

Report Title: **DEVELOPMENT OF A NOVEL CATALYST FOR NO DECOMPOSITION**

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ABSTRACT

Air pollution arising from the emission of nitrogen oxides as a result of combustion taking place in boilers, furnaces and engines, has increasingly been recognized as a problem. New methods to remove NO_x emissions significantly and economically must be developed. The current technology for post-combustion removal of NO is the selective catalytic reduction (SCR) of NO by ammonia or possibly by a hydrocarbon such as methane. The catalytic decomposition of NO to give N_2 will be preferable to the SCR process because it will eliminate the costs and operating problems associated with the use of an external reducing species.

The most promising decomposition catalysts are transition metal (especially copper)-exchanged zeolites, perovskites, and noble metals supported on metal oxides such as alumina, silica, and ceria. The main shortcoming of the noble metal reducible oxide (NMRO) catalysts is that they are prone to deactivation by oxygen. It has been reported that catalysts containing tin oxide show oxygen adsorption behavior that may involve hydroxyl groups attached to the tin oxide. This is different than that observed with other noble metal-metal oxide combinations, which have the oxygen adsorbing on the noble metal and subsequently spilling over to the metal oxide. This observation leads one to believe that the Pt/ SnO_2 catalysts may have a potential as NO decomposition catalysts in the presence of oxygen. This prediction is also supported by some preliminary data obtained for NO decomposition on a Pt/ SnO_2 catalyst in the PI's laboratory.

The main objective of the proposed research is the evaluation of the Pt/ SnO_2 catalysts for the decomposition of NO in simulated power plant stack gases with particular attention to the resistance to deactivation by O_2 , CO_2 , and elevated temperatures. Therefore, it is proposed to perform temperature programmed desorption (TPD) and temperature programmed reaction (TPRx) studies on Pt/ SnO_2 catalysts having different noble metal concentrations and pretreated under different conditions. It is also proposed to perform NO decomposition tests in a laboratory-size packed-bed reactor to obtain long-term deactivation data.

In the current reporting period first the GC-MS system was calibrated. Then the TPD runs for the 15% Pt/ SnO_2 catalyst after treatment with NO and subsequent treatments with NO and O_2 were done. For these runs the catalyst was pretreated with dry helium for 2 hours at 40°C .

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LIST OF GRAPHICAL MATERIAL

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Figure 2. Species evolved during injections of 1-ml doses of 1.6% NO in He on 15% Pt/SnO₂ catalyst at 313 K.

Figure 3. Species evolved during injection of 1-ml doses of 1.6%NO in He on 15% Pt/SnO₂ catalyst at 313 K.

Figure 4. Species evolved during injection of 1-ml doses of 3.6% O₂ in He on 15% Pt/SnO₂ catalyst after treatment with NO, at 313 K.

Figure 5. Species evolved during TPD after treatment of 15% Pt/SnO₂ catalyst with NO at 313 K.

Figure 6. Species evolved during TPD after the treatment of 15% Pt/SnO₂ catalyst with NO and O₂ subsequently at 313 K.

EXECUTIVE SUMMARY

Air pollution arising from the emission of nitrogen oxides as a result of combustion taking place in boilers, furnaces and engines, has increasingly been recognized as a problem. New methods to remove NO_x emissions significantly and economically must be developed. The current technology for post-combustion removal of NO is the selective catalytic reduction (SCR) of NO by ammonia or possibly by a hydrocarbon such as methane. The catalytic decomposition of NO to give N_2 will be preferable to the SCR process because it will eliminate the costs and operating problems associated with the use of an external reducing species.

The most promising decomposition catalysts are transition metal (especially copper)-exchanged zeolites, perovskites, and noble metals supported on metal oxides such as alumina, silica, and ceria. The main shortcoming of the noble metal reducible oxide (NMRO) catalysts is that they are prone to deactivation by oxygen. It has been reported that catalysts containing tin oxide show oxygen adsorption behavior that may involve hydroxyl groups attached to the tin oxide. This is different than that observed with other noble metal-metal oxide combinations, which have the oxygen adsorbing on the noble metal and subsequently spilling over to the metal oxide. This observation leads one to believe that the Pt/ SnO_2 catalysts may have a potential as NO decomposition catalysts in the presence of oxygen.

