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Phillips CO-Oxidation Catalysts for Long-Lived CO₂ Lasers: Activity and Initial Characterization Studies

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Summary

Four different catalysts have been developed specifically for use in sealed carbon dioxide lasers. The catalysts have been designed to be low dusting, stable to shock and vibration, have high activity at low temperatures and have long active lifetimes. Measured global CO oxidation rates range from 1.4 to 2.2 cc CO converted per minute per gram of catalyst at ambient temperature. The catalysts also retain substantial activity at temperatures as low as -35 C. The Phillips laser catalysts are prepared in a variety of different shapes to meet the different pressure drop and gas flow profiles present in the many different styles of lasers. Each catalyst has been tested in sealed TEA* lasers and has been shown to substantially increase the sealed life of the laser. Activity measurements made on the precious metal catalysts which were prepared with and without activity promoters showed that the promoter materials increase catalyst CO oxidation activity at least an order of magnitude at ambient temperature. Initial studies using H₂ and CO chemisorption, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) have shown that the activity promoters do not significantly affect the precious metal crystallite size or the electronic structure around the precious metal. In addition, the formation or lack of formation of solid solutions between the precious metal and promoters has also been shown not to affect the activity of the promoted catalyst.

Introduction

The operation of pulsed CO₂ lasers over long periods of time in a sealed-off condition requires that a technique be developed to control the build-up of oxygen that occurs during the normal operation of the laser. The presence of oxygen has been thought to be one of the most important factors which cause discharge instability (1-4). The use of gas phase additives in sealed CO₂ lasers has had some success in extending the useful sealed life of the laser. However, when the laser must operate over several million pulses or at high repetition rates it becomes necessary to use a catalyst which recombines carbon monoxide and oxygen to carbon dioxide at a rate which is at least equal to or greater than that at which they are being formed during operation of the laser. Many of the CO oxidation catalysts which have been tested in pulsed CO₂ lasers have been based upon Pt or other precious metals supported on SnO₂ which may contain other metal promoters to enhance catalytic activity (5-9). Laser testing of the tin catalysts has clearly shown that catalytic recombination of CO and O₂ can extend the sealed usable life of pulsed CO₂ laser systems.

During the past several years Phillips Petroleum has developed a series of four proprietary catalysts (designated LC-0100, LC-0200, LC-0300 and LC-0400) which have

*transversely excited atmospheric pressure configuration

been shown, on several occasions, to be effective at substantially extending the sealed-off lifetime of pulsed CO₂ lasers at temperatures as low as -35 C. Each of the different catalysts have been designed to have minimal dust formation, be stable to shock and vibration, have high activity at low temperatures, and have long active lifetimes.

Experimental

Catalytic activity measurements were made using a continuous flow system schematically shown in Figure 1. Carbon monoxide was continuously monitored using an Anarad infrared analyzer. Oxygen and carbon dioxide were spot checked using gas chromatography. The catalyst reactor consisted of a 7 mm i.d. quartz tube fitted with thermocouple well, which was in contact with either the upstream or downstream edge of the catalyst bed. The LC-0100 and LC-0400 catalysts were loaded as full size particles (1 or 2 grams); the LC-0300 catalyst was broken to approximately 3/16 inch particles. Void spaces between catalyst particles were packed with 16/30 mesh quartz chips to enhance flow characteristics and transfer heat away from the catalyst particles during the highly exothermic CO oxidation reaction. By using this packing method the increase in gas temperature across the catalyst bed was kept to less than 10 C. The LC-0200 catalyst, which is a monolith supported material, was tested as a 1 inch diameter by 1 inch deep cylinder in a quartz reactor just slightly larger than the monolith or as material which had been crushed to approximately 1/8 inch particles.

Unless otherwise specified, all of the catalysts were reduced in flowing hydrogen at 300 C for two hours prior to each experiment. After reduction, the catalyst was cooled under a helium purge. The standard experiment consisted of passing 400 sccm of simulated laser blend containing 1.20% CO, 0.60% O₂, 32% CO₂, and 32% He with the balance being nitrogen. Reactor and inlet gas temperatures were controlled by placing the reactor and inlet gas lines in a Thermotron environmental chamber. Global rates are expressed as ml of CO at STP converted per minute per gram of catalyst. Although this method of activity measurement introduces sometimes severe limitations due to external and internal heat and mass transfer effects, the authors have found the global rates calculated in this manner to be very useful in determining how much catalyst would be needed in various laser applications, using the known carbon monoxide or oxygen production rates of each laser and the gas recirculation rates within the laser.

