

SYMPOSIUM ON CHEMISTRY OF FLUE GAS CLEANUP PROCESSES
FOR PREPRINTS OF THE FUEL CHEMISTRY DIVISION
AMERICAN CHEMICAL SOCIETY
DENVER, CO MEETING, MARCH 28-APRIL 2, 1993

ACTIVATED CARBON FOR SELECTIVE REMOVAL OF NITROGEN OXIDE
FROM COMBUSTION FLUE GAS

By

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

Keywords: NO, selective adsorption, activated carbons

INTRODUCTION

A new concept for non-catalytic NO removal from combustion flue gas is being developed at the University of Kentucky Center for Applied Energy Research (CAER). Flue gas cleanup would be achieved through the use of activated carbons for the selective capture of NO_x at stack temperatures between 70-120°C followed by desorption of a concentrated stream of NO_x at elevated temperatures, near 140-150°C. Processing would involve repeated NO_x adsorption/desorption cycles using the same adsorbent carbon.

Previous work on the removal and adsorption of NO over carbaceous materials has focused on the heterogeneous reduction of NO by carbon to CO, CO₂, and N₂¹⁻⁶. The proposed reaction mechanisms involve the chemisorption of NO on carbon at temperatures near 200°C resulting in the formation of a carbon-NO complex which rearranges to form a carbon-oxygen complex and molecular nitrogen². The amount of NO adsorbed was less than 2 wt% of the carbon and, upon desorption, 40-50 wt% of the carbon is gasified^{2,6}. Some work has been done toward the use of activated carbon to remove NO_x from moist off-gases in nitric acid plants at ambient temperatures and in the presence of O₂. The NO adsorptive capabilities found were low and near 0.16 to 0.7 mg NO/g carbon⁷. No information has been found in the literature concerning NO/NO₂ adsorption on active carbon under conditions found in combustion flue-gases.

During this study, the mechanisms and kinetics of NO_x adsorption/desorption on activated carbon under conditions typical to combustor stacks were investigated by thermogravimetry/mass spectrometry (TG/MS). Information was obtained concerning the requirements for NO_x capture, the NO_x adsorption capacity of an activated carbon, the effect of repeated adsorption/desorption cycles on NO_x adsorption, and the mechanism of adsorption.

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 conditions kept constant during the acquisition of adsorption/desorption profiles were: sweep gas flow rate of 200 ml/min metered at room temperature and pressure and a constant carbon sample volume weighing approximately 20 mg. The MS was scanned over a 0-100 amu range with measurement intervals of approximately 30 seconds. NO (mass 30) or NO₂ (mass 30 and 46) were identified by comparing amu 30/46 ion ratios. These ratios were determined for all combinations of gases flowing through the TG-MS system both with and without carbon in the TG sample pan.

The TG heating regime used to produce NO_x adsorption/desorption profiles incorporated segments for outgassing, cooling, adsorption, desorption, and temperature-induced desorption. Table I shows a typical heating program for a single adsorption/desorption cycle. During outgassing and subsequent cooling of the carbon sample to an adsorption temperature (segments a and b, Table I), an inert (He) gas sweep was usually used. However, O₂ and CO₂ pretreatments of the carbon were also done during these steps for some experiments. Maximum outgassing temperature was always the same as the maximum used during temperature programmed desorption (step e). After preconditioning of the carbon, NO or NO₂ was introduced in a simulated flue gas atmosphere containing either O₂ or CO₂, or both O₂ and CO₂. After completion of an adsorption interval (30 or 60 minutes), He was again used to purge the system during segments d and e. Two maximum desorption temperatures were used, 300 and 400°C. Multiple and consecutive adsorption/desorption cycles were performed by recycling the temperature programmer to segment b.

Materials and simulated flue gas composition

A commercially (Carbo Tech) produced coal-based carbon was used. This carbon was produced by physical activation and had a N₂ BET surface area of 450 m²/g.

During this study, the concentrations of gases used during adsorption and pretreatments were: 2% or 0.3% NO or NO₂; 5% O₂, 15% CO₂ and He as the balance. NO adsorption capacity of the activated carbon studied was determined for the following combinations of gases: 2% NO with O₂ and CO₂; 2% NO in He alone; 0.3% NO in O₂ and CO₂; 0.3% NO in either O₂ or CO₂; 0.3% NO in He with carbon presaturated with either O₂ or CO₂; 0.3% NO in He alone; and 0.3% NO₂ in O₂ and CO₂.

RESULTS AND DISCUSSION

Capacity of activated carbon to selectively capture NO_x

Both single cycle and repeated cycles TG-MS adsorption/desorption profiles were used to show effective and rapid removal of NO from simulated flue gas by activated carbon.

