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

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DISCLAIMER

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 previous reporting period the GC-MS system was calibrated and 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^oC.

In the current reporting period The Temperature Programmed Reaction (TPRx) of NO and $NO+O_2$ mixtures on the catalysts containing 15 % Pt and 10 % Pt were completed.

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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.

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In the previous 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.

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 an s d O_2 amounts in the exit gas reaching a steady state level or that NO continues to chemisorb at a steady rate. 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 low levels of N2O 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.

 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.

In this reporting period temperature programmed reaction runs on the 15% Pt and 10% Pt catalysts were performed using NO+He and NO+O_2+He reactant gas mixtures. For the TPRx of NO on both the 15% Pt an 10% Pt catalysts, appreciable NO conversions were obtained above 700 K. With reactant gas mixtures that do not contain added oxygen, N_2O production was observed below 700 K, but the amounts produced were very small for the second and subsequent runs. With the reactant gas mixtures containing up to O_2/.NO ratio of 1, the NO decomposition activity decreased for the second and subsequent runs and leveled off after the third run. The final conversion level was higher on the 15% Pt catalyst compared to that on the 10% Pt catalyst.

To explain the observed results, two different NO decomposition processes, one occurring on the Pt sites and the other taking place at the Pt-SnO_2 interface and involving the lattice oxygen of SnO_2 and the NO adsorbed on the Pt surface are proposed. The second mechanism involves the formation of surface nitrite/nitrate species as intermediates. There was strong indication of irreversible reduction of SnO_2 upon heating above 600 K under a reactant gas containing no added oxygen.

EXPERIMENTAL

a. Temperature-Programmed Reaction Experiments

Temperature-Programmed Reaction (TPRx) Experiments were used to evaluate the reactions of NO and NO - O_2 mixtures on the catalysts and to identify the product species. For this purpose, a Micromeritics Pulse Chemisorb 2705 with TPD/TPR Option was used. A mass spectrometer-gas chromatograph system (SATURN 2000MS/3800GC) from Varian was used for the identification of the reaction products.

A typical TPRx 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. Replace the carrier gas by NO+He or NO+O_2+He reactant gas mixture and heat the catalyst to 800 K at a rate of 3K/min. Measure the amount of species in the exit gas stream.
   Flow rate: 40 ml/min
   Temperature range: 308 K – 800 K

3. Cool to 308 K under He and flush the sample with a stream of dry helium at 308 K for 2 hours.

4. Repeat this procedure for more cycles as needed.

RESULTS AND DISCUSSION

The processes that are expected to occur on the catalyst are summarized below:

- Oxygen adsorption on the platinum sites
- NO adsorption on Pt sites
- Decomposition of NO to form N_2 and O_2
- Desorption of N_2 and at higher temperatures desorption of O_2
- Formation of nitrite and nitrate species on SnO_2 probably through the interaction of adsorbed NO on Pt with the lattice oxygen of SnO_2 at the Pt-SnO_2 interface.
- Decomposition of these species to form N_2, O_2, N_2O and NO depending on the temperature and the gas phase composition.

The observations during the TPRx runs will be interpreted using these steps.

Temperature Programmed Reaction of NO on 15%Pt/SnO$_2$ Catalyst

Although the reactant gas is 634 ppm NO-He mixture, there is always a small amount of oxygen in the system (a limitation of the TPD/TPR apparatus). From Figures 1 - 3 it can be seen that

oxygen adsorbs on the catalyst up to 520 K. There is no NO decomposition, but some N_2O formation above 370 K, which peaks at 520 K. There also seems to be a smaller N_2O peak around 620 K, but no N_2O is present above 750 K. Above 520 K, oxygen and nitrogen in the gas start increasing at about the same rate while NO decreases rapidly, indicating significant NO decomposition at temperatures above 520 K.

Two different NO decomposition mechanisms are expected to take place on the catalyst. One occurring on the Pt surface and the other involving intermediate nitrate and nitrite species formation on the oxide and their subsequent decomposition giving N_2 and O_2. The existing small amount of O_2 and the O_2 formed during NO decomposition is expected to preferentially adsorb on the Pt surface. Both the oxygen adsorption and the formation of the nitrite/nitrate species can explain the decrease of oxygen concentration up to about 520 K. Again both the O_2 desorption and O_2 formation as the result of the decomposition of surface nitrate /nitrite species can explain the increase in O_2 concentration above 520 K.

Initially some NO is retained on the catalyst, probably due to NO adsorption on Pt, and this NO is later released increasing the NO concentration in the gas phase slightly above the feed gas concentration. This can be explained by the preferential adsorption of O_2 on the Pt sites. After a broad peak, which becomes broader with aging, NO concentration starts decreasing rapidly. This corresponds to about 520 K on fresh catalyst. The start of NO decomposition is pushed to about 625 K during subsequent runs with the same catalyst, but the rate appears to be faster so that the NO concentration in the gas at 900 K is the same for fresh and used catalysts, which corresponds roughly to 50% conversion of NO. The changes in the gaseous NO concentration can also be explained by the two NO decomposition processes mentioned above. The desorption of O_2 at high temperatures may free up Pt sites for the NO reactions, and higher temperatures may increase the rate of decomposition of the nitrate/nitrite surface species.

The peak in the N_2O formation corresponds to the minimum in the gaseous O_2 concentration and the maximum in the gaseous NO concentration indicating the contribution of N_2O formation to the decrease in the gaseous O_2 concentration. The N_2O formation on the used catalysts is significantly smaller than that on the fresh catalyst.

Temperature Programmed Reaction of NO+O_2 on 15%Pt/SnO$_2$ Catalyst

Figures 4 and 5 show the TPRx of a gas mixture containing O_2 and NO in He with O_2/N_2=1.1. Clearly the presence of oxygen inhibits the decomposition of NO and promotes the formation of N_2O. The small amount of decomposition activity starts around 425 K on fresh catalyst. During the second run the NO decomposition activity does not start until 575 K, but appears to be faster than on fresh catalyst. On the other hand more N_2O formation was observed during the second TPRx run. The species concentrations appear to follow the same trends explained for the runs without added oxygen in the feed except some fluctuations were observed in the N_2 concentration especially during the second run. At this point these fluctuations could not be correlated with any process expected to occur on the catalyst.

