

SELECTIVE CATALYTIC SORBENTS FOR NO_x FROM COMBUSTION FLUE GAS FOR PREPRINTS OF THE FUEL CHEMISTRY DIVISION, ACS

A. Rubel, M. Stewart, J. Stencel
University of Kentucky
Center for Applied Energy Research
3572 Iron Works Pike
Lexington, KY 40511-8433

Keywords: coal-based sorbents, selective NO_x capture, combustion flue gas

INTRODUCTION

A process which uses coal-based activated carbons as selective catalytic sorbents for the removal of NO_x from combustion flue gas is under investigation at the University of Kentucky, Center for Applied Energy Research (CAER) (1-3). Flue gas cleanup would be achieved through the selective capture of NO_x at stack temperatures of 70-120°C followed by desorption of a concentrated stream of NO₂ at elevated temperatures (140-150°C). Processing would involve repeated NO_x adsorption/desorption cycles using the same adsorbent carbon.

Numerous investigations have been conducted on the decomposition of NO_x over carbonaceous materials with respect to the heterogeneous reduction of NO_x (4-9). Under the reaction conditions used, the amount of NO adsorbed was less than 2 wt% of the carbon and, due to the high reaction temperatures, 40-50 wt% of the carbon was gasified (2,6). Our work has concentrated on the use of activated carbons as selective sorbents for NO_x at flue gas stack conditions without added chemicals. Our data suggests that an environmentally benign process is possible which eliminates problems associated with ammonia slippage, and provides possibilities for by-product generation such as nitrates for agricultural purposes, nitric acid, or other nitrated compounds.

This paper will discuss NO_x adsorption on coal-based sorbents, catalytic reactions involved in the adsorption process, identification of the desorbed oxide, and the possibility of making HNO₃ from adsorbed NO_x.

EXPERIMENTAL

Instrumentation. NO_x adsorption/desorption profiles were obtained using a Seiko TG/DTA 320 coupled to a VG Micromass quadrupole MS. The two instruments were coupled by a heated (170°C) fused silica capillary transfer line leading from above the sample pan in the TG to an inert metrasil molecular leak which interfaced the capillary with the enclosed ion source of the MS. The TG was connected to a disk station which provided for programmable control of the furnace, continuous weight measurements, sweep gas valve switching, data analysis, and export of data to other computers. The MS has a Nier type enclosed ion source, a triple mass filter, and two detectors (a Faraday cup and a secondary emissions multiplier). The MS was controlled by a dedicated personal computer which was also used to acquire and review scans before export to a spreadsheet for data manipulation.

TG-MS procedures. The TG heating regime used to produce NO_x adsorption/desorption profiles incorporated segments for outgassing, cooling, adsorption, desorption, and temperature-induced desorption. The details of this heating program have been discussed previously (1). Other TG conditions used have also been published (1,2).

The MS was scanned over a 0-100 amu range with a total measurement interval of approximately 30 s per 100 amu; NO (mass 30) or NO₂ (mass 30 and 46) were identified by comparing amu 30/46 ion ratios.

NO_x scrubbing test procedures. NO_x breakthrough profiles were acquired using a 7.2 ml cylindrical reactor loaded with approximately 1 g of sorbent. A small fraction of the effluent gas leaving the reactor was routed to a mass spectrometer for continuous monitoring of gas composition. The sample was outgassed at 300°C for 1 hour with a He purge at a flow rate of 150 ml/min metered at room temperature and pressure. The coal-based carbon was then cooled to an adsorption temperature of 80°C. Once this temperature was achieved, the purge gas was switched to a simulated combustion flue gas containing 2% NO, 5% O₂, and a balance of He. Subsequent to testing, the reactor was cooled and the sorbent retrieved for analysis.

Nitric acid production tests. Activated carbon which had been completely saturated with NO_x was subjected to two different wash solutions, distilled/deionized water and 3% H₂O₂ in distilled/deionized water. The washes were saved for analysis. A control, non-treated sample of sorbent was also washed with both solutions for comparison.

Analytical procedures. The sorbents were subjected to surface area determinations performed on a Quantachrome Autosorb-6 using a N₂ static volumetric flow procedure. Surface areas were calculated using the standard BET equation between relative pressures of 0.05-0.25 (10). Wash solutions from the nitric acid production testing were analyzed by ion chromatography on a Dionex 2020i instrument according to standard procedures. The pH of the wash solutions was determined by ASTM D3838-80.

Materials and simulated flue gas composition. Two coal based activated carbons, produced commercially by steam activation, were tested during this study. For the purposes of this paper, the two carbons will be identified as **a** and **b**. They had N₂ BET surface areas of 460 and 850 m²/g, respectively.

