

PRESSURE ENHANCED REVERSIBLE ADSORPTION OF NO_x BY ACTIVATED CARBONS

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INTRODUCTION

Although a tremendous amount of research has been and continues to be performed on the catalytic reduction of NO_x^{1,2}, the development of selective adsorbents for NO_x could provide a chemically benign option for the control of these emissions through a process which sequesters and then concentrates NO_x. One requirement for an adsorption/desorption process is a material with a high, reversible adsorption capacity. A number of potential adsorbents have been examined, including metal oxides^{3,4}, zeolites^{5,6}, activated carbons⁷⁻¹¹, and carbon fibers^{12,13}. Activated carbons in the absence of O₂ have slow NO adsorption kinetics and low NO adsorption capacities^{14,15}. However, at temperatures between 20-120°C and in the presence of O₂, recent studies have shown that both the kinetics and capacities are enhanced dramatically⁷⁻¹¹. The research suggested that activated carbon catalytically converted $\text{NO} + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_2$, which then condensed within the micropores of the carbon. At atmospheric pressure and 70°C, the NO_x adsorption capacities were as high as 150 mg NO₂ (g carbon)⁻¹. Other coreactants such as CO₂ and H₂O did not inhibit nor were significantly adsorbed.

Our data suggested that the site(s) of NO → NO₂ conversion was different from the micropores in which the NO₂ condensed¹⁰. Therefore, it may be possible to pressure enhance micropore filling and improve the overall kinetics and capacities for NO_x adsorption over a greater temperature range. Such pore filling is influenced by a gas' van der Waals attractive force constant, α^3 ¹². For example, the α constant for NO₂ is 25 times greater than that for NO¹⁶, making NO₂ the preferred adsorbate. However, increased temperature has a disordering effect, decreasing the van der Waals attraction¹⁷ and impacting negatively the overall adsorption capacity.

Since no work has been reported for pressurized adsorption-desorption of NO_x over activated carbons, this study was initiated. In the current paper, the effects of pressure on the NO_x adsorption capacity and kinetics over an activated carbon were studied, with specific attention to the effect of pressure on the storage of irreversible versus reversible NO_x species.

EXPERIMENTAL

A Cahn C1100 high pressure microbalance and accompanying reactor was used for this study. The balance controls were interfaced to a personal computer for data acquisition. A cylindrical porous (100 m) stainless steel bucket, 10 mm O.D., 8 mm I.D. and 20 mm in length, was used as the sample holder. This bucket when loaded was suspended by a platinum wire and hook from the balance beam to a position within the heated portion of the high pressure cell. The reactor was enclosed within a vertical, split tube, furnace which was regulated by a programmable temperature controller. Pressure in the reactor was maintained by a back pressure regulator. Gases flowing into the reactor were controlled by high pressure mass flow controllers.

A VG Micromass quadrupole MS was used to monitor the gases leaving the reactor immediately down stream from the back pressure regulator. A heated (170°C) fused silica capillary was used to transfer a small aliquot of the gases leaving the pressure cell to an inert metrasil molecular leak which interfaced the capillary with the enclosed ion source of the MS. 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.

The identification of desorbed gases was done by using the major mass ions, 44, 32, and 18, for CO₂, O₂, and H₂O respectively. The major mass ion for both NO and NO₂ is 30. The relative abundance of mass 46 for NO₂ gas is approximately 40% but in mixtures of gases this value can change. Therefore, NO and NO₂ were identified by comparing peak intensities of the mass ion ratio, 30/46, during desorption and relating these intensities to those obtained using mixtures of NO or NO₂ and all combinations of gases used during our study.

Approximately 0.6 to 0.7 g of carbon were loaded in the zeroed sample bucket. The weight of the carbon was monitored continuously. Each batch of carbon was subjected to several adsorption and

desorption cycles. The flow rate through the reactor was measured at room temperature and pressure and was maintained at 100 ml/m during the entire experiment which involved gas switching between He and the combustion gas mixture. The sample was first pre-conditioned by heating to 180-200°C in a flow of He to remove any pre-adsorbed NO_x. The carbon was then cooled to the desired adsorption temperature before the first exposure to the simulated combustion flue gas.