When the feed O_2/NO ratio was cut by about one half, the N_2O production on the fresh catalyst was significantly reduced, but this improvement did not continue during the second run (Figures 6and7). The reduction in the feed oxygen content also appeared to improve the NO decomposition activity. Figure 6 indicates a significant increase in NO retention at lower temperatures on the fresh catalyst.

The gaseous NO concentration continuously increases up to about 575 K then starts decreasing slowly at higher temperatures. During the run, gaseous NO concentration remained below the feed concentration. A similar behavior was not observed during the second run, which exhibited similar concentration trends as observed in the other runs. The bursts of nitrogen that were observed in Figure 5 were also observed in Figure 7. During the second run there was no NO decomposition activity up to about 550 K. At higher temperatures the NO decomposition rate increased and this increase was similar to that observed with the feed containing no added oxygen.

Temperature Programmed Reaction of NO on 10%Pt/SnO$_2$ Catalyst

The reactions taking place on fresh 10% Pt/SnO2 catalyst were similar to those observed on the 15% Pt/SnO$_2$ catalyst above 500 K except that the amount of N$_2$O formed was larger on the 10% Pt catalyst (Figure 8). The NO conversion on both fresh catalysts were about 20% at 773 K. Below 500 K, concentrations of all gaseous components fluctuated appreciably. This may be attributed to the lower O$_2$ and NO adsorption capacity.

Second run on the 10% Pt catalyst (Figure 9) was very similar to that on the 15% Pt catalyst giving about 16% conversion at 773 K. The amount of N$_2$O formed was also similar. Conversion of NO on the 10% Pt catalyst during the third run (Figure 10) at 773 was slightly lower (about 14.5%) compared to that on the 15% Pt catalyst (about 18.5%). Therefore, a fourth run on the 10% Pt catalyst was done (Figure 11), which produced again 14.5% NO conversion. Therefore, it was concluded that the slight drop in conversion after the second run was not an indication of continuous deactivation of the 10% Pt catalyst. The N$_2$O production on the 10% Pt catalyst for the second through fourth runs was very small.

These observations can also be explained by the two NO reduction mechanisms suggested above. It is known that under reducing atmospheres SnO$_2$ is completely deactivated at temperatures above 600 K and the activity cannot be restored by an oxidation treatment. For the current tests it can be postulated that if the decomposition of NO, and the formation of N$_2$O, on SnO$_2$ involve lattice oxygen, thus effectively reducing SnO$_2$, then the NO decomposition activity of SnO$_2$ will gradually decrease until the SnO$_2$ is deactivated. After that time the only NO decomposition activity will be on the Pt sites. If we accept that the N$_2$O formation occurs only on SnO$_2$, then this will explain the decrease of N$_2$O formation after the first run. It will also explain the initial decrease in NO dissociation activity, which levels off at a higher value on the 15% Pt catalyst.

Temperature Programmed Reaction of NO+O$_2$ on 10%Pt/SnO$_2$ Catalyst

Unfortunately these runs were made with a reactant gas mixture containing more oxygen (O$_2$/NO=2.4) than that used in runs with the 15% Pt catalyst due to an error in setting the gas flow rates and the two sets of results cannot be compared to each other. Therefore they will be repeated using the same O$_2$/NO ratios that were used with the 15% Pt catalyst. The current results (Figures 12-14) for the 10% Pt catalyst show very little activity at temperatures below 800 K and a slightly higher rate of N$_2$O formation. These observations are consistent with the explanation given above in terms of two NO dissociation mechanisms and deactivation of SnO$_2$ by reduction if the surface nitrite/nitrate formation occurs at the Pt-SnO2 interface and requires the adsorption of NO on the Pt sites. Presence of a large amount of oxygen is expected to saturate the Pt sites and leave little room for NO adsorption. Although SnO$_2$ may not be reduced as fast under the O$_2$-containing reactant gas, the formation of nitrite and nitrate surface species is greatly retarded resulting in very little NO decomposition activity.

CONCLUSION

- For the TPRx of NO on both the 15% Pt and 10% Pt catalysts, appreciable NO conversions were obtained above 700 K.

- With reactant gas mixtures that do not contain added oxygen, N_2O production was observed below 700 K, but the amounts produced were very small for the second and subsequent runs.

- With the reactant gas mixtures containing up to $O_2/.NO$ ratio of 1, the NO decomposition activity decreased for the second and subsequent runs and leveled off after the third run. The final conversion level was higher on the 15% Pt catalyst compared to that on the 10% Pt catalyst.

REFERENCES

APPENDIX

Additional Activities

Several students (Jillyan Harlan, Valerie Brown, and Victor Robers) were employed as undergraduate research students. All the experimental runs in this reporting period were conducted by the students.

A poster paper, entitled "Development of a Novel Catalyst for NO Decomposition" will be presented by Jillyan Harlan at the AIChE 2004 Annual Meeting, Austin, TX, Nov.7-12, 2004.

a. Future Plans

During the next reporting period, it is planned to:

1. Complete the TPRxn experiments with the 10% and 5% Pt catalysts.

2. Run the TPD experiments with catalysts containing 10% and 5% Pt.

6. Complete the analysis of data.

Figures

Figure 1. TPRx of NO on Fresh15% Pt/SnO2 Catalyst

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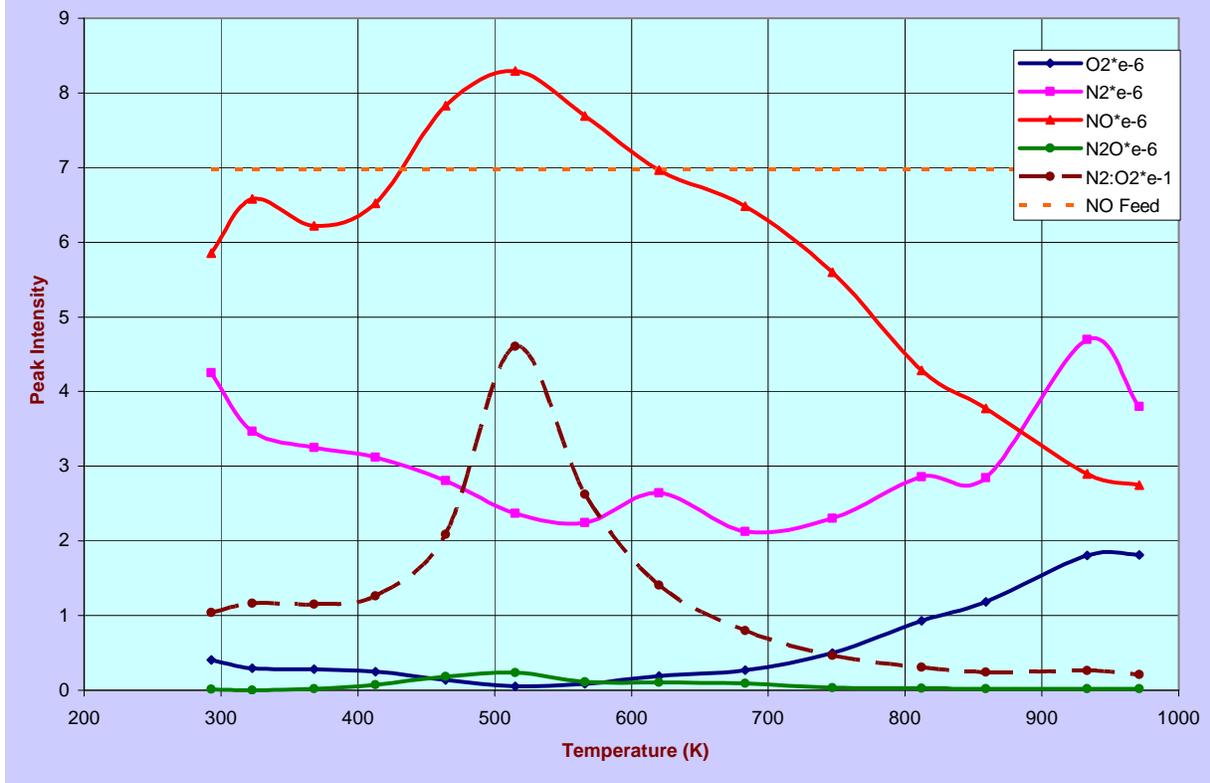
Figure 2. Second TPRx run of NO on 15% Pt/SnO$_2$ Catalyst.
