

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

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Principal Author(s): **Dr. Ates Akyurtlu**
Dr. Jale F. Akyurtlu

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Submitting Organization	Hampton University Chemical Engineering Department Hampton, VA 23668
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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 N₂ 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/SnO₂ 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/SnO₂ catalyst in the PI's laboratory.

The main objective of the research that is being undertaken is the evaluation of the Pt/SnO₂ catalysts for the decomposition of NO in simulated power plant stack gases with particular attention to the resistance to deactivation by O₂, CO₂, and elevated temperatures. Temperature programmed desorption (TPD) and temperature programmed reaction (TPRx) studies on Pt/SnO₂ catalysts having different noble metal concentrations and pretreated under different conditions were done. It is also planned to perform NO decomposition tests in a laboratory-size packed-bed reactor to obtain long-term deactivation data.

In the previous reporting periods, runs were made with catalysts containing 15% Pt and 10% Pt on SnO₂ were done. Catalysts containing 10% Pt resulted in significantly lower activities than 15% Pt catalysts. Therefore, in the following tests 15% Pt/SnO₂ catalysts were used. Runs to elucidate the effects of temperature, oxygen, water vapor, pretreatment temperature, and space velocity on NO dissociation were completed. It was found that the presence of oxygen and water vapor did not affect the activation energy of the NO dissociation reaction indicating the presence of the same rate controlling step for all feed compositions. Activation energy was higher for higher gas velocities suggesting the presence of mass transfer limitations at lower velocities. Presence of oxygen in the feed inhibited the NO decomposition. Having water vapor in the feed did not significantly affect the catalyst activity for catalysts pretreated at 373 K, but significantly reduced catalyst activity for catalysts pretreated at 900 K.

In this reporting period, since no release time was available, no laboratory work was undertaken. Focus was on obtaining equilibrium data on various feed mixtures at temperatures up to 1000 K.

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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.

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 this 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. Temperature programmed desorption (TPD) and temperature programmed reaction (TPRx) studies were done on Pt/ SnO_2 catalysts having different noble metal concentrations and pretreated under different conditions. It is also planned to perform NO decomposition tests in a laboratory-size packed-bed reactor to obtain long-term deactivation data.

In the previous reporting periods 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. Catalysts containing 10% Pt were significantly less active than those containing 15% Pt. Therefore the remaining runs were done using 15% Pt catalysts.

Temperature programmed reaction of $\text{NO} + \text{O}_2 + \text{H}_2\text{O}$ on 15 % Pt/ SnO_2 catalyst was also 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.

Reactions of NO and an equimolar amount of O_2 with and without 5% H_2O were done at 1000 K. Since OH groups are thought to be very active in the O_2 -involving processes on the catalyst surface an additional set of runs were done with catalyst samples pre-treated at 900 K to drive off most of the OH groups.

The BET surface areas of the catalysts were also measured and found to be around $80 \text{ m}^2/\text{g}$.

The experiments to establish the effects of pretreatment, presence of oxygen and water vapor in the feed, and space velocity were completed. Runs were made at varying temperatures between 800 K and 1000 K to establish the variation of NO conversion with temperature. To identify the effect of space velocity, two different gas flow rates, $40 \text{ cm}^3/\text{min}$ and $60 \text{ cm}^3/\text{min}$, were used while keeping the amount of catalyst constant at 150 mg. The conclusions were that the presence of oxygen and water vapor did not affect the activation energy of the NO dissociation reaction indicating the presence of the same rate controlling step for all feed compositions. Activation energy was higher for higher gas velocities suggesting the presence of mass transfer limitations at lower velocities. Presence of oxygen in the feed inhibited the NO decomposition. Having water vapor in the feed did not significantly affect the catalyst activity for catalysts pretreated at 373 K, but significantly reduced catalyst activity for catalysts pretreated at 900 K.

In this reporting period, since no release time was available, no laboratory work was undertaken. Focus was on obtaining equilibrium data on various feed mixtures at temperatures up to 1000 K.

The results confirmed that the dissociation of NO is not limited by equilibrium, but determined by the rates of the reactions involved.

EXPERIMENTAL

No experimental work was performed in this period.

