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 some TPRx runs with the catalysts containing 15 % and 10 % Pt were repeated due to the uncertainty of the oxygen content of the feed. In this reporting period runs were made with feed gas mixtures containing water vapor. Two reaction regimes,one below and the other above 750 K were observed. Presence of water vapor slightly enhanced the catalyst activity, but decreased the selectivity towards N_2 at low temperatures.

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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.

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In the previous 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.

The catalyst was active for NO decomposition only above 600 K and at these temperatures no appreciable N_2O was observed. For feeds containing additional oxygen, the NO decomposition activity was less when fresh and the catalyst lost most of its activity in the subsequent runs. This may be due to the oxidation of Pt, coverage of active Pt sites with oxygen, and the loss of OH groups from the SnO_2 surface. Since these OH groups are thought to be very active in the O_2-involving processes on the catalyst surface, and since water vapor is a component of the power plant stack gas, we plan to repeat the TPRx runs with feeds containing water vapor.

In this reporting period temperature programmed reaction of $NO + O_2 + H_2O$ on 15 % Pt/SnO_2 catalyst was done. The reaction of NO and O_2 in the presence of water vapor appears to show two different reaction schemes, one below and the other above 750 K. Activation energy below 750 K was estimated to be 204 kJ/mol and that at higher temperatures was estimated as 43kJ/mol.

In addition, reactions of dry and wet mixtures of NO and O_2 were carried out for over 3 hours. No apparent deactivation was observed.

EXPERIMENTAL

a. Temperature-Programmed Reaction Experiments

Temperature Programmed Reaction of NO + O_2 + H_2O on the 15 % Pt/SnO_2 catalyst was run to identify the effect of water vapor on catalyst activity and selectivity. 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.

b. Reactions at 800 and 900 K

The reactions of NO + O_2 with and without water vapor were carried out at 800 and 900 K. The reactions were continued for over 3 hours to investigate catalyst deactivation.

RESULTS AND DISCUSSION

a. Temperature Programmed Reaction of NO + O_2 + H_2O

The feed contained 634 ppm NO, an equal amount of O_2 and was saturated with water at 295 K. Figure 1 shows that NO decomposition starts at around 700 K with close to 100 % selectivity to N_2 and O_2. There appears to be two rate controlling processes, one below 750 K and the other above 750 K. Arrhenius plot given in Figure 2 confirms this. The apparent activation energy obtained for temperatures less than 750 K is 204 kJ/mol and that for higher temperatures is 43 kJ/mol. Although 43 kJ/mol might be too high to indicate mass transfer control, this run will be repeated at a higher flow velocity to confirm the absence of external mass transfer limitations.

Effect of the water content of the feed gas

Comparisons of Figures 3 and 4 indicate that at 800 K, the NO conversion is very low. Water content of the feed gas appears to enhance the decomposition activity slightly but also decreases N_2 selectivity as indicated by a slight increase in the N_2O formation. Figures 5 and 6 indicate that at 900 K, NO conversion is higher and presence of H_2O again affects the NO conversion favorably. At this higher temperature the effect of water on N_2O formation is not very significant. This observation contradicts the prediction that the presence of OH ions on the tin oxide will hinder the desorption of surface oxygen and thus adversely affect the catalyst activity. The observed enhancement activity may be due to the attraction of surface oxygen to these hydroxyl groups preventing the coverage of the Pt sites by the adsorbed oxygen. The reactions were continued over 3 hours and no decrease in activity were observed both for wet and dry feeds.

To further investigate the effect of surface hydroxyl groups, we plan to pretreat the catalysts at 1000 K under helium and cool to room temperature under helium before running the reactions at the desired temperature.

CONCLUSIONS

- The reaction of NO and O_2 in the presence of water vapor appears to show two different reaction schemes, one below and the other above 750 K
- Having water vapor in the feed seems to enhance the catalyst activity, but decrease the selectivity towards N_2 especially at lower temperatures.