Results

Each of the Phillips catalysts are based on precious metals, activity promoters, and support materials which not only provide needed structural and flow characteristics but also enhance the activity of the catalytic components. Each one of the four catalysts to be discussed here use a chemically distinct support.

LC-0100 Series. This series of catalysts are prepared on activated cylindrical tablets that are nominally 4.7 mm in diameter and 4.7 mm in height. The average bulk density of the finished catalyst is 1 gram per cc, with nitrogen BET* surface areas in the 50 to 60 m²/gram range. Figure 2 shows a lifetime test for the catalyst at two different activation temperatures. No improvement in catalyst activity is obtained when hydrogen activation is carried out at temperatures above 300 C. As shown in the figure the catalyst has initially high CO conversion

*Brunauer, Emmett, and Teller

activity which declines to a steady state value after approximately 100 hours of testing. After the steady state activity has been reached, (1.4 cc CO/min/gram), no degradation of activity was observed in tests which lasted as long as 35 days. Soaking of the catalyst in a CO₂, N₂ and He blend which contained no CO or O₂ had no detrimental effect on activity. Exposure of the catalyst to atmospheric oxygen for several hours reduced CO oxidation activity by about 90%; however, when the catalyst was reactivated in hydrogen or carbon monoxide at 300 C, its activity returned to that of the fresh catalyst. To illustrate the strong effects of heat and mass transfer, where full size particles had an activity of 1.4 cc CO/min/gram, a one gram sample of the same catalyst crushed to 30/40 mesh and mixed with an equal volume of quartz chips gave 100% CO conversion at virtually any feed rate. In high flow cases the catalyst temperature easily exceeded 150 C.

Figure 3 shows catalyst activity as a function of inlet gas temperature. The three different curves are for catalysts prepared using the same method over a 14 month interval to check synthesis repeatability. Figure 4 shows low temperature data over a several hour test period. Catalysts used in both Figures 3 and 4 were brought to their steady state activity level at ambient temperature before temperature testing was begun.

LC-0200 Series. This series of catalysts are prepared by supporting the active catalyst components on a standard cordierite monolith. Activity testing of the crushed monolith catalyst (1/8 inch particles) gave a steady state rate of CO conversion of approximately 2 cc CO/min per gram of supported catalyst material (does not include weight of cordierite monolith). Testing of a 1 by 1 inch monolithic cylinder having 100 cells/inch gave 100% conversion under our test conditions. Figure 5 is a photograph of a Phillips monolith catalyst that was used successfully in high pulse rate TEA laser tests.

LC-0300 Series. The LC-300 series of catalysts have been designed specifically for applications where large volumes of gas must be passed over the catalyst with low pressure drop. This catalyst is also the hardest and most durable of any of the Phillips laser catalysts. The catalyst is supplied as 15.9 mm diameter by 9.5 mm thick tablets with seven 3.2 mm holes to improve diffusion and pressure drop characteristics (see Figure 6). Average bulk density of the finished catalyst is 0.8 grams/cc with an N₂ BET surface area of 50 m²/g. As shown in Figure 7 the catalyst has a steady state activity of 1.5 cc CO/min per gram of catalyst. This catalyst is not as susceptible to reversible poisoning by atmospheric oxygen as the LC-0100 catalyst.

LC-0400 Series. The LC-0400 series of catalysts have been designed specifically to reduce the reversible poisoning of the catalyst by atmospheric oxygen during shipment and loading into the CO₂ laser. The catalyst is normally supplied as 3.2 mm diameter spheres. Catalysts having diameters of 4.8, 7.9 or 12.7 mm can also be prepared. The average bulk density of the finished catalyst is 0.72 grams/cc with an N₂ BET surface area in the 250 to 300 m²/gram range. As shown in Figure 8 the catalyst is quite tolerant to exposure to oxygen and moisture. The data were taken after the catalyst had been stored in the shipping container for thirty days then exposed to laboratory atmosphere for 6 hours before pretreatment and testing.

Characterization Studies

As mentioned earlier, each of the Phillips catalysts contains precious metals, support material and activity promoters. Comparative tests of pairs of catalysts prepared by identical

procedures, one with and the other without the activity promoters, showed that the activity promoters increased the rate of CO oxidation at ambient temperature by at least one order of magnitude. Catalysts that contained only the supported promoters were totally inactive for CO oxidation.

