

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

Report Type: Semi-Annual	Reporting Period Start Date: 03/14/2006 End Date: 09/14/2006
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Report Issue Date: October 14, 2006	DOE Award No.: DE-FG26-03NT41911
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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 research that is being undertaken 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 on Pt/ SnO_2 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 SnO_2 were done. Catalysts containing 10% Pt resulted in significantly lower activities than 15% Pt catalysts. Therefore, in the following tests 15% Pt/ SnO_2 catalysts were used.

In the current reporting period 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.

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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 $80 \text{ m}^2/\text{g}$.

In this reporting period 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.

EXPERIMENTAL

a. Temperature-Programmed Reaction Experiments

In this reporting period 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 cm³/min and 60 cm³/min, were used while keeping the amount of catalyst constant at 150 mg. The Temperature Programme Reaction (TPRx) runs were performed using the Micromeritics Pulse Chemisorb 2705 with TPD/TPR Option. A mass spectrometer-gas chromatograph system (SATURN 2000MS/3800GC) from Varian was used for the identification of the reaction products.

b. Bench Scale Laboratory Reactor Runs

The bench scale laboratory setup will be used for long term deactivation studies. In this reporting period the setup was repaired and made functional. To test the operation of the setup, runs were made to investigate the effects of NO and O₂ concentrations on NO conversion. NO measurements were done using the Thermoenvironmental 42H chemiluminescence NO_x analyzer.

RESULTS AND DISCUSSION

The results of all the runs are summarized in Table 1. If the only reaction occurring is the decomposition of NO according to the equation $\text{NO} \rightarrow \frac{1}{2} \text{N}_2 + \frac{1}{2} \text{O}_2$, there will be no change in the total number of moles and the ratio of the change in NO concentration to N₂ concentration will be 2 and the ratio of the change in N₂ concentration to the change in O₂ concentration will be 1. Therefore, to identify the presence of complex reaction processes, the changes in the concentrations are also reported in Table 1.

Table 1 indicates that $\Sigma\Delta$ is generally not close to zero but this discrepancy is likely to be the result of experimental errors and not due to the presence of different reaction mechanisms as suggested in an earlier report based on a few preliminary data. For most runs $\Delta\text{O}_2/\Delta\text{N}_2$ is between 0.87 and 1.61, which is sufficiently close to one as expected. The few exceptions are for relatively small changes and appear to be the result of the inaccuracies in the measurements. No further conclusions could be drawn at this point.

Two different pre-treatment methods were used. One at 373 K under flowing He for 2 hours mainly to drive off the air and other physically adsorbed gases, the other at 900 K under flowing He for 2 hours to drive off most of the OH groups attached to the tin oxide that contribute to the non-specific adsorption of emission effluent species that might mitigate the catalytic activity. Figure 1 indicates that pretreatment at 900 K results in a higher activity for dry runs, but this effect is reversed for feeds containing water vapor as seen in Table 2. This result was anticipated because the presence of water will replenish the surface hydroxyl groups.

Figure 1 also shows that the presence of equimolar amount of O₂ drastically inhibits the dissociation of NO. In the presence of oxygen, the NO conversion is reduced from 30 % to 13% at 1000 K. The Arrhenius plots shown in Figure 1 indicate that the presence of oxygen and the pretreatment temperature do not significantly affect the activation energy, indicating the presence of the same rate controlling reaction step in all cases.

Figure 2 shows the Arrhenius plots for the NO dissociation in the presence of equimolar amount of oxygen at two different space velocities. It can be seen that the apparent activation energy at the lower space velocity is lower, suggesting the presence of mass transfer limitations at lower space velocities.

Table 1. Summary of results for this period. Δ s indicate the difference between the feed and product concentrations in ppm. $\Sigma\Delta$ indicates the sum of concentration changes for NO, N₂, and O₂.