NO EQUILIBRIUM STUDIES

For this purpose CHEMKIN Release 4.0.2 was used. The mixtures used were pure NO, 50 % NO – 50 % O₂, 60 % O₂ – 40 % NO, 67 % O₂ – 33 % NO, 98 % He – 1 % Air – 1% NO, 97 % He – 1 % Air – 1 % O₂ – 1 % NO, and 99% He – 1 % NO. The mixtures with He simulate the experimental conditions. Product species considered were O, O₂, N₂, NO, NO₂, N₂O, N₂O₃,

N₂O₄, N. It would have been very informative if we could add tin oxides and tin nitrates to this list, but CHEMKIN library does not contain them. Our preliminary literature search did not provide the required data to include these solid components.

RESULTS AND DISCUSSION

The results of chemical equilibrium computations are presented in figures 1 through 7. Figures 1 through 4 indicate that the only effect of excess oxygen is the slight suppression of N₂O formation. At all temperatures investigated (300 K to 1000 K), equilibrium favors oxygen and nitrogen formation. The equilibrium amounts of NO₂, NO and N₂O increase with temperature, N₂O being favored at low temperatures and NO at high temperatures, the crossover taking place around 750 K. No other nitrogen species exist in the equilibrium mixture below 1000 K.

Figure 1. NO dissociation equilibrium at 1 atm. Pure NO.

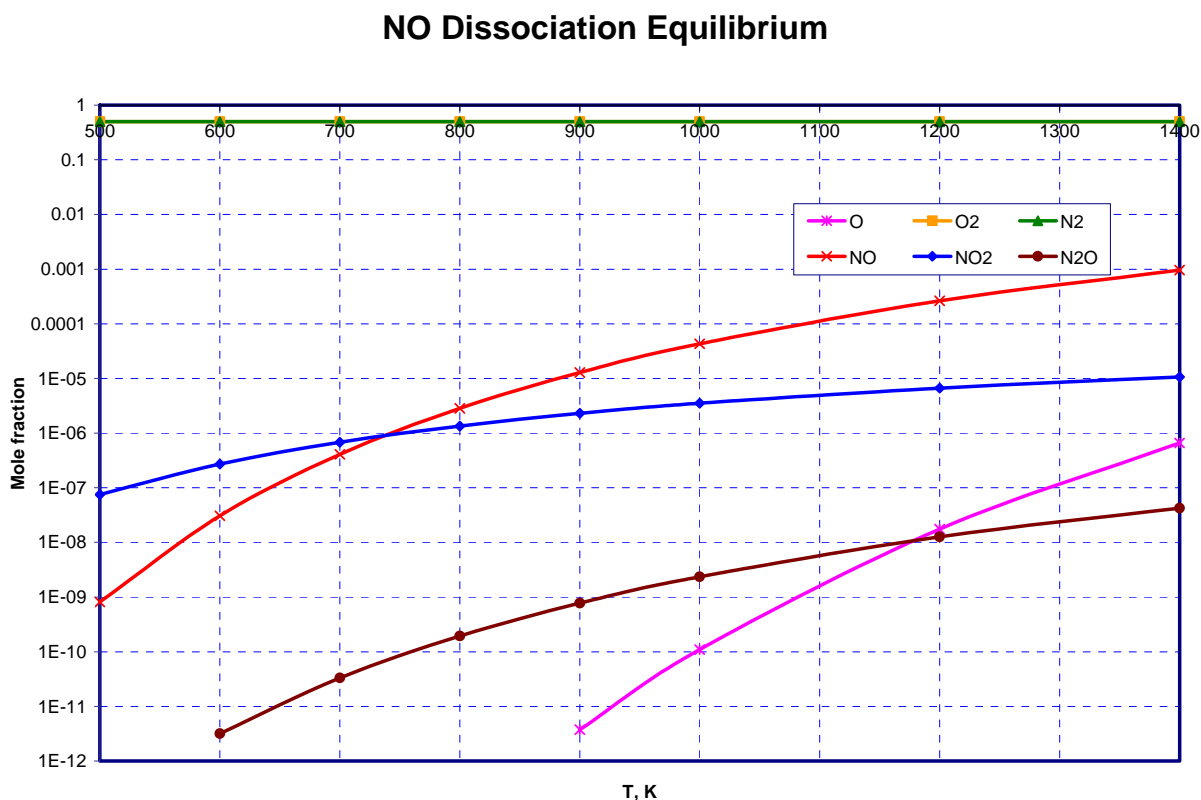


Figure 2. NO dissociation equilibrium for 50 % NO – 50 % O₂ at 1 atm.

