

ALTERNATIVE CATALYSTS FOR LOW-TEMPERATURE CO OXIDATION

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ABSTRACT

MnO_x, Ag/MnO_x, Au/MnO_x, Cu/MnO_x, Pd/MnO_x, Pt/MnO_x, Ru/MnO_x, Au/CeO_x and Au/Fe₂O₃ were synthesized and tested for CO oxidation activity in low concentrations of stoichiometric CO and O₂ at 30-75°C. Catalytic activity was measured for periods as long as 18000 minutes. At 75° Au/MnO_x is most active sustaining nearly 100% CO conversion for 10000 minutes. It also retains high activity at 50 and 30°C with negligible decay in activity. A direct comparison between an unpretreated 10% Au/MnO_x catalyst and an optimized 19.5% Pt/SnO₂ (pretreated) catalyst shows that the Au/MnO_x catalyst exhibits much higher catalytic activity and far superior decay characteristics. Other catalysts including Au/CeO_x and Au/Fe₂O₃ also perform well. The Cu/MnO_x exhibits a high initial activity which decays rapidly. After the decay period the activity remains very stable making Cu/MnO_x a potential candidate for long-term applications such as CO₂ lasers in space.

INTRODUCTION

The catalytic oxidation of carbon monoxide near ambient temperatures has important applications. Closed-cycle CO₂ lasers produce CO and O₂ in the laser discharge resulting in a rapid loss of output power. This problem can be overcome by incorporating a low-temperature CO oxidation catalyst into the laser system which converts the dissociated products back into CO₂ (1-3). Also, air filtration devices often contain catalysts to oxidize dangerous levels of toxic CO. Such devices are utilized in fire safety equipment and in underground mines as respiratory aids.

Consequently, the development of low-temperature CO oxidation catalysts has received considerable attention (1-19). Although significant progress has been made with regard to understanding the reaction mechanism (6,7,10,13), there remains a need for development of catalysts which exhibit higher activities for prolonged periods at low temperatures (typically less than 100°C) and in the diverse range of oxidation environments which are encountered. Factors which determine oxygen availability and gaseous impurities often have a pronounced effect on catalyst performance. CO oxidation in ambient air has the advantages of excess O₂ and low CO₂ concentrations which facilitate the reaction considerably. Consequently, numerous materials are known to oxidize CO in excess O₂ at low temperatures (4,5,14-17), but complications due to presence of humidity and/or air pollutants are often detrimental to their activity. In CO₂ lasers, CO and O₂ are present in small stoichiometric quantities in a large amount of CO₂. Although the catalytic reaction benefits from the fact that the lasers usually operate at temperatures somewhat above ambient (25-100°C), catalytic CO oxidation is difficult under these conditions.

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Recently, Haruta and coworkers prepared supported-gold catalysts on various base-metal oxides including MnO_x , Fe_2O_3 , Co_3O_4 , NiO and CuO and determined their catalytic activities toward the oxidation of H_2 and/or CO (18,19). Most of the CO oxidation runs were carried out using 1 volume % CO in dry air. At 0°C $\text{Au/Fe}_2\text{O}_3$ and Au/NiO maintain essentially 100% CO conversion under the flow conditions used over a 7-day test period. Similar performance was also observed for $\text{Au/Fe}_2\text{O}_3$ and $\text{Au/Co}_3\text{O}_4$ at 30°C in 76% relative humidity. Therefore, these catalysts appear to be quite useful in air purification devices, but activities in the presence of air contaminants were not determined. These catalysts may be useful in CO_2 lasers even though the reaction conditions are quite different as described above. It is interesting to note that Haruta and coworkers apparently did not examine the behavior of Au/MnO_x toward CO oxidation.

Catalysts consisting of Pt and/or Pd supported on tin oxide have been researched extensively for use in CO_2 lasers (1-13). Although these materials can exhibit considerable CO oxidation activity in this application, there are complications which must be overcome. Acceptable activity is observed only after the catalyst undergoes a reductive pretreatment. Unfortunately, such pretreatments often lead to considerable induction periods often lasting several days during which the observed activity declines before reaching a maximum (7). Even after acceptable activity is recovered these materials exhibit a steady decay in performance over time. Efforts to understand and correct these problems continue (6-10).

The purpose of the present study is to explore the behavior of materials other than platinized tin oxide as catalysts for low-temperature CO oxidation particularly with regard to CO_2 laser applications. Several materials were synthesized and screened for CO oxidation activity using small concentrations of stoichiometric CO and O_2 in He and temperatures between 30 and 75°C . The tests were run for periods as long as 18000 minutes in order to observe the induction and decay characteristics of the catalysts.

CATALYSTS PREPARATION

A review of the literature provided a basis for selection of support materials examined in this study which include iron oxide (Fe_2O_3), nonstoichiometric manganese oxides (MnO_x), and ceria (CeO_x) where x is between 1.5 and 2. The materials investigated were synthesized using established impregnation and coprecipitation techniques (20). The samples prepared include MnO_x , Pt/MnO_x , Ag/MnO_x , Pd/MnO_x , CuO/MnO_x , Au/MnO_x , Au/CeO_x and $\text{Au/Fe}_2\text{O}_3$.

The MnO_x was used as received from the Kerr-McGee Company, U.S.A. It was prepared by the electrolytic oxidation of manganous sulfate and has a B.E.T. surface area of $74 \text{ m}^2/\text{g}$. The MnO_x served as a sample itself as well as an impregnation support for other materials.

Two Pt/MnO_x samples (0.2 wt% Pt) were prepared by impregnation of MnO_x using an aqueous solution of $\text{Na}_2\text{Pt}(\text{OH})_6$. Sample #1 was dried in air at 280°C for 4.5 hours while sample #2 was dried in air at 75°C for 3 hours. Pd/MnO_x (0.2 wt% Pd) was prepared by impregnating MnO_x with an aqueous solution of PdCl_2 . The product was dried in air at 280°C for 4.5 hours.