During a single NO adsorption/desorption cycle using a simulated flue gas with a high NO concentration (2% NO, 15% CO₂, and 5% O₂ with a balance of He), 0.14 g NO/g carbon was adsorbed in 30 minutes as evidenced by the increased weight of the carbon (Figure 1). Increasing the adsorption time to 60 minutes only marginally increased NO capture to 0.16 g NO/g carbon. Desorption of NO_x from the carbon through both physisorption and temperature programmed desorption was confirmed by the mass spectra showing a major peak in the ion intensity of amu 30 (the primary ion mass for both NO and NO₂) coinciding with the TG monitored weight loss. A small peak was also observed for amu 46, a secondary ion mass for NO₂. The temperature of maximum desorption occurred at 140°C.

Repeated cycling of the same carbon through three NO_x adsorption/desorption cycles, resulted in a 15% total loss of adsorptive capacity (Figure 2). The maximum desorption temperature (400°C) used during this experiment was higher than the 250-300°C required for complete NO_x desorption. Since the loss in adsorptive capacity of the carbon coincided with a 0.5-1.0 wt% loss of carbon, possibly through oxidation/gasification, lowering the desorption temperature should reduce this already small loss in adsorptive capacity.

Effect of flue gas constituents on NO_x adsorption

To determine the effect of typical flue gas constituents on the kinetics of NO adsorption, a parametric study was done using 0.3% NO in various combinations with O₂ (5%), CO₂ (15%), and He (balance) (Figure 3). Adsorption time for all experiments was kept constant at 60 minutes. NO capture was dependent on the presence of O₂ but was not significantly affected by the presence of CO₂. Presaturation of carbon with O₂ followed by NO adsorption in He increased adsorption from 1 wt% using He alone to 6 wt% suggesting a carbon surface reaction mechanism. Control experiments without NO present during adsorption showed that 1% or less of the weight gain during NO adsorption resulted from O₂, CO₂, or He adsorption on the carbon (Figure 3).

Possible reaction mechanism

The dependency of NO adsorption on the presence of O₂ suggests that NO must be converted to a surface species similar to NO₂ during the adsorption step. Simultaneous differential thermal analyses (DTA) conducted during these experiments supported such conversion. A significant exotherm accompanied NO adsorption (Figure 4) whereas, no heat of reaction was associated with NO₂ adsorption (Figure 5).

A comparison of MS ion ratios for masses (30/46) for all combinations of NO or NO₂ and O₂ or CO₂ flowing through the TG-MS system with and without activated carbon in the sample pan shows the differences obtained in these ratios (Figure 6). These differences were used to identify the form of NO_x desorbed from the carbon. Since the (30/46) ion ratios for all combinations of NO or NO₂ with O₂ or CO₂ were less than 20, an experiment where desorption occurred in a He sweep with low baseline levels of O₂ and CO₂ was necessary. This requirement was met by presaturating carbon with O₂ followed by adsorption and desorption in He. The ion ratio during desorption for this experiment was 94 and most closely matched the ion ratio for NO₂ in He (Figure 7). For comparison, the desorption ion ratio for a NO, CO₂, O₂ experiment is also shown.

SUMMARY AND CONCLUSIONS

The data presented provides evidence for the selective capture of NO_x by activated

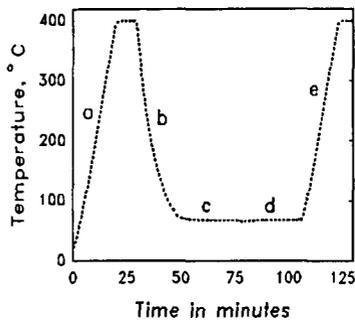
carbons in the presence of typical flue gas components. The NO adsorption capacities approached 0.16 g NO/g carbon. Adsorption of NO was rapid only in the presence of O₂, was not influenced by the presence of CO₂, and involved the exothermic conversion of NO to NO₂-like species at the surface of the carbon. The capacity for NO adsorption was only slightly diminished by repeated adsorption/desorption cycles. At desorption temperature as high as 400°C, the capacity after three cycles decreased to about 85% of the original value with a coincident loss of 0.5-1.0 wt% of the carbon. The results suggested that activated carbon can be used for NO_x flue gas clean-up and would provide a simple alternative to more expensive and complex methods such as selective catalytic reduction.

REFERENCES

1. Smith, R.N., J. Swinehart, and D. Lesnini. *J. Physical Chem.* 63(1959)544.
2. DeGroot, W.F., T.H. Osterheld, G.N. Richards. *Carbon* 29(1991)185.
3. Teng, H., E.M. Suuberg, J.M. Calo, and P.J. Hall. *Proc. 19th Conf. on Carbon*, (1989)574.
4. Suuberg, E.M., H. Teng, and J.M. Calo. *23rd Symposium (International) on Combustion*, The Combustion Institute (1990)1199.
5. Teng, H., E.M. Suuberg, and J.M. Calo. *Preprints of the 200th ACS National Meeting*, Washington, DC, 35,3(1990)592.
6. Gray, P.G., N.J. Desai, and D.D. Do. *Recent Trends in Chem. Rxn Engr.*, B.O. Kulkarni, R.A. Mashelkar, and M.M. Sharma, eds., Wiley Eastern Ltd., 1(1987)383.
7. Richter, E., R. Kleinschmidt, E. Pilarczyk, K. Knoblauch, and H. Juntgen. *Thermochemica Acta* 85(1985)311.