REFERENCES

APPENDIX

Additional Activities

A paper, entitled “Development of a Novel Catalyst for NO Decomposition” was presented by Ates Akyurtlu at the DOE 2005 University Coal Research/Historically Black Colleges and Universities and Other Minority Institutions Contractors Review Conference.

a. Future Plans

During the next reporting period, it is planned to:

1. Repeat the TPRx of NO + O_2 + H_2O at 900 K using a higher flow velocity.
2. Run the TPRxn experiments at 1000 K with the 10% and 15% Pt catalysts with feeds containing water vapor.
3. Run the TPD experiments with catalysts containing 10% and 15% Pt and treated with He containing water vapor.
3. Run TPRxn experiments at 800, 900, and 1000 K on the 10% and 15% Pt catalysts pretreated at 900 K and 1000 K under He, with dry feeds (NO + He and NO +O_2 + He).

Figures

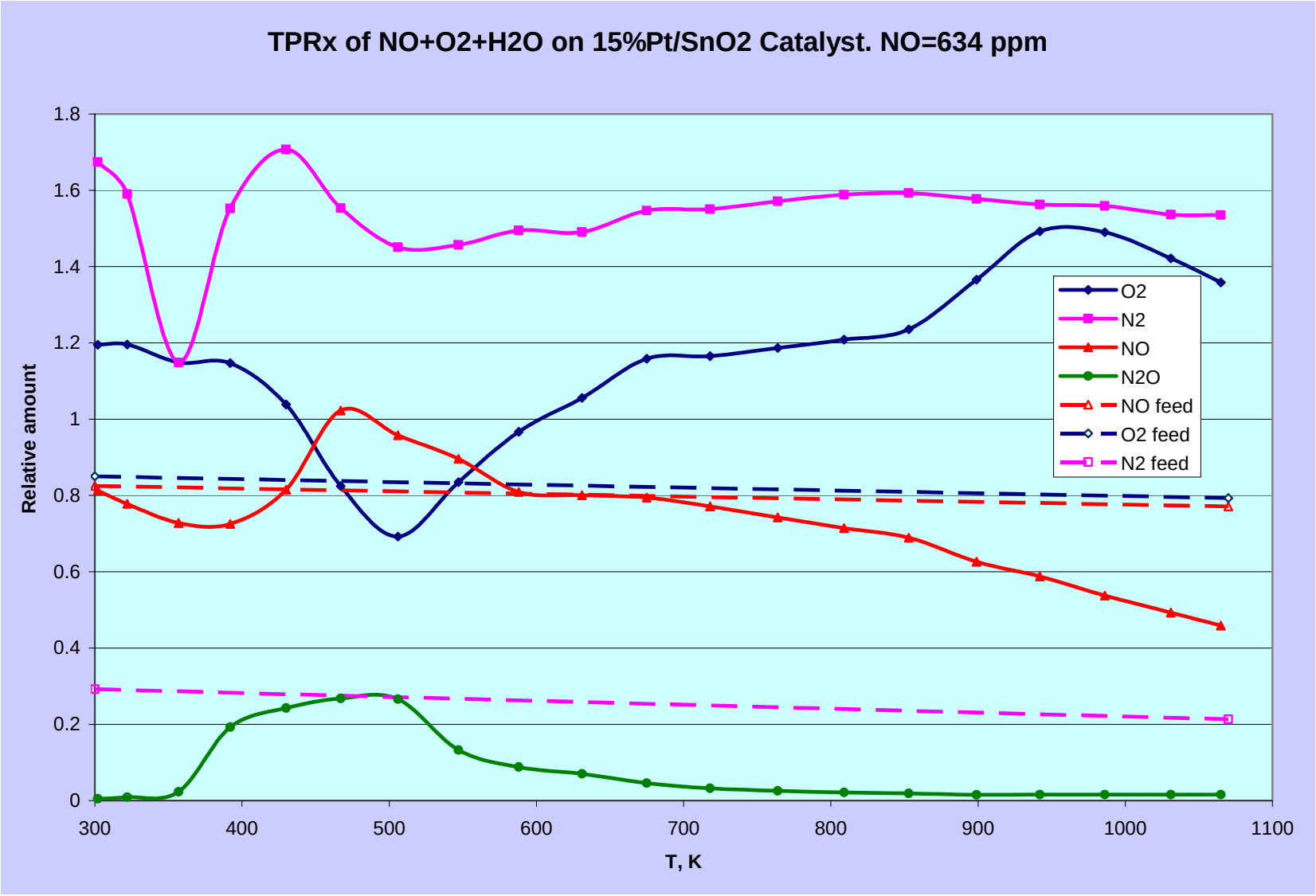
TPRx of NO+O2+H2O on 15%Pt/SnO2 Catalyst. NO=634 ppm
Relative amount
T, K
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
300
400
500
600
700
800
900
1000
1100
O2
N2
NO
N2O
NO feed
O2 feed
N2 feed

