

A COMPARISON OF THE REACTIVITIES OF DIFFERENT CARBONS FOR NITRIC OXIDE REDUCTION

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INTRODUCTION

Carbon has been recognized to play a significant role in reducing NO in some combustion systems (e.g., fluidized beds) and offers the potential as a reducing agent in other, new applications. In order to more fully appreciate this potential, it is useful to explore what factors influence the reactivity of carbons (and, more generally, chars) towards NO. This paper summarizes what is known about the reactivity of different carbons, and examines some questions raised by the comparison, in light of new experimental results.

The reduction of NO by carbons may, for simplicity, be represented by the general reaction:



Other products (for example, N₂O) are possible under certain specific conditions. Likewise, other reaction pathways (involving carbon catalyzed NO reduction by CO) are also possible. Still, the main carbon reduction route involves the products as indicated. Many aspects of this reaction system have been reviewed in recent years [e.g., 1-4]. Many of the published data on the NO-carbon reaction are summarized in Figures 1 and 2. A more complete summary of the available data is in preparation, and will be presented shortly. This summary is intended to convey the essential features of what is known about the kinetics of the reaction.

Figure 1 presents the data on the rate constant for the reaction, expressed as an NO consumption rate, on a per unit mass of carbon basis. The assumption has been made, consistent with most reports in the literature, that the reaction is first order with respect to NO [1, 2, 5- 8]. Several features are immediately apparent. First, there is a significant spread in the rates of reaction. The variation is of two to three orders of magnitude, which may not initially be surprising inasmuch as the data were not normalized based on surface areas, *vide infra*. It is apparent that there is quite commonly a shift in apparent activation energy of the rate constant. The "breaks" occur at temperatures ranging from about 900 to 1050 K, and always involve an increase in activation energy with increasing temperature. This break has been earlier noted by several groups. It must involve a change in mechanism, as opposed to an encroachment of heat and/or mass transfer effects, since the shift is in the direction of higher activation energies with increasing temperature. A hypothesis to explain the two regimes has been previously advanced [2]. The individual studies offer a wide range of activation energies, with some sets showing no evidence of the "break". There are surprisingly few clear trends with the nature of the carbon. For example, a highly pyrolyzed resin char exhibits a lower reactivity than does a graphite. De-ashing of a lignite char shows only a modest effect on reactivity. A cellulose char with low inorganic impurity content is seen to have a higher reactivity than coal chars.

Figure 2 presents a comparison of literature data on a surface area-normalized basis. The surface areas were taken as reported by the investigators themselves, and include some measured by nitrogen sorption and others with carbon dioxide. It should be noted that the data sets represented in Figures 1 and 2 are not identical, because the data were not always available to include results on both plots. It is perhaps surprising that converting data to a surface area basis does little to reduce the amount of scatter in the data. It is worth noting that the degree of scatter is not unlike that observed in similar summary plots of data on the oxygen-carbon reaction [9]. Thus it appears as though there is a high degree of variability of carbon reactivity towards NO, just as there is towards oxygen. This has been attributed to differences in the numbers of active sites per unit surface area. It is not yet possible to predict this value. It is interesting to note that the graphites exhibit relatively high reactivities per unit surface area. There is, however, no clear trend in reactivity with the nature of the carbon.

The results of Figures 1 and 2 present a confusing picture of the factors that influence the reactivity of carbons towards NO. While small subsets of the data can be compared and logical hypotheses drawn regarding the influence of certain variables, there is not yet an ability to predict reactivity to better than orders of magnitude uncertainty. The problem with an approach based upon comparing reactivities from literature accounts is that there are a number of experimental variables that may have had an influence on reactivity, and these are never completely controlled or reported. Most of these variables have to do with how the carbon is prepared, but some might also have to do with how the reactivities were determined. The remainder of this paper will explore how measured reactivities can be influenced by a number of experimental factors.

EXPERIMENTAL

Two different reactor systems were selected for study, in order to represent the two most widely employed techniques for study of this reaction. The first reactor system was a thermogravimetric

analyzer (TGA). In this case, a TA Instruments TGA was employed. As compared with the Cahn TGA system in which we had performed most of our earlier work [1,2], the TA Instruments TGA has a somewhat smaller enclosed gas volume. Thus, the experiments were performed with a continuous gas flow through the TGA to ensure that depletion of NO was not significant. The TGA work was performed, as earlier [1,2], at quite high NO partial pressures, ranging from about 1 to 10 kPa of NO partial pressure.

Many of the studies reported in the literature have employed packed bed reactors. One of the advantages of these systems is that they more realistically simulate possible "end-of-pipe" reduction systems. They also tend to be less complicated to operate, allowing for a steady flow of NO-containing gas which is continuously analyzed using an NO_x analyzer. Operation at lower, more realistic, NO concentrations is also possible. Operation of a TGA at low NO concentrations is often considered impractical, because of the long times needed to achieve significant burnoff (weight loss).

In our case, we employed a 4 mm ID packed tubular reactor, made of quartz. A bed of between 20 and 200 mg of carbon (char) was packed into a predetermined length of between 1 and 30 mm, depending upon the conditions to be studied. The bed was held in place with quartz wool. Blank runs indicated no significant NO reduction in the absence of carbon (this was not the case if ordinary glass wool was employed). A carrier flowrate between 70 and 125 cc/min of helium was passed through the reactor. In the work considered here, the only other component in the inlet gas was NO. The inlet NO concentration ranged between 100 and 300 ppm. The particle size in the bed was approximately 200 μm in all cases. Before all runs, the surface of the char was cleaned of oxides by heating at 1173 K for one to two hours.

RESULTS AND DISCUSSION

Several different carbons were tested in the TGA, using a consistent protocol. The samples examined were a resin char (ex-phenolformaldehyde) that we had earlier extensively studied [1,2], a graphite powder (from AESAR/Johnson Matthey Company), a coconut char (from Fisher Scientific), and a Wyodak coal char, prepared from a sample obtained from the Argonne Premium Coal Sample Program. The results are shown in Figure 3.

The results of Figure 3 show that this wide range of carbons gives fairly consistent rates, when the results are represented on a unit surface area basis. The one exception is the rates from our earlier work [1,2], and the reasons for this will be discussed below. It should be noted that the carbons range from those of quite high purity (the phenolic resin char and the graphite) to a mineral-containing coal char. The good agreement between the carbons and chars might be attributable to the fact that an effort was made to compare highly heat treated materials, in this case. The coconut char and graphite were used as-received (apart from surface cleaning at 1273 K for one hour). The phenolic resin char and the Wyodak char were prepared by a two-hour pyrolysis at 1223 K, and then surface cleaned prior to use. Thus for carbons and chars which may be considered as "old" there is quite good agreement in reactivity. Further tests, which will be reported separately, have not surprisingly indicated that the "age" of a char (i.e., how severely it is heat treated) does indeed have some effect on its reactivity. Here, however, it came as a surprise that the aging seems to lead to similar reactivities towards pure NO, despite significant differences in contents of impurities.

Figure 3 also indicates that the "break" in the Arrhenius plots depends upon the type of carbon. It can be seen that the break occurs at a much higher temperature in the graphite than in the other carbons. The agreement between the reactivities of the different carbons, on a per unit mass basis, was not nearly as good. In fact, the results gave a spread similar to that seen in Figure 1. Thus it appears that the reactions occur in Zone 1, and that the micropore area of the carbons is significant.