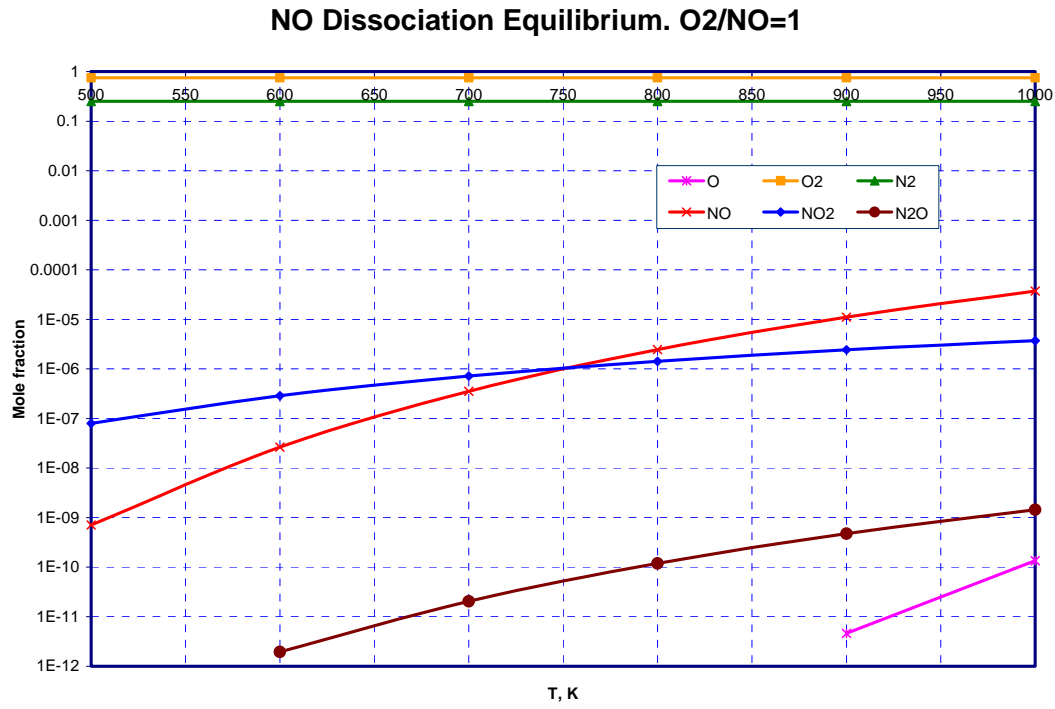


Figure 3. NO dissociation equilibrium at 1 atm. 60 % O₂ – 40 % NO

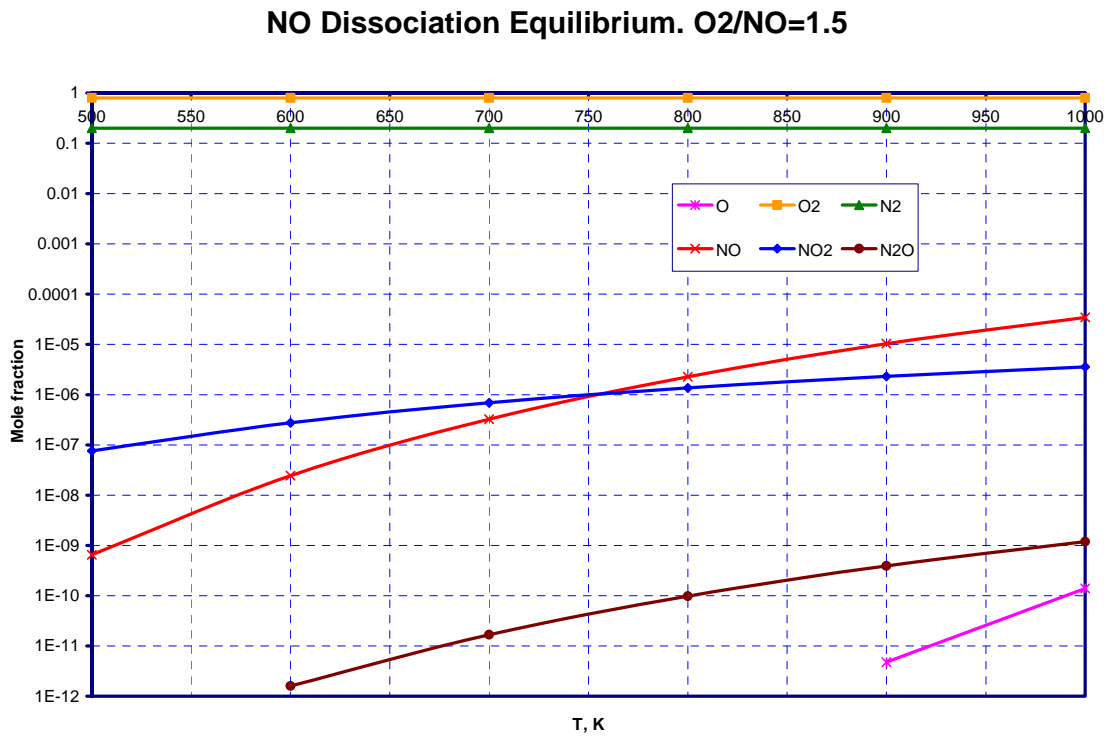