As the carbon approached saturation with adsorbate, the gases flowing through the reactor were switched to He and reactor pressure was lowered to atmospheric beginning a pressure release desorption step. Weight loss was monitored until no further changes were observed. The weight loss during this period was attributed to reversibly adsorbed species. System pressure was then re-established with flowing combustion gas mixture and another adsorption cycle was begun. The amount of irreversibly adsorbed material was determined by temperature induced desorption after reversible desorption was complete during some experiments. The adsorption variables studied were temperature (70 and 100°C) and pressure (14.7, 150, 250, and 400 psi).

A commercially produced activated carbon was used in this study. The carbon was physically activated using steam and had N₂ BET total, mesopore and micropore surface areas of 460, 20, and 440 m²/g, and volumes of 0.69, 0.45, and 0.24 ml/g, respectively. The NO_x adsorption capacity of this carbon determined by thermal analysis-mass spectrometry was 120 mg NO₂ (g carbon)⁻¹ at atmospheric pressure and 70°C when a simulated flue gas, containing 2.0% NO, 5% O₂, 15% CO₂, 0.4% H₂O and He as the balance, was used. The reactant gas used for this work had the same composition. The gases were added simultaneously except during experiments where the carbon was presaturated with CO₂/O₂ before NO was added to the reactant mixture.

Control adsorption experiments were performed to determine the contributions of He and CO₂/O₂ to the total weight gained by the carbon. The gases and gas mixtures used during these experiments were: He alone; NO in He; O₂/CO₂ in He; and O₂/NO in He.

RESULTS

Figure 1 shows results of an experiment with three consecutive adsorption - reversible desorption steps at a pressure up to 250 psi (points a-to-b) which followed a pre-conditioning step (up to point a), and one temperature induced desorption of the irreversibly adsorbed species (from point c). The mass uptake of NO₂ was 200 mg (g carbon)⁻¹ at a temperature of 70°C. The weight loss following pressure release at point b was attributed to a reversibly adsorbed species. After pressure release (to point c) approximately 40 mg (g carbon)⁻¹, or 20% of the weight gain, remained on the carbon even after 1700 minutes of purging with He at 70°C. This more strongly bound adsorbate, considered as the irreversibly bound species, required temperature induced desorption to 180-200°C to be completely removed. The adsorption capacity associated with the reversibly adsorbed species was not affected by repeated adsorption - desorption cycles; as many as 10 cycles were performed using the same sample without loss of capacity.

The effect of pressure on the adsorption of combustion flue gas components was studied using the adsorption - desorption profiles just described. Figure 2 is a plot of the amount of total, reversibly, and irreversibly adsorbed NO₂ versus pressure at a temperature of 70°C. Pressure improved total adsorption and increased the amount of reversibly adsorbed material while reducing the amount of irreversibly adsorbed species. Plotting the reversible adsorption data as the ratio of NO₂ volume adsorbed (carbon microporous volume)⁻¹, V_{NO₂}/V_μ, versus the total pressure, P, results in a typical Type I isotherm¹⁸. This type of isotherm suggested that micropore volume filling is important for NO₂ uptake, with the formation of a monolayer at pressures near 150 psi (Figure 3).

Figures 4a, 4b and 4c show the weight loss and intensities of mass spectral peaks as a function of time during pressure release to atmospheric from either 400 psi or 250 psi, and during temperature induced desorption. For simplicity, only trends for masses 30, 32 and 44 are displayed. The mass ion ratio, 30/46, for the data in Figure 4 was compared to the mass ion ratio obtained from standard mixtures. This comparison defined NO₂ as the only detectable nitrogen oxide species evolved during pressure release and thermal desorption.

Increasing the adsorption pressure from 250 to 400 psi caused increased intensity for ion mass 30 (NO₂) and decreased or held constant the intensity for ion masses 32 (O₂) and 44 (CO₂) during pressure release desorption. The data in Figure 4a and 4b, when compared to the data in Figure 3, indicate that O₂ and CO₂ may be important components of the reversibly adsorbed species (see below). Subsequent to eliminating the reversibly adsorbed species, the temperature induced desorption data in Figure 4c show that very little O₂ evolved from the carbon, whereas significant amounts of CO₂ and NO₂ were present.

The time sequence by which NO₂, O₂ and CO₂ were desorbed was different during pressure release versus temperature induced desorption. During pressure release, the evolution of O₂ and CO₂ began immediately and maximized at approximately 115 s before the peak in the NO₂ desorption. During a thermal desorption cycle, the peak for NO₂ occurred 150 s before the CO₂ desorption peak; the temperatures of these maxima were 140 and 155°C for NO₂ and CO₂, respectively. It is likely that, whatever the source of the CO₂ in the mass spectral data, the origin of the CO₂ detected during pressure release was different than the origin of CO₂ during temperature induced desorption. Because only a trace amount of O₂ was detected during temperature induced desorption, its evolution time was not quantified.