When our earlier TGA results on the same resin char are compared with those from the present study, there appears to be a significant difference (see Figure 3). This turned out to be a consequence of how the sample was prepared, and indicates an important consideration in developing experimental testing procedures. The extent to which the resin char surface was cleaned of oxides was responsible for the differences in the observed rates. In our earlier work [1,2], the reactivity of the resin char was established as a function of temperature, merely by varying temperature and recording what appeared to be pseudo-constant rates. This might be considered a "normal" experimental procedure. In this more recent work, it was learned that by cleaning the surface of oxides, by heating at 1273 K for an hour between each temperature to be studied, the resulting pseudo-steady mass loss rate was significantly higher. This means that the oxide population on the char surface is a function of the reaction history of the sample, and that this, in turn, influences the observed rate. What may appear to be a pseudo-steady state rate might actually be slowly evolving, as the oxide population readjusts on a timescale longer than that used to obtain the rate. We had actually noted the same problem earlier, in connection with determination of the reaction order with respect to NO [1]. Failure to clean the surface between different partial pressures gave an apparently less than unit order with respect to NO, since the surface oxide population could only very slowly adjust to the new NO partial pressure. Thus it is essential to report how kinetic experiments are performed, in order to establish a sample reaction history. Without this information, comparison of rate data from the literature may be quite misleading. Once this aspect of the process was noted, all our experiments were performed on a self-consistent basis, with surface oxide cleaning between each temperature step. Because we are measuring rates

on a virgin surface in each case, issues related to the influence of remaining oxides on rate are minimized. Further experiments in the TGA again established that the reaction is unequivocally first order with respect to NO partial pressure, validating the form of the rate constant used in Figures 1 through 3 (see Figure 4).

Generally, good agreement was obtained between the rate constants from the TGA and packed bed experiments, despite the fact that there was about a two order of magnitude difference in the concentrations of NO in the two reactor systems (around 2% in the TGA vs. 200 ppm in the packed bed reactor). Results for the coconut char in Figure 5, illustrate this conclusion. Further discussion of the small differences will be presented elsewhere. Thus apparently large differences in reactivity in Figures 1 and 2 are not attributable to what type of reactor system is used for testing, nor to the concentration level of NO employed. It is clear that the purity of the gas feed is important in determining the apparent reactivity; small amounts of oxygen affect rates significantly. This will be reported on elsewhere. We have further established, consistent with an earlier presented hypothesis [10], that it is difficult to obtain reliable reaction order information from packed bed experiments. This will also be reported elsewhere.

ACKNOWLEDGEMENT

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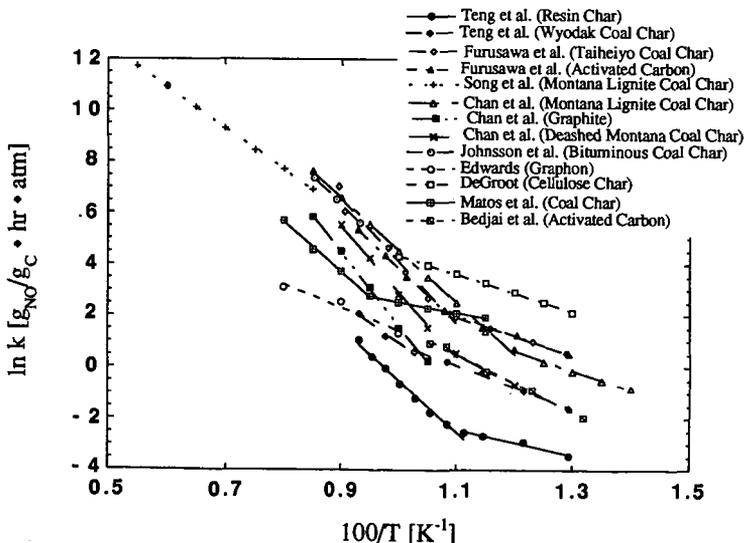


Figure 1. NO-carbon reaction rate constant, per unit mass of carbon reactant.

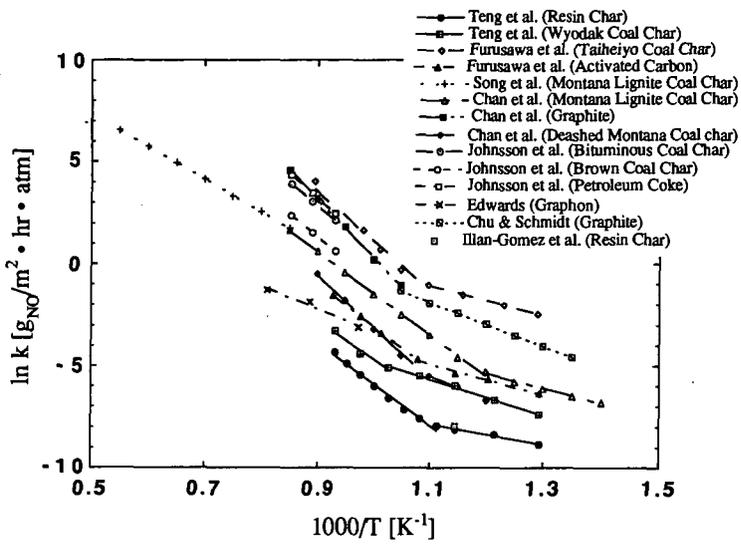


Figure 2. NO-carbon reaction rate constant expressed on a surface area basis

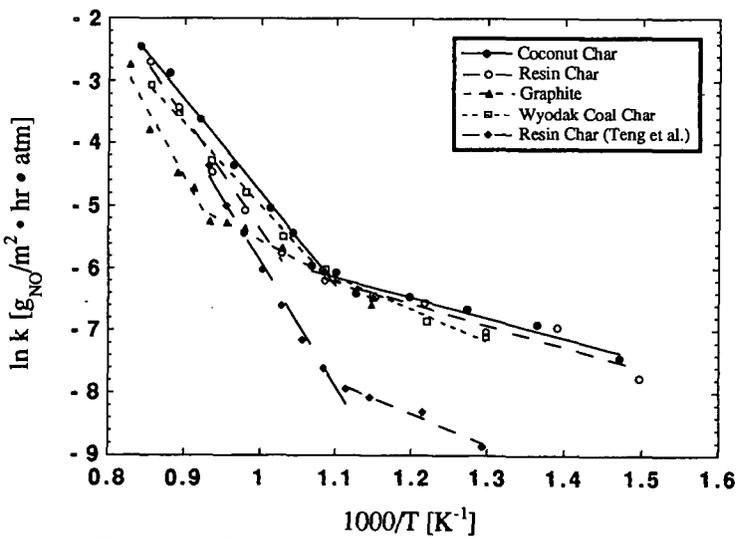


Figure 3. NO-carbon reaction rates from TGA experiments.

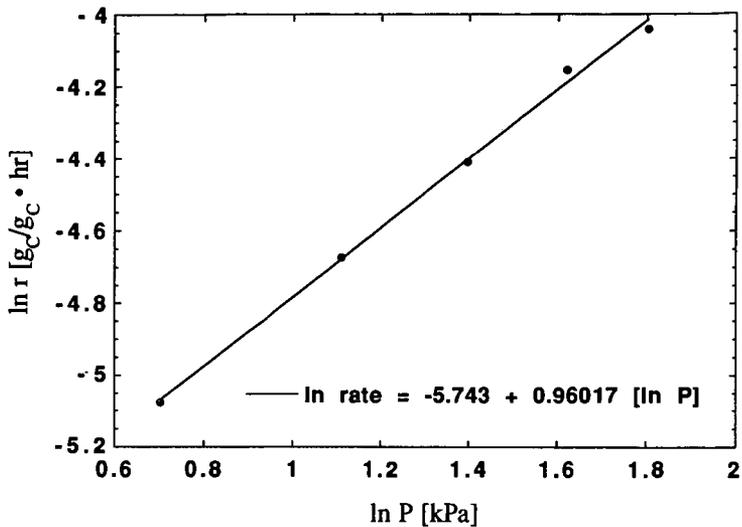


Figure 4. Reaction rate of resin char in the TGA, showing first order rate. ($T=600^\circ\text{C}$)