Reactants	Pre-treatment	Flow rate ccpm	Temp. K	Δ NO	Δ O ₂ /N ₂	$\Sigma\Delta$	Conv. NO
NO+O ₂	He 373 K 2 h	40	1000	-103	1.41	37	9.0
NO+O ₂	He 373 K 2 h	40	1000	-109	1.15	93	9.3
NO+O ₂ +H ₂ O	He 373 K 2 h	40	1000	-100	1.58	99	8.9
NO+O ₂ +H ₂ O	He 373 K 2 h	40	900	-114	1.05	636	9.0
NO+O ₂ +H ₂ O	He 373 K 2 h	40	900	-128	3.44	130	8.1
NO+O ₂ +H ₂ O	He 373 K 2 h	40	800	-103	0.907	-21	6.4
NO+O ₂	He 373 K 2 h	40	800	-94	1.56	242	5.6
NO+O ₂	He 900 K 2 h	40	1000	-148	1.19	373	12.7
NO+O ₂	He 900 K 2 h	40	950	-141	1.61	171	11.6
NO+O ₂	He 900 K 2 h	40	900	-93	1.06	388	8.0
NO+O ₂	He 900 K 2 h	40	850	-124	1.19	205	9.2
NO	He 900 K 2 h	40	1000	-401	1.30	255	29.7
NO	He 900 K 2 h	40	950	-417	0.968	79	26.3
NO	He 900 K 2 h	40	900	-284	1.24	288	21.5
NO	He 900 K 2 h	40	850	-239	1.34	147	16.3
NO+O ₂ +H ₂ O	He 900 K 2 h	40	900	-54	2.35	23	4.7
NO+O ₂	He 900 K 2 h	60	850	-43	1	-43	3.5
NO+O ₂	He 900 K 2 h	60	900	-78	1	-38	6.3
NO+O ₂	He 900 K 2 h	60	950	-79	2.91	-36	6.4
NO+O ₂	He 900 K 2 h	60	1000	-110	1.48	-56	9.0
NO+O ₂	He 373 K 2 h	60	900	-75	1.42	85	8.0
NO+O ₂	He 373 K 2 h	60	900	-64	1.09	74	7.3
NO+O ₂	He 373 K 2 h	60	900	-67	1.21	86	6.7
NO+O ₂ +H ₂ O	He 373 K 2 h	60	900	-65	0.870	79	6.4

Table 2 shows that the presence of water vapor in the feed causes a small decrease in NO conversion for samples pretreated at 373 K, but inhibits catalyst activity significantly for catalysts pretreated at 900 K.

Table 2. Effect of water in the feed. Since the 8 % conversion obtained for the reaction of NO +

O₂ on catalyst pretreated at 900 K was an outlier, the conversion obtained at 900 K through the regression of the data was also included in the table in brackets.

Reactants	Pre-treatment	Flow rate ccpm	Temp. K	Δ NO	Δ O ₂ /N ₂	$\Sigma\Delta$	Conv. NO
NO+O ₂	He 373 K 2 h	40	1000	-109	1.15	93	9.3
NO+O ₂ +H ₂ O	He 373 K 2 h	40	1000	-100	1.58	99	8.9
NO+O ₂	He 900 K 2 h	40	900	-93	1.06	388	8.0[9.7]
NO+O ₂ +H ₂ O	He 900 K 2 h	40	900	-54	2.35	23	4.7
NO+O ₂	He 373 K 2 h	60	900	-67	1.21	86	6.7
NO+O ₂ +H ₂ O	He 373 K 2 h	60	900	-65	0.870	79	6.4

