DOE/PC/92521--T228

TECHNICAL REPORT
March 1 through May 31, 1995

Project Title: **NOVEL TECHNOLOGIES FOR SO_x/NO_x REMOVAL FROM FLUE GAS**

DOE Cooperative Agreement Number: DE-FC22-92PC92521 (Year 3)
ICCI Project Number: 94-1/2.1A-2P
Principal Investigator: Harold Kung, Northwestern University
Other Investigators: Mayfair Kung, Northwestern University
David Alt, Northwestern University
James J. Spivey, Research Triangle Institute
Ben W. Jang, Research Triangle Institute
Project Manager: Frank I. Honea, ICCI

ABSTRACT

The goal of this project is to develop a cost-effective low temperature deNO_x process. Work done in previous quarters suggested that the best approach for NO_x removal between 120°C and 150°C was the catalytic oxidation of NO to NO_2, followed by adsorption of NO_2 with an effective sorbent. Since preliminary investigation of this approach has demonstrated that effective sorbents can be found, the effort this quarter was concentrated on further evaluation of catalysts for NO oxidation. This included more detailed studies of Co/Al_2O_3 (best NO oxidation catalysts investigated previously) and searching for other active and stable catalysts. The initial increase and subsequent decline in NO oxidation activity of Co/Al_2O_3 in the presence of SO_2 in the feed was investigated by measuring the dependence of NO oxidation activity on the time of pretreatment in a stream of 0.1% SO_2, 4% O_2 and 10% H_2O. The results suggested that NO oxidation to NO_2 might be effected by SO_3 that was formed by the oxidation of SO_2, and the subsequent decline in activity might be due to the formation of stable inorganic sulfate ($SO_4^=$). Other catalysts evaluated included those containing Au as the essential active component, because these catalysts are active for low temperature CO oxidation, and Au does not form stable nitrates or sulfates. Au/Al_2O_3, despite being a good low temperature CO oxidation catalyst, was ineffective for NO oxidation. However, a 5 wt.% Au/Co_3O_4 catalyst (prepared by co-precipitation with Na_2CO_3 as the precipitating agent) showed high activity. At a W/F of 0.0071 g-min/cc, and a feed composition of 400 ppm NO and 4% O_2, a NO conversion of 45% to NO_2 at 200°C was obtained, but no activity was observed at 150°C. When H_2O and SO_2 were included in the feed, NO conversions between 48%-50% were observed between 120 and 150°C. The enhancement of NO oxidation activity by the presence of SO_2 is of particular interest in view of the high sulfur content of the Illinois coal. Furthermore, this activity was stable for the 15 h duration that the catalyst was tested.

EXECUTIVE SUMMARY

In view of the phasing in of more stringent environmental regulations, in order for Illinois coal to remain competitive, the development of more efficient SO_x/NO_x processes has become an urgent priority. The objective of this project is to develop a cost-effective $deNO_x$ process that can be integrated into the low temperature (RTI-Waterloo) $deSO_x/deNO_x$ process that is designed for retrofit applications. One approach is the use of environmentally benign reductants to remove NO_x by catalytic reduction. Another approach is to use a practical catalyst to oxidize NO to NO_2 and an effective sorbent for NO_2.

In the previous quarter, it was determined that the second approach is more likely to succeed. This is because the catalysts active for low temperature NO_x reduction by hydrocarbons deactivate due to the formation of coke on the catalysts. However, preliminary investigation of the second approach showed that effective sorbents for NO_2 can be found. However, for this approach to become practical, a low temperature NO oxidation catalyst of sufficient activity and stability need to be found. The preliminary data also showed that Co/Al_2O_3 is a promising catalyst. Thus, efforts were spent to evaluate this catalyst in greater detail.

At 150°C, Co/Al_2O_3 showed no oxidation activity for NO in the absence of SO_2. With the introduction of SO_2 into the feed, the activity increased to a maximum after 6 h and then declined slowly with longer time on stream. Investigation of the effect of SO_2 on this catalyst showed that the initial NO oxidation activity in a feed of 0.1% NO, 0.1% SO_2, 4% O_2 and 10% H_2O could be greatly enhanced by pretreating the catalyst in a stream of 0.1% SO_2, 4% O_2 and 10% H_2O. The highest initial activity of 65% NO conversion to NO_2 was obtained after 3 h of pretreatment. This high initial activity, however, was not sustained. After 5 h of time on stream, the NO oxidation activity dropped to a level slightly lower than that of a sample without the SO_2 pretreatment. A sample that was pretreated for 16 h in SO_2 deactivated more rapidly, showing only 10% conversion of NO at the end of 2.5 h on stream. These results suggested possible oxidation of NO by SO_3, and that deactivation might be a result of the formation of stable metal sulfate, probably $CoSO_4$ rather than $Al_2(SO_4)_3$. To test the latter hypothesis, a Co/TiO_2 catalyst was tested, as $Ti(SO_4)_2$ is less stable than $Al_2(SO_4)_3$. Co/TiO_2 was an inferior NO oxidation catalyst in a stream of 0.1% NO, 0.1% SO_2, 4% O_2 and 10% H_2O.

Au containing catalysts were tested for NO oxidation as Au is very inert and does not form stable nitrate or sulfate. Au/Al_2O_3, despite being active for CO oxidation at room temperature, was not active for NO oxidation at 150°C. In the absence of H_2O and SO_2, a 5 wt. % Au/Co_3O_4 catalyst showed 92% conversion of NO to NO_2 at 250°C in a feed of 400 ppm NO and 4% O_2, and a W/F of 0.007 g-min/cc (SV~4000 h^{-1}). The conversion fell to 45% when the temperature was lowered to 200°C, and the catalyst was inactive for NO oxidation at 150°C. However, when 10% H_2O and 0.1% SO_2 were included in the feed, a 48% NO conversion to NO_2 was observed, and this improved slightly to 50% when the temperature was lowered to 120°C. Furthermore, the activity of the catalyst was stable for the duration of the test (15 h) conducted in the 120-150°C temperature regime.