Figure 4. NO dissociation equilibrium at 1 atm. 67 % O₂ – 33 % NO.

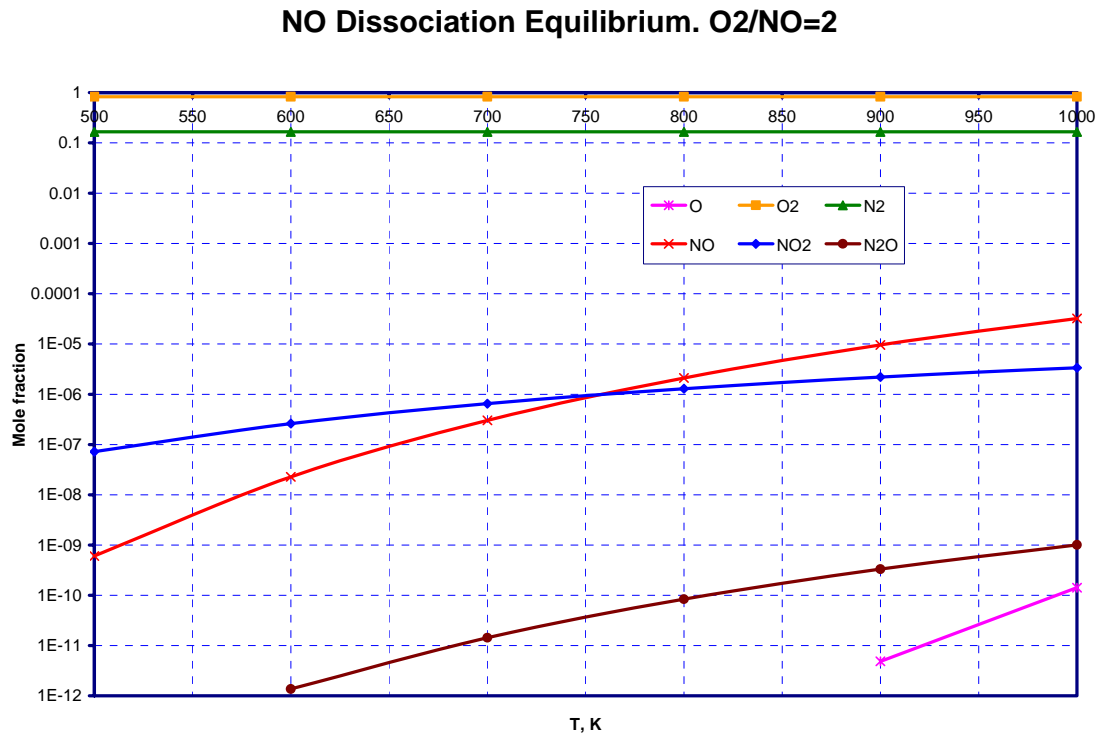


Figure 5. NO dissociation equilibrium at 1 atm. 99 % He – 1 % NO.