Table I. Typical TG heating regime for acquisition of NO_x heating profile.

Step	Temp C	Rate C/min	Hold min
a	0-400	20	10
b	400-70	50	10
c	70 (1)	0	30-60
d	70 (2)	0	30
e	70-400	20	10



¹Adsorption step
²Physidesorption step

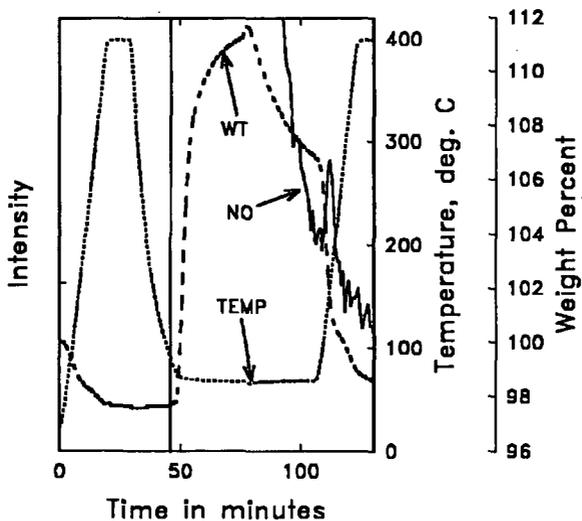


Figure 1. Single adsorption/desorption profile. Adsorption atmosphere: 2% NO, 5% O₂, 15% CO₂, and He balance; adsorption time: 30 min.

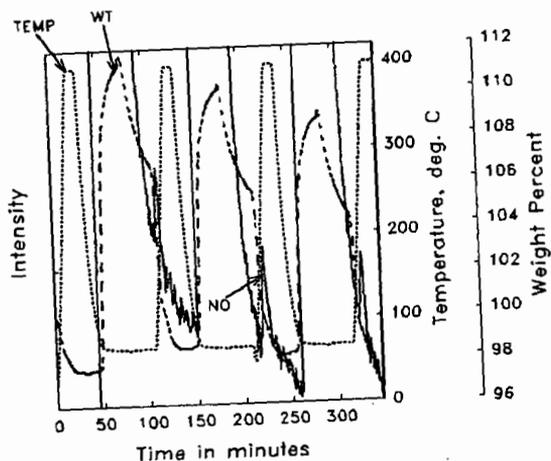


Figure 2. Three consecutive adsorption/desorption cycles using the same carbon sample. Adsorption atmosphere: 2% NO, 5% O₂, 15% CO₂, and He balance; adsorption time: 30 min.

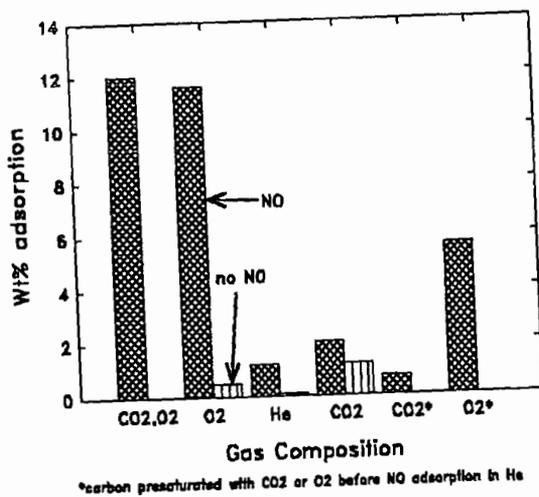


Figure 3. Study of the effect of O₂ and CO₂ on NO adsorption on activated carbon. Gases: 0.3% NO, 5% O₂, 15% CO₂, and He balance; adsorption time: 60 min.

