
60
40
20
0
PERCENT CHANGE
0
1000
2000
3000
4000
5000
TIME, MINUTES
O2 % LOSS
CO % LOSS
CO2 % YIELD
Sample:
.12 G 2% Pt/SnO2
Pretreatment:
5% CO in He
2 Hours at 225° C; 5 SCCM
Test:
1% CO + .5% O2 in He
85° C; 5 SCCM

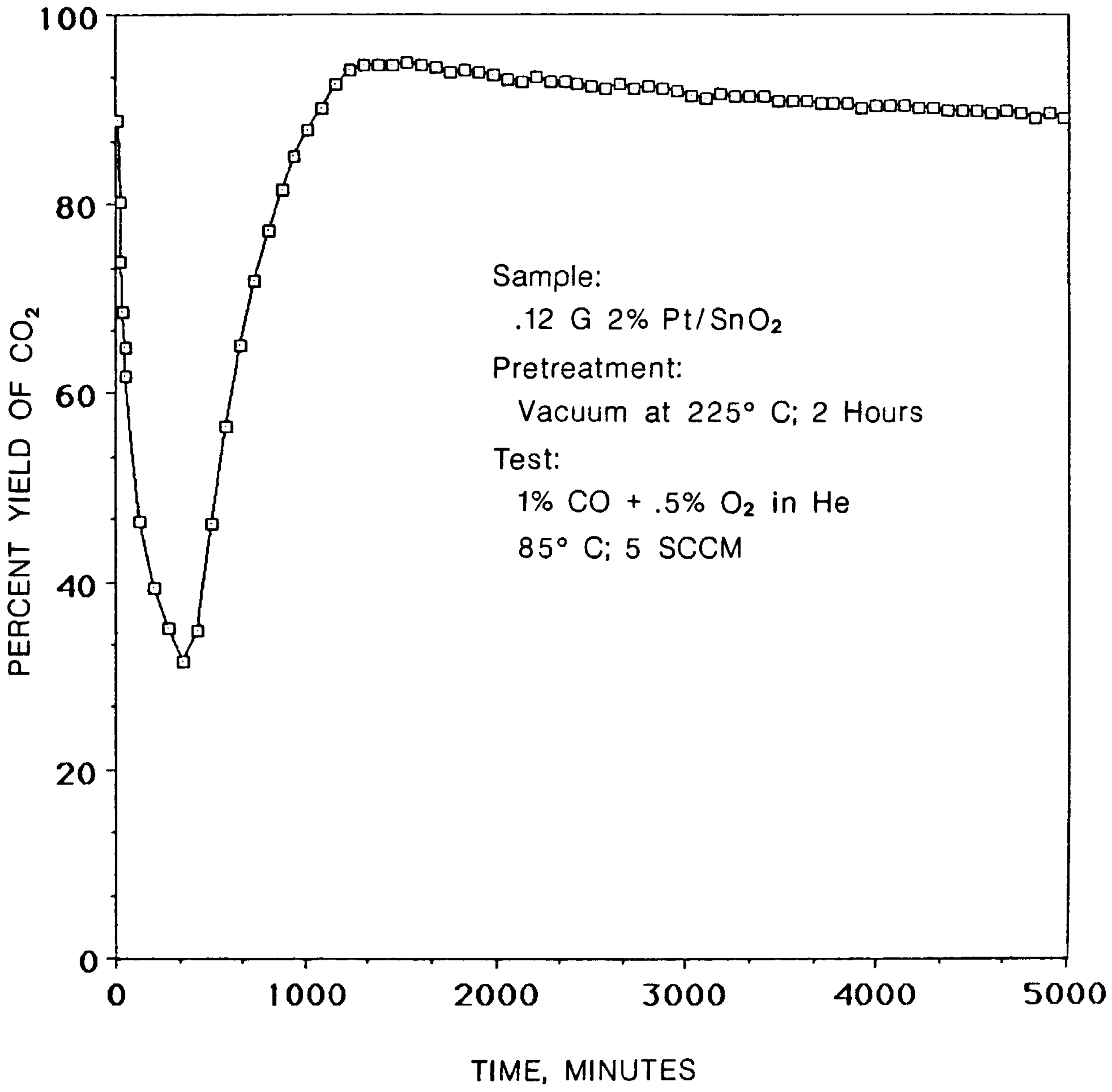

Sample:
.12 G 2% Pt/SnO$_2$
Pretreatment:
2 Hours at 225° C; 5 SCCM
Test:
1% C + .5%O$_2$ in He
85° C; 5 SCCM
CO
H$_2$
O$_2$
He
PERCENT YIELD OF CO$_2$
100
80
60
40
20
0
1000
2000
3000
4000
5000
TIME, MINUTES