We are now engaged in a series of studies aimed at understanding the specific role played by the promoters in increasing so dramatically the low temperature activity of these catalysts. We report here preliminary results of X-ray diffraction studies, H₂ and CO chemisorption studies, and XPS analysis for catalysts in the LC-0100 series.

XRD studies. The purpose of the XRD studies was, on the one hand, to determine the influence of the promoters on the crystallinity and the sintering characteristics of the precious metals and, on the other hand, to establish whether solid solutions of the precious metals and of the promoters are formed and whether their formation is responsible for the increased catalytic activity.

For this work, in order to obtain XRD patterns of sufficient intensity for peak shape analysis, it was necessary to use catalysts with significantly higher contents of precious metals and promoters than the catalysts used in the activity tests. Three catalysts were investigated: one contained only the support and a precious metal (Catalyst 1), the other two also contained promoters (Catalysts 2 and 3). The latter two catalysts had identical composition, but were prepared by different procedures referred to here as A and B.

After reduction of these catalysts in hydrogen at 300 C, the precious metal XRD pattern of the catalyst prepared by procedure A (Catalyst 2) was very similar to that of the catalyst without promoters (Catalyst 1). In contrast, both the breadth and the shape of the precious metal peaks were affected by the promoters in the catalyst prepared by procedure B (Catalyst 3). This difference is illustrated in Figure 9 for the metal [111] peak. The asymmetry of the metal peaks in Catalyst 3 reflects alterations of the metal lattice constant and consequent shifts in the XRD peak arising from the formation of solid solutions of the precious metal and the promoters with a broad range of stoichiometries. Despite these differences in the XRD patterns, there was little difference in activity between catalysts prepared by procedure A and by procedure B.

In the absence of promoters, the average crystallite size of the precious metals, as measured from the breadth of the [111] peak using Scherrer's equation, was a function of the temperature at which the catalyst was reduced in hydrogen, increasing with increasing temperature. The same trend was observed in the presence of the promoters, but, because of the peak broadening described above, only a qualitative comparison of Catalyst 1 with Catalyst 3 was possible.

These results indicate that the promoters do not influence significantly the crystallinity of the precious metal or its sintering as a function of temperature. They also show that bulk solid solutions of the precious metals and the promoters may be formed, but that their formation is not necessary for promoting the activity of the precious metals.

Chemisorption measurements. H₂ and CO chemisorption measurements were made on catalysts containing the same amounts of precious metal and promoters as in the activity tests. Three catalysts were studied containing the same amount of precious metal: one without

promoters (Catalyst 4), and the other two with the same amounts of promoters; of these, one (Catalyst 5) was prepared by procedure A, and the other (Catalyst 6) by procedure B. The catalysts were reduced at 200 or 300 C in hydrogen, and were evacuated overnight at 250 C, before the chemisorption measurements. Isotherms were measured at ambient temperature (22-25 C). As shown in Table 1, there was no significant difference in the total volumes of gas absorbed by the unpromoted and the promoted catalysts. These results are in accord with the results of the XRD experiments and indicate that the promoters do not affect the dispersion of the precious metals.

XPS studies. Two of the catalysts used in the chemisorption measurements, catalysts 4 and 5, were also subjected to XPS analysis. The XPS spectrometer is equipped with a chamber for the pretreatment of the samples at high temperatures, so that the samples could be oxidized and reduced in the chamber and moved directly into the instrument. Only data for the reduced samples are reported here.

As anticipated from the results of the XRD studies and of the chemisorption studies, the relative surface coverage of the precious metal was essentially identical in the two samples. More significantly, the binding energies of the representative precious metal lines were the same, within experimental error, for the two samples. This indicates that the promoter produces no significant changes in the electron density around the precious metal.

Altogether, the results reported here lead to the conclusion that the observed changes in catalytic activity produced by the addition of the promoters are not related to the formation of bulk alloys, nor can they be attributed to changes in the dispersion of the precious metal, to changes in the electronic density around the precious metal atoms, or to changes in the CO chemisorption capacity of the catalyst. It is likely that more subtle electronic phenomena are responsible for the effects of the promoters on the catalytic activity.