A sample which contained admixtures of CuO and MnO_x was prepared from the products of several procedures. Procedure A involved coprecipitation from aqueous solutions of CuSO_4 + sucrose and KMnO_4 . The precipitate was washed with water and dried in air at 105°C for 15 hours. The Cu:Mn molar ratio was approximately 1.4. In procedure B the former product was dried in air at 280°C for 2 hours. In procedure C MnO_x was precipitated from aqueous solutions of sucrose and KMnO_4 . The precipitate was washed and dried as outlined in procedure A. The final product consisted of an admixture of 0.4 grams from procedure A, 0.7 grams from procedure B, 0.3 grams from procedure C and 0.2 grams of commercial CuO powder.

A technique in which $\text{Mn}(\text{OH})_2$ was precipitated in the presence of ultra-fine Ru powder was utilized to prepare a 2 wt% Ru/ MnO_x sample. A solution of $\text{Mn}(\text{NO}_3)_2$ was added dropwise to a stirred mixture of Ru powder in NH_4OH . The resulting product was dried and calcined at 400°C for 2 hours.

Four supported Au samples were synthesized via coprecipitation from aqueous HAuCl_4 and the nitrate of the corresponding support metal. The composition of the materials is approximately 5 at% Au/ MnO_x , 10 at% Au/ MnO_x , 20 at% Au/ CeO_x and 5 at% Au/ Fe_2O_3 on a Au/metal basis. In each case the appropriate precursor solutions were added dropwise to a stirred solution of sodium carbonate at room temperature. After washing and drying the precipitates were calcined in air at 400°C for 4 hours. Two Au/ Fe_2O_3 samples were prepared which differed only in the temperature of the wash water utilized (25°C and 80°C).

EXPERIMENTAL

The reactor used to test the CO oxidation activity of the catalysts has been described previously (11). Screening of catalysts for CO oxidation has typically been carried out using a test gas consisting of a few percent CO in air (excess oxygen), but the catalytic behavior under stoichiometric CO and O_2 and in the presence of CO_2 has not been determined. Since the catalytic behavior can vary considerably under different environments as described above, it is necessary to perform such experiments. Except for the data shown in figure 9, all tests were conducted using 0.15 grams of catalyst and a reaction gas mixture of 1% CO, 0.5% O_2 and 2% Ne in helium at a pressure of 1 atm. flowing at 10 sccm. The reaction temperatures investigated were 75, 50 and 30°C as noted. The conversions are quite high under these conditions which correspond to operating the reactor in an integral mode.

In most cases the catalysts were tested as prepared without additional pretreatments. Unless noted otherwise, each catalyst was loaded in the reactor and exposed to flowing helium for about one hour as the reaction temperature stabilized. Then the helium flow was changed to the reaction gas mixture and product sampling was begun. At predetermined time intervals, an automated sampling valve directed a small fraction of the reaction products to a gas chromatograph for analysis of % CO_2 yield, %CO loss and % O_2 loss, and the results were plotted versus time.

RESULTS AND DISCUSSION

During these initial activity screening experiments, emphasis is placed upon characteristics of the overall CO oxidation activity curves with respect

to temperature and time. An appropriate catalyst for use in CO₂ lasers must not only exhibit high activity at low temperatures (25-100°C) but also maintain acceptable activity over a lifetime of up to 3 years. Since a catalyst cannot be practically tested for a 3-year lifetime, its activity profile must be extrapolated with reasonable confidence. Nevertheless, it is necessary to exercise caution when evaluating potential catalysts for CO₂ lasers because a catalyst which exhibits the best activity initially might succumb to decay mechanisms which render it inferior after extended use. Consequently, a catalyst exhibiting only marginal activity initially may become the optimal choice if the corresponding activity decay remains negligible.

CO oxidation activity curves for several MnO_x-based catalysts appear in figure 1. Initially, MnO_x and Cu/MnO_x exhibit the highest CO oxidation activities although their performance rapidly deteriorates. However, after about 2000 minutes the reaction curve for Cu/MnO_x appears to approach a steady-state conversion with negligible activity decay. MnO_x may approach a more active steady-state conversion but more extensive testing is required to be certain. Even though the Pt/MnO_x #1 and Ag/MnO_x samples display superior activity throughout most of the test period, extrapolation of the data in figure 1 indicate that Cu/MnO_x may be the optimal catalyst in a long-term run.

Figure 1 also depicts an interesting comparison between the catalytic activities of Pt/MnO_x #1 (dried for 4.5 hours at 280°C) and Pt/MnO_x #2 (dried for 3 hours at 75°C). The poor activity exhibited by Pt/MnO_x #2 may be the result of incomplete removal of surface impurities (such as Na, Cl or OH) associated with the impregnation step. However, as found in previous studies of MnO₂ and MnO₂-CuO catalysts (21-23), the inactivity is most likely the result of incomplete surface activation. MnO_x-based catalysts usually require heating between 100-200°C in air or oxygen to produce an active surface. The heat treatments apparently activate the surface through the creation of reactive sites via partial surface reduction depletion of adsorbed water or surface hydroxyl groups, and/or concurrent micropore generation.

An interesting observation is that the reaction profiles of Pt/MnO_x #1 and Ag/MnO_x are remarkably similar. This is unexpected based on the different catalytic properties of Pt and Ag. It is possible that this behavior results primarily from exposure of MnO_x to similar basic solutions followed by drying in air at 280°C for 4.5 hours. The activity curve for pure MnO_x (as-received and common to both samples) is quite different in character, which is consistent with this hypothesis. Nevertheless, both materials performed well during the 10000-minute test period oxidizing 70-80% of available CO at 75°C.