A comparison of desorption spectra from 150, 250, and 400 psi experiments clearly demonstrated that the amount of NO₂ released from the carbon increased with increasing adsorption pressure. In contrast, the amounts of stored O₂ and CO₂ did not appear to be uniformly affected by pressure. To quantify the relative contribution of NO₂, CO₂, and O₂ to the total mass uptake, control experiments were used to provide the relative amount of weight gain which could be related to each of these adsorbates. For example, data in Figure 5, for experiments performed at 250 psi, confirmed our previous findings at atmospheric pressure that less than 10 mg NO₂ (g carbon)⁻¹ was adsorbed if O₂ was not present in the reactant gas⁷⁻¹¹. This value is approximately 2% of the mass uptake for the case of simultaneous exposure to NO + O₂. During the CO₂/O₂ adsorption displayed in Figure 5, the mass uptake was as great as 78 mg (g carbon)⁻¹, or about 36% of the total uptake when NO is also present in the reactant stream. In addition, Figure 6 shows that the relative contributions of the reactants to the total mass uptake were sensitive to temperature with less than 10% of the total uptake at 100°C resulting from CO₂/O₂. The remainder of the mass uptake for the carbons was the result of NO + ½ O₂ → (NO₂)_{adsorbed}.

The relative percent of reversibly and irreversibly adsorbed NO₂ removed from the sample is given in Figure 7. At 70°C and atmospheric pressure, approximately 65% of the NO₂ in the carbon was reversibly desorbed; this percentage increased to 80% at 250 psi. At 100°C and atmospheric pressure, approximately 75% of the NO₂ in the carbon was reversibly desorbed; this percentage increased to greater than 95% at 250 psi. Hence, increased pressure decreased the relative amount of NO₂ which was irreversibly adsorbed at each temperature.

DISCUSSION

The Type I isotherm in Figure 3 suggests micropore filling. We have applied both Langmuir theory and BET adsorption theory to these data with the identical conclusion that the NO₂ adsorbed within the carbon was primarily located within the micropores and that a monolayer capacity within these pores was reached at total pressure near 150 psi¹⁹. Other work has shown that micropore filling is not effective for gases which have critical temperatures less than the temperature used during adsorption³. NO₂ is the only gas in this study with a critical temperature (158 °C) that is greater than the adsorption temperatures which were used. Hence, the amounts of NO, O₂, and CO₂ adsorbed in the micropores should be expected to be small in comparison to the amount of NO₂ (see Figure 6). However, at 250 psi and 70°C, the amount of CO₂ adsorbed was 78 mg (g carbon)⁻¹, a value representing 36% of the total uptake of the carbon. This uptake was possibly a consequence of the increased pressure affecting CO₂ condensation since the critical temperature for CO₂ is 31°C which is close to the adsorption temperature, 70°C. The low value of the critical temperature for NO (-93°C) also indicates that it would not be a stable, adsorbed species in the carbon's micropores.

Another factor which favors NO₂ adsorption is its high van der Waals force constant, *a*, which is 1.5 times greater than the *a* constant for CO₂. Therefore, the attractive force between NO₂ molecules upon entering the pores would be greater than for CO₂. This difference may account for the desorption of CO₂ before NO₂ during pressure release. During temperature induced desorption, the evolution of CO₂ subsequent to NO₂ desorption may be related to the gasification of carbon at C-O bonds.

The total amount of gaseous NO₂ (at STP) adsorbed into the activated carbon at 400 psi and 70°C is approximately 70 ml (g carbon)⁻¹. This value is significantly larger than the amount of NO reported to occupy the microporosity of cation-exchanged zeolites². In addition, the amount of irreversibly adsorbed NO₂ in the activated carbon at 250 psi and 100°C is less than 5% of the total amount of adsorbed NO₂. Such a value is as good as or less than values reported for the cation-exchanged zeolites.

SUMMARY AND CONCLUSIONS

The amount of NO₂ reversibly adsorbed on activated carbons increased with pressure over a range of pressures from 15-400 psi. At 100°C and 250 psi pressure, the amount of NO₂ adsorbed was nearly the same as at 70°C and atmospheric pressure and 3 to 4 times greater than at 100 °C and

atmospheric pressure. The NO_2 adsorption Type I isotherm suggested that the reversible NO_2 adsorption mechanism involved micropore filling. The time profiles during pressure release and temperature programmed desorptions were consistent with important roles for critical temperature and pressure and van der Waals forces in the adsorption and condensation of NO_2 , CO_2 , and O_2 within the micropores of the carbon.