Conclusions

The preceding discussion has described four different catalysts that have been developed by Phillips Petroleum for use in carbon dioxide lasers. Each of the catalysts has been proven to be effective in numerous pulsed CO₂ TEA laser tests. Using simulated laser test conditions, the full size catalyst particles have global CO conversion rates between 1.4 and 2.2 cc CO converted per minute per gram of catalyst. The different particle shapes available allow optimization of pressure drop and gas flow profiles. Initial chemisorption studies, XRD and XPS studies have been conducted in an attempt to explain the role of activity promoters and how they increase CO conversion rates by over an order of magnitude. These studies have shown that the promoters do not significantly affect the precious metal dispersion or the electronic structure around the precious metal; in addition, the formation of solid solutions between the precious metals and promoters also do not seem to affect catalyst activity. Characterization studies are continuing which may allow us to elucidate what the exact role of the activity promoters are.

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Table 1. Relative volumes of H₂ and CO chemisorbed at 100 torr by unpromoted and promoted catalysts.

A. Reduction temp=200 C. Promoted catalyst prepared by procedure A.

	Promoted	Unpromoted
H ₂	1.0	0.9
CO	1.0	1.0

B. Reduction temp=300 C. Promoted catalyst prepared by procedure B.

	Promoted	Unpromoted
H ₂	1.0	1.0
CO	1.0	1.1

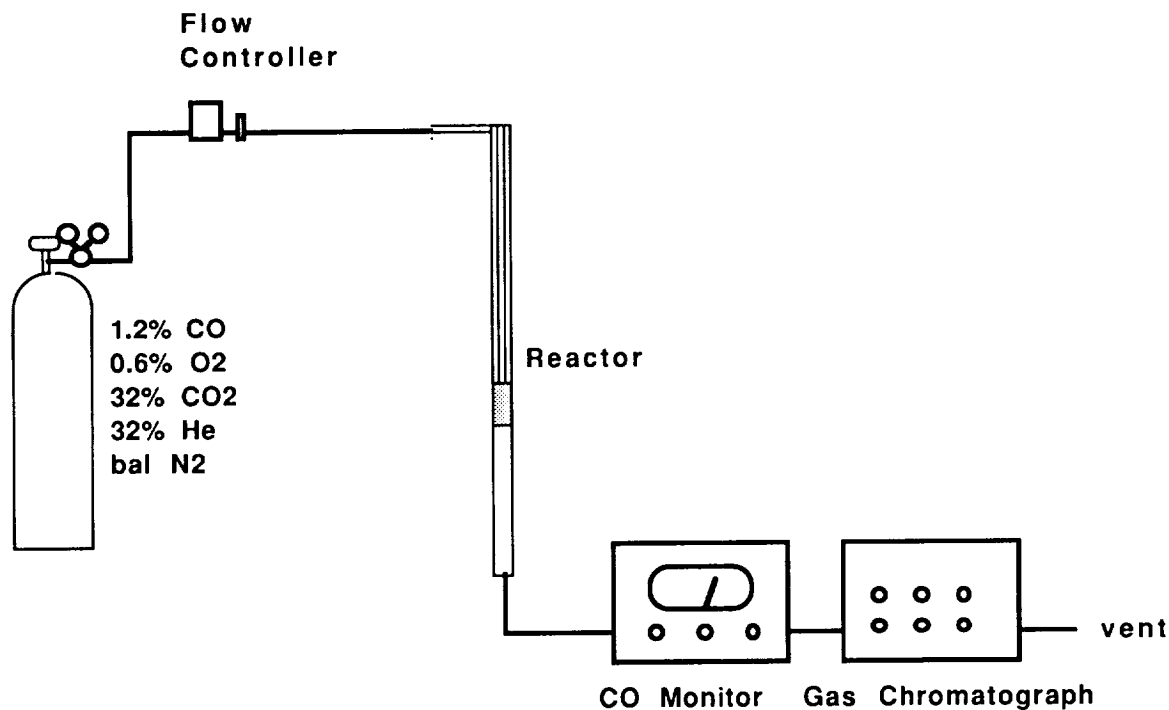


Figure 1. Apparatus used to measure CO oxidation rates.