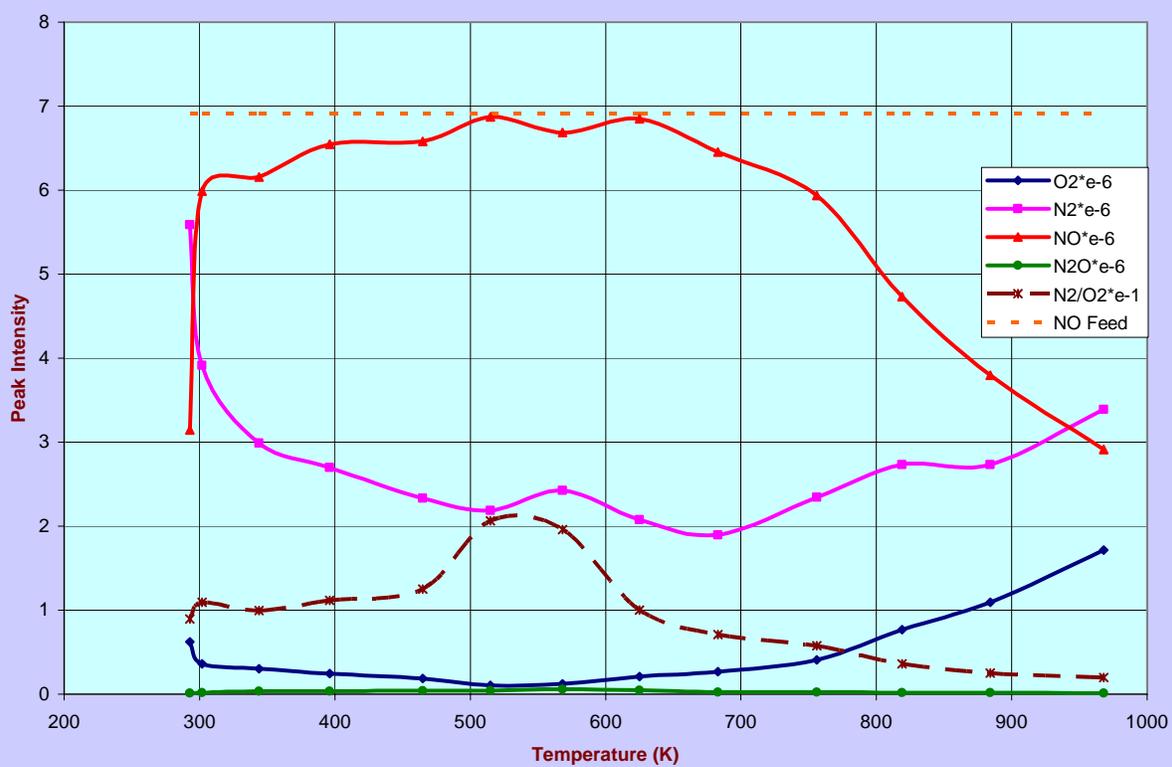
Figure 3. Third TPRx run of NO on 15% Pt/SnO2 Catalyst.
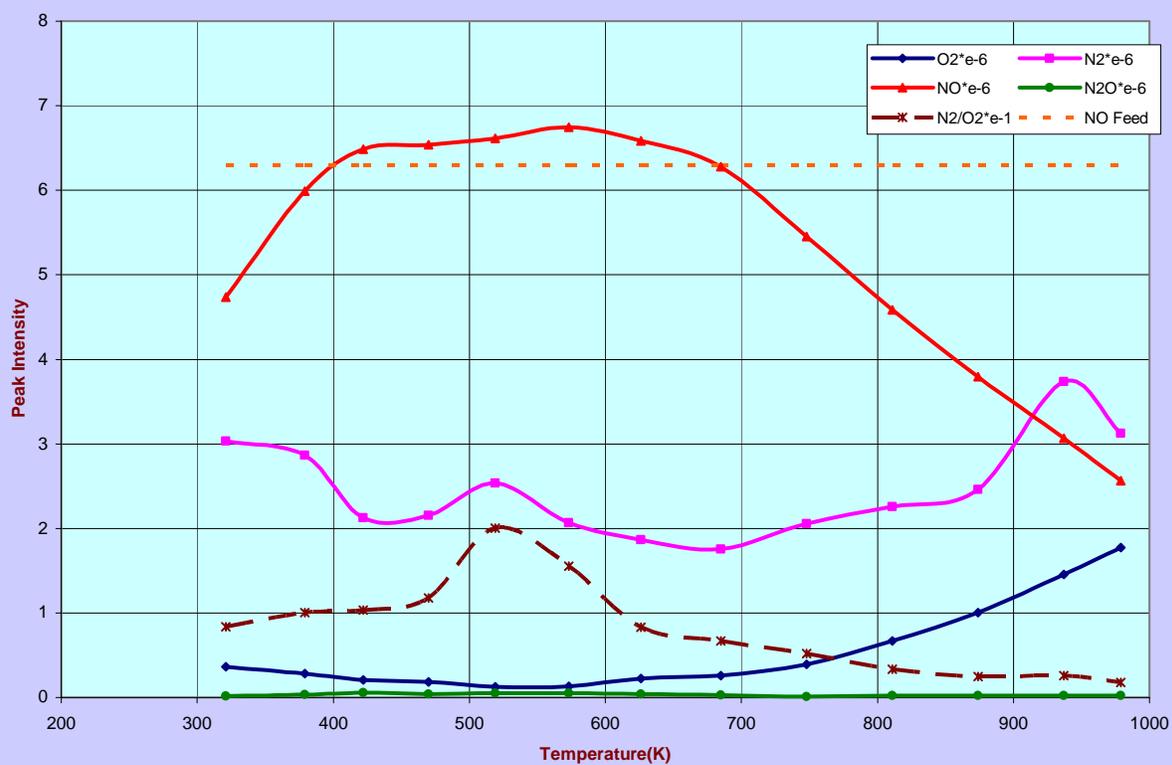
Figure 4. TPReaction on fresh NASA 15% Pt/SnO2 Catalyst. Feed O2/NO=1.1
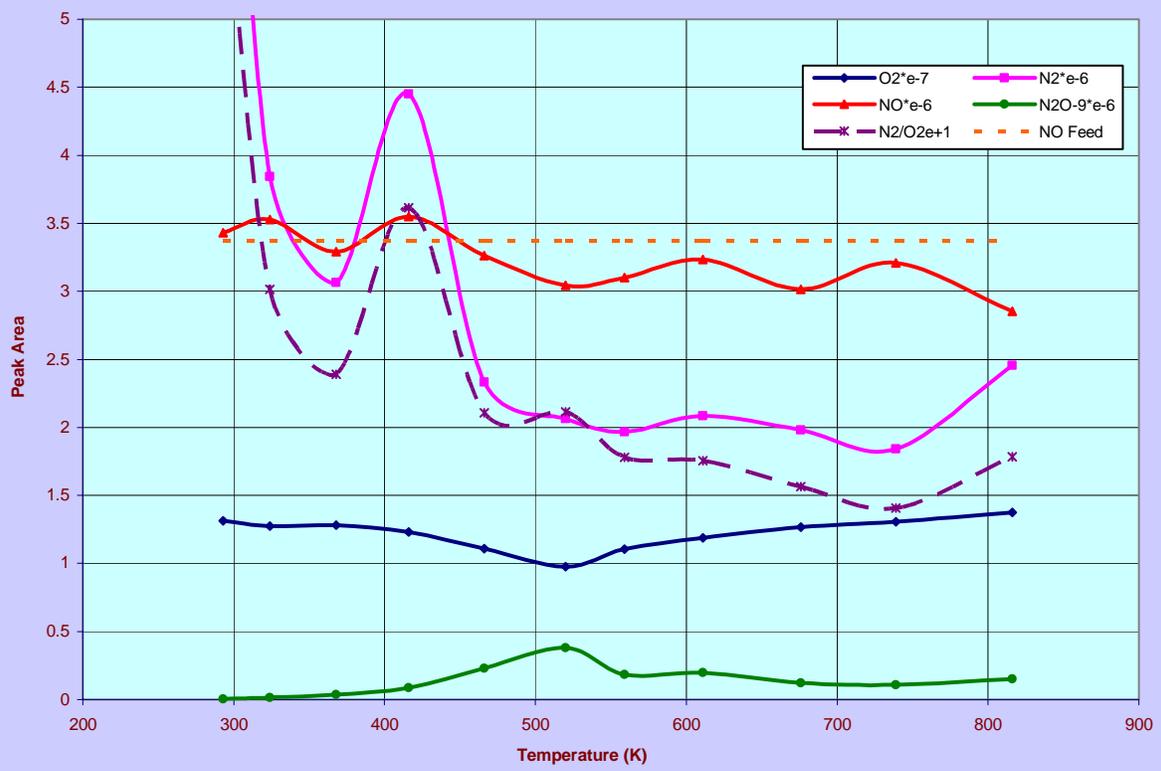
Figure 5. Second TPReaction Run on NASA 15% Pt/SnO$_2$ Catalyst. Feed O$_2$/NO=1.1