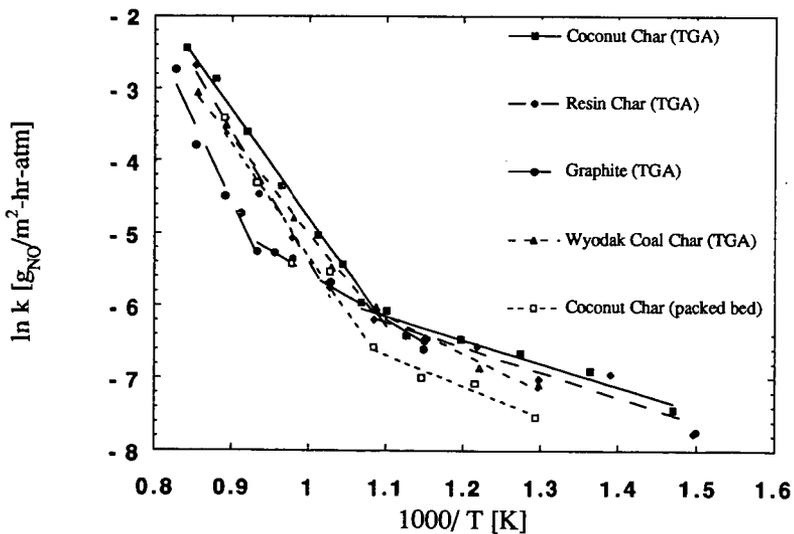


Figure 5. Comparison of rates obtained on various samples, in the TGA and packed bed reactor.

REMOVAL OF NO_x OR ITS CONVERSION INTO HARMLESS GASES BY CHARCOALS AND COMPOSITES OF METAL OXIDES

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Keywords: adsorption, charcoal, metal oxide

Introduction

In recent years, much attention has been devoted to environmental problems such as acid rain, photochemical smog and water pollution. In particular, NO_x emissions from factories, auto mobiles, etc. in urban areas have become worse. To solve these problems on environmental pollution on a global scale, the use of activated charcoal to reduce air pollutants is increasing. However, the capability of wood-based charcoal materials is not yet fully known. The removal of NO_x or its conversion into harmless gases such as N₂ should be described.¹⁾ In this study, the adsorption of NO over wood charcoal or metal oxide-dispersed wood charcoal was investigated.

In particular, carbonized wood powder of Sugi (Cryptomeria japonica D. Don) was used to study the effectivity of using these materials in adsorbing NO_x. Since wood charcoal is chemically stable, metal oxide with the ability of photocatalysis was dispersed into wood charcoal to improve its adsorption and capability to use the light energy effectively.

Experimental method

1. Carbonization method

Wood meal of Sugi (Cryptomeria japonica D. Don) was carbonized in electric furnace with the desired carbonization temperatures of 300, 400, 500, 600, 700 and 800°C. The temperature was increased at the rate of 4 °C/min, and then kept constant for 1 hour after reaching the desired temperature.

2. Metal oxide-dispersed wood charcoal

Wood charcoal with a weight of 0.5 g was soaked in solution of Titanium (IV) alkoxide dissolved in about 5 ml 1-propanol. The charcoal was then oven-dried at 105 °C for 24 hours.

3. Adsorption method

NO_x gas of about 100 ppm was passed through the reaction tube with 0.5 g of wood charcoal or metal oxide-dispersed wood charcoal. The concentration of NO_x gas was measured by gas detectors. During measurement, the reaction tube was lighted up or covered by black shield.

Results and Discussion

The relationship between carbonization temperature and adsorption of NO in light and dark reactions is shown in Fig. 1. Based from the results, the adsorption was highest in 600°C. It was previously thought that in using wood charcoal, there will be no difference between light reaction and dark reaction. However, based from the results, adsorption was better in dark reaction than light reaction. As reflected, higher adsorption is observed in all the carbonization temperatures in the light reaction.

As shown in Fig. 2, adsorption of NO is different when charcoal is soaked in titanium oxide. Adsorption is better in light reaction when greater amount of titanium oxide is used as observed in all the carbonization temperatures studied. It seems that titanium oxide oxidized NO gas by light energy. However, in this study the source of light reaction was a fluorescent light. If the light with the suitable wavelength is irradiated to the titanium oxide-dispersed wood charcoal, the adsorption ability may be better.

Fig. 3 shows the relationship between carbonization temperature and adsorption of NO in light and dark reaction using the same percentage of titanium oxide. It is clear that adsorption is better in light reaction than dark reaction in all the carbonization temperatures. This is because titanium oxide plays an important role in the light reaction. Further, higher adsorption is observed in high temperature carbonized materials.

Conclusion

The adsorption of NO over wood charcoal was better in dark reaction than light reaction. Higher adsorption is observed in all the carbonization temperatures in the dark reaction although the highest adsorption is observed in 600 °C.

On the other hand, 800 °C was observed to adsorb more when soaked in titanium oxide. It can be concluded that the use of titanium oxide is very effective in improving the adsorption of NO especially in light reaction. Further, adsorption is better in light reaction when greater amount of titanium oxide is used as observed in all the carbonization temperatures studied. It seems that titanium oxide oxidized NO gas by light energy.

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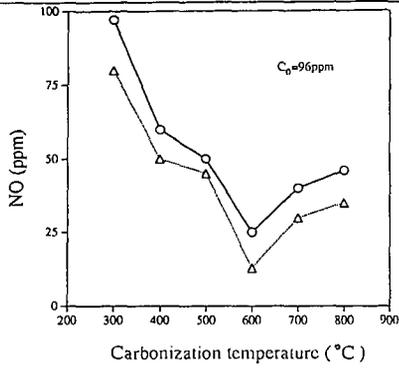


Fig.1 Adsorption of NO over charcoal
Notes: C_0 : Initial concentration of NO

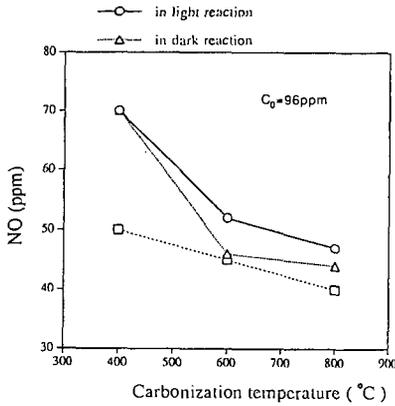


Fig.2 Adsorption of NO over charcoal materials in light reaction

Notes: C_0 : Initial concentration of NO

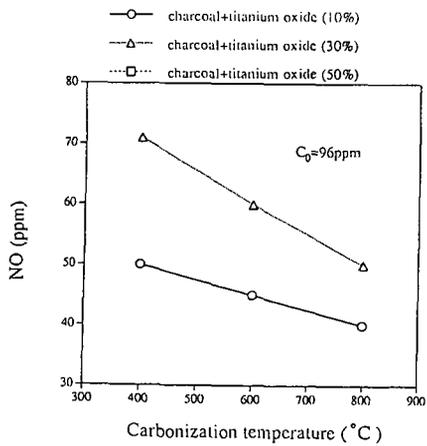


Fig. 3 Adsorption of NO over charcoal materials

Notes: C_0 : Initial concentration of NO

- charcoal+titanium oxide (50%) in light reaction
- △ charcoal+titanium oxide (50%) in dark reaction

NO REDUCTION BY POTASSIUM CONTAINING COAL BRIQUETTES. EFFECT OF
MINERAL MATTER CONTENT AND COAL RANK

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INTRODUCTION

Carbons and activated carbons have been proposed as reducing agents for NO removal from exhaust gases as well as for applications to vehicles and other small sources¹⁻³. The use of carbon for NO reduction could present advantages over gaseous reactants used in conventional technologies⁴. Moreover, coals could be bindered and pyrolyzed in order to obtain carbon briquettes with good mechanical strength that will resist abrasion⁵.