The NO_x adsorption capacity of the activated carbons was determined using the following concentrations of gases during adsorption: 2% NO, 5% O₂, 15% CO₂, 0.4% H₂O and He as the balance. Helium was used by itself during degassing, physisorption, and temperature programmed desorption.

The range of concentrations of flue gases studied during this work are as follows: 0.3 to 2.0% NO or NO₂; 5 to 20% O₂; 0 to 15% CO₂; 0.4 to 6% H₂O and He as the balance. During some tests, the sorbent was pre-saturated with O₂ or CO₂ to determine their contribution to the adsorption mechanism.

RESULTS AND DISCUSSION

Adsorption Capacities and sorbent gasification. Adsorption/desorption profiles, as shown in Figure 1 for sorbent **a** were used to determine adsorption capacities and recycle potential for the two carbons. On exposure to NO and in the presence of O₂ and CO₂, the weight gained in 30 minutes by sorbent **a** was 13.6%. Desorption of NO₂ from the carbon through both physisorption and temperature programmed desorption was confirmed by mass spectra showing a major peak at amu 30 (the primary mass ion for both NO and NO₂) which coincided with the TG monitored weight loss. A peak was also observed at amu 46, a secondary mass ion for NO₂. The temperature at which maximum desorption occurred was 140°C.

Repeated cycling of the sorbent indicated that gasification and adsorption capacity losses were very small. Carbon **a**, subjected to three NO_x adsorption/desorption cycles, lost approximately 1.5% of its total adsorptive capacity (Figure 1). This loss was partially related to a small amount of carbon gasification (0.5-1.0 wt%). Since the temperature at which maximum desorption occurred, 140°C, is significantly lower than the 400°C to which the samples were heated during temperature-induced desorption, these losses can be reduced by lowering the maximum temperature to which the carbons are exposed. Results for carbon **b** were similar to those for carbon **a** except the adsorption capacity for NO_x was slightly less at 10.7 g NO₂ / 100 g carbon.

NO_x scrubbing test. The response of the mass spectrometer (amu 30) during NO_x scrubbing using sorbent **a** showed removal of NO to near the lowest detection limits of the MS over a 16 minute period (Figure 2). This implies that the NO₂ loading on the carbon was 9.1 g NO₂ / 100 g carbon.

Requirements of adsorption. To better understand adsorption mechanisms and requirements, the adsorption capacity of sorbent **a** was determined for various combinations of NO or NO₂ combined with CO₂ and/or O₂, and for NO or NO₂ on carbon pre-saturated with CO₂ or O₂ (Figure 3). The relative capacity for the combination of gases was defined as the amount of adsorption measured for each case with respect to the base case for both NO and NO₂ adsorption. The base case was the adsorption of NO or NO₂ in CO₂ and O₂. The weight gained by the carbon was the same for both base cases.

It was found that O₂ was required for significant NO adsorption and that CO₂ did not interfere with adsorption. Adsorption of NO in CO₂/O₂ was the same as for NO in O₂ alone. Almost no adsorption of NO occurred in the presence of He or CO₂. These data are consistent with other literature which show low levels of NO_x adsorption at temperatures above 200°C and in the absence of O₂ (4-9). Pre-saturating carbon with O₂ followed by NO adsorption in He improved NO adsorption over the comparable He case, but whether this was due to binding of O₂ to the carbon or slightly higher gaseous O₂ levels as a result of the inability to completely purge O₂ from the TG-MS system could not be determined. There was a slight increase in the weight (approximately 0.5 wt%) of the carbon during O₂ pre-treatment. In contrast to NO adsorption, the relative adsorption of NO₂ was found to be nearly independent of the presence or absence of CO₂ and/or O₂. The amount of NO₂ adsorbed in He was only slightly less than

in O₂.

Control experiments for the above series of experiments indicated that O₂, CO₂ and H₂O were not significantly adsorbed on the sorbent (Figure 4). For comparison, results from a base case with carbon exposed to the simulated flue gas containing NO_x, O₂, CO₂, and H₂O is also shown in Figure 4.

Adsorbed Oxide. Since identical weight was gained by the carbon when it was exposed to identical concentrations of either NO or NO₂ in the presence of O₂, the adsorbed oxide must be the same for both cases. During the adsorption of NO in O₂, a significant exotherm was observed which did not occur when NO₂ was used (Figure 5). The heat of adsorption determined from these dta curves was -1.6 kcal/g NO₂ which is consistent with the conversion of NO + O to NO₂. Detection of this heat of adsorption by the instrumentation requires that the reaction occurred at the surface or within the pores of the sorbent, suggesting the carbon's catalytic role in the conversion of NO to NO₂.