As mentioned above Pt/SnO₂ catalysts have received considerable attention for use in CO₂ lasers. Figure 2 shows a comparison of CO oxidation performance between the Pt/MnO_x #1 sample (see figure 1) and a commercial Pt/SnO₂ catalyst manufactured by Engelhard Industries. At 75°C the Pt/MnO_x #1 sample exhibits superior activity after approximately 2500 minutes of reaction. Due to the limited reaction data for Pt/SnO₂, further comparisons require data extrapolation. Pt/MnO_x #1 represents the optimal catalyst over an extended time period assuming that the indicated trends continue. This also is true for Ag/MnO_x which behaves identically to Pt/MnO_x #1.

Figure 2 represents a valid comparison because the sample size and experimental parameters used were identical in both tests. It should be noted,

however, that the Pt/SnO₂ was pretreated in a 5% CO/He stream at 225°C for 1 hour prior to activity testing. Such reductive pretreatments significantly enhance the performance of Pt/SnO₂ catalysts (7). A surface characterization study of the changes induced during pretreatment of the Engelhard catalyst has been carried out by Drawdy et al. (10). The fact that no pretreatments were used for the MnO_x-based catalysts is an advantage. Furthermore, since the precious metal loading for the Pt/MnO_x #1 and Ag/MnO_x samples is only 0.2 wt% (compared with 2 wt% for the Pt/SnO₂ catalyst), there also appears to be an economic advantage over the Engelhard catalyst. Of course, the Ag/MnO_x catalyst is the least costly.

The fact that reductive pretreatments activate Pt/SnO₂ catalysts provided motivation to investigate the effects of similar pretreatments on Pt/MnO_x catalysts. Two pretreatment conditions were used in which the Pt/MnO_x #1 sample was exposed to 5% CO/He for 1 hour at 125 and 225°C. The effects on catalytic performance are shown in figure 3. It is clear that the pretreatments are detrimental to the CO oxidation activity of Pt/MnO_x. In fact, the observed activity of Pt/MnO_x decreases with increasing pretreatment temperature; a trend opposite to that which is observed for Pt/SnO₂ catalysts (7). A possible explanation may involve the reducibility of the MnO_x and SnO₂ supports. It appears that catalysts based upon these materials require a certain degree of surface reduction for optimal activity. There is evidence that a completely dehydroxylated or an entirely oxygenated MnO_x surface is not active toward low-temperature CO oxidation (21,22). Similarly, surface hydroxyl groups are believed to be instrumental in the CO oxidation mechanism over Pt/SnO₂ (7-10). Given the relative instability of MnO_x with respect to SnO₂, such an optimum degree of surface reduction most likely results from milder pretreatments than those used to generate the data shown in figure 3. In fact, heat treatments in air or oxygen appear to be more beneficial for MnO_x CO oxidation catalysts (21,22,24-26). Although the CO reductive pretreatments at 125 and 225°C are appropriate for Pt/SnO₂, they apparently are too severe for Pt/MnO_x.

Additional insight on the pretreatment effects may be gained by considering the initial reaction characteristics with regard to CO₂ production, CO loss and O₂ loss (determined by GC analysis). These data are shown in figures 4, 5 and 6 for Pt/MnO_x catalysts which were not pretreated, pretreated at 125°C and pretreated at 255°C respectively. For unpretreated Pt/MnO_x #1, figure 4 shows that a considerable amount of catalyst surface oxygen is utilized in CO₂ formation during the early stages of reaction because the O₂ loss is much lower than the CO₂ production. The participation of catalyst oxygen during CO oxidation has been observed for MnO_x catalysts previously (14,25-27). After a 125°C CO pretreatment, the catalyst activity is decreased, and this decrease is accompanied by a decrease in the utilization of catalyst oxygen as shown in figure 5. Since the curves now nearly coincide, the early stages of CO oxidation on this pretreated surface appears catalytic in nature with only gas-phase oxygen being utilized. The data of figure 6 obtained after pretreating in CO at 225°C indicate essentially opposite behavior to that shown in figure 4. That is, the surface appears to have been reduced to a point where gas-phase oxygen is utilized not only in CO₂ formation but in catalyst regeneration as well. Even though the catalyst surface acquires excess oxygen from the gas phase, this fresh surface oxygen does not appear to participate in the reaction or restore the catalytic activity which was lost during the pretreatment.

A consistent interpretation of the data in figures 4-6 may be realized by invoking a surface REDOX mechanism for CO oxidation. The active surface in figure 4 appears to reach a situation wherein both surface and gas-phase oxygen participate in the reaction. The active surface is partially reduced after the first 30 minutes of reaction, and the extent of reduction depends upon the relative rates of surface reduction by CO and reoxidation by gas-phase O_2 . During the CO pretreatments, the surface can be reduced to such an extent that catalyst oxygen is not available for reaction. Therefore, the resulting surfaces are not as active toward CO oxidation. These data suggest that it might be possible to determine optimal pretreatment conditions and that these optimal conditions would be less severe than the ones used in this study. The exact form(s) of the active surface oxygen species remains to be determined.

Figure 7 shows the CO oxidation performance of Au/CeO_x , Au/Fe_2O_3 #1 and Au/Fe_2O_3 #2 at 75, 50 and 30°C. Several important features appear in these activity curves. The Au/CeO_x exhibits very high activity at 75°C oxidizing greater than 80% of the available CO. Also, the reaction profile exhibits negligible decay over 10000 minutes. This represents a significant improvement over the performance of Pt/MnO_x #1 and Ag/MnO_x shown in figure 1. At 50°C Au/CeO_x continues to perform well maintaining a 43% CO_2 yield.

Figure 7 also provides an interesting comparison between Au/Fe_2O_3 #1 (washed with hot water) and Au/Fe_2O_3 #2 (washed with cold water). The activity of Au/Fe_2O_3 #1 is clearly superior although some decay in performance is evident. Surface Cl is generally believed to inhibit low-temperature CO oxidation. Therefore, the difference in activity of the two samples may be attributable to poisoning by surface chlorine (originating from the gold precursor $HAuCl_4$) which is not as effectively removed by washing with cold water compared to hot water. Nevertheless, it is interesting to note that the activity of Au/Fe_2O_3 #2 steadily increases with time (negative or inverse decay). This behavior may be a consequence of some surface process which removes the surface Cl as the reaction proceeds.