The main objective of the proposed research is the evaluation of the Pt/ SnO_2 catalysts for the decomposition of NO in simulated power plant stack gases with particular attention to the resistance to deactivation by O_2 , CO_2 , and elevated temperatures. Therefore, it is proposed to perform temperature programmed desorption (TPD) and temperature programmed reaction (TPRx) studies on Pt/ SnO_2 catalysts having different noble metal concentrations and pretreated under different conditions. It is also proposed to perform NO decomposition tests in a laboratory-size packed-bed reactor to obtain long-term deactivation data.

In the current reporting period first the GC-MS system was calibrated. Then the TPD runs for the 15% Pt/ SnO_2 catalyst after treatment with NO and subsequent treatments with NO and O_2 were done. For these runs the catalyst was pretreated with dry helium for 2 hours at 40°C .

When the catalyst sample is subjected to NO pulses, it is expected that some NO be retained on the catalyst and form surface nitrite and nitrate species while some may dissociate or react to form other gaseous species. Experimental results showed that a significant portion of NO is either dissociated into N_2 and O_2 with both the N_2 and O_2 amounts in the exit gas reaching a steady state or that NO continues to chemisorb at steady state. To obtain more information on what actually was taking place, the N_2/O_2 ratios in the steady state region were calculated. These essentially remained close to 3.8, which is approximately the ratio in air. Very little N_2O formation was observed and NO_2 was not detected.

When the catalyst treated with NO was subjected to 1-ml pulses of 3.6% O_2 , no NO and N_2O were observed indicating that the chemisorbed nitrogen species were stable at 313 K. The N_2 and O_2 amounts did not vary with the number of injections.

During the TPD runs with the catalyst treated with NO, only a large N_2O peak at 473 K and a large NO peak at 513 K were observed. A similar increase in nitrogen was observed during N_2O desorption with no change in the oxygen amount. On the other hand, nitrogen sharply decreased with NO desorption. A slight dip in the amount of oxygen was observed during NO desorption. The

N_2/O_2 ratio had two peaks, one corresponding to the maximum in the N_2O curve (480 K) and the other to the end of the NO curve (590 K).

During the TPD runs with the catalyst treated with subsequent pulses of NO and O_2 , the N_2O and NO peaks occurred at the same temperatures as in the case of only NO chemisorption, but in this case, the N_2O peak was larger than the NO peak. The N_2 and O_2 amounts sharply increased at the start of the N_2O peak (at about 350 K), then after about 400 K the rate of increase of N_2 became constant for the rest of the run while the O_2 amount started decreasing at the same temperature. The amount of oxygen became minimum at the N_2O peak temperature (490 K) and then slowly increased. The N_2/O_2 ratio also peaked at 490 K and eventually reached 3.8, the N_2/O_2 ratio in air, at 750 K.

The species observed, especially the variation of O_2/N_2 ratio, during TPD runs after NO chemisorption and after subsequent NO and O_2 chemisorptions cannot be explained by considering a simple dissociation of a nitrite or nitrate species, indicating the presence of a more complicated reaction mechanism and the existence of different reaction schemes at different temperature intervals.

At this time only the TPD runs for the 15% Pt/ SnO_2 catalyst after treatment with NO and subsequent treatments with NO and O_2 were done. Therefore at this point it is difficult to come to any definite conclusions, especially before the completion of the temperature programmed reaction studies.