Desorbed Oxide. During all our experimentation, MS mass ion ratios were determined by monitoring amu 30/46. This ratio has been determined for all our experimental conditions and for all combination of the gases. As previously stated, mass 30 is the primary ion for both NO and NO₂ while NO₂ also exhibits a secondary mass ion at 46. The 30/46 mass ion ratio during temperature induced desorption, clearly suggests that the desorbed oxide is primarily NO₂ (Figure 6).

Nitric acid production. The catalytic conversion of NO to NO₂ by the carbon and the desorption of NO₂ as the major product suggests that nitric acid production would be a possible by-product of a process using coal-based sorbents for combustion flue gas clean-up. When carbon a, exposed to simulated combustion flue-gas, was washed with either distilled/deionized water or 3% H₂O₂, the pH of the wash solutions decreased dramatically (Table I). This decreased was caused by an increase in the nitrate ion concentrations of the solutions (Table II). More work needs to be done in this area but these results suggest the possibility that nitric acid could be produced directly from the captured NO_x without additional reactions or chemicals.

SUMMARY AND CONCLUSION

NO_x in the presence of O₂ and CO₂ was selectively captured by coal based activated carbons. The measured heat of adsorption indicated that NO present in the flue gas was catalytically converted to NO₂ at the surface of or within the carbon. The desorbed oxide species was identified as NO₂ by mass ion ratios (30/46). The presence of adsorbed NO₂, which can be simply washed from the carbon as nitrate ion, suggests that the production of nitric acid as a by-product is possible. Our research has shown that coal based sorbents have the potential to be used in an environmentally benign process to selectively remove NO_x from combustion flue gas.

REFERENCES

1. Rubel, A.M.; Stencil, J.M.; Ahmed, S.N. *Preprints Symposium on Flue Gas Cleanup Processes*; ACS, Division of Fuel Chem.: Denver, CO, 1993; 38(2), 726-733.
2. Rubel, A.M.; Stencil, J.M.; Ahmed, S.N. *Proceeding of the 1993 AIChE Summer National Meeting*; AIChE: Seattle, WA, 1993; Paper no. 77b.
3. Rubel, A.M.; Stewart, M.L.; and Stencil, J.M. *Preprints Symposium on NO_x reduction*, ACS, Division of Petroleum Chem.: San Diego, CA, 1994; 39(1), 137-140.
4. Smith, R.N., J. Swinehart, and D. Lesnini. *J. Physical Chem.* 63(1959)544.
5. DeGroot, W.F., T.H. Osterheld, G.N. Richards. *Carbon* 29(1991)185.
6. Teng, H., E.M. Suuberg, J.M. Calo, and P.J. Hall. *Proc. 19th Conf. on Carbon*, (1989)574.
7. Suuberg, E.M., H. Teng, and J.M. Calo. *23rd Symposium (International) on Combustion*, The Combustion Institute (1990)1199.
8. Teng, H., E.M. Suuberg, and J.M. Calo. *Preprints of the 200th ACS National Meeting*, Washington, DC, 35,3(1990)592.
9. Gray, P.G., N.J. Desai, and D.D. Do. *Recent Trends in Chem. Rxn Engr.*, B.O. Kkulkarni, R.A. Mashelkar, and M.M. Sharma, eds., Wiley Eastern Ltd., 1(1987)383.
10. Brunauer, S.; Emmett, P.H.; Teller, E. *J.A.M. Chem. Soc.* 1938, 60, 309.

Table I. pH of wash solutions from nitric acid production tests

Wash solution	pH	Wash solution	pH
H ₂ O Control	6.0	3% H ₂ O ₂ /H ₂ O Control	4.8
H ₂ O, Unused C	6.7	3% H ₂ O ₂ , Unused C	6.4
H ₂ O, NO _x exposed C	2.1	3% H ₂ O ₂ , NO _x exposed C	1.9

Table II. Nitrate ion concentration in wash solutions determined by IC

Wash solution	%NO ₃ ⁻	Wash solution	%NO ₃ ⁻
H ₂ O, Unused C	< 1 ppm	3% H ₂ O ₂ , Unused C	< 1 ppm
H ₂ O, NO _x exposed C	0.18	3% H ₂ O ₂ , NO _x exposed C	0.23