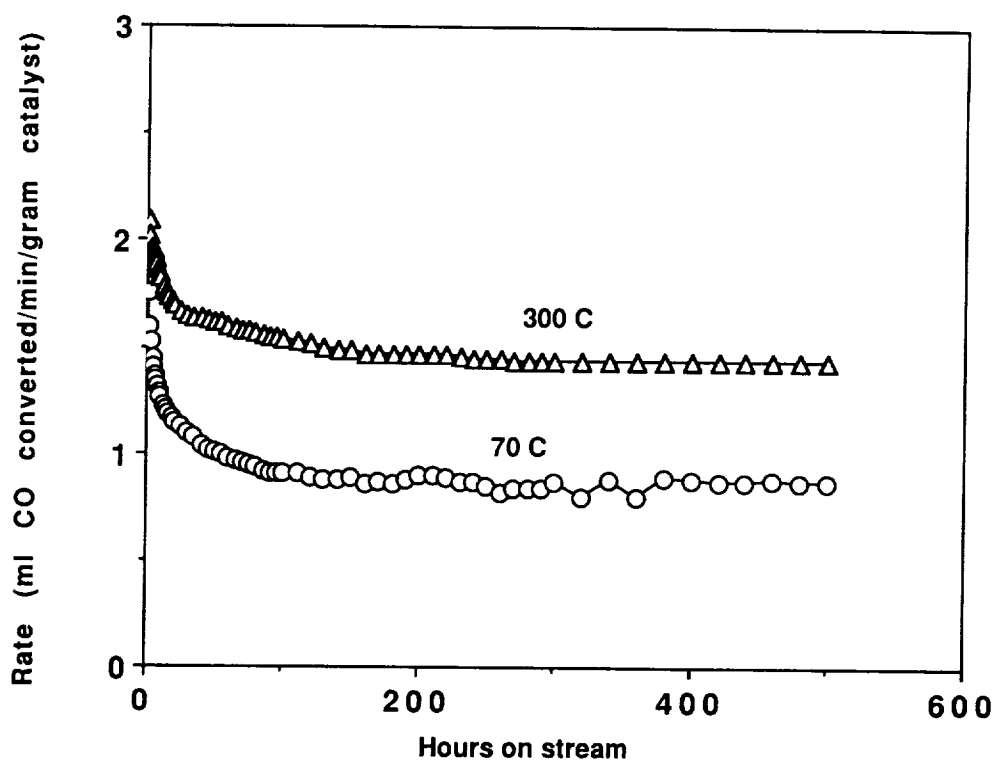


Figure 2. Activity of LC-0100 catalyst at ambient temperature after two hour activation in hydrogen at 70 C and 300 C.

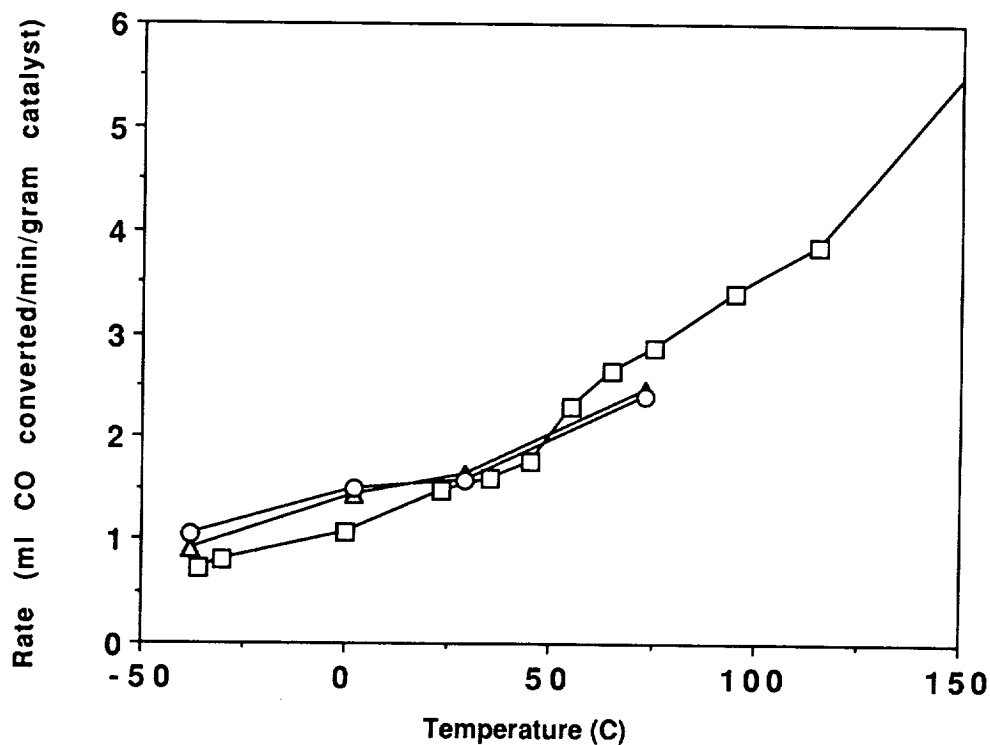


Figure 3. Activity of LC-0100 catalyst as a function of temperature for three samples of catalyst prepared over a 14 month interval.