Figure 1. Arrhenius Plot for NO dissociation

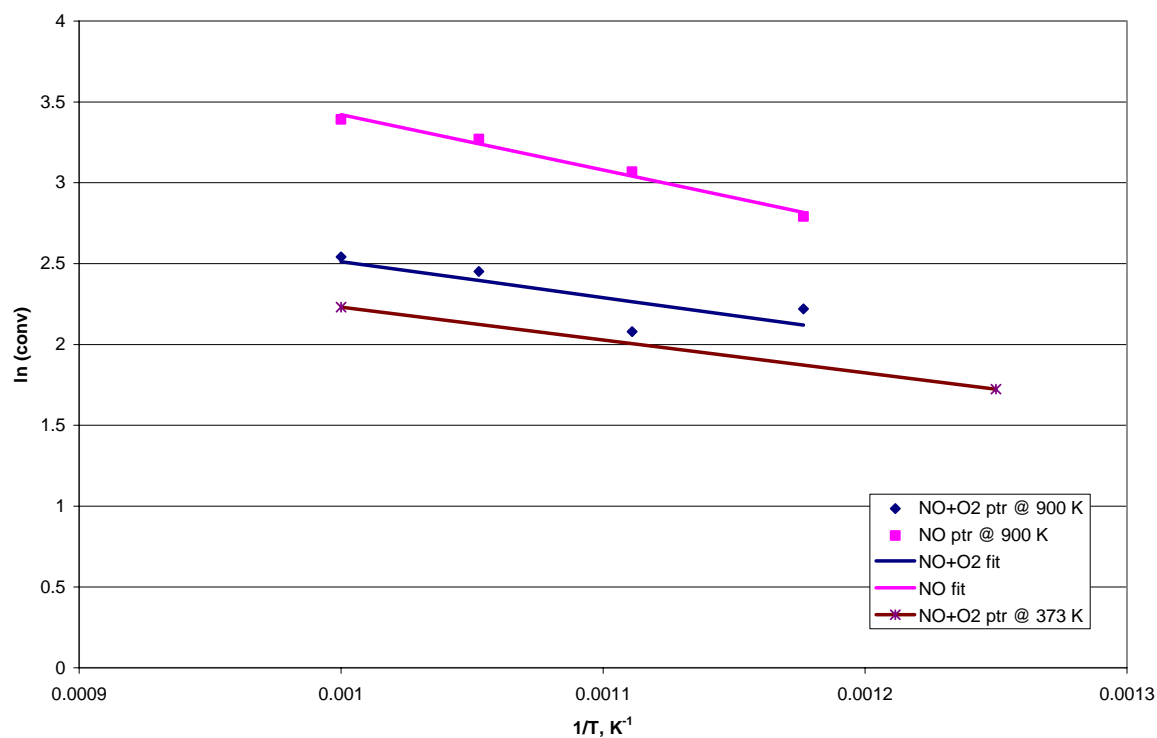
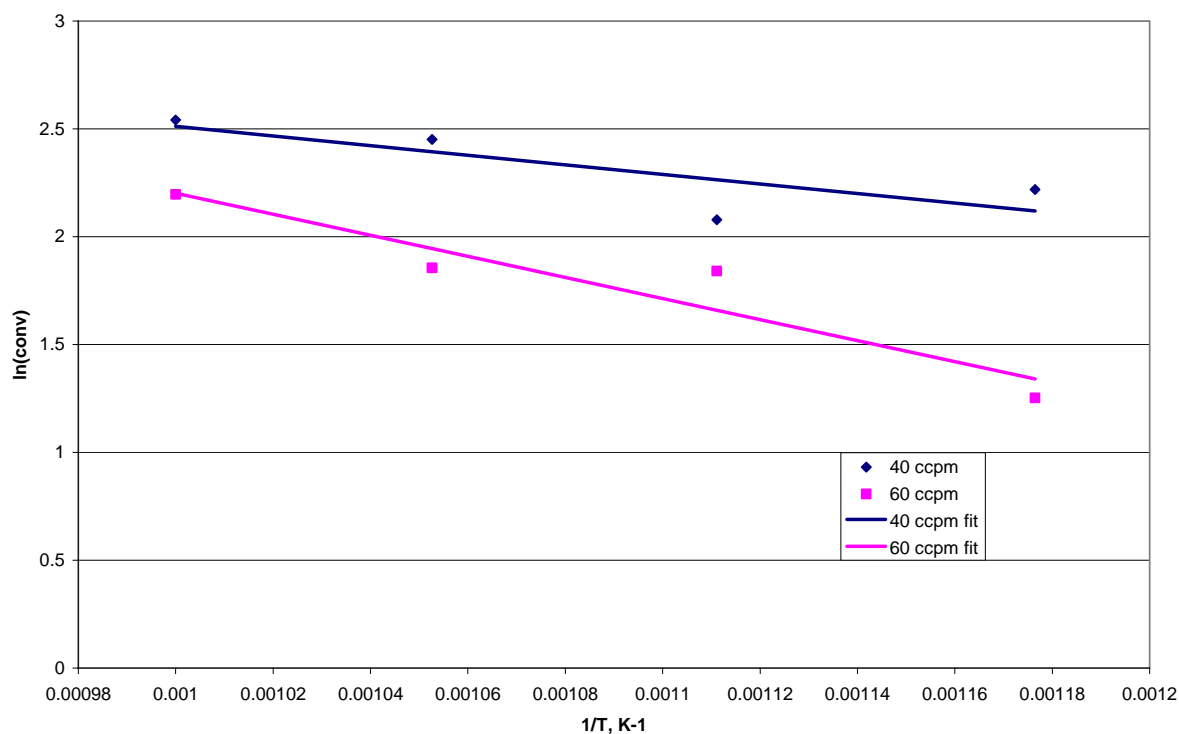


Figure 2. Effect of space velocity on NO conversion. 150 mg 15 % Pt/SnO₂ catalyst pretreated at 900 K



Bench scale reactor tests

The results of the runs using 2g 15% Pt/SnO₂ catalyst in the bench scale packed bed reactor system are summarized in Table 3. The results show that, within the concentration ranges used, the NO conversion did not depend significantly on the reactant concentrations.

Table 3. Effect of reactant concentrations on NO conversion on the 15% Pt/SnO₂ catalyst at 900 K.

NO conc. ppm	O ₂ Conc. ppm	Conversion
630	0	9.9
520	0	10
410	0	10
280	0	9.0
600	900	7.1
750	1500	7.2

CONCLUSIONS

- The presence of oxygen and water vapor does 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 severely inhibits NO decomposition.
- Having water vapor in the feed does not significantly affect the catalyst activity for catalysts pretreated at 373 K, but significantly reduces catalyst activity for catalysts pretreated at 900 K

REFERENCES

APPENDIX

a. Additional Activities

A paper, entitled “A Novel Catalyst for NO Decomposition” will be presented at the 2006 AIChE Annual Meeting in San Francisco.

b. Future Plans

During the next reporting period, it is planned to:

1. Obtain equilibrium compositions using CHEMKIN.
2. Run experiments with feeds containing SO₂.
3. Make long duration runs to obtain data on catalyst stability.