Figure 1

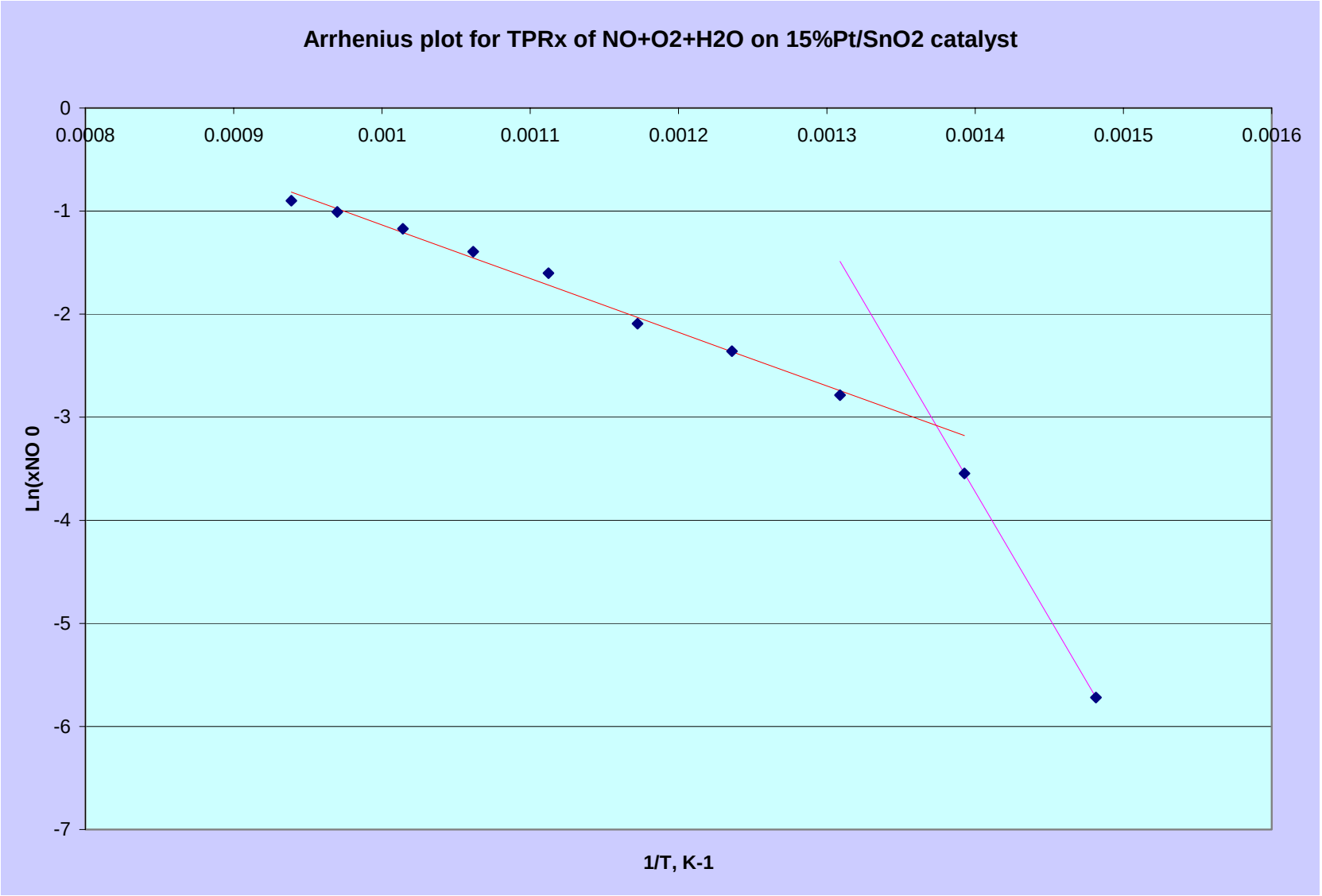
Arrhenius plot for TPRx of NO+O2+H2O on 15%Pt/SnO2 catalyst
0
0.0008
0.0009
0.001
0.0011
0.0012
0.0013
0.0014
0.0015
0.0016
-1
-2
-3
-4
-5
-6
-7
Ln(xNO 0
1/T, K-1

Figure 2.