Recently, a method for briquette preparation and its use as NOx reducing agent has been presented⁶. This novel manufacture method presents the advantage of using a binder agent which inherently contains potassium. Illán et al.^{7,8} found that potassium acts as catalyst of the NO-carbon reaction. In a previous paper⁹, it was found that potassium containing coal briquettes have an activity similar to that of activated carbons with potassium remaining from the preparation method although, they were not as active as activated carbon oxidized with HNO₃ and ion exchanged with potassium acetate⁸. The study⁹ was conducted using only one type of coal precursor but, as the NO-carbon reaction is a gasification reaction, it is expected that both the coal rank and the mineral matter content affect the NO reduction¹⁰.

The objective of this study is to analyze the effect of coal rank and mineral matter content in the NO reduction activity of potassium containing coal briquettes.

EXPERIMENTAL

Four coals of different rank have been selected as raw material for the briquette preparation. An anthracite (UA1), a high volatile A bituminous (A3), a high volatile C bituminous (P) and a lignite (LY). To study the effect of mineral matter content, two fractions of coal A3 with very different ash content (8% and 25%), denoted as A3 and A3' respectively, have been used. These fractions were obtained using two portions of the raw coal with different particle size ($0.71 < \phi < 1.40$ and $\phi < 0.71$ mm, respectively). To prepare the briquettes raw coals were grounded and sieved to a particle size of $0.1 < \phi < 0.2$ mm.

Commercial humic acid (liquid with a density of 1.12 g/cm³ and a potassium content of 0.049 g/cm³) has been used as binder agent for briquette preparation. The method was previously described^{6,9}. In summary, a coal sample is impregnated with a variable binder volume depending on the humic acid/coal ratio desired, mixed for 30 min, dried at 110°C, pressed (1-2 Kg/cm²) and pyrolyzed in N₂ for 2 h at 700°C. Potassium content was determined after the pyrolysis step by atomic absorption spectroscopy by AES-ICP.

After pyrolysis, a test was conducted to determine mechanical

strength of the briquettes. The impact strength test was previously described⁹. All the briquettes described in this paper have satisfactory values, independently of the humic acid/coal ratio.

The kinetics of the NO-carbon reaction were studied at atmospheric pressure in a fixed-bed flow reactor (15 mm, i.d.; ca. 300 mg sample) connected to a gas chromatograph (Hewlett Packard, Model 5890A). The reactant mixture used was: 0.5% NO in He using a 60 ml/min flow rate, which resulted in a bed residence time of 0.56 s. NO, N₂, N₂O, CO₂ and CO were analyzed using a Porapak Q 80/100 column and a thermal conductivity detector. Briquettes were ground to < 1.5 mm to introduce them in the microreactor.

Two types of experiments were performed: i) a temperature programmed reaction (TPR) at a linear heating rate of 5°C/min up to a maximum temperature of 900°C; and ii) an isothermal reaction at 300, 400, 500 and 600°C for 120 minutes. The samples were treated in helium at 50°C/min, up to 900°C for 10 minutes prior to the reaction. In case i), the temperature is lowered to ambient temperature and He replaced by the reactant mixture. In case ii), the temperature is lowered to the desired level and the isothermal experiment is initiated by substituting He by the NO/He mixture. The reaction products were monitored in both cases, thus allowing detailed oxygen and nitrogen balances to be determined.

RESULTS AND DISCUSSION

Table 1 presents the results for sample preparation, consisting of coal precursor, humic acid to coal ratio (HA/C), yields of the pyrolysis process and sample nomenclature including final potassium content. It is interesting to note that samples prepared, with the same HA/C (1.20), using the different coal precursors present a very different potassium content which is higher as coal rank decreases. This fact must be due to two phenomena, the increase in weight lost during pyrolysis from the anthracite to the lignite, as observed in the values of pyrolysis yield (Table 1) and the higher oxygen surface groups as coal rank decreases¹¹, that are mainly responsible for potassium anchorage¹².

For a fixed coal, an increase in HA/C produces an increase in potassium content up to a limit value, this could be observed in the series prepared from coals P and LY (Table 1). For coal P, an increase from 0.8 to 1.2 in HA/C only produces a 20% increase in potassium content while from 0.4 to 0.8 it increases in 100%. The specific activity (per gram of potassium) decreases, for a given coal precursor, with increasing potassium content. This behaviour was previously observed and explained for potassium impregnated activated carbons⁸.

To study the effect of coal rank, briquettes with similar potassium contents have been prepared from coals UA1, P and LY. Figure 1 presents the results of specific activity determined at steady state conditions, at different temperatures, as a function of percentage of fixed carbon in the coal precursor. It is clearly observed a decrease in activity as the coal rank increases. Briquettes prepared from lignite (LY) has a much higher activity. It may be observed that the same value is found for sample LY-1.9 at 400°C and for sample P-1.5 at 600°C. A reduction of 200°C in the process temperature is very important for a practical point of view. It is also interesting to note that the ash content of coal LY is very low (0.5 wt%) in comparison to UA1 (7.0 wt%) or P (16.7 wt%). Both low rank and low ash content could be responsible for

the high activity, as we will discuss later. Sample LY-1.9 has an activity as high as that of an activated carbon, oxidized with HNO_3 and ion-exchanged with potassium acetate¹³. The behaviour of both samples for NO reduction in the temperature range studied (300-600°C) is very similar. These results confirm that, if very reactive low rank coals are used as precursors, the briquetting process can produce very active samples, with the advantage of higher mechanical strength and in a very simpler procedure.

Figure 2 shows the activity plots for briquettes A3-4.7 and A3'-3.6. As already mentioned in the experimental section, these samples were prepared from two portions of coal A3 containing different ash content. At 600°C the behaviour is not very different for the two samples although, at steady state conditions the activity level is more constant for the sample prepared with low ash content coal. At 500°C, the difference is dramatic. Sample A3'-3.6 very much deactivates presenting a very low activity at steady state conditions.

To explain these results, the analysis of reaction products, mainly N_2O , N_2 , NO, CO_2 and CO, during TPR experiments are presented in Figures 3 and 4. Similar results were obtained for potassium containing activated carbons⁸. The profiles can be described as follows:

i) An initial period from 100 to 300°C with NO uptake reaching a maximum about 150°C. In this zone N_2O and N_2 are the only products.

ii) A second period from 300 to 600 °C, where NO reduction activity increases with temperature. In this zone N_2 and CO_2 are the main products.

iii) Above 600°C, N_2 becomes constant, the 100% NO reduction is reached and CO begins to evolve being the majority product at about 800°C. The CO appearance coincides with the complete disappearance of NO.

However, an important difference is observed in these plots in comparison to those of potassium containing activated carbons. The CO_2 evolution reaches a maximum at 620-650°C that is typical of most of the briquette samples⁹.

For potassium containing activated carbons⁸, an excess CO_2 in relation to N_2 (both the main reaction products at this temperature range) was observed forming a broad band but, no single peak appeared. In a previous study⁹, the CO_2 peak, appearing in the TPR of coal briquettes has been attributed to K_2CO_3 decomposition, considering the temperature range of appearance. The area under the peak allows to calculate the carbonated potassium during TPR experiment. This portion of the metal will be inactive as catalyst for the reaction⁸. The results in Figures 3 and 4 explain the large difference in activity at 500°C for samples A3-4.7 and A3'-3.6. For the second one (Figure 4) an 88% of the catalyst is in the carbonated form while only 25% for the former one (Figure 3). At 600°C, the K_2CO_3 decomposition starts and the activity is very similar for both samples.

At present, it is not probed the origin of the negative effect of mineral matter, present in the raw coal, that produces an increase in the K_2CO_3 formation. The hypothesis that is being investigated,

it is that mineral matter acts as a sink for potassium, producing a lower dispersion and consequently larger particles that will be easier carbonated in the reaction conditions since most part of the catalyst is not in contact with the carbon substrate.