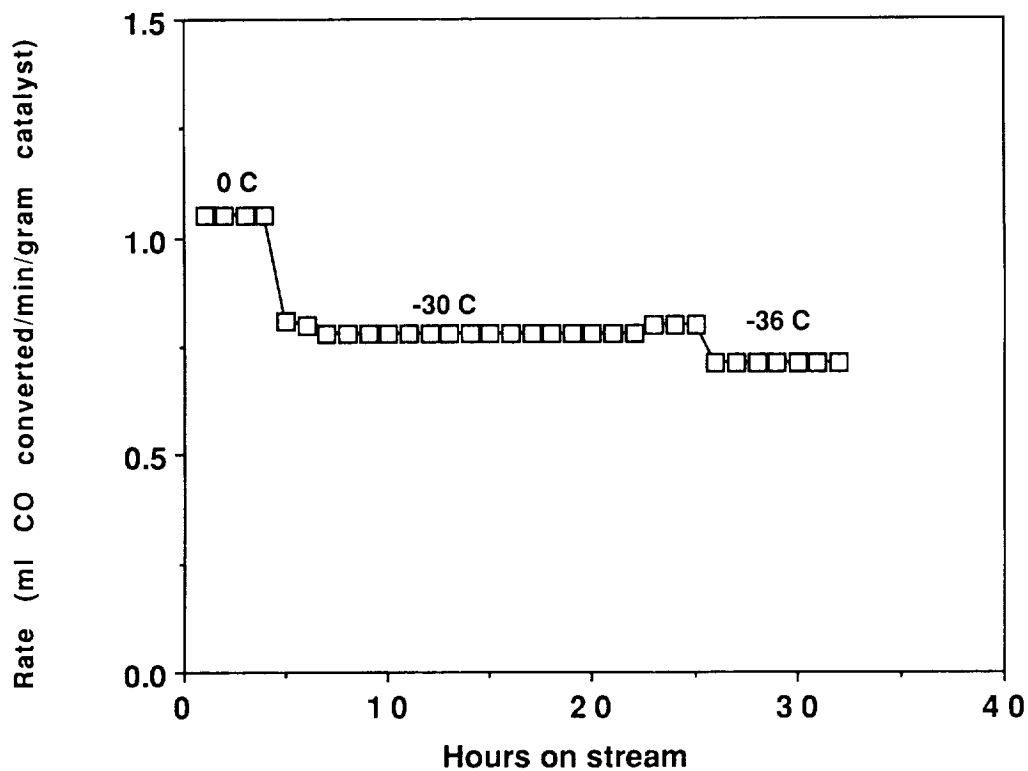


Figure 4. Low temperature data for the LC-0100 catalyst as a function of hours on stream after reaching steady-state activity.

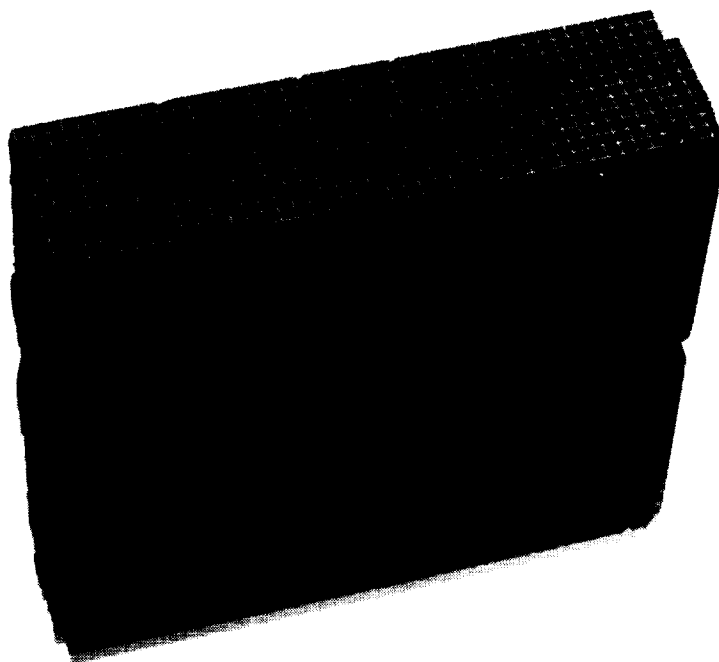


Figure 5. Phillips LC-0200 cordierite monolith CO oxidation catalyst.