There is evidence that the activity of the Au/Co_3O_4 catalyst can be improved further. In the preliminary experiments, another preparation of a small quantity of 5 wt.% Au/Co_3O_4 (sample II) showed a 35% conversion of NO at 150°C in the absence of H_2O and SO_2, compared with 0% conversion for the sample mentioned above (sample I). Sample II could also oxidize C_3H_6 readily at 175°C, whereas sample I could only oxidize C_3H_6 at 250°C. These data suggested that sample II has higher oxidizing power than sample I. These two samples differed in the details of their preparation procedures: a less vigorous washing procedure and a reduction in the amount of the precipitating agent (Na_2CO_3) relative to Au and Co were used in preparing sample I than sample II. New samples of 5 and 10 wt.% Au/Co_3O_4 were synthesized recently. Preliminary test of the 10 wt.% sample in the absence of H_2O and SO_2 indicated that this catalyst behaved like sample II.

In the coming quarter, a detailed evaluation of the NO oxidation activity of the new Au/Co_3O_4 samples will be carried out. The emphasis of the characterization will be on the effect of SO_2 concentration and the long term stability of the catalytic activity. The effect of preparation variables such as concentration of the precipitating agent (Na_2CO_3), precipitation temperature, and calcination conditions such as heating rate will be explored to improve the catalytic performance. The effect of Au loading will also be investigated.

OBJECTIVES

The goal of this research is to develop a cost-effective low temperature deNO_x process that could be integrated readily into the novel RTI-Waterloo SO_x/NO_x process. It involves either the development of a cost-effective low temperature catalyst that promotes the selective reduction of NO by hydrocarbons or alcohols, or the development of an efficient NO_x sorbent. In the previous quarters, it was found that the problem of catalyst coking encountered in low temperature catalytic NO reduction can only be reduced but not totally eliminated. Thus, the second approach of low temperature NO_x sorption was explored. It was found that the efficiency of NO_2 sorption with inorganic sorbents was high. In screening for an active NO oxidation catalyst, it was found that Co/Al_2O_3 showed a 25% NO conversion to NO_2 after 20 h of reaction in a feed of 0.1% NO, 4% O_2, 0.2% SO_2 and 10% H_2O. Thus, the objectives for this quarter are to: 1) further study Co/Al_2O_3 in order to improve its catalytic performance, and 2) investigate Au based catalysts to determine their potential as practical low temperature NO oxidation catalysts.

INTRODUCTION AND BACKGROUND

Recent stringent environmental regulations makes the development of a more effective SO_x/NO_x process especially urgent for Illinois as its large reserve of coal has a high sulfur content. This project is to develop a low temperature deNO_x process which can be integrated easily into the novel RTI-Waterloo process. In the course of the investigation, it was found that the process could be integrated also into the existing commercial STEAG process with only minor modifications.

The RTI-Waterloo process involves SO_2 removal by carbon before NO_x removal. The SO_2-free gas is then slightly reheated with incoming flue gas, blended with ammonia and passed over another bed of different modified carbon to remove the NO_x. The process of SO_2 removal, however, lowers the temperature of the flue gas to around 150°C, which is substantially lower than the operational temperature (350-400°C) of practical SCR (selective catalytic reduction) catalysts. Although a modified carbon catalyst used in the second bed works at low temperature, its activity is low. Furthermore, the reductant used in the process is NH_3, which itself is environmentally harmful. Thus, the goal of this research could be met if an efficient NO_x sorbent could be developed. An economic analysis of this sorption process (1) showed it to be competitive with the reduction process.

The commercial STEAG flue gas cleanup process uses char to remove SO_x, fine particulates, and trace elements such as mercury from the flue gas. If NO_x is to be removed, the flue gas is reheated after the char bed, and passed over a separate SCR catalyst bed. Thus, an efficient NO_x sorption process can be integrated also into the STEAG process.

In the previous quarters, it was found that coking of the catalysts was the major obstacle towards achieving low temperature reduction of NO over both the inorganic Cu-ZrO_2 catalyst and the carbon based catalysts. The considerable effort expended in solving this problem managed to only alleviate but not eliminate it. In the meantime, the screening for NO oxidation catalyst yielded a Co/Al_2O_3 catalyst that was found to have a relatively stable activity of 25% NO conversion after 20 hours on stream, in a flow of 1000 ppm NO, 10% H_2O, 4% O_2 and 0.2% SO_2. However, this activity was only half of the maximum activity recorded around 6 hours after the start of the reaction. It appeared that with improvement this might be a viable catalyst. The screening for NO_x sorbent also showed that inorganic sorbents are very effective for NO_2 adsorption. Thus, adsorption of NO_2 appeared to be a more promising approach than NO_x reduction for low temperature removal of NO_x. However, for it to be practical, a more active and stable NO oxidation catlayst than Co/Al_2O_3 needs to be found. Thus, the primary objective this quarter was to develop a better NO oxidation catalyst.

EXPERIMENTAL PROCEDURES

Catalyst Preparation

CoO/Al_2O_3: These catalysts were prepared by impregnation of Al_2O_3 with cobalt nitrate solution. Cobalt nitrates and γ-Al_2O_3 pellets were purchased from Johnson Matthey.

Cu/active carbon: Active carbon was refluxed in 1M HCl solution overnight to remove alkali metals. 30 cc of 1M HCl solution was used per gram of carbon. The active carbon was then washed with distilled water and dried at 110°C followed by impregnation with 5% Cu and vacuum drying.

