

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 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°C . The Temperature Programmed Reaction (TPRx) of NO and $\text{NO}+\text{O}_2$ mixtures on the catalysts containing 15 % Pt and 10 % Pt were also performed.

In this 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.

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LIST OF GRAPHICAL MATERIAL

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Figure 2. Second TPRx run of NO on 15% Pt/SnO₂ Catalyst.

Figure 3. Third TPRx run of NO on 15% Pt/SnO₂ Catalyst.

Figure 4. TPRx of NO+O₂ on fresh 15% Pt/SnO₂ Catalyst. NO = 634 ppm

Figure 5. TPRx of NO+O₂ on 15% Pt/SnO₂ Catalyst. Second run.

Figure 6. TPRx of NO+O₂ on 10% Pt/SnO₂ Catalyst. Second run.

Figure 7. TPRx of NO+O₂ with no Catalyst. NO = 634 ppm.

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 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.

During pulse chemisorption of NO, about half of NO is either dissociated into N_2 and O_2 or retained on the catalyst at a steady rate. Based on the N_2/O_2 ratio, the latter is deemed a more probable explanation. The N_2 , N_2O , and NO peaks were separated by about 25 K. There were two O_2 minima, one corresponding to the N_2O peak and the other to the termination of NO peak. The observed NO peak could be due to the presence of free surface nitrite or nitrate species, but the presence of N_2O_4 and N_2O_3 is more likely. The 25 K separation between the N_2 and N_2O peaks suggests that these two species are produced, at least partially, by different surface reaction schemes.

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 after successive adsorptions of NO and O_2 , the N_2O and NO peaks and the single O_2 minima were all observed around 490 K suggesting that in the presence of excess O_2 , both N_2O and NO were produced by parallel surface reactions.

Presence of excess oxygen increased the production of N_2O .

In this reporting period temperature programmed reaction runs on the 15% Pt and 10% Pt catalysts were performed using NO+He and NO+O₂+He reactant gas mixtures.

The catalyst was active for NO decomposition only above 600 K and at these temperatures no appreciable N₂O 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 SnO₂ surface. Since these OH groups are thought to be very active in the O₂-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.

EXPERIMENTAL

a. Temperature-Programmed Reaction Experiments

Temperature-Programmed Reaction (TPRx) Experiments were used to evaluate the reactions of NO and NO - O₂ 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.

TPRx of catalysts containing 15% and 10% Pt were repeated. This time temperatures were increased up to 900 K and close attention was paid to making sure that a steady feed composition was obtained before starting the TPRx runs. For some runs the feed composition after the TPRx runs were also measured.

RESULTS AND DISCUSSION

Temperature Programmed Reaction of NO and NO + O₂

For the TPRx of NO the feed contained 634 ppm NO. Although no additional oxygen or nitrogen was added to the feed gas, the feed contained some oxygen and nitrogen due to the impurities in the bottled NO-He mixture and some small air leaks in the equipment. For the TPRx of NO + O₂, the feed NO concentration was kept at 634 ppm and an equal molar amount of oxygen was added. As mentioned above, the feed contained some oxygen and nitrogen due to gas impurities and air leaks. As a result, the graphs presented with this report, show a different NO/O₂ ratio.

The general result obtained are summarized below:

- There was no NO decomposition below 520 K, but some N₂O formation above 370 K, which peaked at 520 K, but no N₂O was present above 750 K. NO desorption started at 520 K and increased with temperature.
- The N₂O formation on the used catalysts was significantly smaller than that on the fresh catalyst.
- The start of NO decomposition is pushed to 625 K during subsequent runs with the same catalyst, but the rate is 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 presence of oxygen inhibits the decomposition of NO and promotes the formation of N₂O. On catalysts with 15% Pt, some decomposition activity starts around 425 K on fresh catalyst. During the second run NO decomposition does not start until 575 K. During the second run there was no NO decomposition activity up to about 550 K, but significantly less N₂O formation was observed.

- On fresh catalysts with 10% Pt, there was very little decomposition activity, but at lower temperatures N_2O was formed. During the second run NO dissociation activity increased and N_2O formation decreased.

CONCLUSION

- The catalyst is 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.