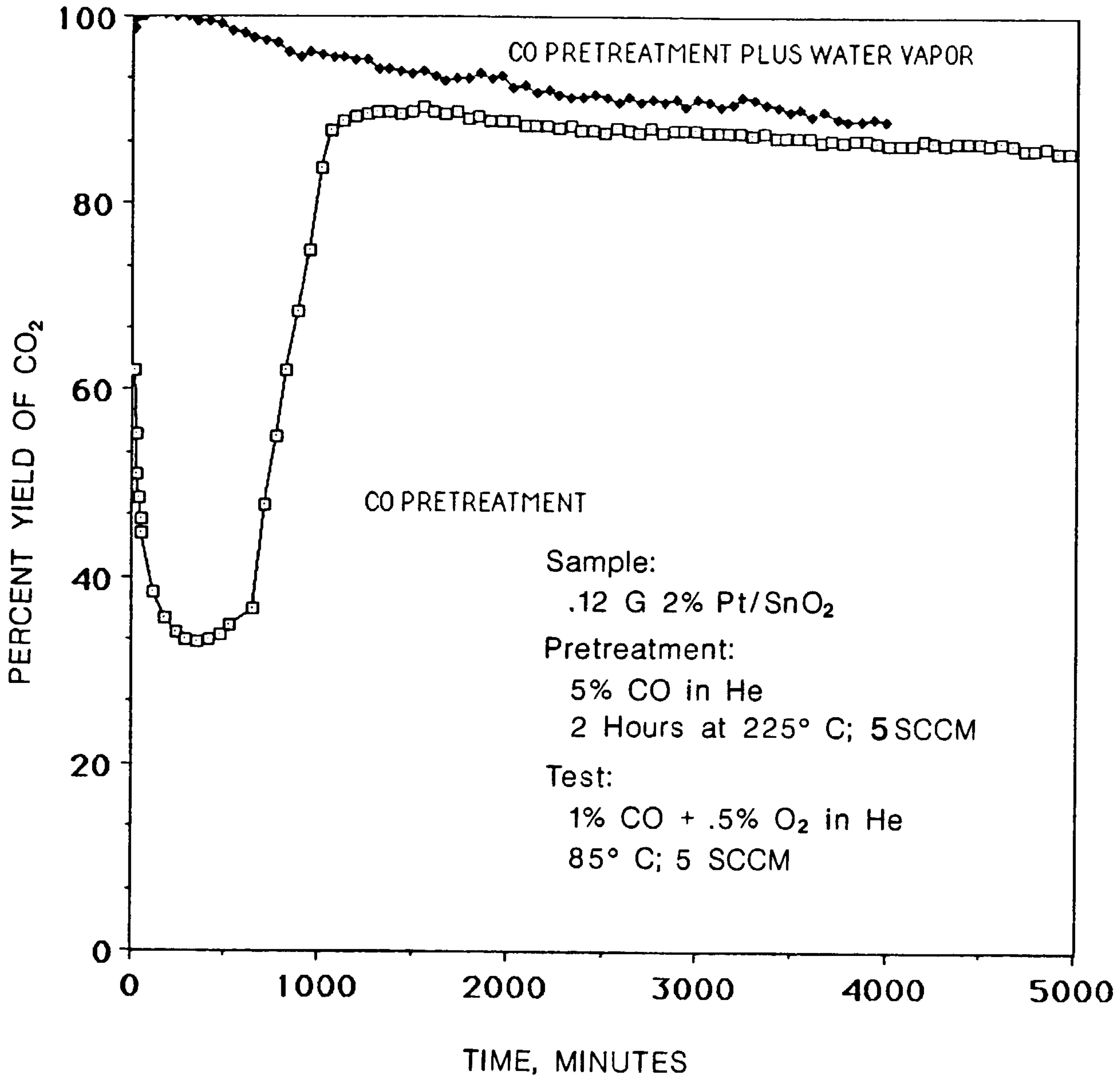

PERCENT YIELD OF CO_2
100
90
80
70
60
50
40
30
20
10
0
0
1000
2000
3000
4000
5000
6000
TIME, MINUTES
1 Hr pretreatment
20 Hr pretreatment
No pretreatment
Sample:
.15 G 2% Pt/SnO_2
Pretreatment:
5% CO in He
225° C; 10 SCCM
Test:
1% CO + .5% O_2 in He
75°C; 10 SCCM