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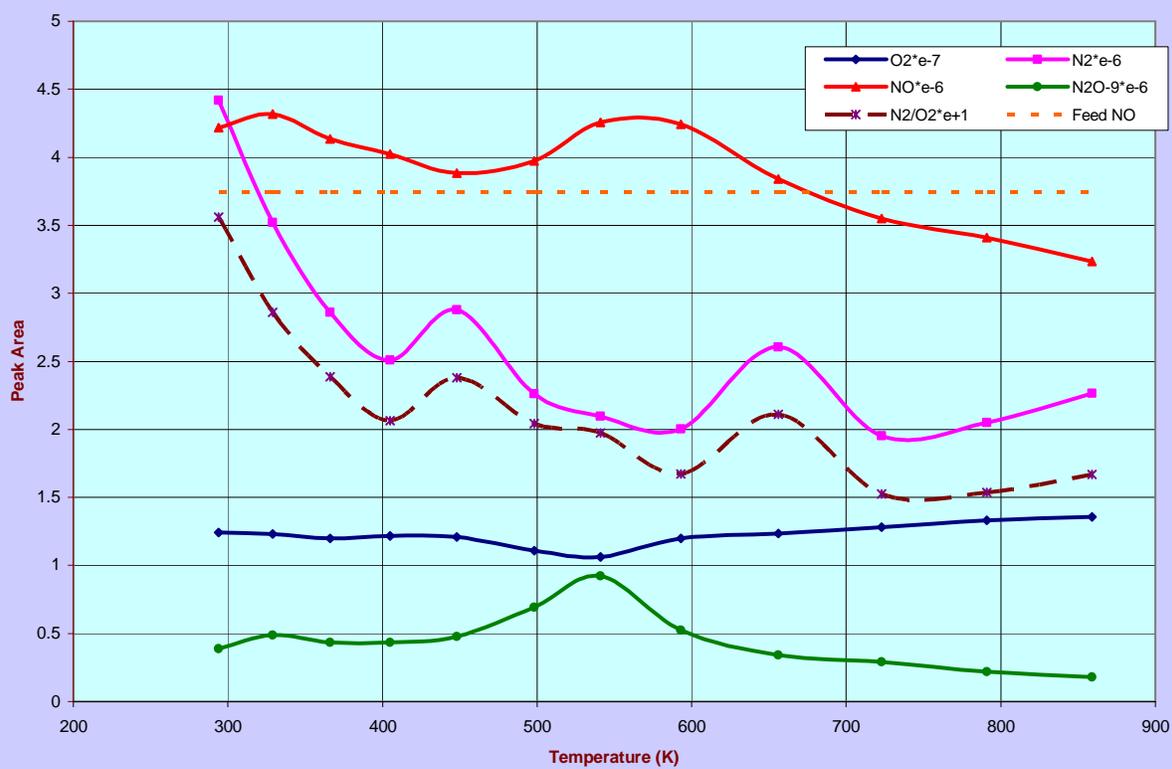
Figure 6. TPRx on Fresh NASA 15% Pt/SnO2 Catalyst. Feed O2/NO= 0.49