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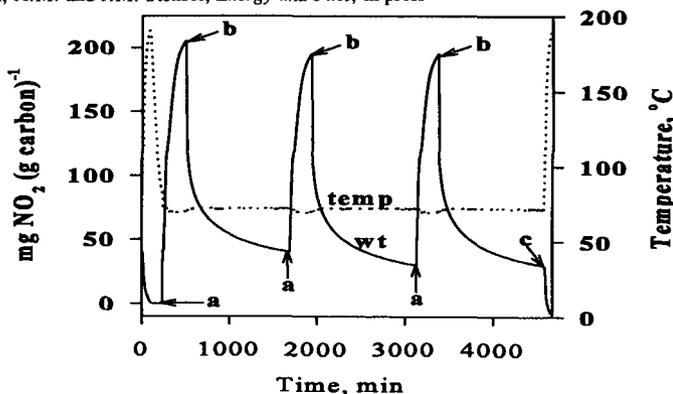


Figure 1. Adsorption - desorption profile for activated carbon.

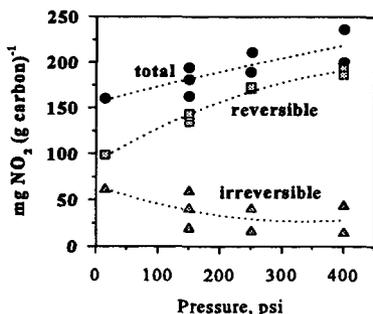


Figure 2. Plot of total, irreversible, and reversible adsorption versus pressure.

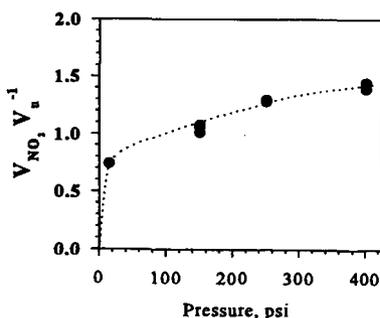


Figure 3. The type I adsorption isotherm for 70°C adsorption on activated carbon.