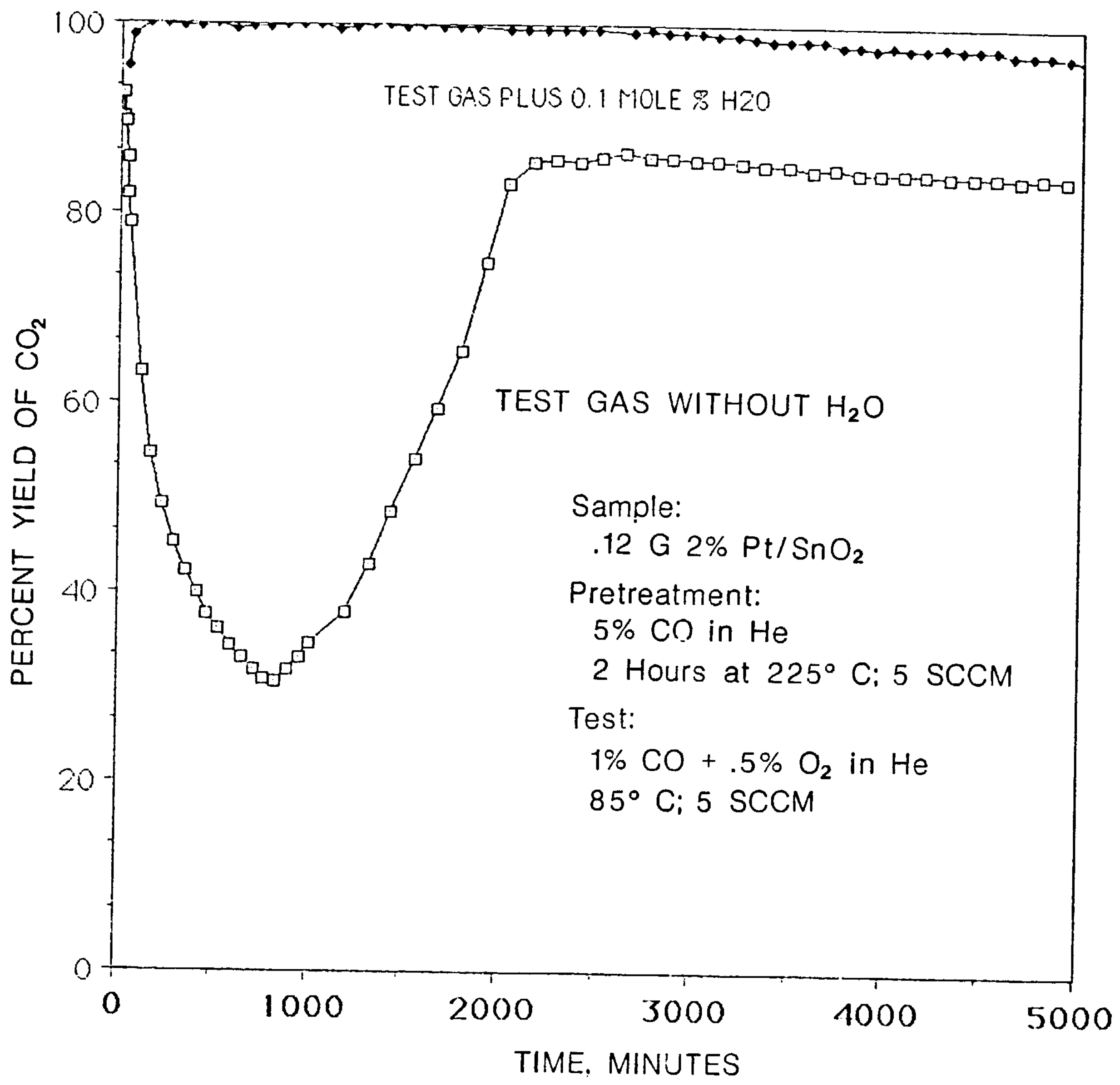

PERCENT YIELD OF CO2
TIME, MINUTES
0
10
20
30
40
50
60
70
80
90
100
0
1000
2000
3000
4000
5000
6000
Pretreatment temp.: 125°C; 175°C; 225°C
Pretreatment temp.: 100°C
No pretreatment
Sample:
.15G 2% Pt/SnO2
Pretreatment:
5% CO in He
1 Hr at 10 SCCM
Test:
1% CO+.5% O in He
75° C at 10 SCCM


Sample:
1.5 G 2% Pt/SnO$_2$
Pretreatment:
He, 20 Hours at 225° C; 10 SCCM
Test:
1%CO + .5%O$_2$ In He
75° C; 10 SCCM
PERCENT YIELD OF CO$_2$
0
10
20
30
40
50
60
70
80
90
100
TIME, MINUTES
0
4000
8000
12000
16000
20000
24000
28000
32000
36000
40000


125° C Pretreatment
175° C Pretreatment
Sample:
.15 G of 2% Pt/SnO2
Pretreatment:
5% CO In He
1 Hour at 10 SCCM
Test gas:
1% CO + .5% O2 In He
75° C at 10 SCCM
PERCENT YIELD OF CO2