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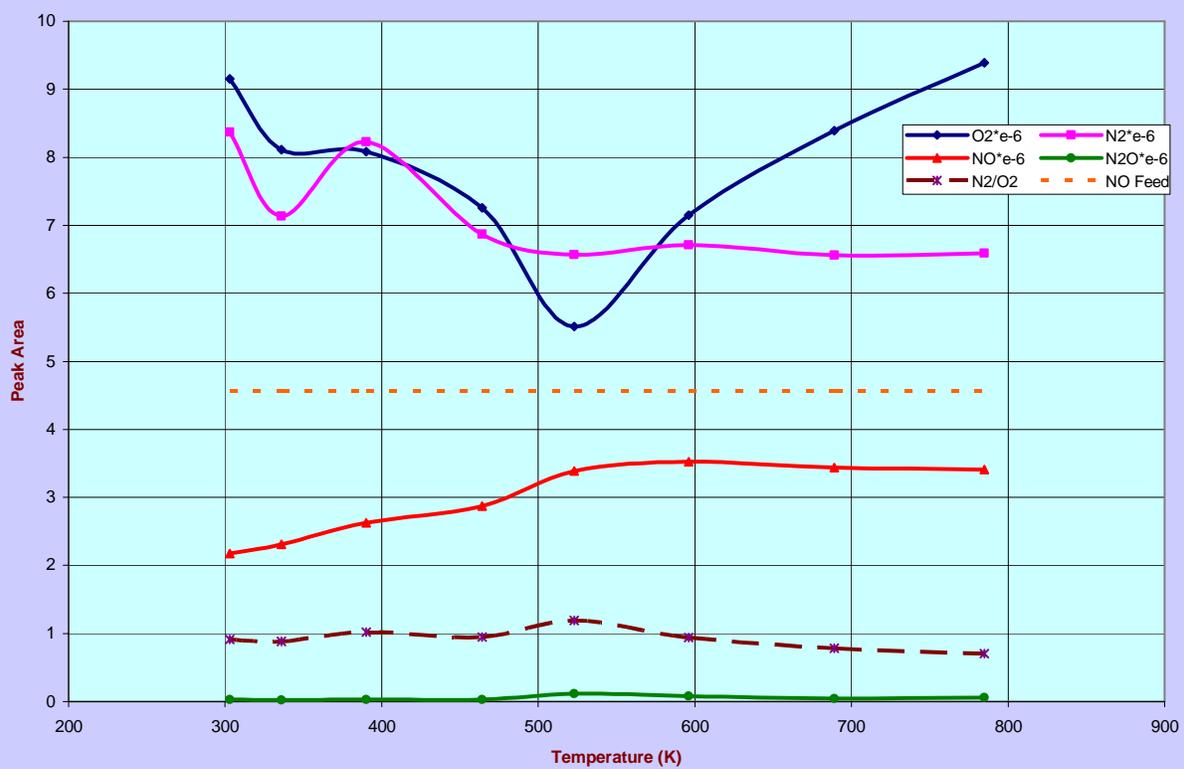
Figure 7. Second TPRx Run on NASA 15% Pt/SnO$_2$ Catalyst. Feed O$_2$/NO= 0.49
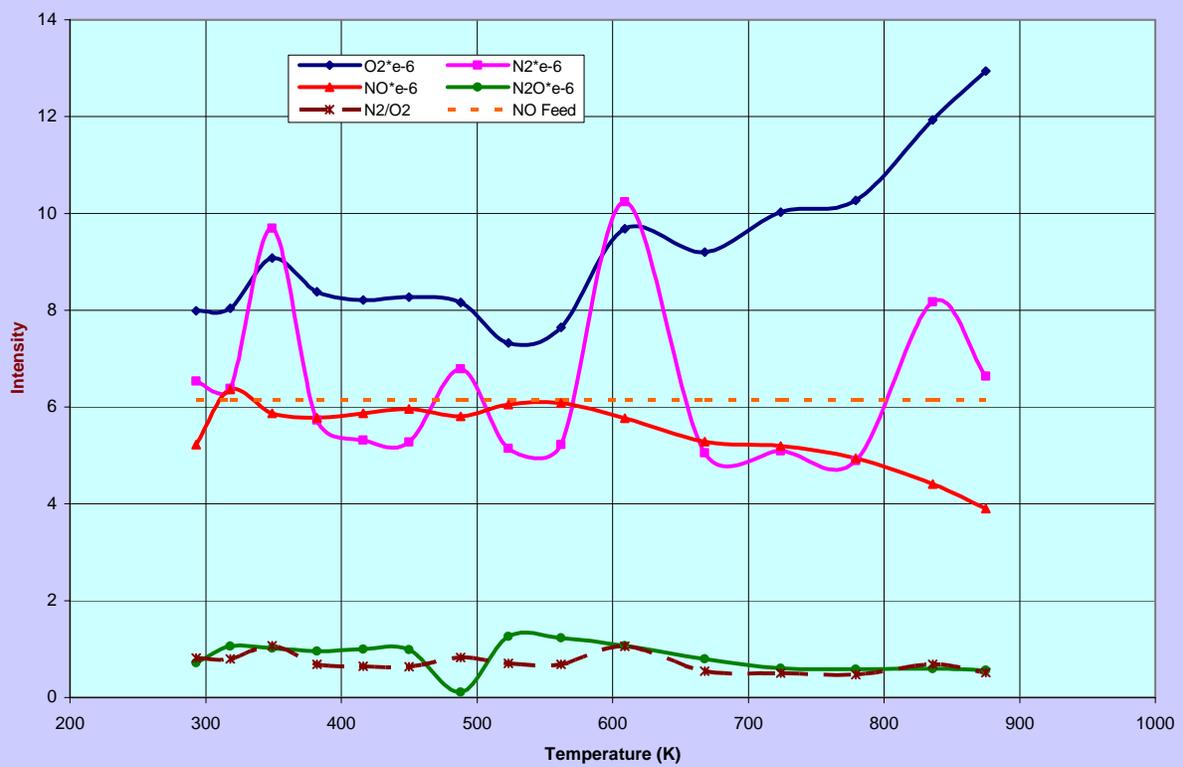
Figure 8. TPRx of NO on Fresh10% Pt/SnO$_2$ Catalyst. Feed Gas: 634 ppm NO in He
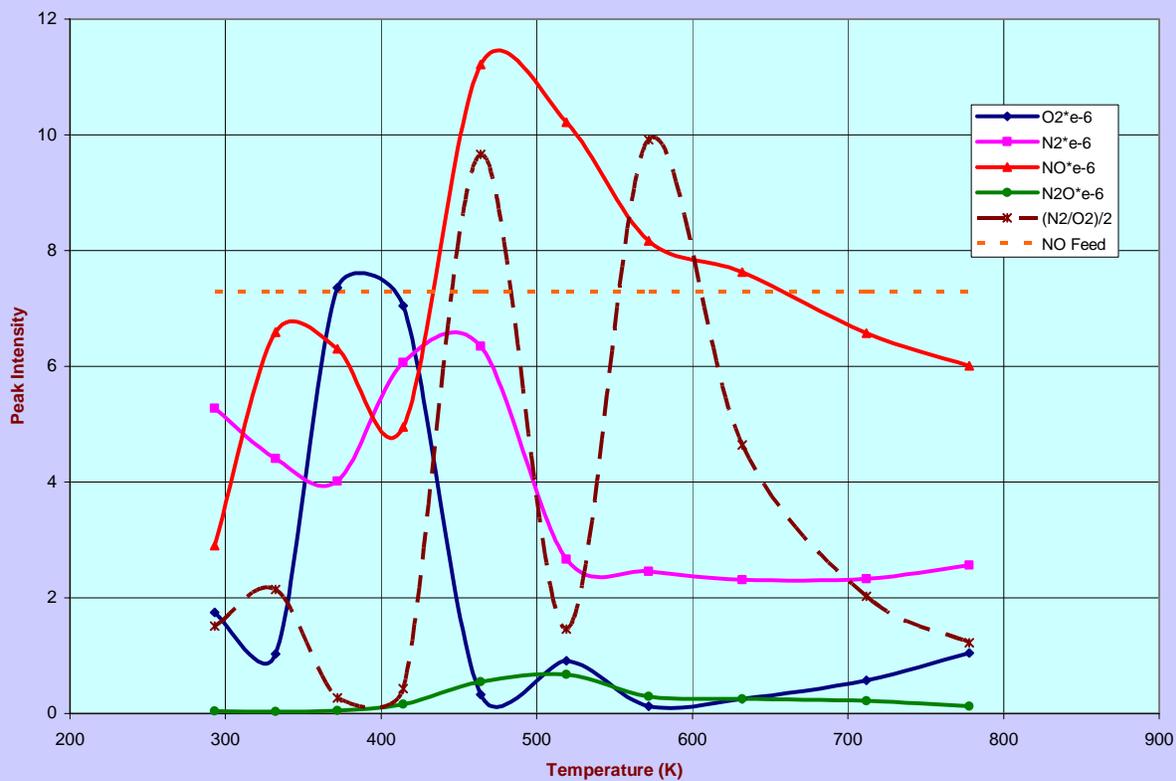