REFERENCES

APPENDIX

Additional Activities

A poster paper, entitled “Development of a Novel Catalyst for NO Decomposition” was 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. Run the TPR_{xn} experiments with the 10% and 15% Pt catalysts with feeds containing water vapor.
2. Run the TPD experiments with catalysts containing 10% and 15% Pt and treated with He containing water vapor.
6. Complete the analysis of data.

Figures

Figure 1

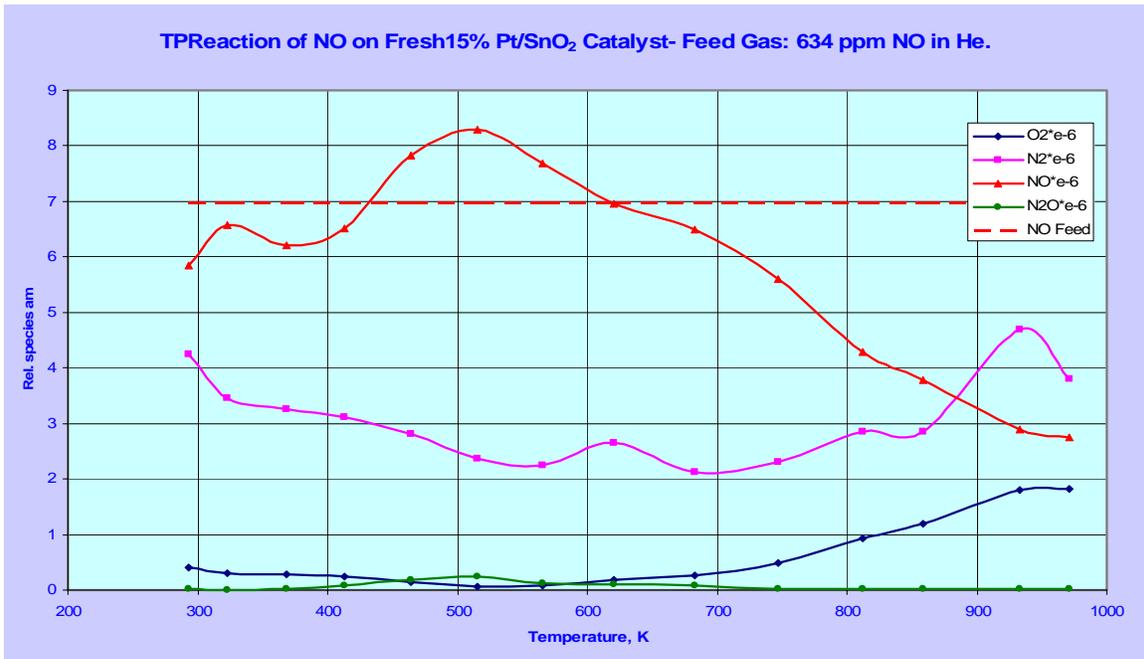


Figure 2

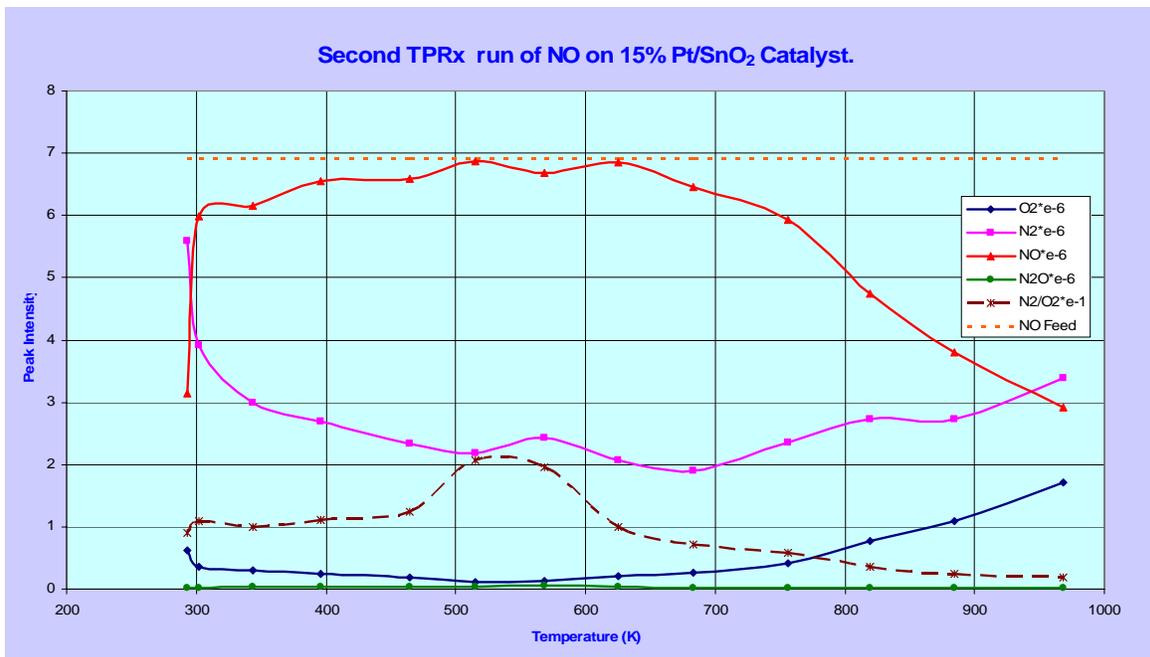


Figure 3