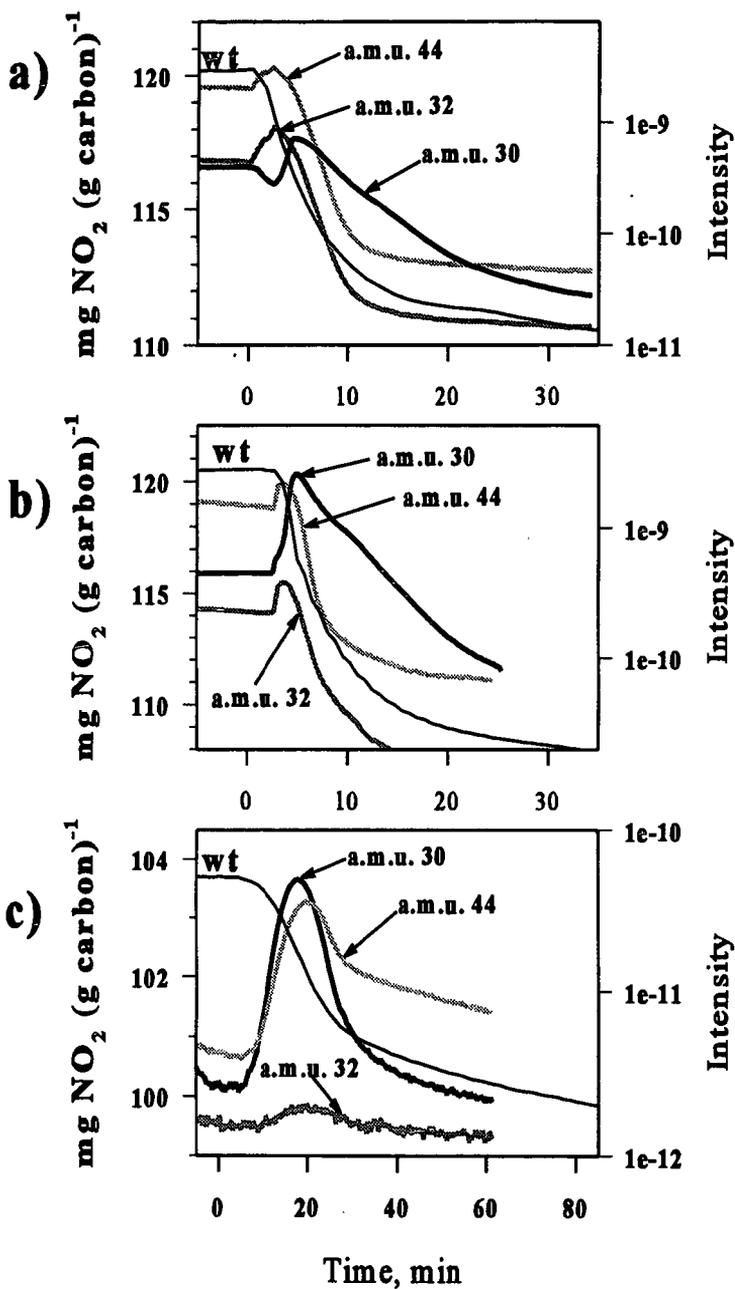


Figure 4a, b, c. Integrated weight loss - mass spectral data for pressure-release and thermal-induced desorptions; 4a) pressure-release from 250 psi; 4b) pressure-release from 400 psi; 4c) thermal-induced desorption.

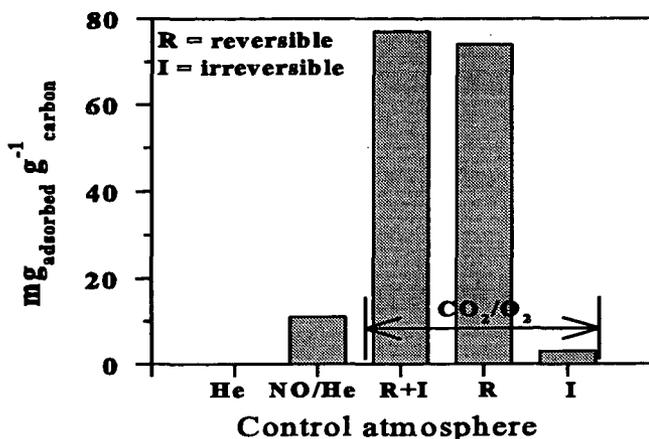


Figure 5. Contributions of He, NO, and CO₂/O₂ to total adsorption.

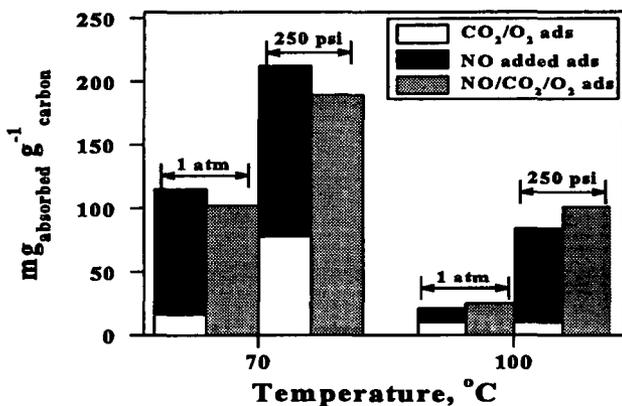


Figure 6. Effect of temperature on the relative contribution of CO₂/O₂ to total uptake.

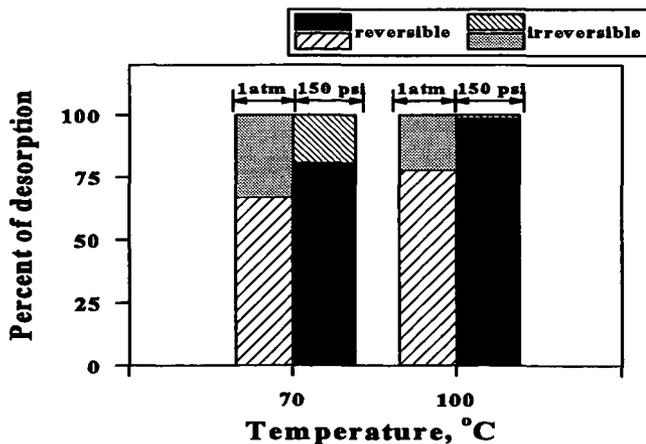


Figure 7. Effect of temperature and pressure on the relative percentage of reversibly and irreversibly adsorbed NO₂ removed from the carbon.