Figure 9. Second TPRx of NO on 10% Pt/SnO$_2$ Catalyst. Feed Gas: 634 ppm NO in He
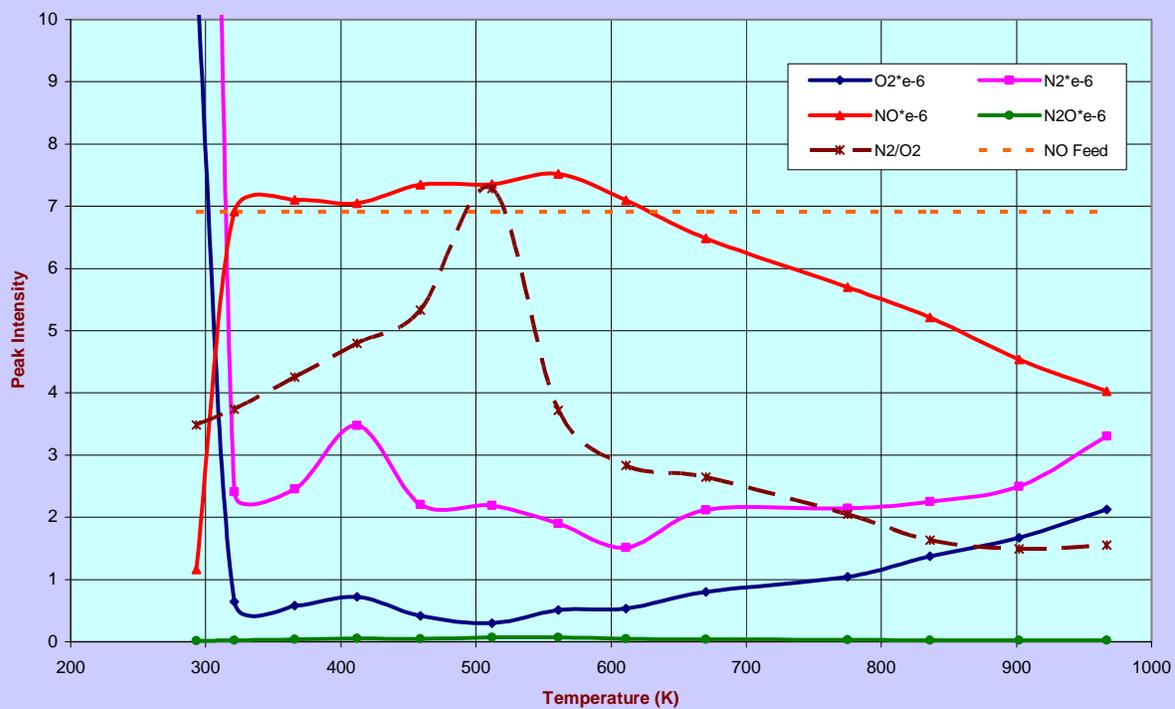
Figure 10. Third TPRx of NO on 10% Pt/SnO$_2$ Catalyst. Feed Gas: 634 ppm NO in He
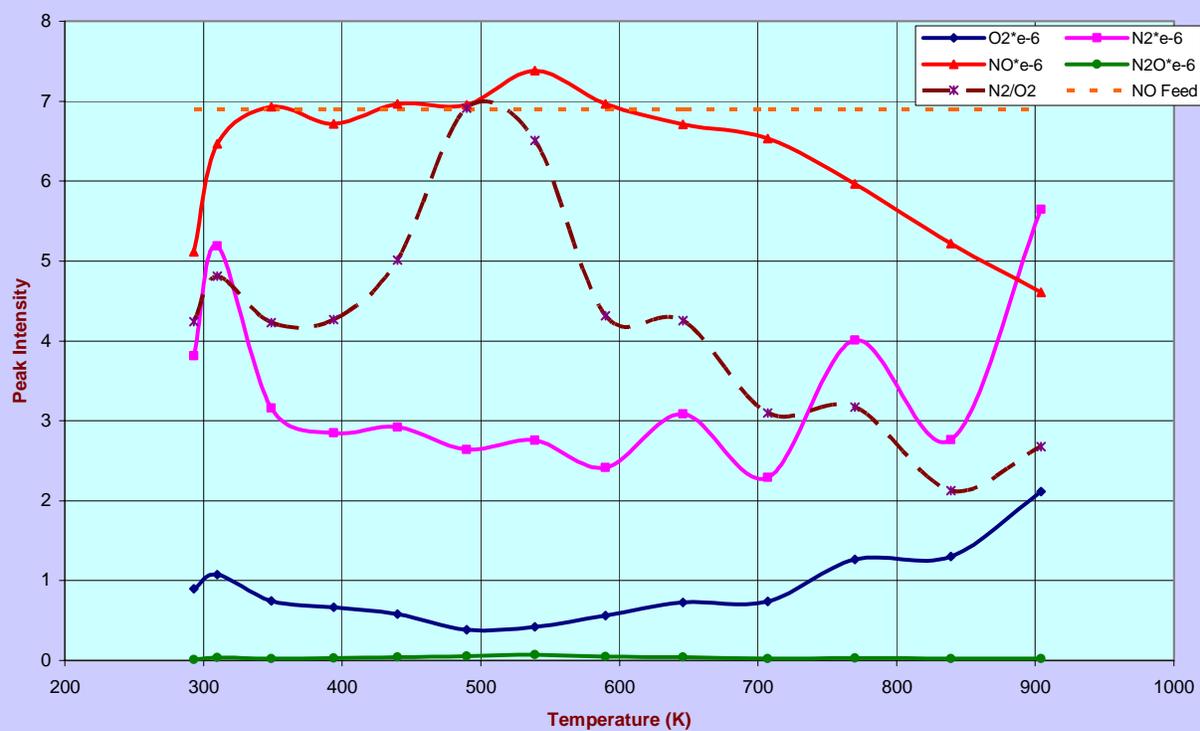
Figure 11. Fourth TPReaction of NO on 10% Pt/SnO$_2$ Catalyst. Feed Gas: 634 ppm NO in He