CONCLUSIONS

NO reduction activity of potassium containing coal briquettes depends on coal precursor rank. Regarding samples with similar potassium content the activity increases with decreasing coal rank. Coal rank also affects potassium content of the briquettes. Using a similar humic acid to coal ratio the lower the coal rank the higher the potassium content. Briquettes prepared from low rank coals are as active as potassium ion-exchanged activated carbons which need a much more complicated preparation method. Mineral matter in the coal precursor produces deactivation of potassium catalyst, favoring the K_2CO_3 formation in reaction conditions.

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TABLE 1. Briquette preparation

Coal precursor	Humic acid/ coal ratio	pyrolysis yield (%)	Briquette nomenclature
UA1	1.20	88.1	UA1-1.3
A3	1.20	72.0	A3-4.7
A3'	1.20	---	A3'-3.6
P	0.40	---	P-1.5
P	0.80	---	P-3.2
P	1.20	65.2	P-3.9
LY	0.25	52.1	LY-1.9
LY	0.78	53.4	LY-6.0
LY	1.20	53.4	LY-7.2

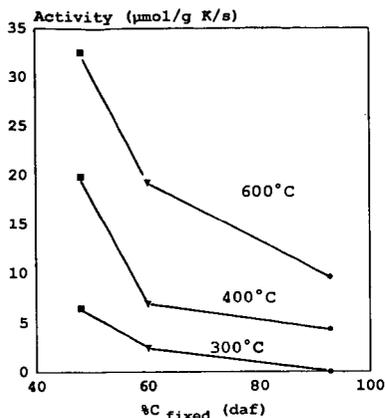


Figure 1. Briquette specific activity for NO reduction versus fixed carbon of coal precursors. (•UA1-1.3, ▼P-1.5, ■LY-1.9)

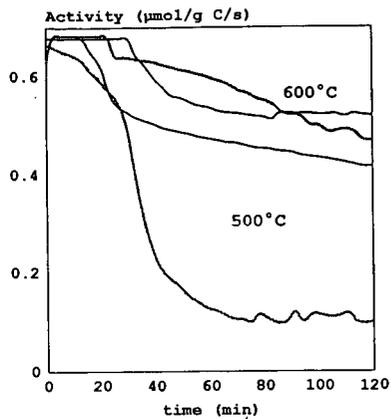


Figure 2. NO reduction activity curves. (—A3-4.7, —A3'-3.6)

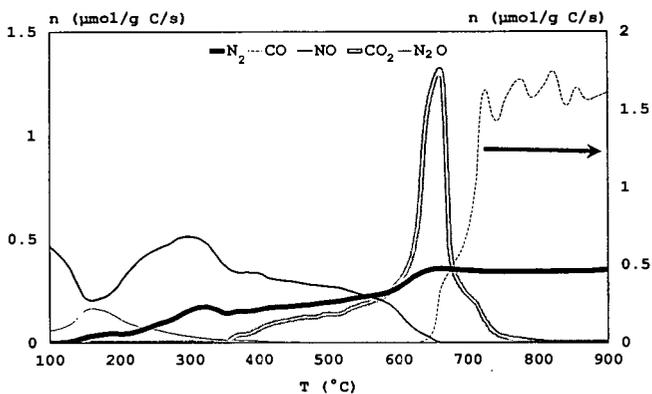


Figure 3. TPR gas composition profiles for briquette A3'-3.6.

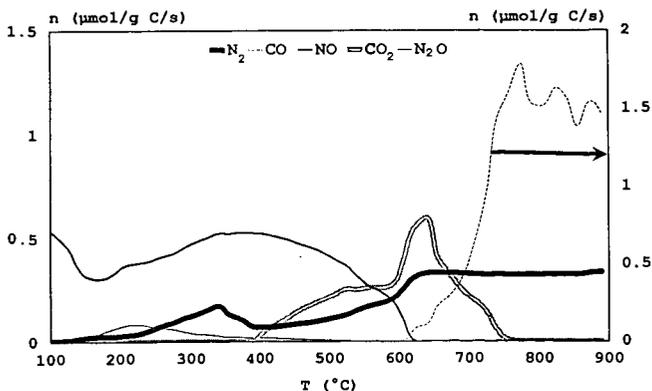


Figure 4. TPR gas composition profiles for briquette A3-4.7.

ACTIVATED CARBON USE IN TREATING DIESEL ENGINE EXHAUSTS

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Keywords: Diesel engines; NOx control

INTRODUCTION

Diesel engines, both stationary and mobile, are major sources of air pollution. Pollutants of concern are solid and liquid particulates, nitrogen oxides (NOx), toxic hydrocarbon gases, and, in some cases, sulfur dioxide (SO₂). Approaches considered in the past to reduce these pollutants have included modifying the engine design, modifying the fuel composition, recirculating the exhaust gases, and installing a device or system on the exhaust gas stream to remove or modify the undesirable constituents. Of particular concern to the U.S. Air Force are the high levels of NOx that are present in their diesel engine exhaust gases. Sorbent Technologies Corporation (Sorbtech) engineers, during the past two years, have been examining and developing ways to remove NOx from these exhaust gases.

The principal NOx species in diesel engine exhaust gases is nitric oxide (NO). Typical NO levels range from 100 to 1200 ppm. Higher NO levels generally occur with higher engine loads that result in higher engine temperatures.

Both stationary and mobile diesel engines are employed at Air Force sites. Typical stationary engines produce back-up electrical power at critical sites, such as at computer or hospital locations. Mobile diesel engine applications include portable or mobile generators, air heaters, air-conditioners, and incinerators, small and large trucks, and buses. Each engine application presents its own problems because each has different space constraints and each produces gases with different characteristics of temperature, flow rates, and composition.

At least four different methods have been used in the past to remove nitrogen oxides (NOx) from waste gases. These methods include (1) selective catalytic reduction, (2) selective non-catalytic reduction, (3) reaction of the oxides with water or alkali solutions, and (4) sorption by a solid sorbent. The first two methods are receiving most attention today. In selective catalytic reduction, ammonia is commonly injected into the waste gas stream and the combination is passed across a catalyst to reduce nitrogen oxides to nitrogen and water. Disadvantages of this approach include high cost, narrow temperature range of applicability, and ammonia emissions into the atmosphere. In selective non-catalytic reduction, ammonia or urea is injected into the engine or combustor itself or into the gas leaving the engine where temperatures are very high. Disadvantages of this approach are low NOx removals and the problems associated with the handling of ammonia or urea. Reaction of the oxides with water or alkali has seen only limited success because of NO, the principal NOx species in most gases, does not readily dissolve in water or react with alkali in aqueous solutions.

APPROACH

Sorbtech engineers have adopted two separate approaches in treating exhaust gases from stationary diesel sources and from mobile diesel sources. Each approach involves the use of activated carbon, but in different manners.

Few materials sorb NOx well. An exception is activated carbon under certain conditions. Specially prepared activated carbons can sorb 10 percent or more of their weight in NOx under ideal conditions. After NOx is sorbed at a low temperature, heating the carbon to a higher temperature can release it. This process of sorbing NOx at a low temperature with activated carbon and releasing it at a high temperature has been used commercially in the past. This approach was pursued in treating exhaust gases from mobile sources.

An observation by Sorbtech engineers made possible a second approach for use with stationary sources. It was found that certain activated carbons, when saturated with NOx, act as a catalyst for the rapid conversion of NO to NO₂, in the presence of oxygen. The resulting gas stream containing principally NO₂, instead of NO, was then observed to be readily treatable with water alone or with alkali solutions. This approach was pursued in treating exhaust gases from stationary sources.