100
90
80
70
60
50
40
30
20
10
0
0
200
400
600
800
TIME, MINUTES


100
80
60
40
20
0
PERCENT YIELD OF CO_2
0
1000
2000
3000
4000
5000
TIME, MINUTES
Sample:
.12 G 2% Pt/SnO_2
Pretreatment:
Vacuum at 225° C; 2 Hours
Test:
1% CO + .5% O_2 in He
85° C; 5 SCCM


CO PRETREATMENT PLUS WATER VAPOR
CO PRETREATMENT
Sample:
.12 G 2% Pt/SnO$_2$
Pretreatment:
5% CO in He
2 Hours at 225° C; 5 SCCM
Test:
1% CO + .5% O$_2$ in He
85° C; 5 SCCM
PERCENT YIELD OF CO$_2$
100
80
60
40
20
0
0
1000
2000
3000
4000
5000
TIME, MINUTES


100
80
60
40
20
0
PERCENT YIELD OF CO2
0
1000
2000
3000
4000
5000
TIME, MINUTES
TEST GAS PLUS 0.1 MOLE % H2O
TEST GAS WITHOUT H2O
Sample:
.12 G 2% Pt/SnO2
Pretreatment:
5% CO in He
2 Hours at 225° C; 5 SCCM
Test:
1% CO + .5% O2 in He
85° C; 5 SCCM