EXPERIMENTAL

a. Temperature-Programmed Desorption Experiments

Temperature-Programmed Desorption (TPD) Experiments were used to evaluate the NO, NO₂, and O₂ chemisorption capacity of the catalysts and to identify the surface species and desorption species. For temperature-programmed experiments, a Micromeritics Pulse Chemisorb 2705 with TPD/TPR Option is used. A mass spectrometer-gas chromatograph system (SATURN 2000MS/3800GC) from Varian is used for the identification of desorbed species and reaction products.

A typical TPD run is described below:

1. Pretreat all the samples in He (40 ml/min) at 313 K for 2 hours. This thermal treatment will prevent any appreciable oxygen uptake.
2. Carry out NO (NO+O₂ or O₂) adsorption at 313 K by flowing a NO/He mixture (or a similar mixture containing other adsorbents) containing 1.94 % NO in He, 3.6 % O₂ in He. Measure the species in the exit gas stream at the time corresponding to the maximum in the desorption curve.
Flow rate: 40 ml/min
Temperature range: 35 °C – 500 °C
Temperature ramp: 3 °C/min
3. Flush the sample with a stream of dry helium at 313 K to eliminate gaseous NO and weakly adsorbed NO (or any other adsorbent).
4. When no NO (or any other adsorbent) is observed, heat the sample to 773 K in flowing He stream. Record the desorbed species.
5. Repeat this procedure for two more cycles. Cool the sample to 323 K.

RESULTS AND DISCUSSION

a. Reproducibility of species measurements during adsorption

Figures 1 through 3 show the analysis of the exit gas during injections of 1-ml pulses of 1.94% NO in He on the 15% Pt/SnO₂ catalyst for 3 replicate runs. Although the reproducibility of the results for the NO measurements are satisfactory, the amount of air present in the test cell initially, affects the nitrogen and oxygen concentrations in the exit gas significantly. It was observed that even when

the catalyst is stored overnight in the sample cell, the initial amount of air present changed. No source of leak was found with the helium leak detector. These tests will be repeated with the same catalyst pretreated under helium at 473 K for 2 hours immediately prior to pulsing with NO at 313 K.

b. Species observed during NO injections

When the catalyst sample is subjected to NO pulses it is expected that some NO be retained on the catalyst and form surface nitrite and nitrate species while some may dissociate or react to form other gaseous species. Figures 1-3 show that after four 1-ml pulses of 1.94% NO in He, the retention of NO on the 150-g catalyst sample reached steady state for the subsequent pulses. The mean NO content of the pulse gas is also shown on the figures. Comparison indicates that a significant portion of NO is either dissociated into N₂ and O₂ with both the N₂ and O₂ amounts in the exit gas reaching a steady state or continues to chemisorb at steady state. To obtain more information on what actually was taking place, the N₂/O₂ ratios in the steady state region were calculated. These essentially remained close to 3.8, which is same ratio in air. Very little N₂O formation was observed, NO₂ was not detected.

c. Species observed during subsequent O₂ injections

Figure 4 shows the species observed in the exit gas during 1-ml pulses of 3.6% O₂ in He on the 15% Pt/SnO₂ catalyst treated with NO. No NO and N₂O were observed indicating that the chemisorbed nitrogen species were stable at 313 K. The N₂ and O₂ amounts did not vary with the number of injections.

d. TPD after NO chemisorption

Figure 5 presents the species desorbed during the controlled heating of the 15% Pt/SnO₂ catalyst treated with NO only. A large N₂O peak at 473 K and a large NO peak at 513 K were observed. A

similar increase in nitrogen was observed during N₂O desorption with no change in the oxygen amount. On the other hand, nitrogen sharply decreases with NO desorption. A slight dip in the amount of oxygen was observed during NO desorption. The N₂/O₂ ratio has two peaks, one corresponding to the maximum in the N₂O curve (480 K) and the other to the end of the NO curve (590 K).

e. TPD after subsequent NO and O₂ chemisorptions

Figure 6 shows the species evolved during 3 K/s heating of the 15% Pt/SnO₂ catalyst treated with subsequent pulses of NO and O₂. The N₂O and NO peaks occur at the same temperatures as in the case of only NO chemisorption (Figure 5), but in this case, the N₂O peak is larger than the NO peak. The N₂ and O₂ amounts sharply increase at the start of the N₂O peak (at about 350 K), then at about 380 K rate of increase of N₂ slows down and becomes constant for the rest of the run while the O₂ starts decreasing at the same temperature. The amount of oxygen becomes a minimum at N₂O peak temperature (490 K) and then slowly increases. The N₂/O₂ ratio also peaks at 490 K and eventually reaches 3.8, the N₂/O₂ ratio in air, at 750 K.