It is interesting to compare the performance of Au/Fe_2O_3 #2 with that of a Au/Fe_2O_3 catalyst investigated by Haruta et al. (18,19). They observed that Au/Fe_2O_3 is essentially 100% efficient in oxidizing 1% CO in air even below 0°C. The lower activities found in this study apparently are due to the difficulties involved in oxidizing CO in a stoichiometric mixture as described above.

CO oxidation activity curves for a second set of MnO_x -based materials appear in figure 8. The data indicate that Au/MnO_x is clearly the most active catalyst examined in this study. At 75°C, Au/MnO_x sustains nearly 100% CO_2 yield over a 10000 minute period, and excellent activity is also observed at 50 and 30°C. At all temperatures the activity profiles are exceptional in that they exhibit negligible decay over the entire test period.

Figure 8 also shows the activity curves for two Ag/MnO_x samples (0.2 wt% and 1.0 wt% Ag). As stated above, the two samples were prepared in a similar manner differing only in Ag content. The data indicate that small Ag loadings result in better catalytic behavior. Both reaction profiles are similar up to 1000 minutes of reaction after which the 1 wt% Ag/MnO_x sample exhibits accelerated decay in activity.

Although Pd/MnO_x and Ru/MnO_x are the least active catalysts according to the data in figure 8, significant conversions are nevertheless observed. However, both these two materials and the others used in this study probably would be improved by optimizing preparation and pretreatment techniques. Such optimization studies will be carried out for the more promising catalysts particularly Au/MnO_x.

Most of the effort related to developing a low-temperature CO oxidation catalyst thus far has been expended on platinized tin oxide systems. Therefore, it is important to compare the behavior of the Au/MnO_x and Pt/SnO₂ catalysts. This comparison is shown in figure 9 for an optimized 19.5% Pt/SnO₂ catalyst and a 10% Au/MnO_x catalyst using 0.1 g of each and a flow rate of 10 sccm at about 50°C. The Pt/SnO₂ catalyst was optimally pretreated, and the Au/MnO_x catalyst was not pretreated. The optimized Pt/SnO₂ catalyst is nearly twice as active as the Engelhard Pt/SnO₂ catalyst. As observed in figure 9, the activity of the Pt/SnO₂ catalyst is high initially but rapidly drops to about 42% and then continues to decline slowly. Outgassing results in the catalyst regaining its initial high activity followed by a rapid loss in activity to value of about 35% with continuing decline in activity. The activity of the Au/MnO_x catalyst is initially about 78%. It rises rapidly to almost 90% and then remains constant over the duration of the test. Outgassing has little effect on the activity of the Au/MnO_x catalyst. This direct comparison demonstrates that the Au/MnO_x catalyst is vastly superior to the optimized Pt/SnO₂ catalyst with respect to both catalytic activity and decay characteristics. Furthermore, the Au/MnO_x catalyst is much less costly than the Pt/SnO₂ catalyst because about half the amount of Au is required per unit weight of catalyst, Au costs about three-fourths as much as Pt, and the activity of Au/MnO_x is more than twice that of Pt/SnO₂ so less than half the total weight of the Au/MnO_x catalyst would be required for a given application. The fact that no pretreatment is required for the Au/MnO_x catalyst is also a significant advantage with regard to laser applications. Taking all of these considerations into account, there is no justification for further development of platinized tin oxide systems for low-temperature CO oxidation applications. Efforts are continuing by Hoflund, Gardner, Schryer and Upchurch to support the Au/MnO_x catalysts on monolith supports, test these monolith supported catalysts, and characterize the Au/MnO_x catalysts.

SUMMARY

Selected materials have been prepared and tested as low-temperature CO oxidation catalysts for long-term use in CO₂ lasers. The materials were prepared utilizing impregnation and coprecipitation techniques and include MnO_x, Pt/MnO_x, Ag/MnO_x, Pd/MnO_x, Cu/MnO_x, Ru/MnO_x, Au/MnO_x, Au/CeO_x and Au/Fe₂O₃. Each was tested for CO oxidation activity in low concentrations of stoichiometric CO and O₂ at temperatures between 30 and 75°C. Although most of the materials exhibit significant CO oxidation activity, Au/MnO_x is exceptionally active. At 75°C, Au/MnO_x sustains nearly 100% CO₂ yield for 10000 minutes with no evidence of activity decay under the test conditions used. Exceptional activities are also observed at 50 and 30°C. Many of the catalysts tested perform better than a platinized tin oxide catalyst either with regard to activity, decay characteristics or both. For example, Cu/MnO_x has a lower activity than several of the catalysts tested, but it shows negligible decay making it a potential candidate for long-term performance. Pt/MnO_x #1 and Ag/MnO_x exhibit similar and higher activities but decay more rapidly than

Cu/MnO_x and less rapidly than the commercially available platinized tin oxide. Pretreatment in CO at 125 and 225°C decreases the activity. Optimization studies of preparative and pretreatment variables need to be performed in order to further increase the performance of low-temperature CO oxidation catalysts.

A direct comparison between the catalytic behavior of a Au/MnO_x catalyst and an optimized Pt/SnO₂ catalyst has been carried out. The performance of the Au/MnO_x catalyst is vastly superior to that of the Pt/SnO₂ catalyst with regard to both activity and decay characteristics. Combined with the facts that the Au/MnO_x catalyst requires no pretreatment and is less costly than Pt/SnO₂ catalysts, it appears that the Au/MnO_x catalyst is the appropriate choice for CO₂ laser applications.

