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/Fe_2O_3 were synthesized and tested for CO oxidation activity in low concentra-
tions of stoichiometric CO and O_2 at 30-75°C. Catalytic activity was
measured for periods as long as 18000 minutes. At 75°C 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 compari-
son between an unpretreated 10% Au/MnO_x catalyst and an optimized 19.5%
Pt/SnO_2 (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/Fe_2O_3 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 CO_2 lasers in space.

INTRODUCTION

The catalytic oxidation of carbon monoxide near ambient temperatures has
important applications. Closed-cycle CO_2 lasers produce CO and O_2 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 CO_2 (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 activi-
ties 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 pro-
nounced effect on catalyst performance. CO oxidation in ambient air has the
advantages of excess O_2 and low CO_2 concentrations which facilitate the reac-
tion considerably. Consequently, numerous materials are known to oxidize CO
in excess O_2 at low temperatures (4,5,14-17), but complications due to pre-
sence of humidity and/or air pollutants are often detrimental to their activity.
In CO_2 lasers, CO and O_2 are present in small stoichiometric quantities
in a large amount of CO_2. 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\textsubscript{x}, Fe\textsubscript{2}O\textsubscript{3}, CO\textsubscript{3}O\textsubscript{4}, NiO and CuO and determined their catalytic activities toward the oxidation of H\textsubscript{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 Au/Fe\textsubscript{2}O\textsubscript{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 Au/Fe\textsubscript{2}O\textsubscript{3} and Au/CO\textsubscript{3}O\textsubscript{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\textsubscript{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\textsubscript{x} toward CO oxidation.

Catalysts consisting of Pt and/or Pd supported on tin oxide have been researched extensively for use in CO\textsubscript{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\textsubscript{2} laser applications. Several materials were synthesized and screened for CO oxidation activity using small concentrations of stoichiometric CO and O\textsubscript{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\textsubscript{2}O\textsubscript{3}), nonstoichiometric manganese oxides (MnO\textsubscript{x}), and ceria (CeO\textsubscript{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\textsubscript{x}, Pt/MnO\textsubscript{x}, Ag/MnO\textsubscript{x}, Pd/MnO\textsubscript{x}, CuO/MnO\textsubscript{x}, Au/MnO\textsubscript{x}, Au/CeO\textsubscript{x} and Au/Fe\textsubscript{2}O\textsubscript{3}.

The MnO\textsubscript{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 m\textsuperscript{2}/g. The MnO\textsubscript{x} served as a sample itself as well as an impregnation support for other materials.

Two Pt/MnO\textsubscript{x} samples (0.2 wt% Pt) were prepared by impregnation of MnO\textsubscript{x} using an aqueous solution of Na\textsubscript{2}Pt(OH)\textsubscript{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\textsubscript{x} (0.2 wt% Pd) was prepared by impregnating MnO\textsubscript{x} with an aqueous solution of PdCl\textsubscript{2}. The product was dried in air at 280°C for 4.5 hours.
A sample which contained admixtures of CuO and MnO\textsubscript{x} was prepared from the products of several procedures. Procedure A involved coprecipitation from aqueous solutions of CuSO\textsubscript{4} + sucrose and KMnO\textsubscript{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\textsubscript{x} was precipitated from aqueous solutions of sucrose and KMnO\textsubscript{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 Mn(OH)\textsubscript{2} was precipitated in the presence of ultra-fine Ru powder was utilized to prepare a 2 wt% Ru/MnO\textsubscript{x} sample. A solution of Mn(NO\textsubscript{3})\textsubscript{2} was added dropwise to a stirred mixture of Ru powder in NH\textsubscript{4}OH. The resulting product was dried and calcined at 400°C for 2 hours.

Four supported Au samples were synthesized via coprecipitation from aqueous HAuCl\textsubscript{4} and the nitrate of the corresponding support metal. The composition of the materials is approximately 5 at% Au/MnO\textsubscript{x}, 10 at% Au/MnO\textsubscript{x}, 20 at% Au/CeO\textsubscript{x} and 5 at% Au/Fe\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{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\textsubscript{2} and in the presence of CO\textsubscript{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\textsubscript{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\textsubscript{2} yield, %CO loss and %O\textsubscript{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 MnOₓ-based catalysts appear in figure 1. Initially, MnOₓ and Cu/MnOₓ exhibit the highest CO oxidation activities although their performance rapidly deteriorates. However, after about 2000 minutes the reaction curve for Cu/MnOₓ appears to approach a steady-state conversion with negligible activity decay. MnOₓ may approach a more active steady-state conversion but more extensive testing is required to be certain. Even though the Pt/MnOₓ #1 and Ag/MnOₓ samples display superior activity throughout most of the test period, extrapolation of the data in figure 1 indicate that Cu/MnOₓ may be the optimal catalyst in a long-term run.