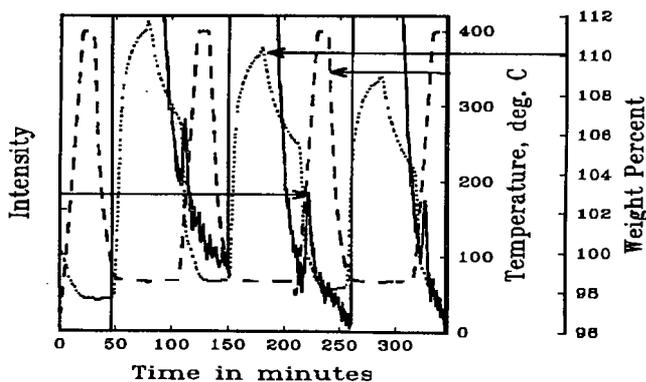


Figure 1. Three cycle ads/des profile for NO_x ads on carbon, a; gases: 2%NO, 5%O₂, 15%CO₂, 0.4%H₂O, balance He

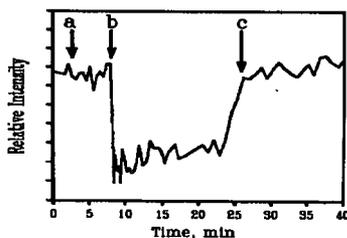


Figure 2. NO_x scrubbing test; mass 30 breakthrough curve; a = baseline NO level, b = gas pass through carbon initiated, c = NO breakthrough

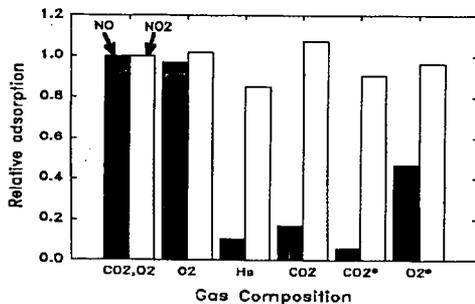


Figure 3. Relative ads of NO_x on carbon, a, in different atmospheres; * = carbon presaturated with O₂ or CO₂; ads in He

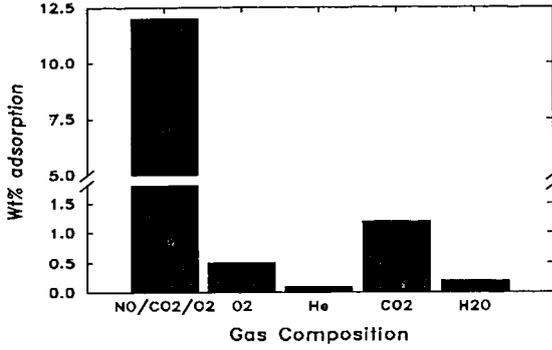


Figure 4. Adsorption of O₂, CO₂, and He on carbon. Gases: 0.6% NO; 5% O₂; 15% CO₂, 6% H₂O; balanced with He

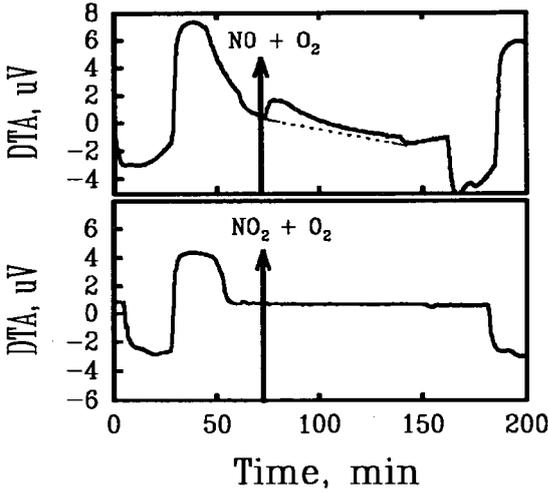


Figure 5. DTA curves for NO vs. NO₂ adsorption in the presence of O₂

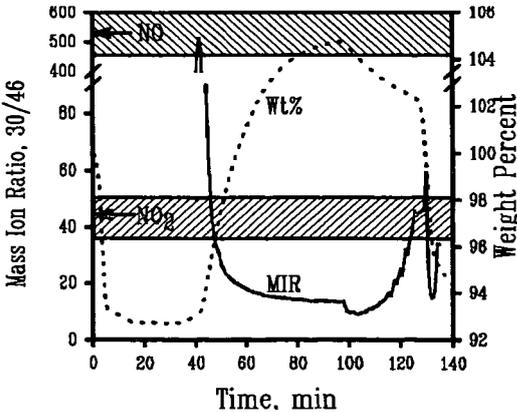


Figure 6. Mass ion ratio (30/46) during desorption