Au/Co_3O_4: Au/Co_3O_4 catalyst was prepared by co-precipitation of hydrogen tetrachloroaurate (III) hydrate (Aldrich Chemical) with $Co(NO_3)_2$ (Aldrich Chemical), as in the methods of Haruta et al. (2). 1 M Na_2CO_3 solution was the precipitating agent. The precipitate was suction filtered and washed many times. Then it was dried in a 100°C drying oven, and then calcined for 5 h at 450°C.

Au/Al_2O_3: Au/Al_2O_3 was prepared by the deposition-precipitation method as in Haruta et al. (3). 2.5 g of Al_2O_3 was put into a solution of 5 mM $AuCl_4$ and the pH was adjusted to 7. The solution was stirred for 30 minutes, and then Mg citrate was added to prevent the coagulation of Au. After the addition of Mg citrate, the solution was stirred for another 1.5 h before it was suction filtered. The resulting paste was washed, suction filtered many times, and then the catalyst was dried in an oven at 100°C and then calcined at 350°C for 0.5 h.

Catalytic Tests

Details of the procedure for catalytic tests for the selective reduction of NO by propene have been described in previous quarterly reports [1]. Briefly, at Northwestern, the catalysts were tested in a fused silica, U-tube reactor. The flow rate and composition of the feed gases were controlled by mass flow meters. The typical composition of the feed was 1000 ppm NO, 1000 ppm C_3H_6, 2% H_2O, 4% O_2, and the balance He.

NO oxidation experiments were performed with the catalyst in a similar reaction system. The effluent from the reactor was analyzed with a Mattson Galaxy series 5000 FTIR.

The RTI NO_x reaction system has been described in the earlier report (1). 400 ppm NO, 0.1% SO_2, 4% O_2, and 10% H_2O with a total flow of 400 cc/min were used for NO oxidation reaction over 3 g Au/Co_3O_4 catalyst or 7 g Co/Al_2O_3 catalyst. NO_x analyzer with NO_x mode and NO mode was used to determine both the inlet and outlet concentrations of NO_2 and NO. The conversion was calculated as:

$$\% \text{ NO oxidation to } NO_2 = (NO_{x,out} - NO_{out})/NO_{x,out} \times 100$$

RESULTS AND DISCUSSION

NO Oxidation to NO_2 over Co/Al_2O_3

A 10 wt.% CoO/Al_2O_3 was active for NO oxidation as reported earlier (1). Its activity first increased with time on stream to a maximum of 60% after 6 h, and then slowly decreased with longer time on stream to a relatively stable 25%. In order to understand this activation and deactivation phenomenon, the catalyst was pretreated for different lengths of time in a gas flow of 0.1% SO_2, 4% O_2 , and 10 % H_2O, with helium as the diluent. Afterwards, the NO oxidation activity was tested by adding 0.1% NO into the feed stream. The pretreatment and NO oxidation were both carried out at 150°C.

The results, summarized in Figure 1, showed that the initial NO oxidation activity was a function of the length of pretreatment. The initial NO activities were 0%, 42%, 65% and 42% for zero, 1 h, 3 h and 16 h of pretreatment, respectively. This indicated that the adsorption of oxidized sulfur species may be beneficial to the NO oxidation activity, and that there is an optimum concentration of such adsorbed SO_x species. The NO oxidation activity increased with time on stream for the first 3 h of reaction for the sample with no SO_2 pretreatment, while it remained invariant or decreased for all the samples pretreated with SO_2. This suggested that a possible reaction pathway is NO oxidation by SO_3 to form NO_2 and SO_2. Although the equilibrium constant for this reaction is 8×10^{-5} at 150°C, the rapid and favorable subsequent reoxidation of SO_2 to SO_3 by oxygen in the feed would render the pathway feasible. However, at the same time, the SO_3 formed could also transform the metal oxide to a more stable but catalytically inactive metal sulfate ($SO_4^{=}$), resulting in the loss in activity with longer pretreatment with SO_2. This proposed mechanism needs to be substantiated with measurements of both SO_2 and SO_3 concentrations in the reaction mixture.

The metal sulfate formed could be $Al_2(SO_4)_3$ or $CoSO_4$. It was reported that Al_2O_3 may form sulfate in the presence of SO_2 under flue gas conditions during NO reduction using NH_3 as reductant (4). TiO_2 was reported to be a better support material than Al_2O_3 because it resists SO_2 deactivation. NO oxidation reaction was tested on Co supported on TiO_2, but was found to be poor relative to Co supported on Al_2O_3.

NO Oxidation to NO_2 over Au catalysts (Au/Al_2O_3 and Au/Co_3O_4)

Catalysts containing Au well dispersed in metal oxides are known to be very active for CO oxidation (2). Since there may be similarities between the mechanism of low temperature CO oxidation and NO oxidation, Au dispersed in metal oxides was studied. Au/Al_2O_3 catalysts were tested for NO oxidation and found to be ineffective, even though the same catalysts were active for CO oxidation at room temperature.

A 5 wt.% Au/Co_3O_4 was tested and showed high activity for NO oxidation. Fig. 2 shows the activity evaluated with a space velocity of about 4000 h^{-1} and a feed of 400 ppm of NO and 4% O_2 in He in the following temperature sequence: 250°C, 200°C, 150°C and then 200°C. A total flow of 400 cc/min and 3.0 g of catalysts were used. 92% NO conversion was obtained after 7.5 hours at 250°C. The activity decreased when the temperature was decreased to 200°C, and it stabilized at 45% conversion after 12 hours on stream. However, the activity dropped to zero within 40 minutes when the temperature was further lowered to 150°C. The lost in activity at low temperature was not the result of poisoning, and the activity could be restored by raising the temperature to 200°C.