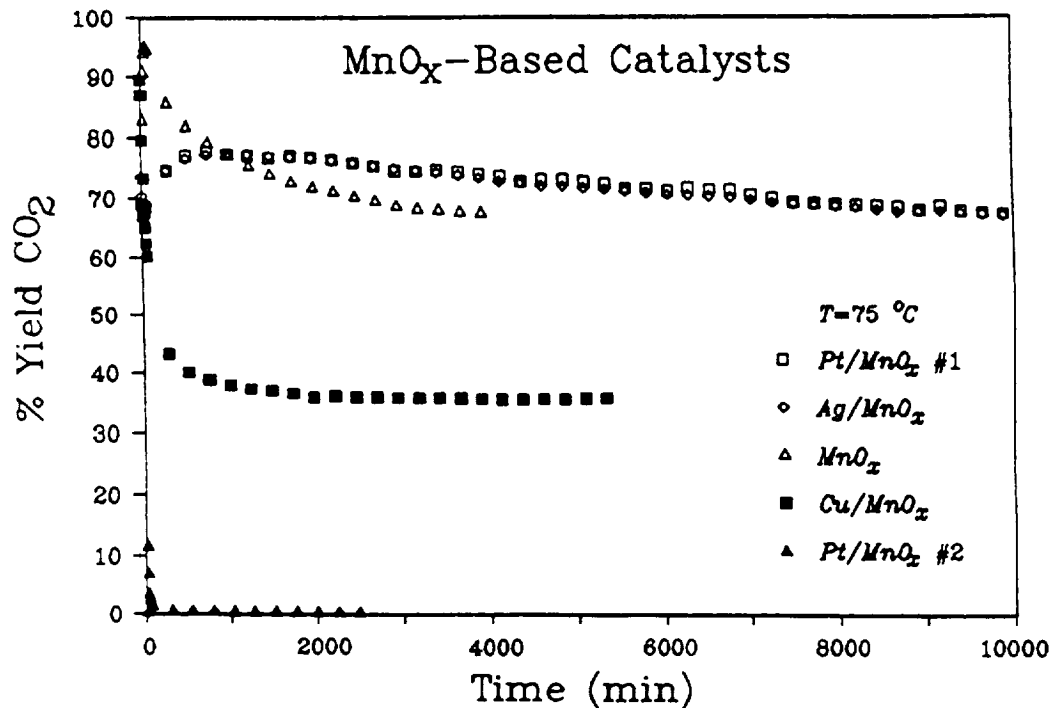


Figure 1. CO oxidation activity of 0.2 wt% Pt/MnO_x #1, 0.2 wt% Ag/MnO_x, MnO_x, 60 at% Cu/MnO_x and 0.2 wt% Pt/MnO_x #2 at 75°C as a function of time.

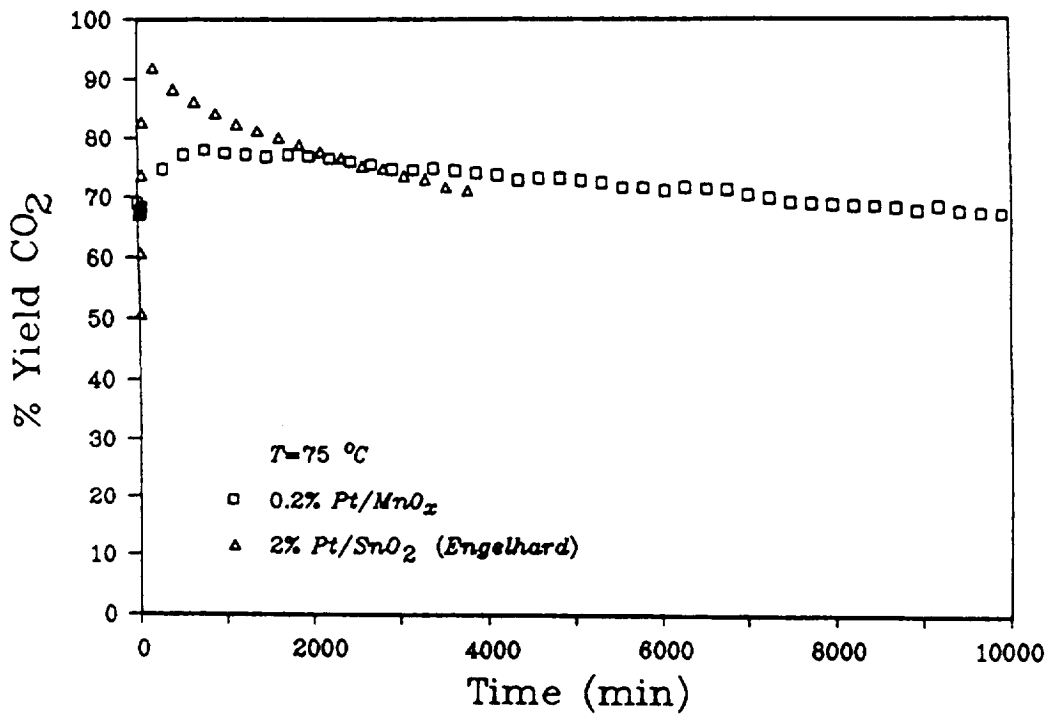


Figure 2. Comparison of CO oxidation activity between 0.2 wt% Pt/MnO_x #1 and a commercial 2 wt% Pt/SnO₂ catalyst at 75°C.