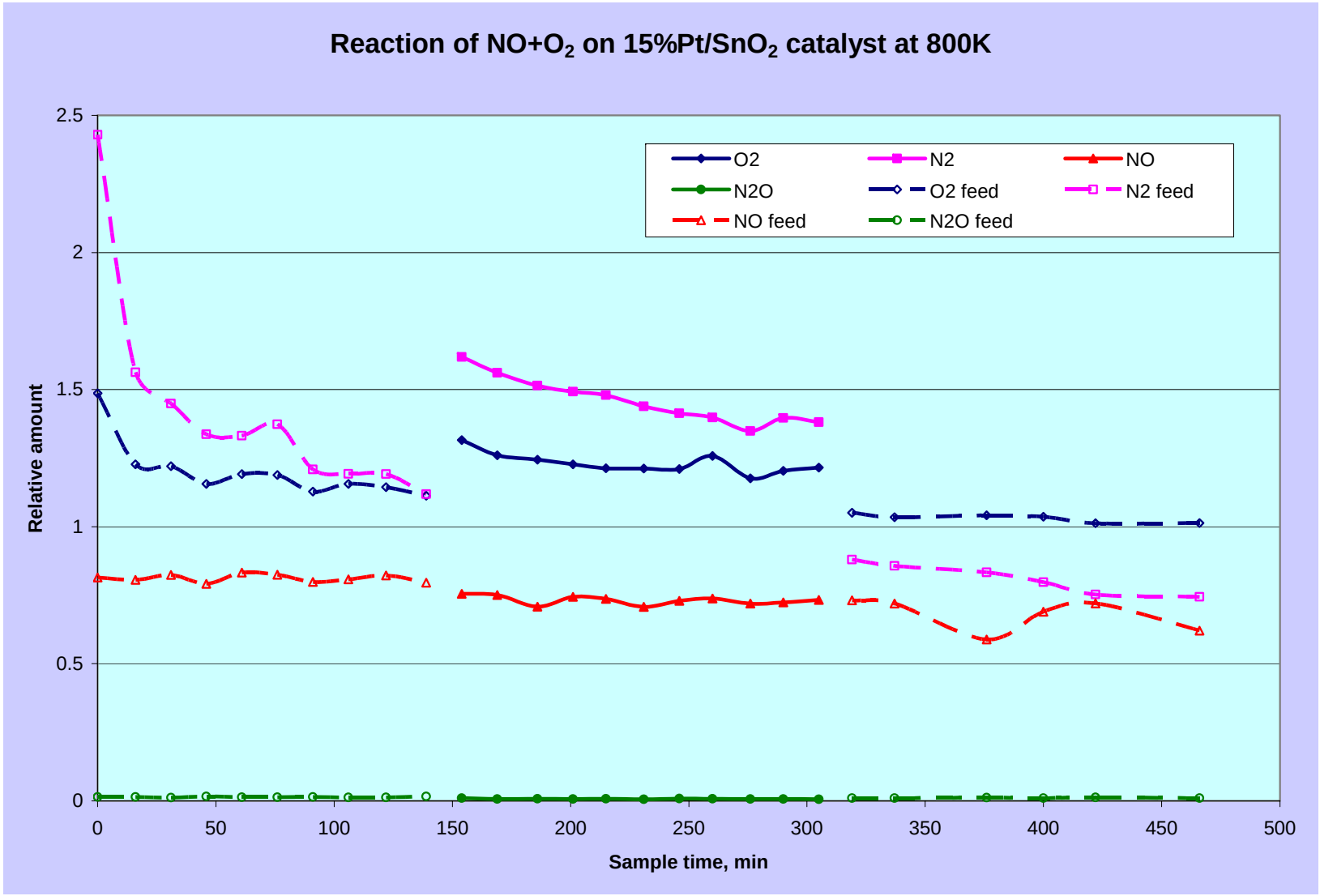
Reaction of NO+O2 on 15%Pt/SnO2 catalyst at 800K
Relative amount
Sample time, min
O2
N2
NO
N2O
O2 feed
N2 feed
NO feed
N2O feed
0
0.5
1
1.5
2
2.5
0
50
100
150
200
250
300
350
400
450
500