The effect of SO_2 and H_2O on NO oxidation was tested with this 5 wt.% Au/Co_3O_4 which had been pretreated with O_2 in helium at 430°C for 1 hour. The results, presented in Figure 3, showed that in the presence of SO_2 and H_2O, a NO conversion of ~35% was obtained after 4 hours at 200°C, which was lowered than the 45% conversion obtained in the absence of SO_2 and H_2O. On the other hand, in the presence of SO_2 and H_2O, 48% NO conversion to NO_2 was observed after 5.5 hours on stream at 150°C. This contrasted dramatically with 0 % conversion without SO_2 and H_2O at this temperature. Further reducing the temperature to 120°C increased the activity slightly to 50%. The activity was stable for the duration of the test (11 hours). These results strongly suggested that Au/Co_3O_4 is a promising catalyst for NO oxidation at low temperatures (120-150°C) under flue gas conditions. When SO_2 was removed from the feed, the oxidation activity decreased from 50 % to 6% within 50 minutes. Thus, the low temperature NO oxidation activity of this Au/Co_3O_4 catalyst, similar to that of the Co/Al_2O_3, was enhanced by the presence of SO_2. However, this catalyst is superior to Co/Al_2O_3 because of its higher activity and much better stability.

The Au/Co_3O_4 catalyst may be even more promising than it appeared from the results reported above. Before the preparation of the 5% Au/Co_3O_4 (sampe I) used in the above study, a small batch 0.5 g was prepared (sample II). Instead of showing no activity for NO oxidation at 150°C in the absence of H_2O and SO_2, sample II showed 35% conversion of NO to NO_2. This sample II could oxidize C_3H_6 readily also at 175°C, whereas sample I could only oxidize C_3H_6 at 250°C. These facts suggested that sample II is a more active oxidation catalyst reaction than sample I. These two samples differed in their preparation procedures. Sample I was prepared using a less vigorous washing procedure and a lower amount of the precipitating agent (Na_2CO_3) relative to Au and Co. New samples of 5 and 10 wt.% Au/Co_3O_4 have been synthesized recently using more Na_2CO_3 and more vigorous washing. Preliminary tests of the 10 wt.% sample in the absence of H_2O and SO_2 indicated that its catalytic activity was close to that of sample II.

NO Reduction over 5%Cu/Active Carbon Treated with HCl

It was suspected that the decline of activity for NO reduction with acetone over Cu supported on activated carbon catalysts was due to K and/or Na impurities on the carbon surface. To test this, the active carbon material was refluxed in 1M HCl solution overnight to remove alkali impurities before loading the Cu. The resulting catalyst was tested for NO reduction with acetone at 150°C. However, no improvement was obtained. The HCl-treated catalysts showed similar deactivation as untreated catalysts.

NO Reduction over Au Catalysts

10 wt. %Au/Co_3O_4 was tested for NO reduction with C_3H_6. Although the catalyst was active for oxidation of C_3H_6 at low temperatures, it was not very active for NO reduction. At 200 °C, 90% of C_3H_6 was oxidized to CO_2. The NO conversion was 34%. Of the NO converted, 24% formed N_2, and 76% formed N_2O.

CONCLUSIONS AND RECOMMENDATIONS

The results for NO reduction were not promising. The catalysts tested either were insufficiently active or deactivated rapidly. On the other hand, NO removal by sorption of NO_x appeared to be very promising.

The $SO_2/O_2/H_2O$ pretreatment had a strong influence on the initial NO oxidation activity of CoO/Al_2O_3. The activity of this catalyst first increased with the duration of the pretreatment time and then decreased for long pretreatment. The presence of SO_2 was also necessary for Au/Co_3O_4 to have high NO oxidation activity at 120 to 150°C. It is speculated that NO oxidation may involve SO_3 intermediate (formed by SO_2 oxidation by O_2). The fact that SO_2 is beneficial to NO oxidation over this catalyst has positive implications on the use of Illinois coal, which has a high sulfur content. The dependence of the reaction on SO_2 concentration in the feed will be investigated further in the next quarter.

The relatively high NO conversion to NO_2 (50% at 120°C) and, more importantly, the high stability of the catalyst suggested that Au/Co_3O_4, with improvement, might be a viable practical low temperature NO oxidation catalyst. The fact that the activity depends on the details of the preparation procedure suggests the possiblity for optimization. Two newly synthesized Au/Co_3O_4 of different Au loadings will be tested thoroughly next quarter. Their long term stability will also be tested. In the mean time, further optimization of the catalyst will be attempted with respect to the preparation variables such as precipitation temperature and calcination temperature.

DISCLAIMER STATEMENT

REFERENCES

1. Quarterly report to ICCI, "Novel Technologies for SO_x/NO_x Removal from Flue Gas", Sept.1-Nov. 30, 1994.

2. M. Haruta, N. Yamada, T. Kobayashi and S. Iijima, J. Catal., **115**, 301 (1989).

3. S. Tsubota, M. Haruta, T. Kobayashi, A. Ueda, and Y. Nakahara in Preparation of

Catalysts V (G. Poncelet, P.A. Jacobs, P. Grange and B. Delmon Eds.) Elsevier, Amsterdam, p. 695 (1991).