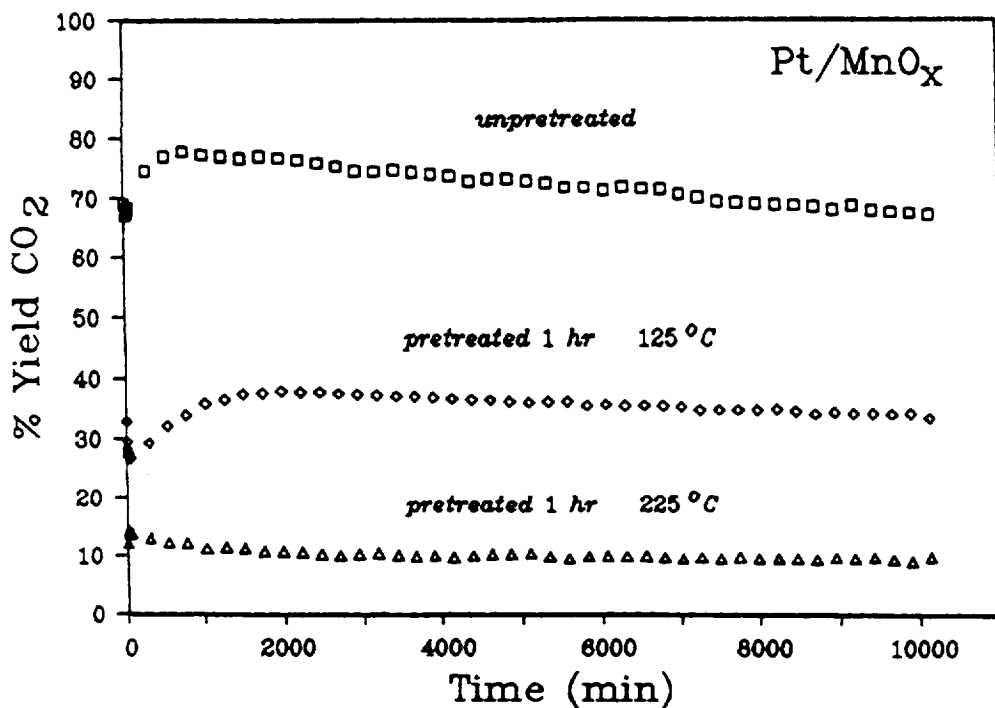


Figure 3. Effect of pretreatment at 125 and 225°C in 5% CO/He for 0.2 wt% Pt/MnO_x #1 on catalytic CO oxidation at 75°C.

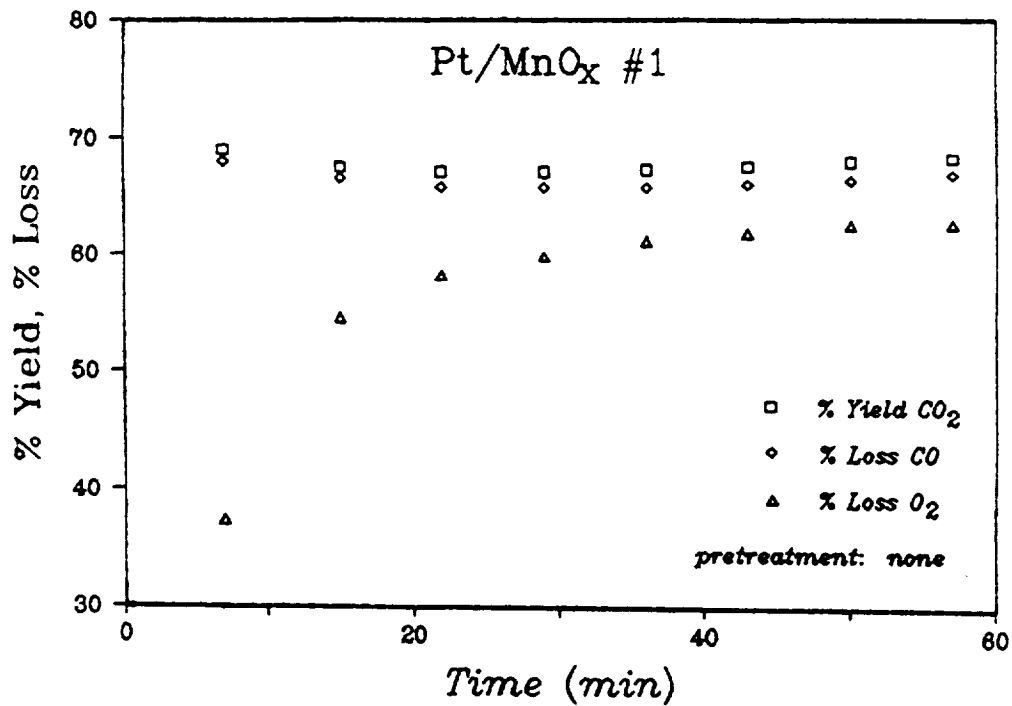


Figure 4. % CO₂ yield with corresponding % loss CO and O₂ for unpretreated 0.2 wt% Pt/MnO_x #1 (75°C reaction temperature).