Figure 3

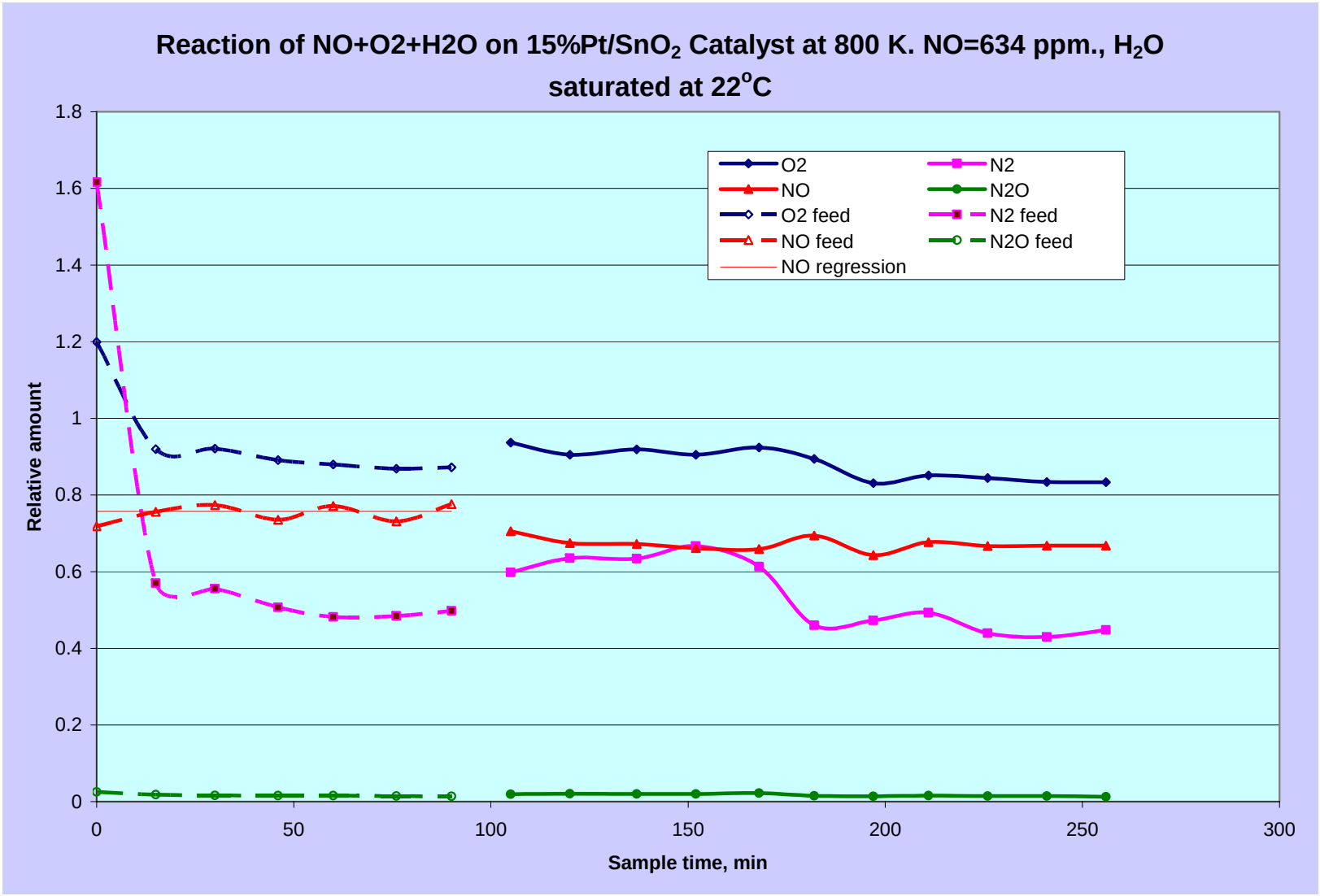
Reaction of NO+O2+H2O on 15%Pt/SnO2 Catalyst at 800 K. NO=634 ppm., H2O saturated at 22°C
Relative amount
Sample time, min
O2
N2
NO
N2O
O2 feed
N2 feed
NO feed
N2O feed
NO regression
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
0
50
100
150
200
250
300