CONCLUSION

At this time only the TPD runs for the 15% Pt/SnO₂ catalyst after treatment with NO and subsequent treatments with NO and O₂ were done. Therefore at this point it is difficult to come to any definite conclusions, especially before the completion of the temperature programmed reaction studies. As a consequence, only some tentative conclusions are presented below.

- From the species observed during NO injections it was tentatively concluded that the catalyst had no dissociation activity at 313 K, but was able to chemisorb significant amounts of NO.
- During subsequent O₂ injections no NO and N₂O were observed indicating that the chemisorbed

nitrogen species were stable at 313 K.

- The species observed, especially the variation of O₂/N₂ ratio, during TPD runs after NO chemisorption and after subsequent NO and O₂ chemisorptions cannot be explained by considering a simple dissociation of a nitrite or nitrate species, indicating the presence of a more complicated reaction mechanism and the existence of different reaction schemes at different temperature intervals.

REFERENCES

APPENDIX

a. Additional Activities

Several students (Shaia Anderson, Shanitra Sanders, Jilyan Harlan, and Victor Robers) were employed as undergraduate research students. They were trained in the laboratory to use the TPR/TPD equipment. They have learnt how to use the GC-MS system.

A poster paper, entitled “Development of a Novel Catalyst for NO Decomposition” will be submitted to the AIChE 2004 Annual Meeting at Austin, TX, Nov.7-12, 2004.

b. Future Plans

During the next year, it is planned to:

1. complete TPD and TPRxn experiments with the 15% Pt catalyst
2. to do TPD and TPRxn experiments with catalysts containing 10% and 5% Pt;
3. complete the analysis of data

FIGURES

Figure 1. Species evolved during injections of 1-ml doses of 1.94% NO in He on 15% Pt/SnO₂ catalyst at 313 K. (Run 1)