4. H. Bosch and F. Janssen, Catal. Today, **2**, 369 (1988).

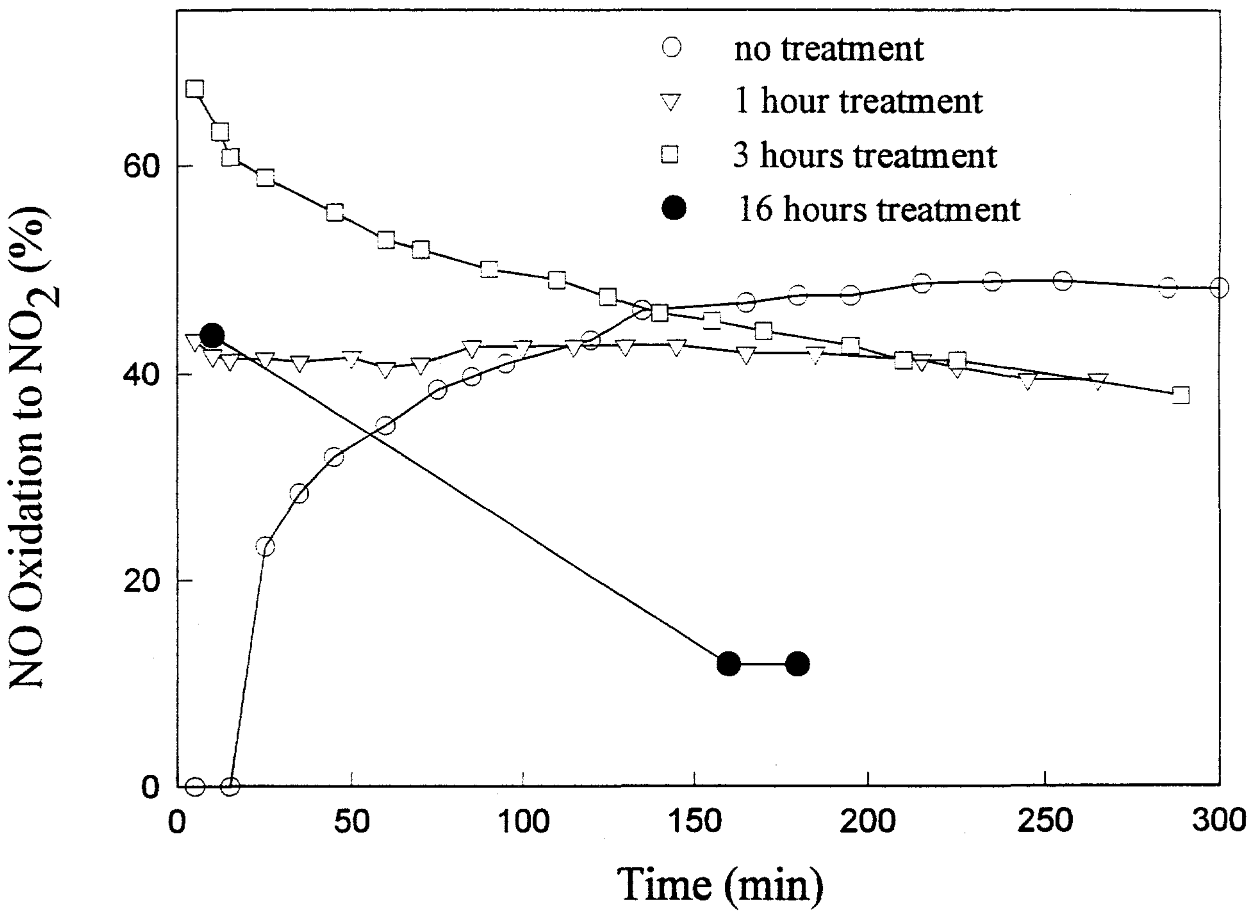


Figure 1. The activity of NO oxidation to NO_2 as function of time over $10\%CoO/Al_2O_3$. Reaction conditions: 0.1% NO, 4% O_2 0.1% SO_2 and $10\%H_2O$ at 150°C, 400 cc/min, 7.0 g catalysts.