Figure 4

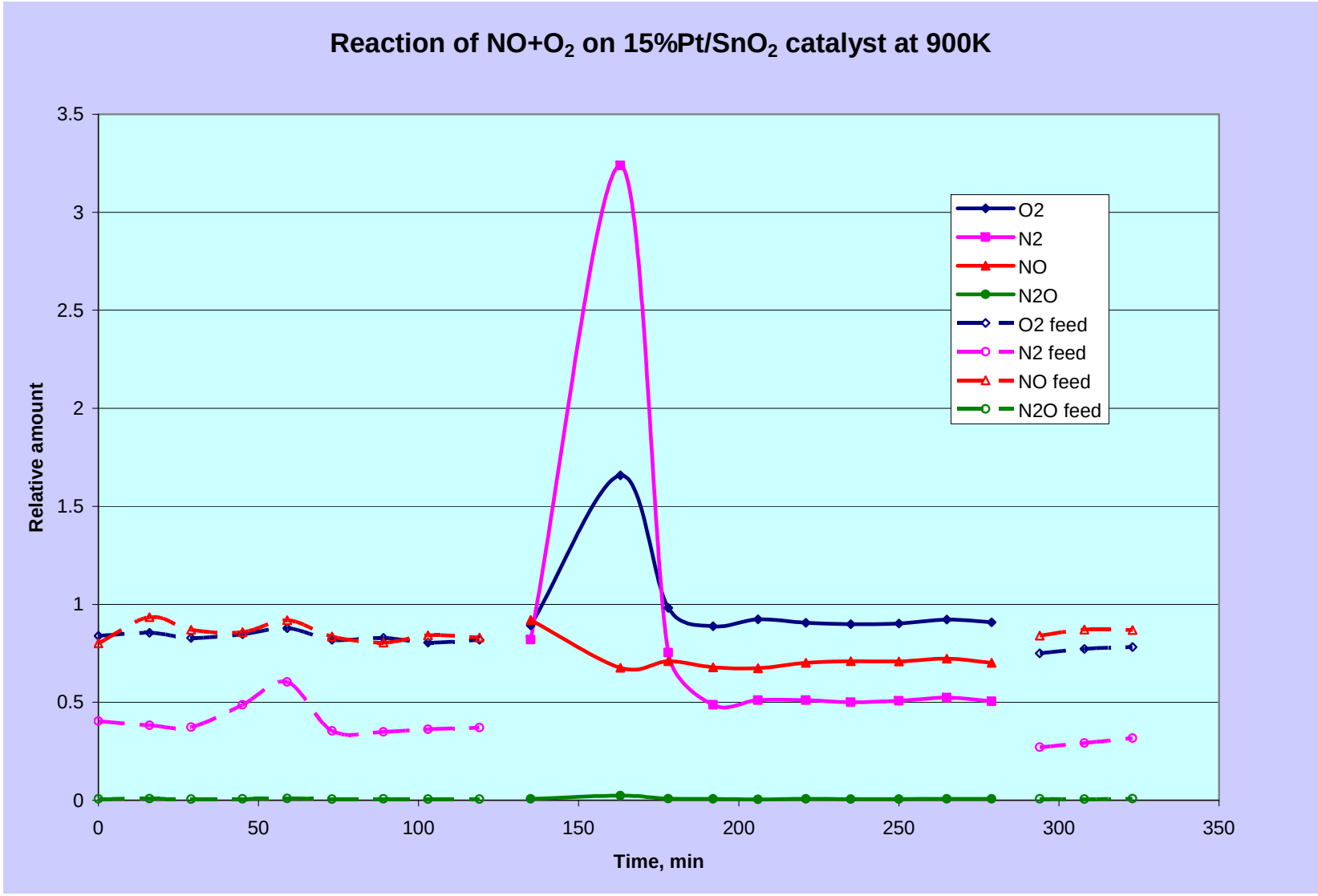
Reaction of NO+O2 on 15%Pt/SnO2 catalyst at 900K
Relative amount
Time, min
0
0.5
1
1.5
2
2.5
3
3.5
0
50
100
150
200
250
300
350
O2
N2
NO
N2O
O2 feed
N2 feed
NO feed
N2O feed