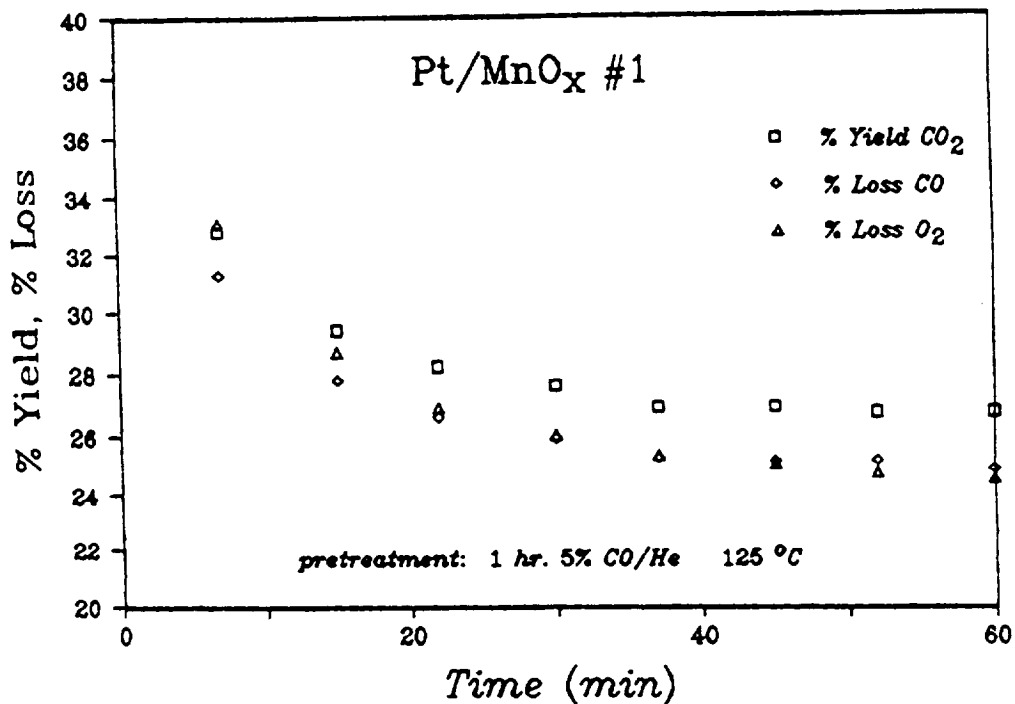


Figure 5. % CO₂ yield with corresponding % loss CO and O₂ for 0.2 wt% Pt/MnO_x #1 pretreated in 5% CO/He for 1 hour at 125°C (75°C reaction temperature).

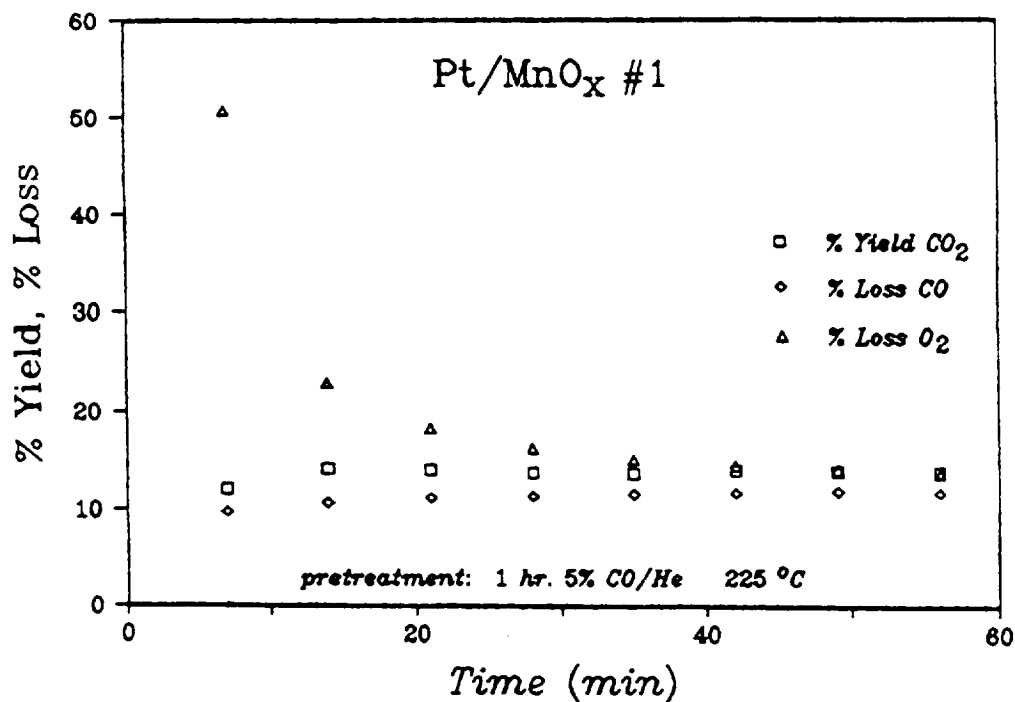


Figure 6. % CO₂ yield with corresponding % loss CO and O₂ for 0.2 wt% Pt/MnO_x #1 pretreated in 5% CO/He for 1 hour at 225°C (75°C reaction temperature).

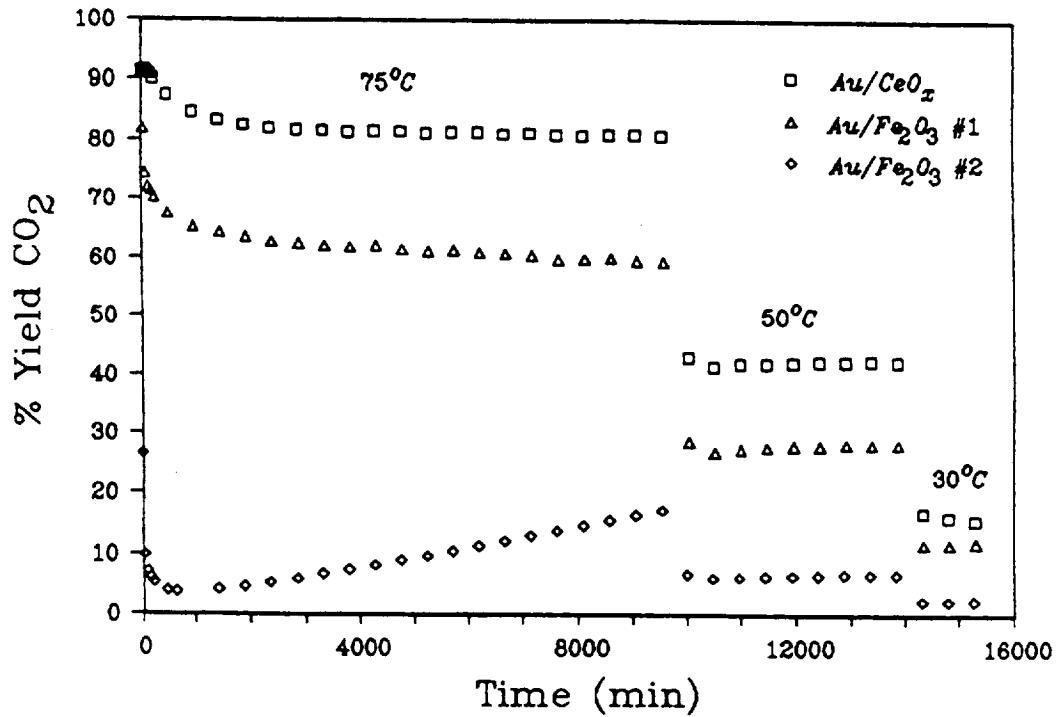


Figure 7. CO oxidation activity of 20 at% Au/CeO_x, 5 at% Au/Fe₂O₃ #1 and 5 at% Au/Fe₂O₃ #2 at 75, 50 and 30°C as a function of time.