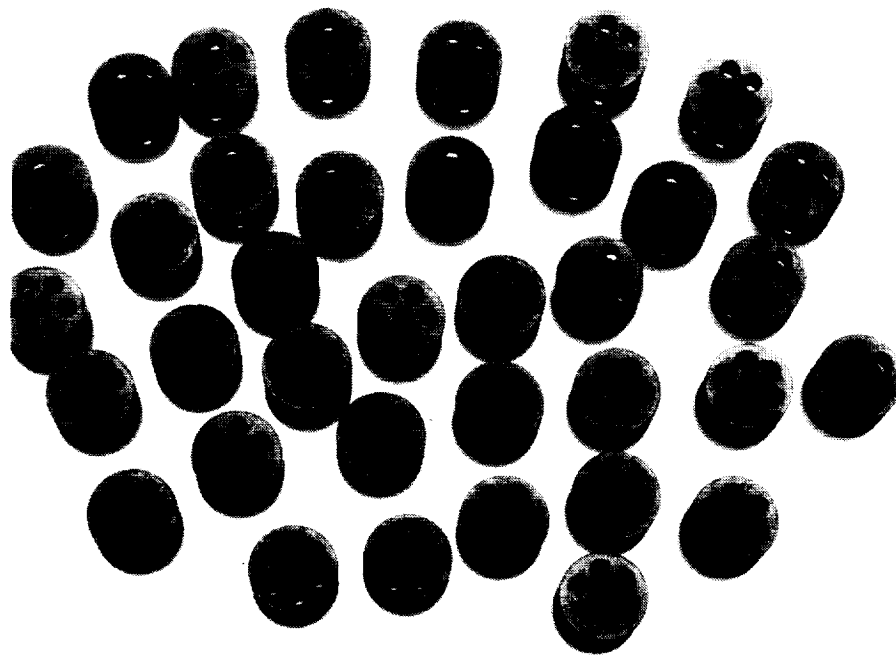


Figure 6. Phillips LC-0300 CO oxidation catalyst.

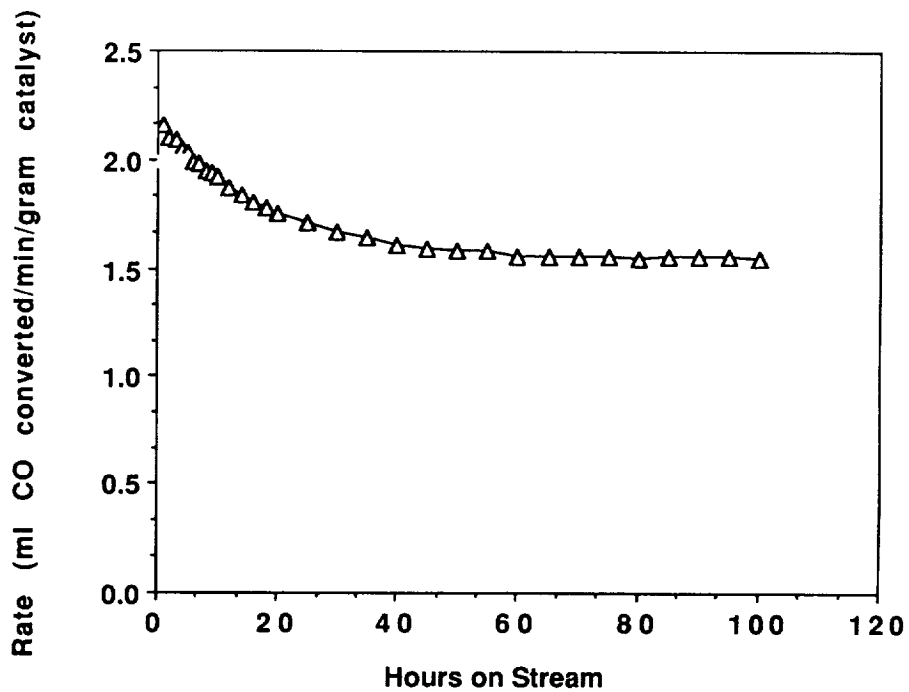


Figure 7. Activity of LC-0300 catalyst at ambient temperature after activation at 100 C in hydrogen prior to testing.