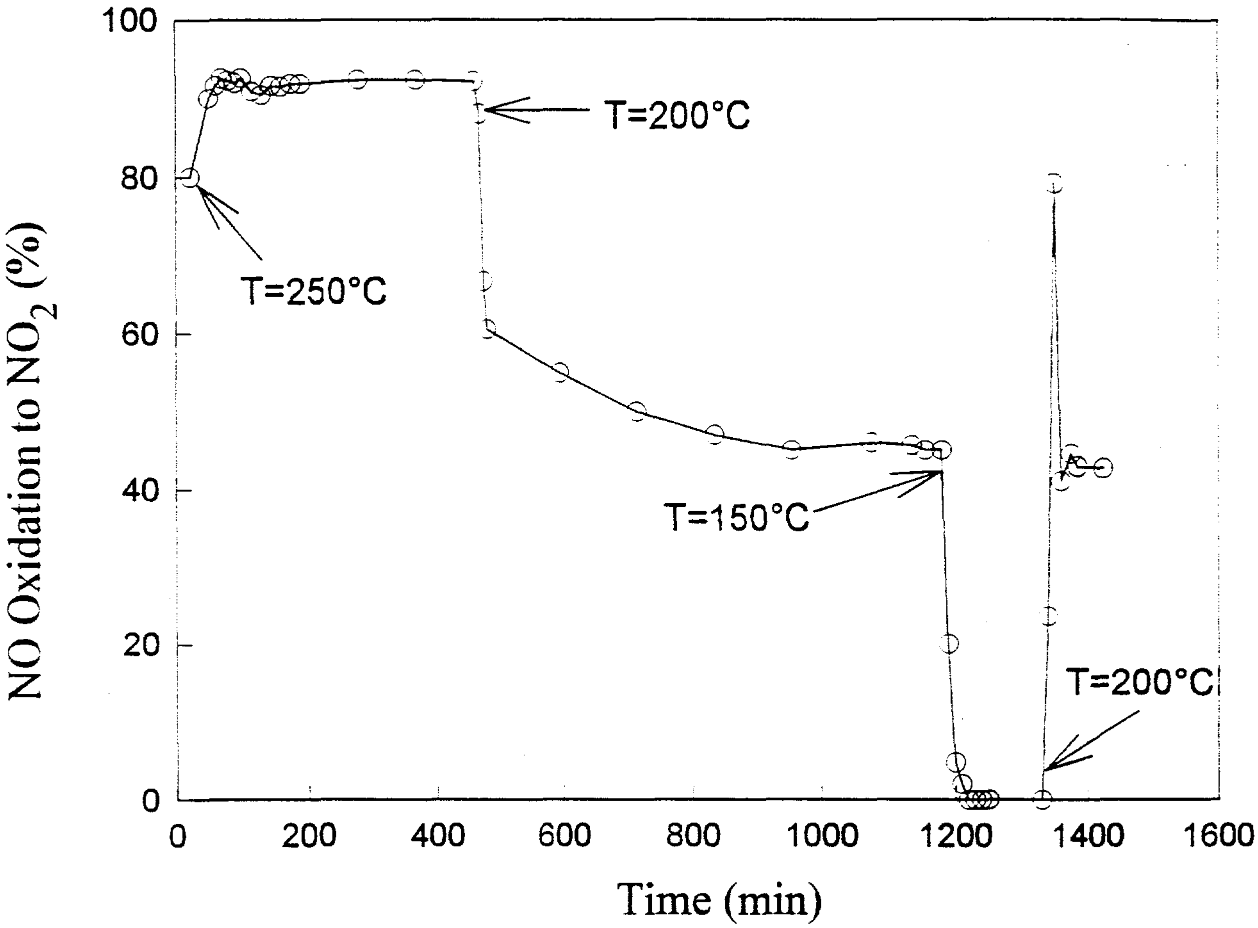


Figure 2. NO oxidation to NO_2 over 5% Au/Co_3O_4 as a functin of time. Reaction conditions: 400 ppm NO, 4% O_2 and 10% H_2O, 400 cc/min, 3.0 g catalysts. Temperature was varied from 250°C to 200°C, then to 150°C and back to 200°C.

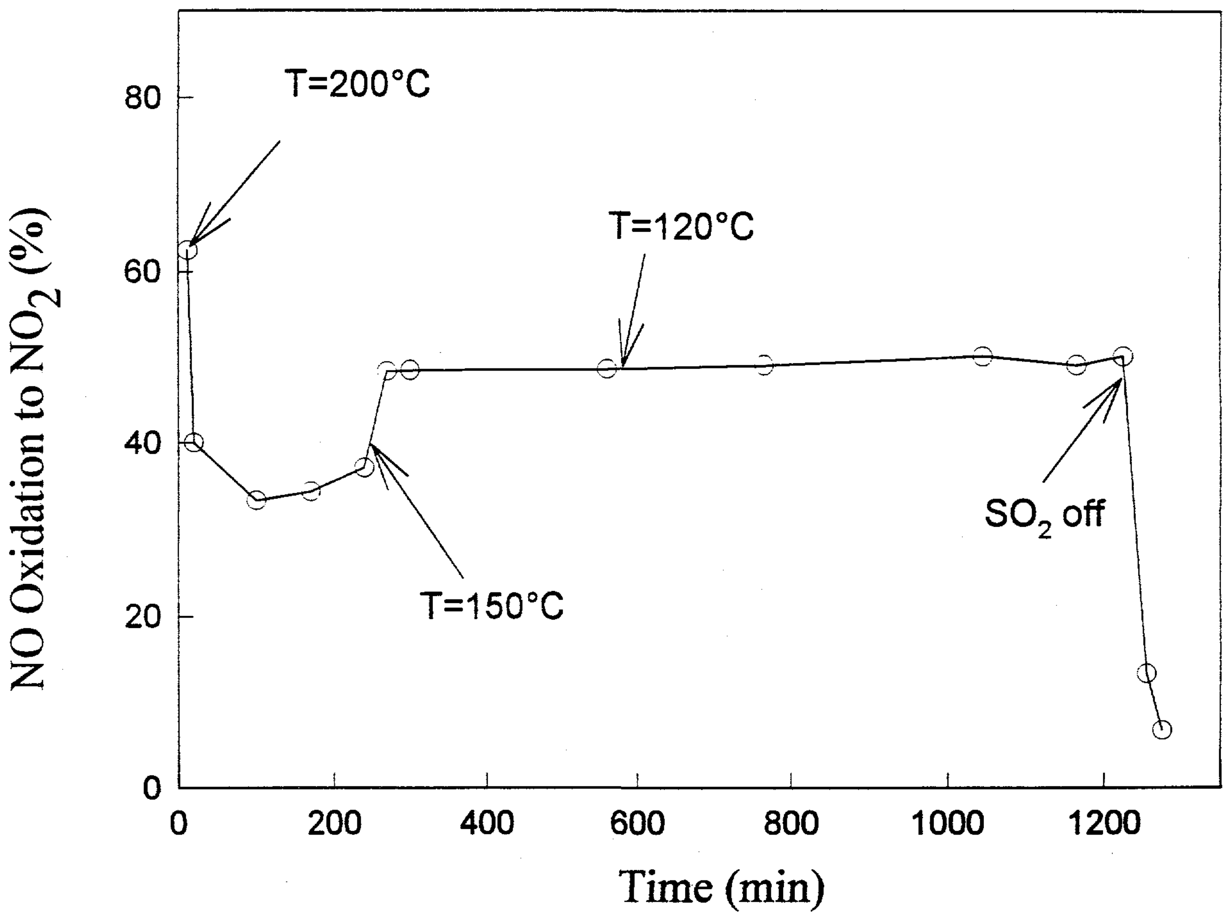


Figure 3. The activity of NO oxidation to NO_2 as function of time over 5%Au/Co_3O_4 in the presence of SO_2 and H_2O. Reaction conditions: 400ppm NO, 4% O2, 0.1% SO2, and 10% H2O, 400 cc/min, 3.0 g catalysts.