MOBILE DIESEL-ENGINE APPLICATIONS

System Design

The concept for mobile applications consists of two steps: (1) capture of NO_x with an activated carbon filter; and (2) regeneration of the filter after it is saturated. The concept is shown schematically in Figure 1. For mobile applications, Steps 1 and 2 are generally performed at two separate locations. In Step 1, the use of a prefilter is recommended to remove particulates before the saturated carbon bed. Diesel engine exhaust gases usually contain huge amounts of particulates. Not only do large puffs of black particulates occur during engine start-up and during power changes, but smaller, PM-10 particles are emitted during all running conditions. Particle traps can be employed to effectively remove these particulates. A special vermiculite-based filter developed by Sorbtech likewise does an effective job in reducing particulates, particularly PM-10 particles. In Step 2, the carbon bed is regenerated by simply heating the bed. The NO_x released during regeneration is destroyed by reaction with natural gas over a special catalyst developed by Sorbtech. The products of reaction are nitrogen, CO₂ and H₂O.

Figure 2 shows a mobile filter cart designed and constructed by Sorbtech to control emissions from Air Force mobile diesel generators. The cart was designed to be attached to the portable generator unit and to move with it to the usage location. Twenty-four separate activated carbon filters are employed on this cart. When saturated, the individual filters are removed from the cart and are processed in a separate regeneration/NO_x-destruction unit.

Experimental Studies

The effectiveness of activated carbon filters in reducing the levels of NO_x and CO in exhaust gases from a mobile diesel generator was examined in studies at Wright Patterson AFB, Ohio. The results of these studies are listed in Table 1. Two filter designs were considered, one consisting of 9 inches of activated carbon alone and a second consisting of 6 inches of a vermiculite-based sorbent followed by 6 inches of activated carbon. The supplier of the carbon was Calgon Carbon Corporation. The exhaust gas was cooled to 60°-100°F before entering the beds. During each run, the activated carbon bed temperatures increased to 110°-120°F due to heat of adsorption. The total run time was several hours. The residence time and flow rate of gas through the filters were 1.0 second and 40 SCFM, respectively.

The results of these runs showed that average NO_x removals of 54 to 64 percent were achieved. These results agreed well with earlier laboratory results. Laboratory results showed that NO_x removals were a strong function of space velocity. Because lower overall gas velocities will occur with the mobile filter cart, higher NO_x removals with this unit can be expected.

STATIONARY DIESEL-ENGINE APPLICATIONS

System Design

The system developed to cleanse NO_x and other contaminants from stationary diesel-engines exhaust gases is shown schematically in Figure 3. This system consists of four components: a prefilter (to remove particulates); a gas cooling means; an activated carbon bed; and a NO₂ scrubber. The key component in this system is the activated carbon bed that converts NO to NO₂.

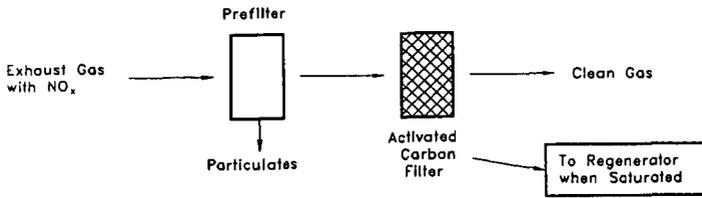
Experimental Studies

A number of carbons were examined for their ability to first sorb NO_x and then convert NO to NO₂. Two materials, one supplied by Calgon Carbon Corporation and one, an experimental char, supplied by the Illinois State Geological Survey proved to be particularly effective.

In one test, for example, an 8.0 gram bed of activated carbon was exposed at 26°C to a simulated exhaust gas having the composition: 460 ppm NO, 50 ppm NO₂, 10 wt% oxygen, and balance nitrogen at a flow rate of 4 liters per minute. The bed was exposed for 60 hours. Figure 4 shows the levels of NO and NO₂ entering and exiting the bed during the 60-hour exposure. In this figure, it can be seen that during an initial period, both NO and NO₂ were sorbed. After this period, however, NO ceased to be sorbed, but instead the NO partially passed through the bed and partially was converted to NO₂. After a time, about 15 hours in this case, an equilibrium occurred in the ratio of NO converted to NO₂ and the level of NO passing through the bed. In this run, a conversion of NO to NO₂ of over 75 percent was achieved.

In separate experiments, the ability of water and alkali solutions to scrub NO₂ and NO from gas streams was studied. Water alone was not effective in removing NO from gas streams, and concentrated alkali solutions were only partially effective. Water alone, however, was effective in removing the majority of the NO₂ present, and alkali solutions removed NO₂ almost completely.

SORPTION



REGENERATION

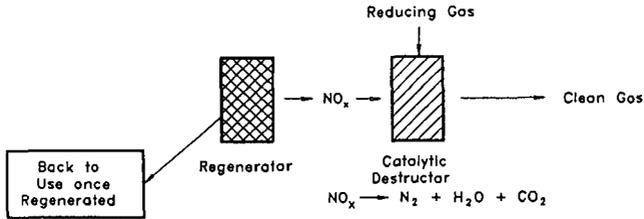


Figure 1. Two-Step Process for NO_x -Control-Mobile Applications

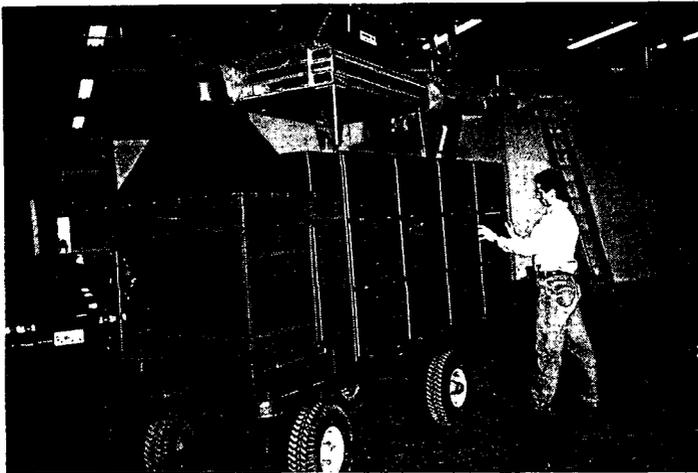


Figure 2. Activated Carbon Beds on a Mobile Filter Cart for Controlling NO_x Emissions

TABLE 1. TEST RESULTS AT WRIGHT PATTERSON AFB
ON MOBILE DIESEL-ENGINE
EXHAUST GASES

Gas Composition			
	Entering Filter	Leaving Filter	Average Removal Rate
9" Activated Carbon			
NO	1000 ppm	320 ppm	68%
NO ₂	200 ppm	120 ppm	40%
NO _x	1200 ppm	440 ppm	63%
CO	200 ppm	200 ppm	0%
O ₂	15%	15%	0%
6" Vermiculite Sorbent + 6" Activated Carbon			
NO	800 ppm	345 ppm	57%
NO ₂	300 ppm	205 ppm	32%
NO _x	1100 ppm	550 ppm	50%
CO	100 ppm	100 ppm	0%
O ₂	16%	16%	0%

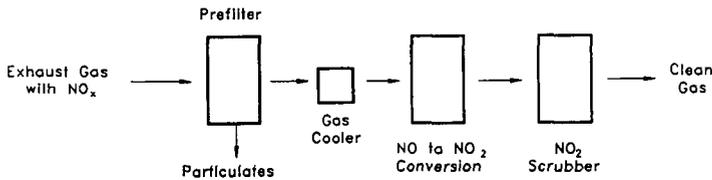


Figure 3. Single-Step Process for NO_x Control-
Stationary Applications

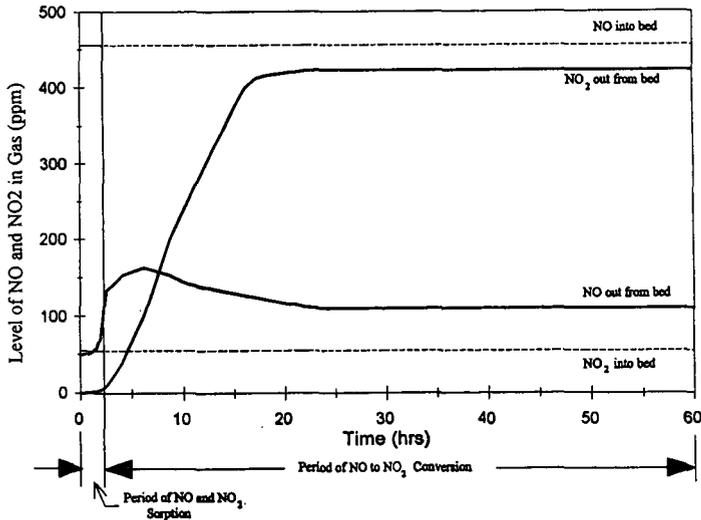


Figure 4. NO to NO₂ Conversion at Room Temperature

PRESSURE ENHANCED REVERSIBLE ADSORPTION OF NO_x BY ACTIVATED CARBONS

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Keywords: NO_x, pressure, adsorption, carbon