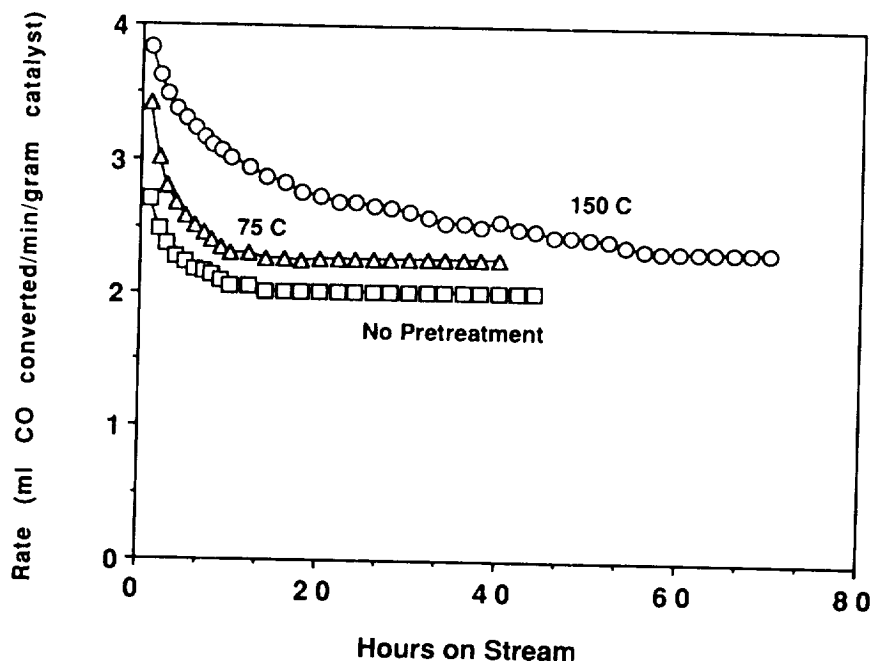


Figure 8. Activity of LC-0400 catalyst at ambient temperature under simulated shipping conditions including air exposure followed by activation in H₂ at temperature shown.

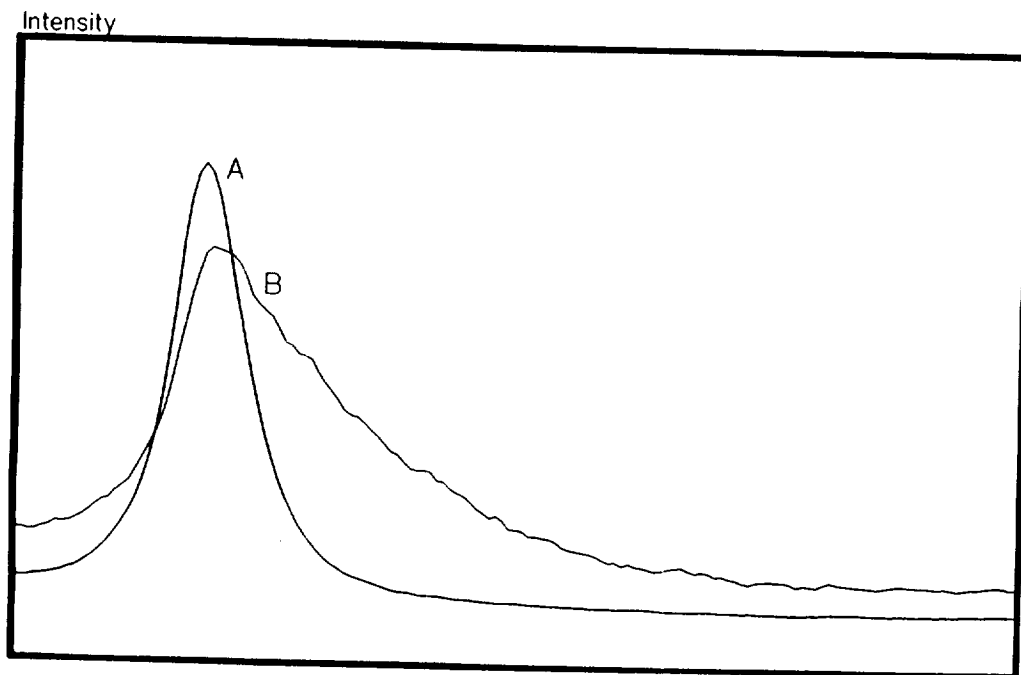


Figure 9. [111] Peak for (A) unpromoted catalyst and (B) promoted catalyst prepared by procedure B.