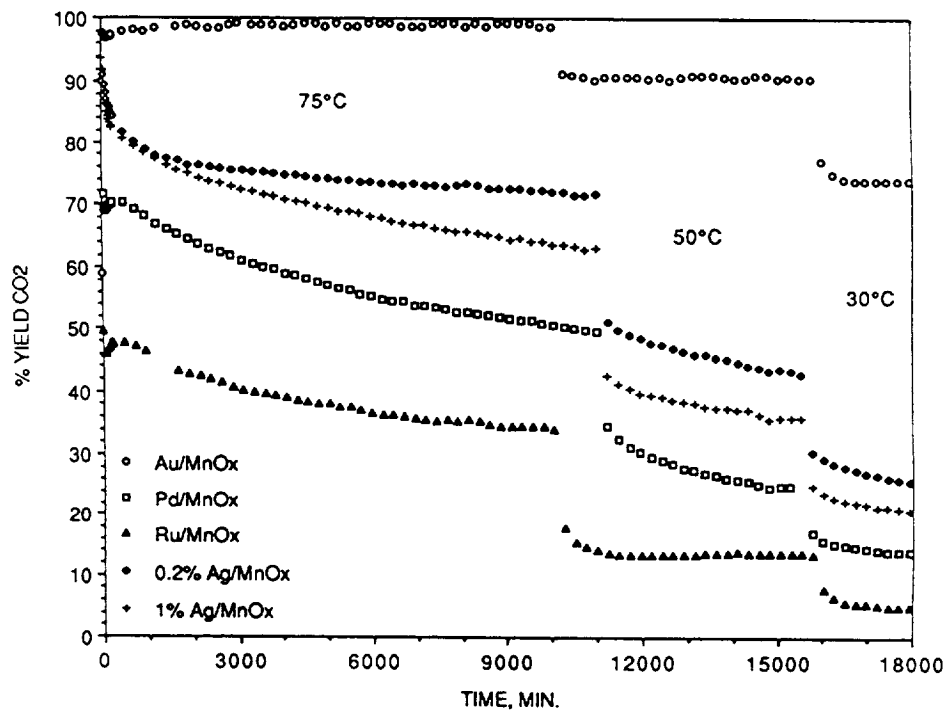


Figure 8. CO oxidation activity of 5 at% Au/MnO_x, 0.2 wt% Pd/MnO_x, 2 wt% Ru/MnO_x, 0.2 wt% Ag/MnO_x and 1.0 wt% Ag/MnO_x at 75, 50 and 30°C as a function of time.

Activity Comparison of Pt/SnO₂ and Au/MnO_x

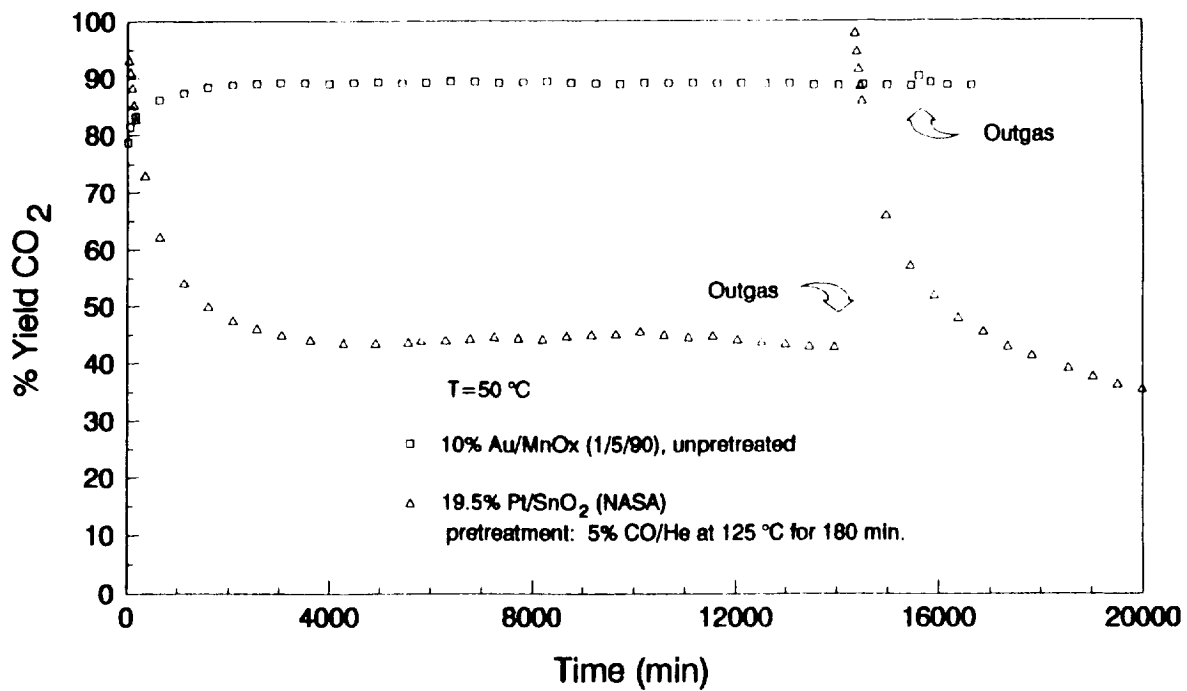


Figure 9. Activity comparison of Pt/SnO₂ and Au/MnO_x.

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