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 NO_2 , O_2 and CO_2 were desorbed was different during pressure release versus temperature induced desorption. During pressure release, the evolution of O_2 and CO_2 began immediately and maximized at approximately 115 s before the peak in the NO_2 desorption. During a thermal desorption cycle, the peak for NO_2 occurred 150 s before the CO_2 desorption peak; the temperatures of these maxima were 140 and 155°C for NO_2 and CO_2 , respectively. It is likely that, whatever the source of the CO_2 in the mass spectral data, the origin of the CO_2 detected during pressure release was different than the origin of CO_2 during temperature induced desorption. Because only a trace amount of O_2 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 NO_2 released from the carbon increased with increasing adsorption pressure. In contrast, the amounts of stored O_2 and CO_2 did not appear to be uniformly affected by pressure. To quantify the relative contribution of NO_2 , CO_2 , and O_2 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 NO_2 (g carbon)⁻¹ was adsorbed if O_2 was not present in the reactant gas⁷⁻¹¹. This value is approximately 2% of the mass uptake for the case of simultaneous exposure to $\text{NO} + \text{O}_2$. During the CO_2/O_2 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 CO_2/O_2 . The remainder of the mass uptake for the carbons was the result of $\text{NO} + \frac{1}{2} \text{O}_2 \rightarrow (\text{NO}_2)_{\text{adsorbed}}$.

The relative percent of reversibly and irreversibly adsorbed NO_2 removed from the sample is given in Figure 7. At 70°C and atmospheric pressure, approximately 65% of the NO_2 in the carbon was reversibly desorbed; this percentage increased to 80% at 250 psi. At 100°C and atmospheric pressure, approximately 75% of the NO_2 in the carbon was reversibly desorbed; this percentage increased to greater than 95% at 250 psi. Hence, increased pressure decreased the relative amount of NO_2 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 NO_2 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. NO_2 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 , O_2 , and CO_2 adsorbed in the micropores should be expected to be small in comparison to the amount of NO_2 (see Figure 6). However, at 250 psi and 70°C, the amount of CO_2 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 CO_2 condensation since the critical temperature for CO_2 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 NO_2 adsorption is its high van der Waals force constant, a , which is 1.5 times greater than the a constant for CO_2 . Therefore, the attractive force between NO_2 molecules upon entering the pores would be greater than for CO_2 . This difference may account for the desorption of CO_2 before NO_2 during pressure release. During temperature induced desorption, the evolution of CO_2 subsequent to NO_2 desorption may be related to the gasification of carbon at C-O bonds.

The total amount of gaseous NO_2 (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 zeolites⁷. In addition, the amount of irreversibly adsorbed NO_2 in the activated carbon at 250 psi and 100°C is less than 5% of the total amount of adsorbed NO_2 . Such a value is as good as or less than values reported for the cation-exchanged zeolites.

SUMMARY AND CONCLUSIONS

The amount of NO_2 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 NO_2 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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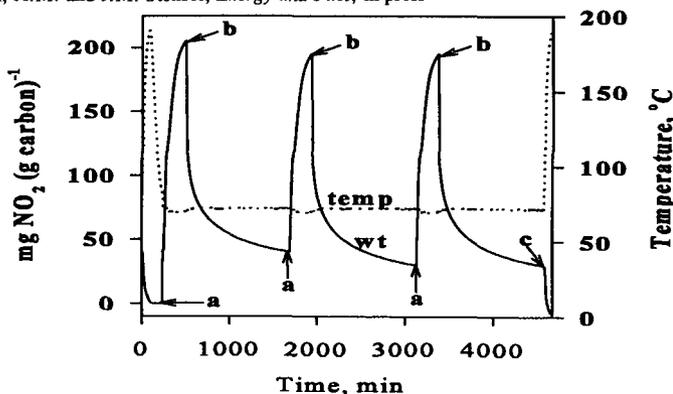


Figure 1. Adsorption - desorption profile for activated carbon.

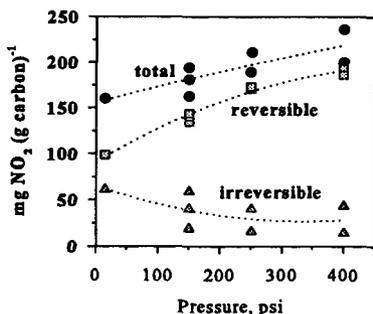


Figure 2. Plot of total, irreversible, and reversible adsorption versus pressure.

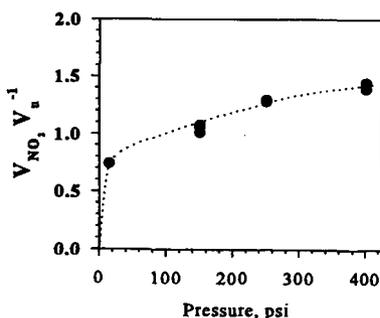


Figure 3. The type I adsorption isotherm for 70°C adsorption on activated carbon.