Figure 1 also depicts an interesting comparison between the catalytic activities of Pt/MnOₓ #1 (dried for 4.5 hours at 280°C) and Pt/MnOₓ #2 (dried for 3 hours at 75°C). The poor activity exhibited by Pt/MnOₓ #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. MnOₓ-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/MnOₓ #1 and Ag/MnOₓ 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 MnOₓ to similar basic solutions followed by drying in air at 280°C for 4.5 hours. The activity curve for pure MnOₓ (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/MnOₓ #1 sample (see figure 1) and a commercial Pt/SnO₂ catalyst manufactured by Engelhard Industries. At 75°C the Pt/MnOₓ #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/MnOₓ #1 represents the optimal catalyst over an extended time period assuming that the indicated trends continue. This also is true for Ag/MnOₓ which behaves identically to Pt/MnOₓ #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/SnO$_2$ 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/SnO$_2$ 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/SnO$_2$ 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/SnO$_2$ 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/SnO$_2$ catalysts (7). A possible explanation may involve the reducibility of the MnO$_x$ and SnO$_2$ 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/SnO$_2$ (7-10). Given the relative instability of MnO$_x$ with respect to SnO$_2$, 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/SnO$_2$, 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 CO$_2$ production, CO loss and O$_2$ 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 CO$_2$ formation during the early stages of reaction because the O$_2$ loss is much lower than the CO$_2$ 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 CO$_2$ 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 O₂. 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/CeOₓ, Au/Fe₂O₃ #1 and Au/Fe₂O₃ #2 at 75, 50 and 30°C. Several important features appear in these activity curves. The Au/CeOₓ 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/MnOₓ #1 and Ag/MnOₓ shown in figure 1. At 50°C Au/CeOₓ continues to perform well maintaining a 43% CO₂ yield.

Figure 7 also provides an interesting comparison between Au/Fe₂O₃ #1 (washed with hot water) and Au/Fe₂O₃ #2 (washed with cold water). The activity of Au/Fe₂O₃ #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 HAuCl₄) 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/Fe₂O₃ #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/Fe₂O₃ #2 with that of a Au/Fe₂O₃ catalyst investigated by Haruta et al. (18,19). They observed that Au/Fe₂O₃ 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 MnOₓ-based materials appear in figure 8. The data indicate that Au/MnOₓ is clearly the most active catalyst examined in this study. At 75°C, Au/MnOₓ sustains nearly 100% CO₂ 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/MnOₓ 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/MnOₓ sample exhibits accelerated decay in activity.
Although Pd/MnOₓ and Ru/MnOₓ 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/MnOₓ.

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/MnOₓ and Pt/SnO₂ catalysts. This comparison is shown in figure 9 for an optimized 19.5% Pt/SnO₂ catalyst and a 10% Au/MnOₓ 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/MnOₓ 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/MnOₓ 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/MnOₓ catalyst. This direct comparison demonstrates that the Au/MnOₓ catalyst is vastly superior to the optimized Pt/SnO₂ catalyst with respect to both catalytic activity and decay characteristics. Furthermore, the Au/MnOₓ 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/MnOₓ is more than twice that of Pt/SnO₂ so less than half the total weight of the Au/MnOₓ catalyst would be required for a given application. The fact that no pretreatment is required for the Au/MnOₓ 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 Uphchurch to support the Au/MnOₓ catalysts on monolith supports, test these monolith supported catalysts, and characterize the Au/MnOₓ 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 MnOₓ, Pt/MnOₓ, Ag/MnOₓ, Pd/MnOₓ, Cu/MnOₓ, Ru/MnOₓ, Au/MnOₓ, Au/CoOₓ 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/MnOₓ is exceptionally active. At 75°C, Au/MnOₓ 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/MnOₓ 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/MnOₓ #1 and Ag/MnOₓ exhibit similar and higher activities but decay more rapidly than
Cu/MnO\textsubscript{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\textsubscript{x} catalyst and an optimized Pt/SnO\textsubscript{2} catalyst has been carried out. The performance of the Au/MnO\textsubscript{x} catalyst is vastly superior to that of the Pt/SnO\textsubscript{2} catalyst with regard to both activity and decay characteristics. Combined with the facts that the Au/MnO\textsubscript{x} catalyst requires no pretreatment and is less costly than Pt/SnO\textsubscript{2} catalysts, it appears that the Au/MnO\textsubscript{x} catalyst is the appropriate choice for CO\textsubscript{2} 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/SnO$_2$ catalyst at 75°C.
Figure 3. Effect of pretreatment at 125 and 225°C in 5% CO/He for 0.2 wt% Pt/MnOₓ #1 on catalytic CO oxidation at 75°C.

Figure 4. % CO₂ yield with corresponding % loss CO and O₂ for unpretreated 0.2 wt% Pt/MnOₓ #1 (75°C reaction temperature).
Figure 5. % CO$_2$ yield with corresponding % loss CO and O$_2$ 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. % CO$_2$ yield with corresponding % loss CO and O$_2$ 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/CeOx, 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/MnOx, 0.2 wt% Pd/MnOx, 2 wt% Ru/MnOx, 0.2 wt% Ag/MnOx and 1.0 wt% Ag/MnOx at 75, 50 and 30°C as a function of time.
Figure 9. Activity comparison of Pt/SnO$_2$ and Au/MnO$_x$.
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