PROJECT MANAGEMENT REPORT
March 1 through May 31, 1995

Project Title: **NOVEL TECHNOLOGIES FOR SO_x/NO_x REMOVAL FROM FLUE GAS**

DOE Cooperative Agreement Number:	DE-FC22-92PC92521 (year 3)
ICCI Project Number:	94-1/2.1A-2P
Principal Investigator:	Harold Kung, Northwestern University
Other Investigators:	Mayfair Kung, Northwestern University
	David Alt, Northwestern University
	James J. Spivey, Research Triangle Institute
	Ben W. Jang, Research Triangle Institute
Project Manager:	Frank I. Honea, ICCI

COMMENTS

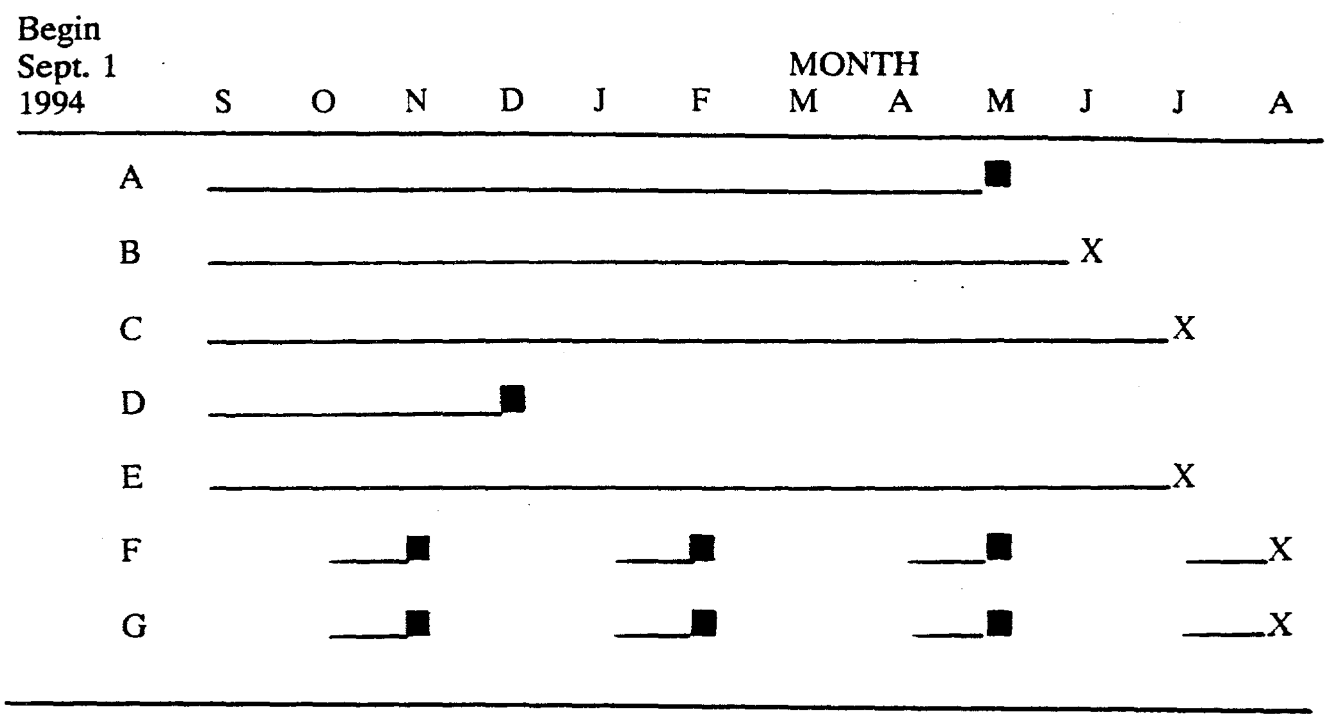
In the second quarter, a new process concept was formulated for NO_x removal, in which NO was first oxidized catalytically to NO_2, which is then removed from the exhaust gas by an absorbent. Preliminary data obtained last quarter demonstrated the feasibility of this process concept, and research proposal to further explore it was submitted to ICCI as a joint effort among Northwestern University, Illinois State Geological Survey, and Research Triangle Institute, with encouragement from representatives of STEAG. Subsequently, other companies have expressed interest about this new process concept to Anthony Lizzio of ISGS.

In this new concept, a major research item is to find a catalyst that has sufficient activity under realistic flue gas conditions to oxidize NO to NO_2, which is also one of the research tasks in this project. Therefore, substantial effort was spent in this quarter to synthesize and test catalysts for this reaction. We are pleased that some of the Au-based catalysts have been found to be very active. We believe that the Au-cobalt oxide catalyst described in the technical report is probably the most active one ever reported. However, the first attempt to scale up the preparation, so as to prepare sufficient quantity for poisoning and long term stability tests, was not successful. Improving the technique for large scale preparation will continue as an effort for the next quarter.

The research expenditure was within expectation. There was a slight delay in the technical progress because the laboratory at RTI was moved to a new location in Research Triangle Park. We expect the research to progress within expectation in the coming quarter.