Figure 5

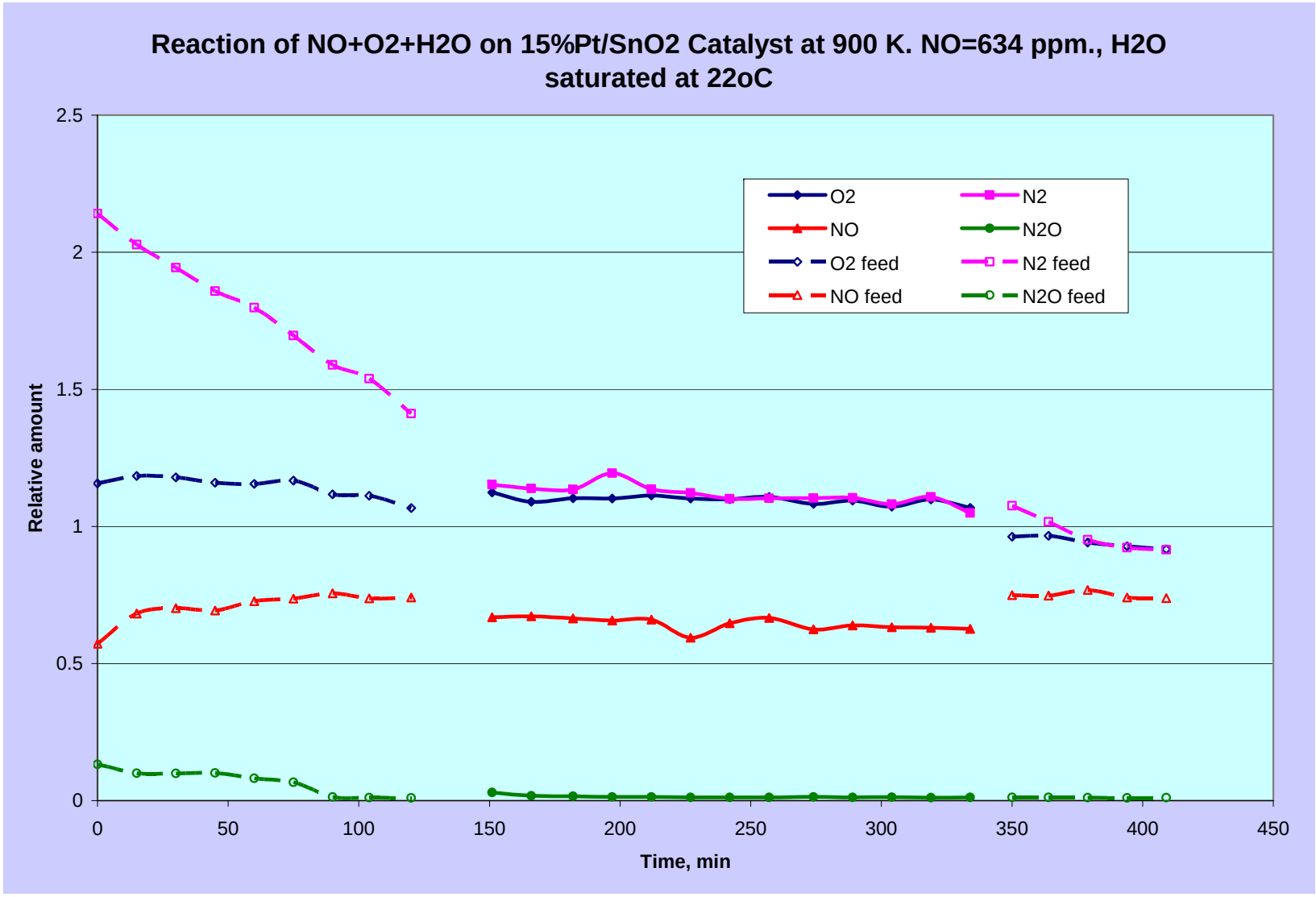
Reaction of NO+O2+H2O on 15%Pt/SnO2 Catalyst at 900 K. NO=634 ppm., H2O saturated at 22oC
Relative amount
Time, min
O2
N2
NO
N2O
O2 feed
N2 feed
NO feed
N2O feed
0
0.5
1
1.5
2
2.5
0
50
100
150
200
250
300
350
400
450

Figure 6