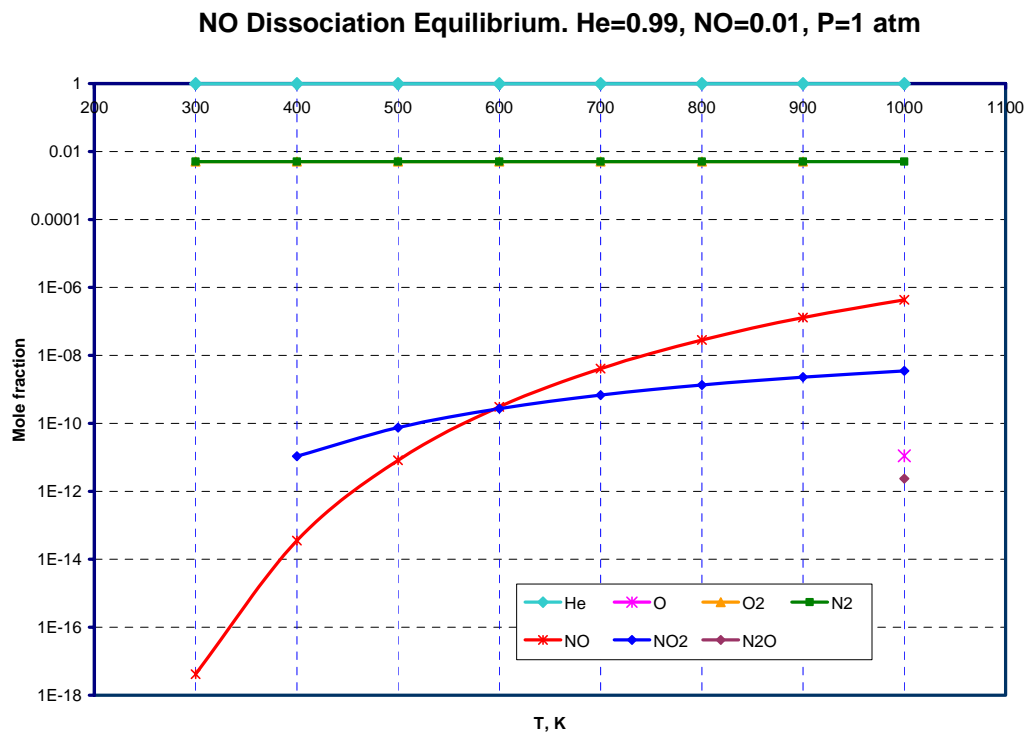


Figure 6. NO dissociation Equilibrium at 1 atm. 98 % He – 1 % NO – 1 % Air.