SCHEDULE OF PROJECT MILESTONES

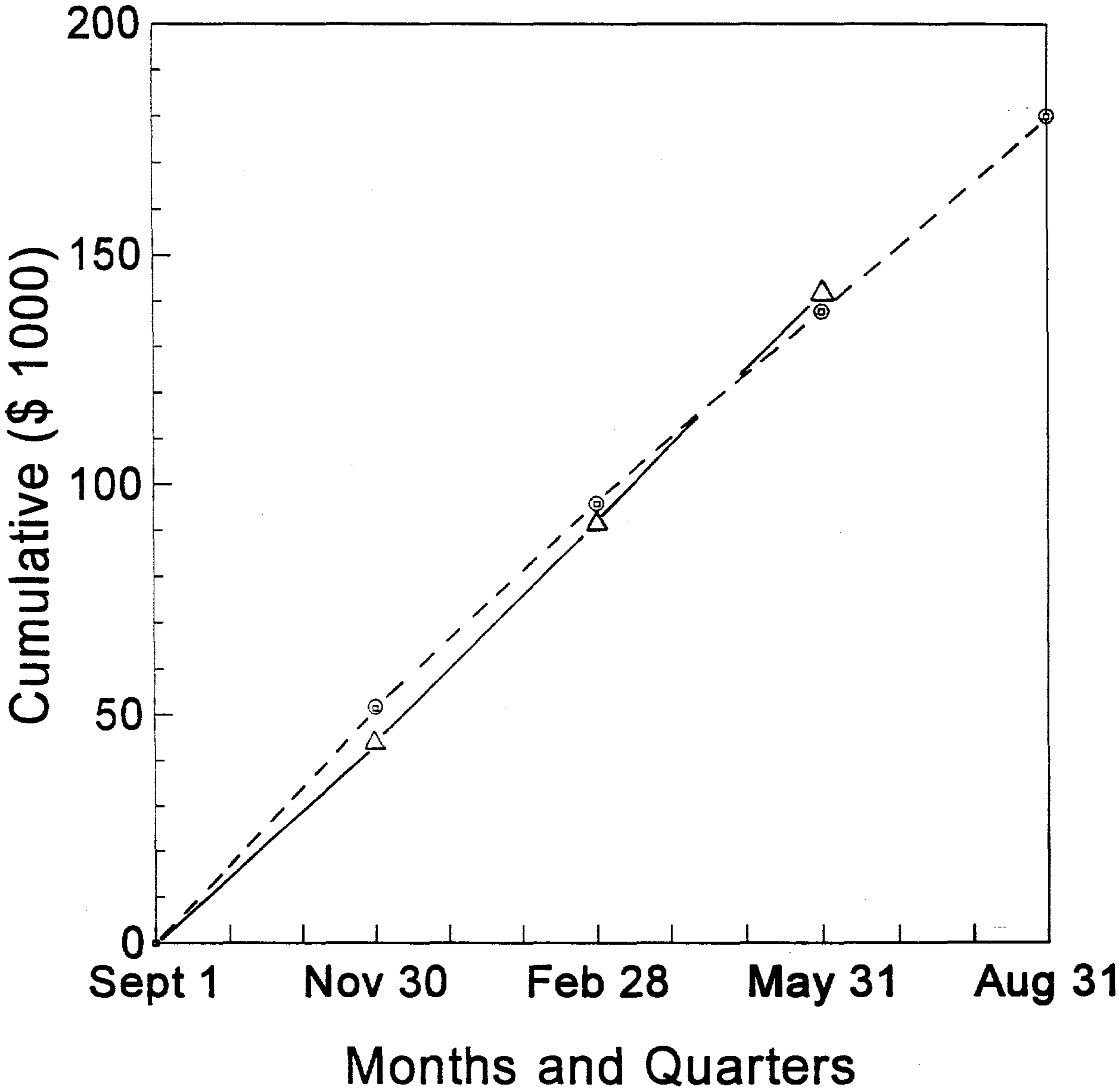
NOVEL TECHNOLOGIES FOR SO_x/NO_x REMOVAL FROM FLUE GAS



Milestones:

A: Synthesis and modification of catalysts completed.
B: Initial tests of new catalysts completed.
C: Long term stability and deactivation tests completed.
D: Test of carbon-supported catalysts completed.
E: Evaluation of feasibility of two-bed catalytic system completed.
F: Technical reports prepared and submitted.
G: Project management reports prepared and submitted.

COSTS BY QUARTER
Novel Technologies for SOx/NOx Removal from Flue Gas



--- ⊙ -- = Projected Expenditure -------
—△— = Estimated Actual Expenditures ———
Total Illinois Clean Coal Institute Award $179,641.00

941130

CUMULATIVE PROJECTED AND ESTIMATED EXPENDITURES BY QUARTER

NOVEL TECHNOLOGIES FOR SO_x/NO_x REMOVAL FROM FLUE GAS

Quarter*	Types of Cost	Direct Labor	Fringe Benefits	Materials & Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sept. 1, 1994 to Nov. 30, 1994	Projected	10,739	2,013	1,500	625	0	19,997	16,567	51,441
	Estimated	11,000	2,062	500	0	0	15,000	13,567	42,129
Sept. 1, 1994 to Feb. 28, 1995	Projected	21,478	4,027	3,000	1,250	0	39,994	26,009	95,758
	Estimated	20,000	3,800	600	0	0	42,000	24,400	90,800
Sept. 1, 1994 to May 31, 1995	Projected	32,217	6,040	4,500	1,875	0	59,991	33,076	137,699
	Estimated	39,700	7,500	2,400	0	0	60,000	33,000	142,600
Sept. 1, 1994 to Aug. 31, 1995	Projected	42,956	8,054	6,000	2,500	0	79,989	40,142	179,641
	Estimated								

*Cumulative by Quarter