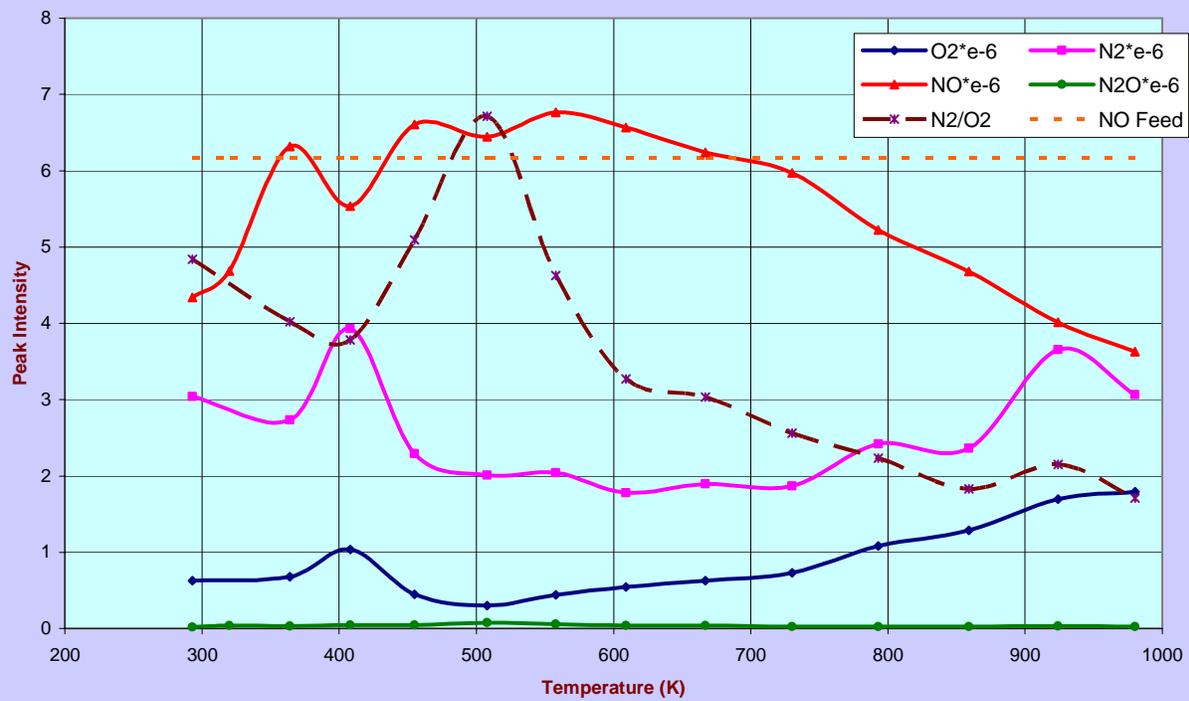
Figure 12. TPRx of NO+O_2 on Fresh10% Pt/SnO_2 Catalyst. Feed O_2/NO= 2.4
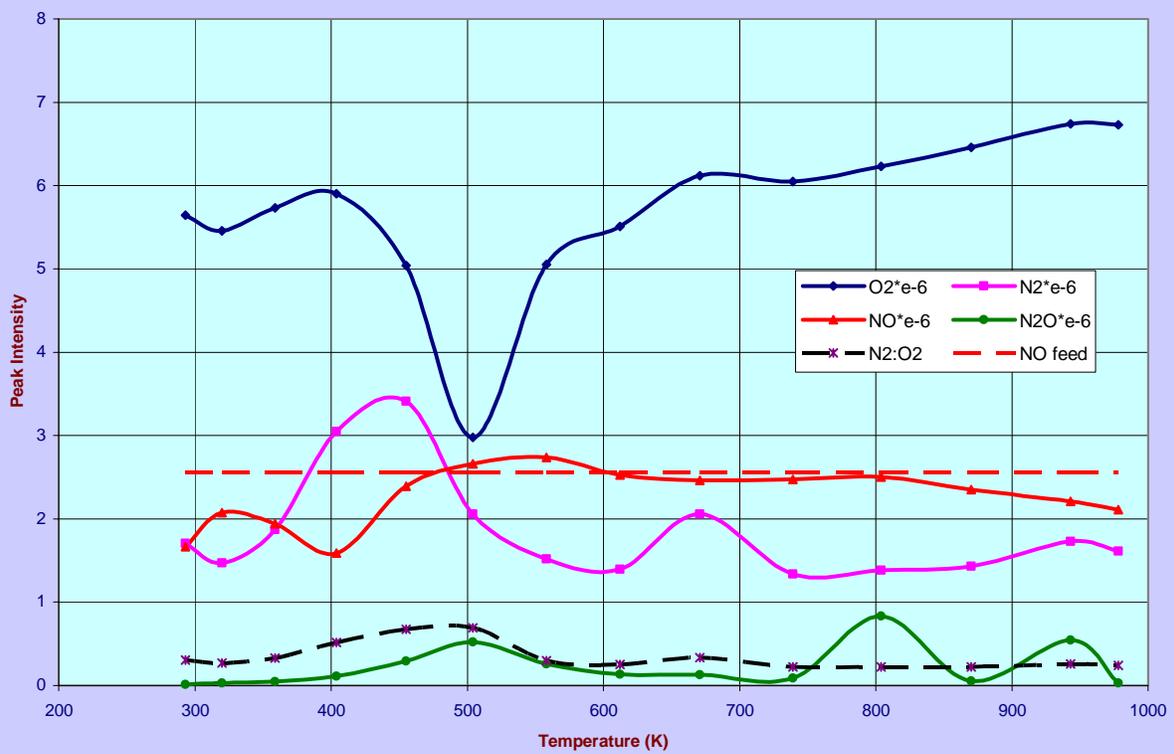
Figure 13. Second TPRx of NO+O_2 on 10% Pt/SnO_2 Catalyst. Feed O2/NO= 2.4
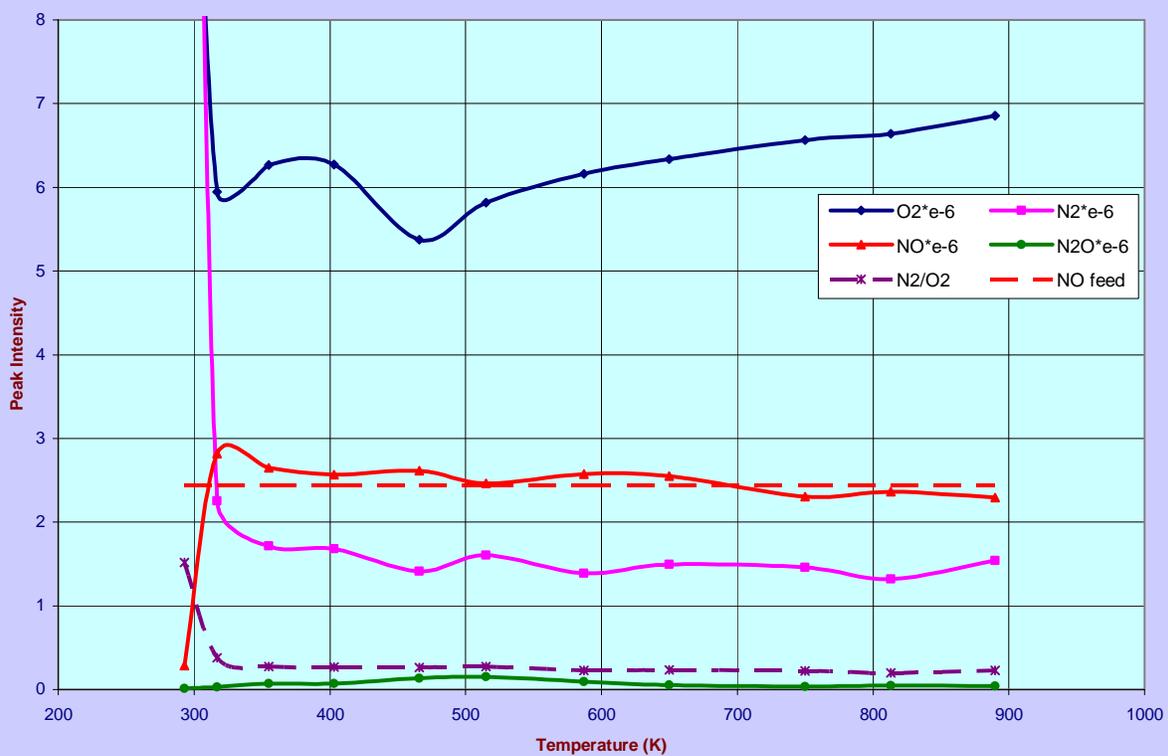
Figure 14. Third TPRx of NO+O_2 on 10% Pt/SnO_2 Catalyst. Feed O2/NO= 2.4