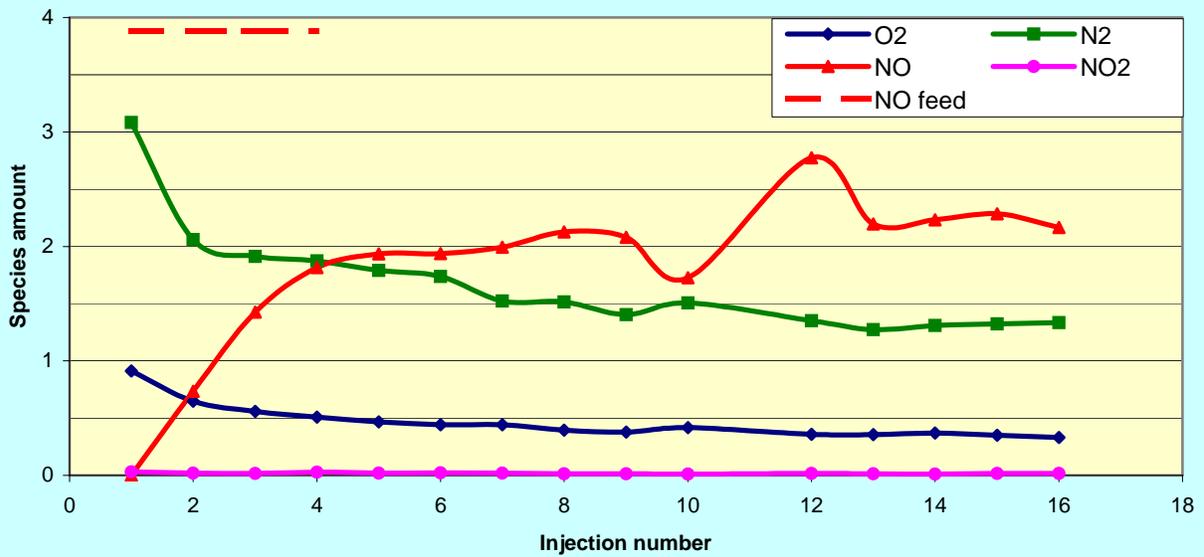


Figure 2. Species evolved during injections of 1-ml doses of 1.6% NO in He on 15% Pt/SnO₂ catalyst at 313 K. (Run 2)

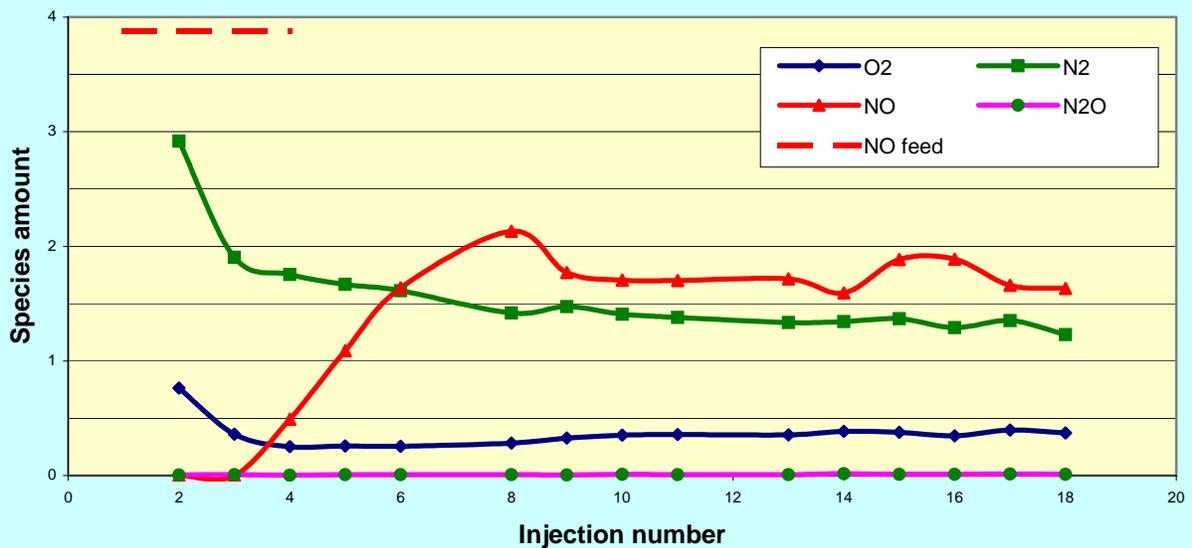


Figure 3. Species evolved during injection of 1-ml doses of 1.6%NO in He on 15% Pt/SnO₂ catalyst at 313 K. (Run 3)

