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 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. For the current reporting period it was decided to finish the runs with water vapor in the feed, check the effect of higher gas flow rate, and run experiments with catalyst treated at 900 K and 1000 K to drive off the OH groups. Unfortunately, shortly into the current period we had to change the gas feed preparation section. Then two flow controllers failed and we had to switch to rotameters and manual flow control as a stop gap measure. This affected the quality of the results and required repeated runs. Currently the results are satisfactory and the experiments are continuing. To take advantage of the down time the surface areas of the 15 % Pt and 10 % Pt catalysts were measured.

The results indicate that when the catalysts are treated at 900 K for 10 hours to remove most of the OH groups on the surface, the activity of the 15 % Pt catalyst increased.

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LIST OF GRAPHICAL MATERIAL

Figure 1. TPRx of NO + O₂ + H₂O on 15% Pt/SnO₂ Catalyst. NO = 634 ppm

Figure 2. Arrhenius plot for TPRx of NO + O₂ + H₂O on 15% Pt/SnO₂ Catalyst

Figure 3. Reaction of NO + O₂ on 15% Pt/SnO₂ Catalyst at 800 K.

Figure 4. Reaction of NO + O₂ + H₂O on 15% Pt/SnO₂ Catalyst at 800 K

Figure 5. Reaction of NO + O₂ on 15% Pt/SnO₂ Catalyst at 900 K.

Figure 6. Reaction of NO + O₂ + H₂O on 15% Pt/SnO₂ Catalyst at 900 K.

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 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 $\text{NO} + \text{O}_2 + \text{H}_2\text{O}$ 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

In this reporting period the focus was on establishing the effects of pretreatment, presence of oxygen and water vapor in the feed, and space velocity. Runs were made at 1000 K and 900 K to establish the variation of NO conversion with temperature. The Temperature Programmed 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. The calibration of the GC-MS was completed and the results for this period were reported as concentration of species in ppm.

At the beginning of this period we needed to construct a new reactant feed system. Since NO+O₂ mixtures were unstable, the gas mixture needed to be prepared from separate bottles. The new feed system was constructed using two existing gas flow controllers. Data at the 60 ccpm flow rate were taken using this system. At the end of these runs the gas flow controllers were accidentally contaminated and became inoperable. To minimize the delay a new feed system was prepared using surplus rotameters and manual valves. Obtaining reliable data with this system required practice and modification of procedures.

RESULTS AND DISCUSSION

The results of the latest 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 the changes in the concentrations are also reported in Table 1.

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	ΔNO	ΔN_2	ΔO_2	$\Sigma\Delta$	Conv. NO
NO+O ₂	He 373 K 2 h	40	1000	-103	58	82	37	9.0
NO+O ₂	He 373 K 2 h	40	1000	-109	94	108	93	9.3
NO+O ₂ +H ₂ O	He 373 K 2 h	40	1000	-100	77	122	99	8.9
NO+O ₂	He 900 K 2 h	40	1000	-148	249	272	373	12.7
NO	He 900 K 2 h	40	1000	-401	285	371	255	29.7
NO	He 900 K 2 h	40	900	-284	260	322	288	21.5
NO+O ₂	He 900 K 2 h	40	900	-93	233	248	388	8.0
NO+O ₂	He 373 K 2 h	60	900	-75	66	94	85	8.0
NO+O ₂	He 373 K 2 h	60	900	-64	66	72	74	7.3
NO+O ₂	He 373 K 2 h	60	900	-67	68	82	86	6.7
NO+O ₂ +H ₂ O	He 373 K 2 h	60	900	-65	77	67	79	6.4

Two different pre-treatment methods were used. One at 373 K under flowing He for 2 hours mainly to drive off the air and 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. Table 1 shows that this effect is in fact present and the NO conversion is higher on the catalyst that has been treated at high temperature (13 % compared to 9 % obtained on the catalyst treated at low temperature).

Table 1. also shows that the presence of equimolar amount of O₂ drastically reduces the conversion from 30 % to 13% for reaction at 1000 K.

Comparison of the results of 40 ccpm and 60 ccpm feed rates indicate that increase of gas velocity and the space velocity does not significantly affect the NO conversion.

The BET surface areas of the 15 % Pt and 10 % Pt catalysts were also measured. The results are reported in Table 2. below.

Table 2. Surface areas (m²/g) of fresh catalysts

15%Pt/SnO ₂	BET
1st run	75.1258 4
2nd run	82.9278 5
10%Pt/SnO ₂	
1st run	77.0777 5
2nd run	82.8865 1

CONCLUSIONS

- Presence of oxygen in the feed severely inhibits NO decomposition.
- Having water vapor in the feed does not significantly affect the catalyst activity.
- Increase in the feed gas flow rate does not seem to have a noticeable effect on NO conversion
- The BET surface areas of the catalysts are around 80 m²/g.

REFERENCES

APPENDIX

Additional Activities

A paper, entitled “A Novel Catalyst for NO Decomposition” was submitted to the 2006 Environmental Controls Conference. An abstract will also be submitted for presentation at the 2006 AIChE Annual Meeting.

a. Future Plans

During the next reporting period, it is planned to:

Figures

Figure 1

Figure 2.

Figure 3

Figure 4

Figure 5

Figure 6