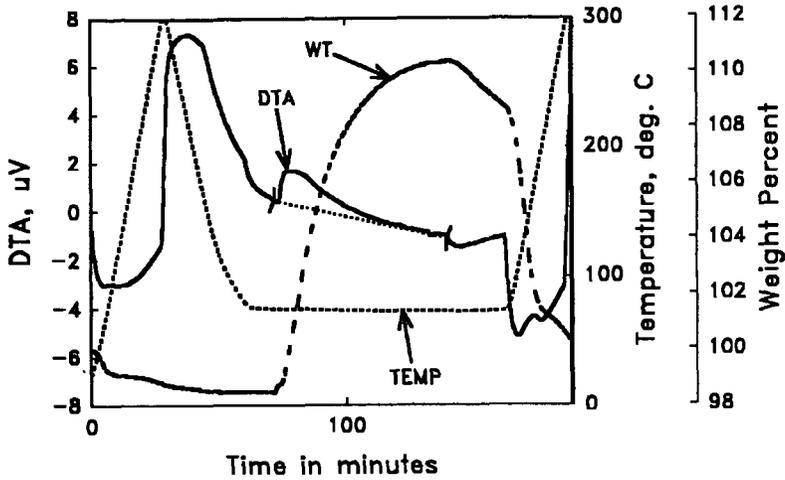


Figure 4. Simultaneous TG/DTA of NO adsorption on activated carbon. Adsorption atmosphere: 0.3% NO, 5% O₂, 15% CO₂, and He balance; adsorption time: 60 min.

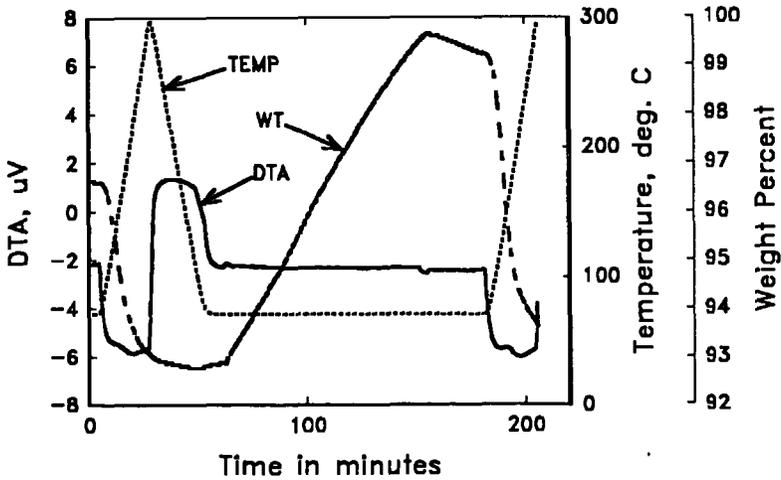


Figure 5. Simultaneous TG/DTA of NO₂ adsorption on activated carbon. Adsorption atmosphere: 0.3% NO₂, 5% O₂, 15% CO₂, and He balance; adsorption time: 60 min.

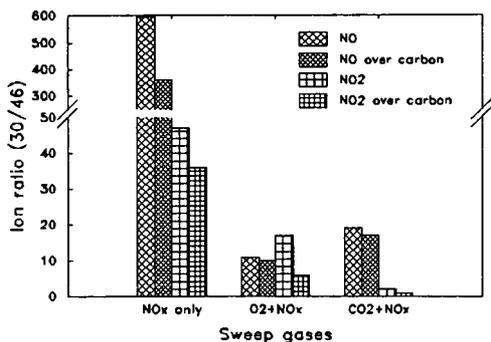


Figure 6. Mass (30/46) ion ratio for various combinations of NO or NO₂ and O₂ or CO₂ with and without the presence of carbon in the TG sample pan as determined by MS.

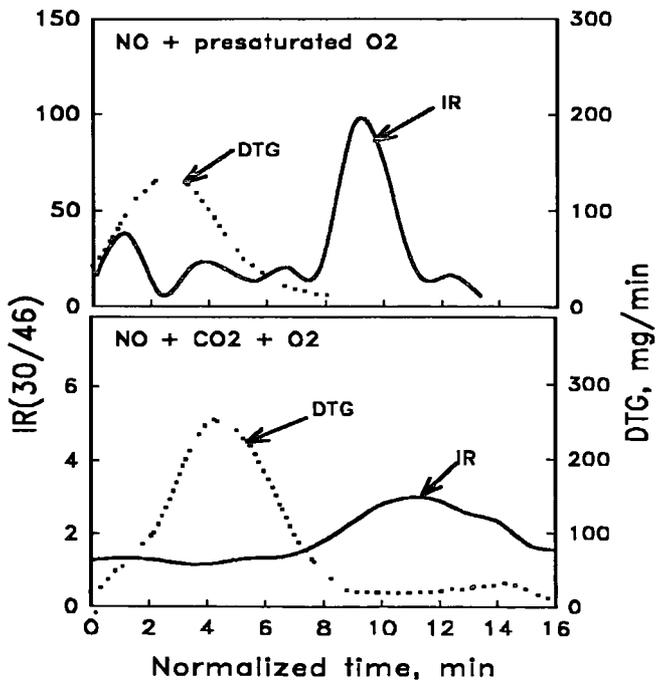


Figure 7. Mass (30/46) ion ratios during desorption of NO_x from activated carbon.