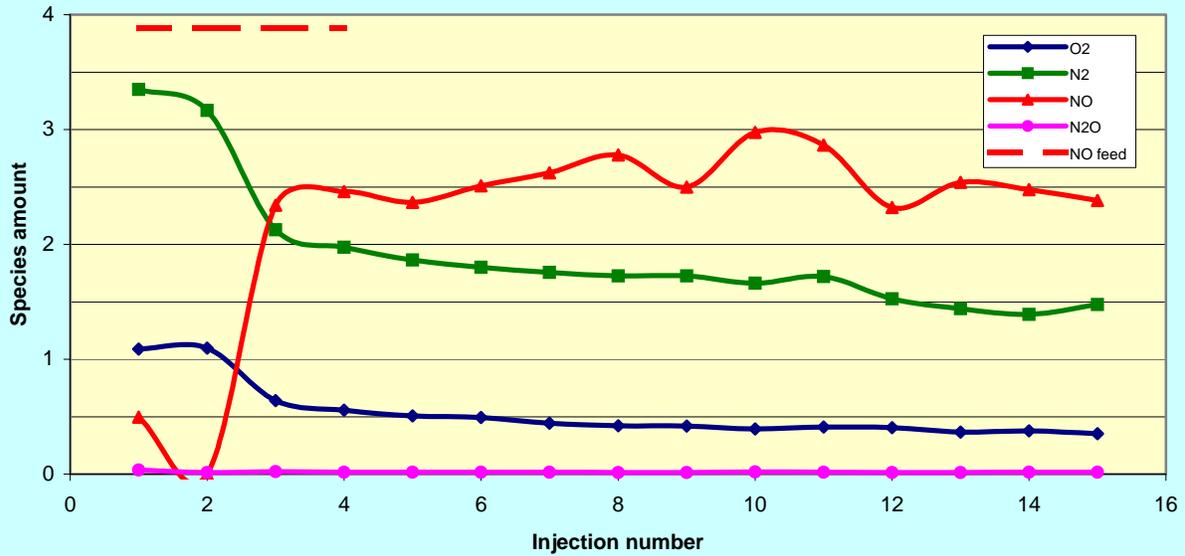


Figure 4. Species evolved during injection of 1-ml doses of 3.6% O₂ in He on 15% Pt/SnO₂ catalyst after treatment with NO, at 313 K.



Figure 5. Species evolved during TPD after treatment of 15% Pt/SnO₂ catalyst with NO at 313 K.

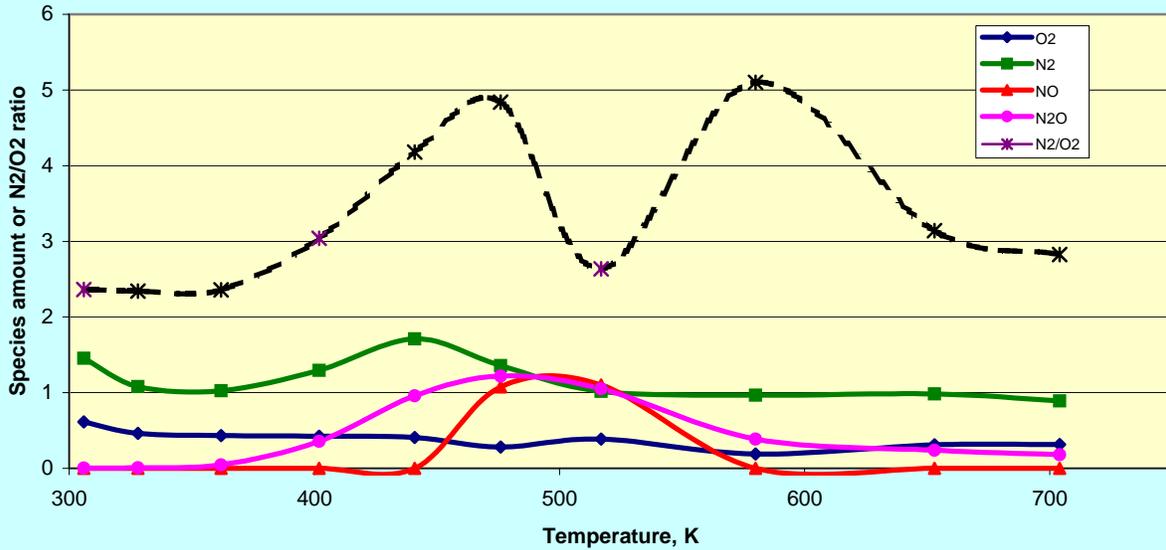


Figure 6. Species evolved during TPD after the treatment of 15% Pt/SnO₂ catalyst with NO and O₂ subsequently at 313 K.