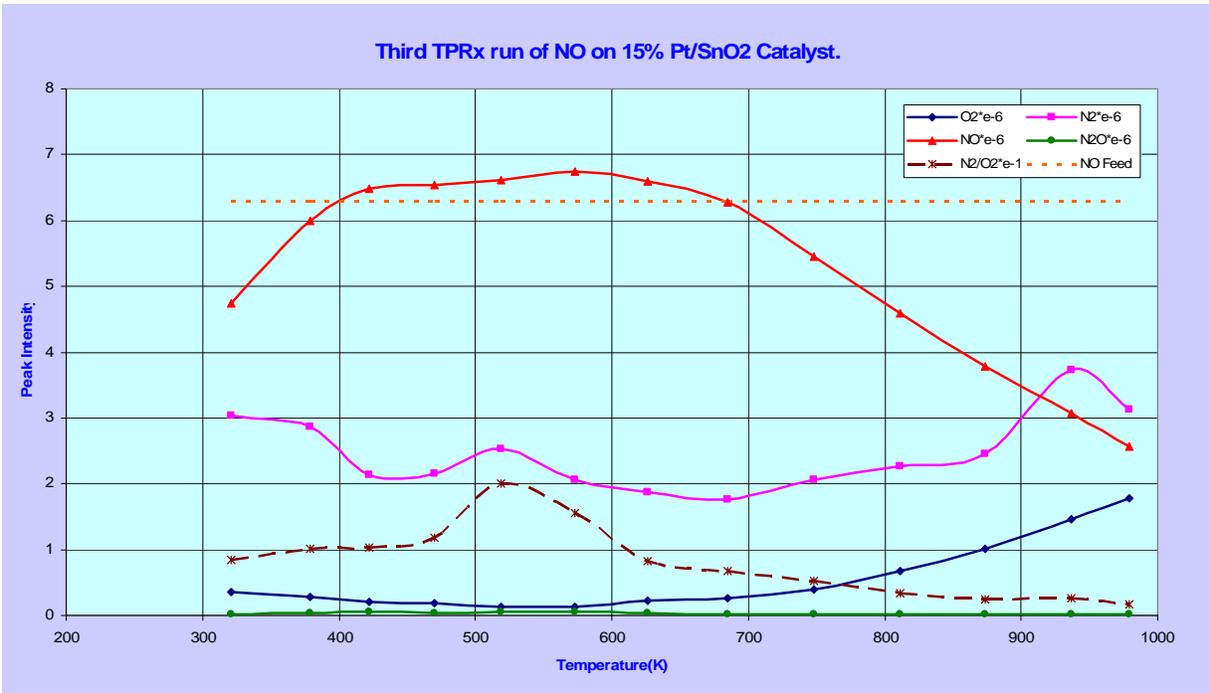


Figure 4

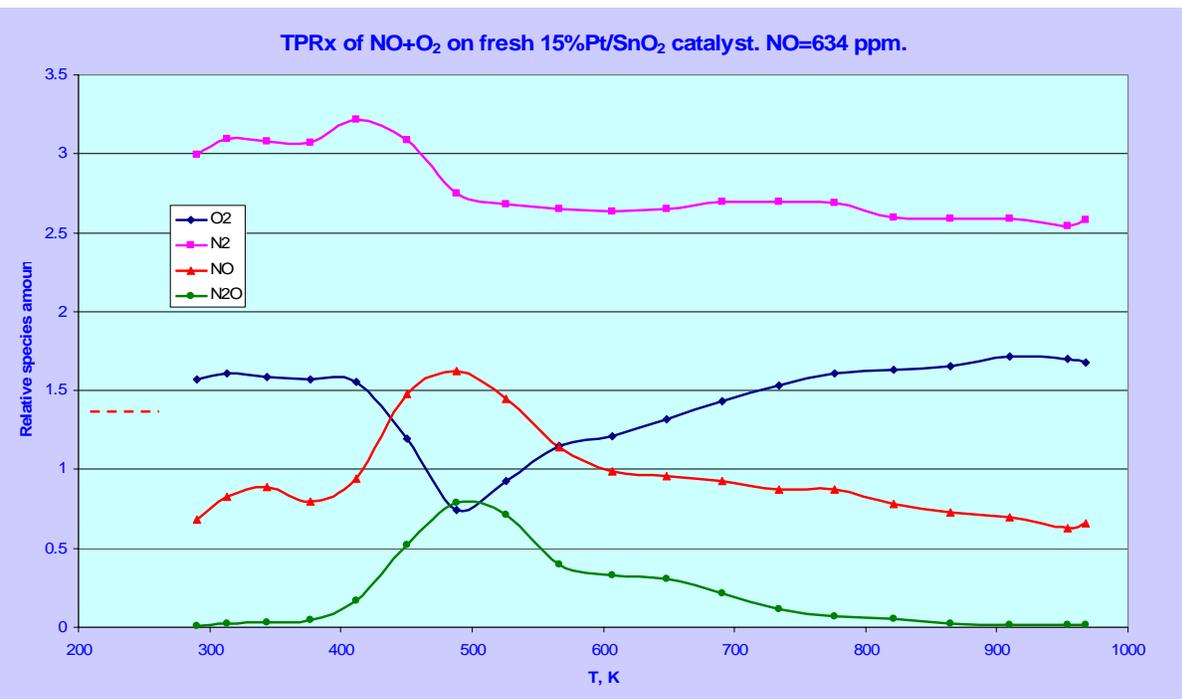


Figure 5

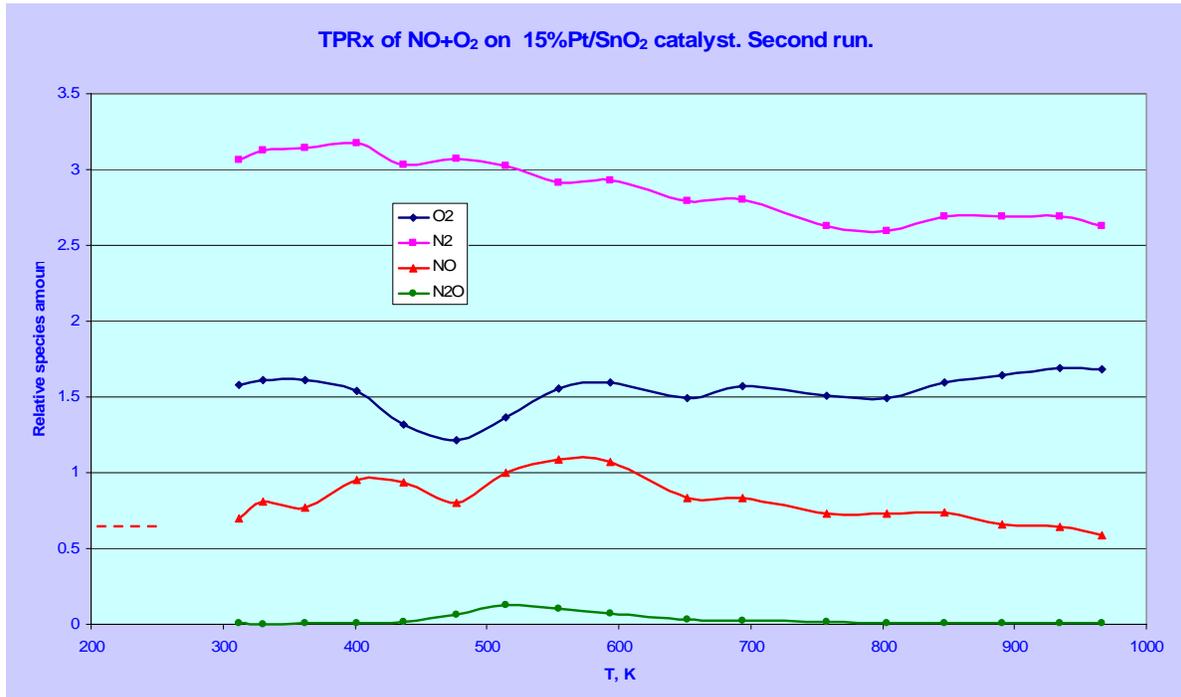


Figure 6

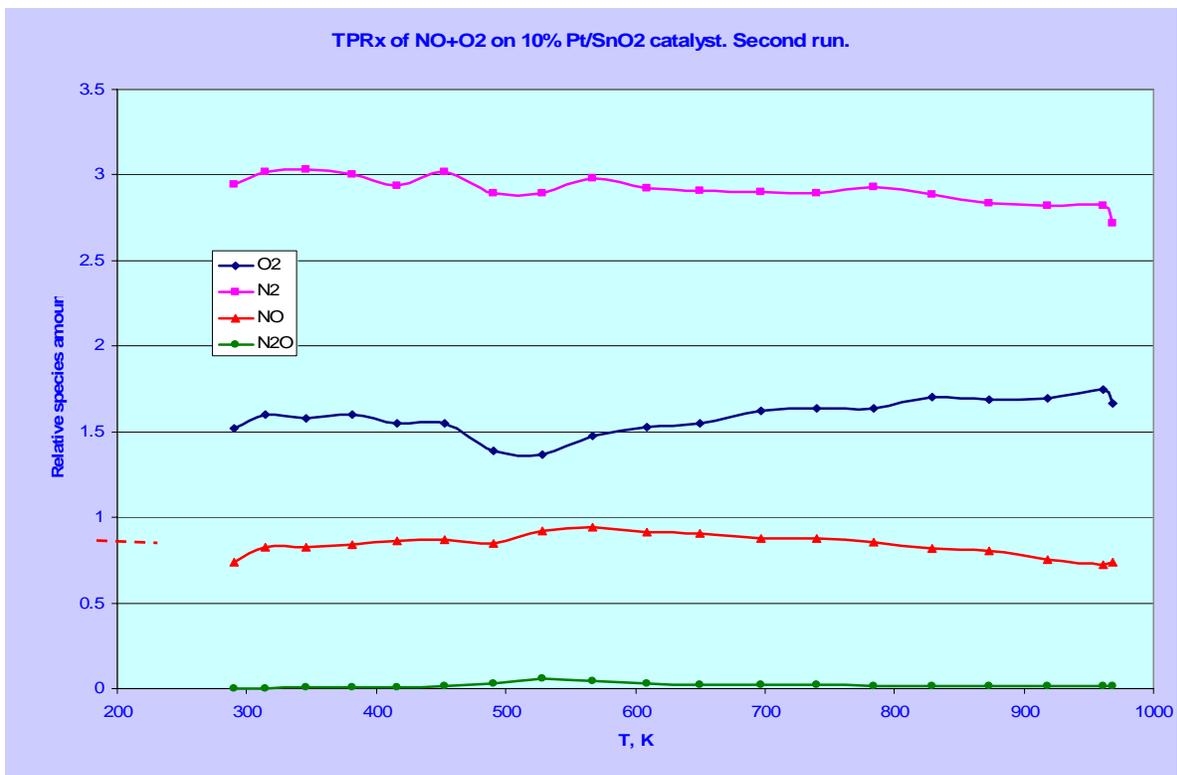


Figure 7