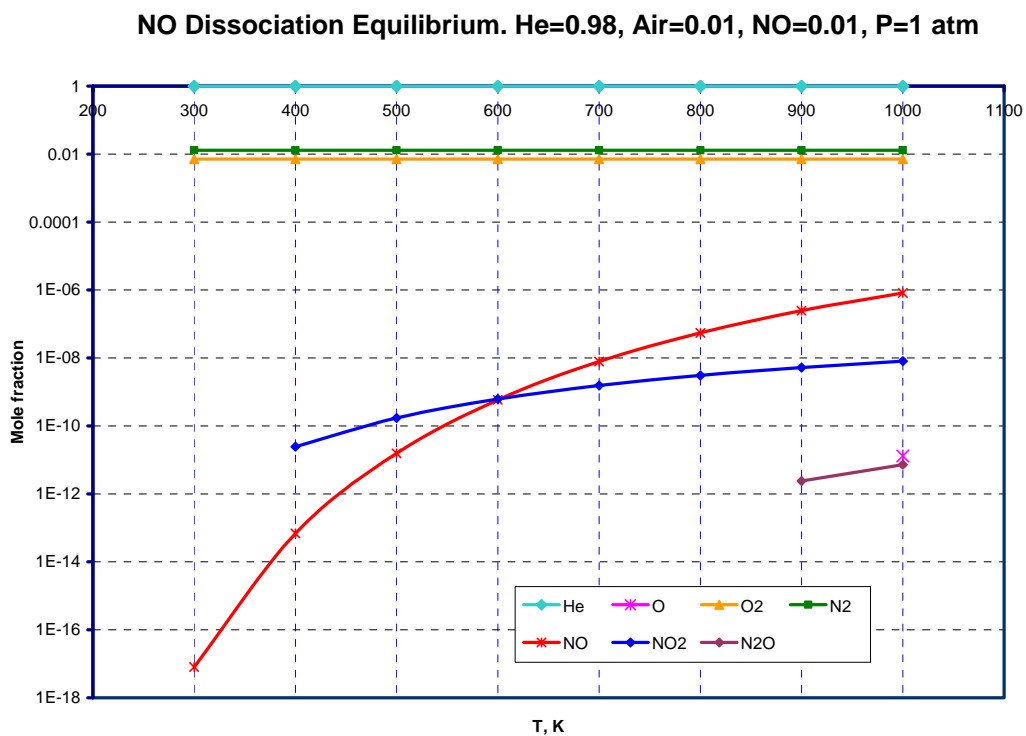
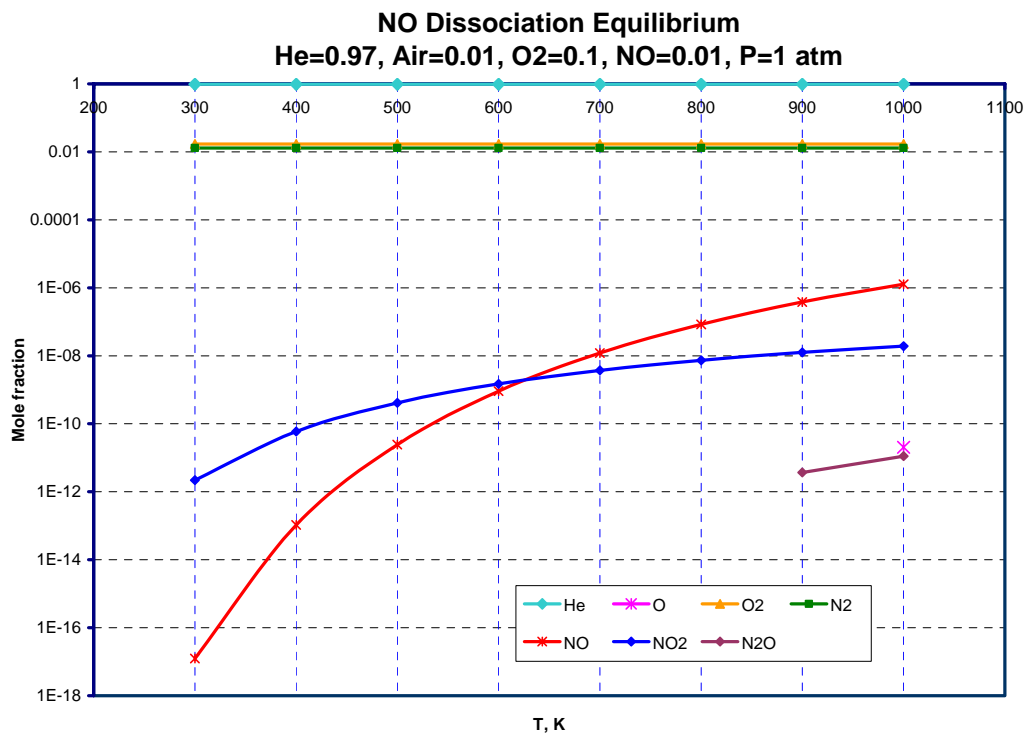


Figure 7. NO dissociation equilibrium at 1 atm. 97 % He – 1 % Air – 1 % O₂ – 1 % NO.



Figures 5 through 7 show that the addition of inert to NO suppresses the amount of NO₂ compared to NO and the crossover takes place at around 600 K. Addition of air to the mixture does not seem to have an effect on the equilibrium composition, but excess oxygen in addition to air favors the formation of NO₂ compared to NO and increases the crossover temperature.

CONCLUSIONS

Equilibrium computations up to 1000 K showed that the main equilibrium products of NO decomposition are oxygen and nitrogen. Small amounts of NO, NO₂, and N₂O also occur in the equilibrium mixture. The only effect of excess oxygen is the slight suppression of N₂O formation. Low temperatures favor NO₂ over NO with the crossover occurring at 750 K.

Addition of inert decreases the fraction of NO₂ compared to NO and decreases the crossover temperature to 600 K.

This confirms that the dissociation of NO is not limited by equilibrium, but determined by the rates of the reactions involved.

REFERENCES

APPENDIX

a. Additional Activities

Xu, Qing, Akyurtlu, Jale F., and Akyurtlu Ates: "Decomposition Of Nitric Oxide By Platinum Supported On Tin Oxide", Paper 280d presented at the 2006 AIChE Annual Meeting, San Francisco, CA, Nov. 14, 2006.

b. Future Plans

During the next reporting period, it is planned to:

1. Run experiments with feeds containing SO₂.
2. Make long duration runs to obtain data on catalyst stability.