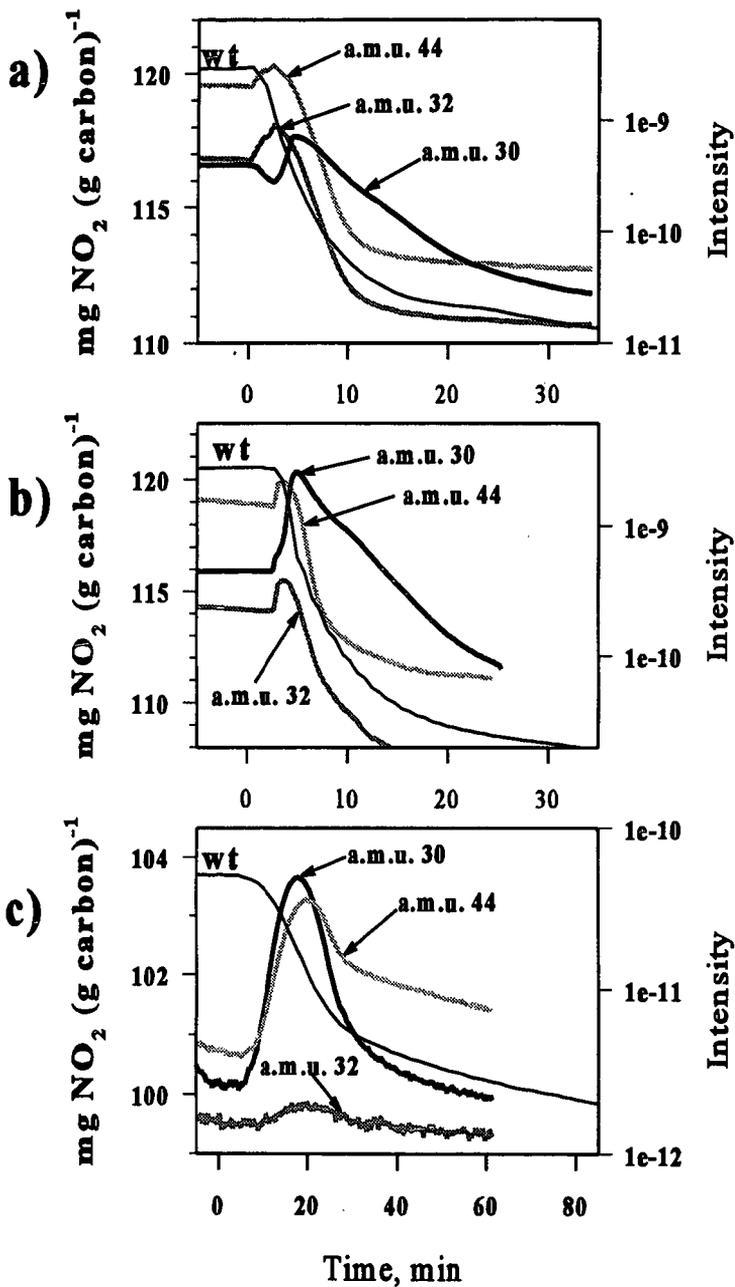


Figure 4a, b, c. Integrated weight loss - mass spectral data for pressure-release and thermal-induced desorptions; 4a) pressure-release from 250 psi; 4b) pressure-release from 400 psi; 4c) thermal-induced desorption.

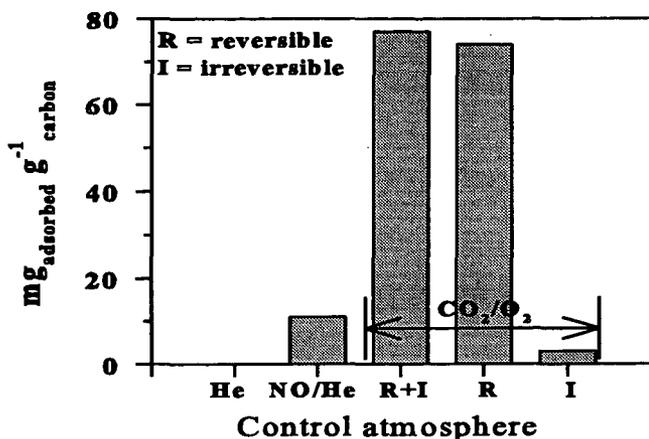


Figure 5. Contributions of He, NO, and CO₂/O₂ to total adsorption.

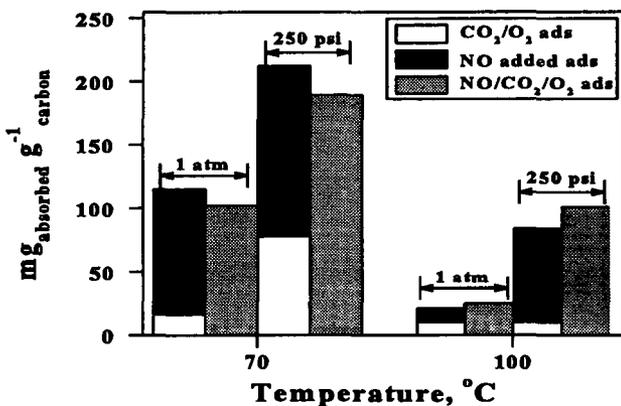


Figure 6. Effect of temperature on the relative contribution of CO₂/O₂ to total uptake.

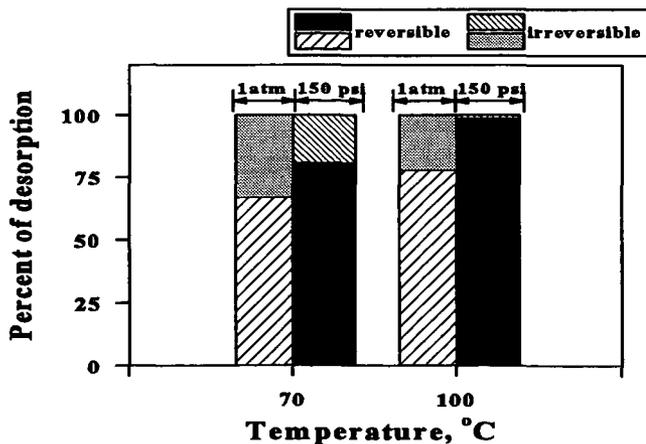


Figure 7. Effect of temperature and pressure on the relative percentage of reversibly and irreversibly adsorbed NO₂ removed from the carbon.

LOW-TEMPERATURE NO_x REMOVAL FOR FLUE GAS CLEANUP

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Key Words: NO_x reduction, NO oxidation, carbons

INTRODUCTION

A wide range of NO_x control processes for electric utilities are under investigation to compete with the current processes such as selective catalytic reduction (SCR). Although SCR using NH₃ is effective for NO reduction, the process suffers from many disadvantages [1]. In addition, current SCR processes must be located at places within the flue gas treatment process where temperatures are near 400 °C. Retrofitting SCR into these locations in the plant is costly because space and access in many power plants are extremely limited [2]. Therefore, there is a need to develop NO_x control technologies that can be located downstream of the particulate control device, near the stack, where temperatures are around 150 °C.

This study investigates the low-temperature selective reduction of NO with hydrocarbons under simulated flue gas conditions over carbon and carbon-supported catalysts. NO oxidation to NO₂ was also investigated as a way of making NO more reactive with hydrocarbons or easier to be removed by absorption at these temperatures.

EXPERIMENTAL

Four active carbon samples including type GI of Barnebey & Sulcliffe Corp. (GI), GmbH from Carbo-Tech (GmbH), PCB from Calgon (PCB), and Rheinbraun AG (AG) and one active carbon fiber (Osaka) provided by Professor Machida (Kyushu U.) were used in this experiment. All the granules were broken into 16/30 mesh particles followed by drying at 120 °C overnight. The carbon-supported catalysts were prepared by pore volume impregnation. The impregnated catalysts were first dried under vacuum at room temperature for 2 h, then at 60 °C for 2 h and 80 °C overnight. All catalysts were treated with 150 cm³/min of helium at 400 °C for 1 h before reaction. The schematic of the experimental system used in this study is the same as shown in the authors' previous report [3]. NO reduction was tested with 400 cm³/min of 0.1% NO, 4% O₂, 8% H₂O, and hydrocarbons in He over 7 g of catalysts. NO oxidation was carried out with 400 cm³/min flow of 0.1% NO, 4% O₂, and balance He over 4 g of catalysts.

RESULTS AND DISCUSSION

NO Reduction

Supports. Four carbon-supported Cu catalysts were tested for the selective reduction of NO at 150 °C. BET surface area measurement was carried out for those carbons. The surface areas ranged from 90 m²/g to 943 m²/g. The activities for NO selective reduction with acetone were investigated in the presence of O₂. The activity over Rheinbraun AG, with the lowest surface area (90 m²/g), was the lowest among the carbons tested. The activity for NO conversion was much better for GmbH from Carbo-Tech with surface area of 440 m²/g. The initial NO conversion for Carbo-Tech carbon was high, but decreased to ~20% after 5 h. PCB from Calgon (927 m²/g) and GI of B&S (943 m²/g) carbons were the two best catalysts for NO reduction with acetone in the presence of O₂. The NO conversions were 26% and 32% after 5 h for GI and PCB, respectively. The results indicate that carbon materials with higher surface area would be better for NO selective reduction with acetone in the presence of O₂. Although the surface area of GI was about the same as PCB, the activity of PCB was somehow more stable than GI. This result suggests that the surface area was not the only factor affecting the activity of carbon catalysts for NO reduction. Factors such as pore size and Cu dispersion could influence the catalytic activity and the stability of reaction.

Reductants. Because the NO reduction activity of PCB was the best among the carbon materials tested, further investigation was focused on supported PCB catalysts. The NO conversion over 5%Cu-2%Ag/C with various hydrocarbons as reductants in the presence of O₂ and H₂O is shown in Table 1, along with the results in the absence of any hydrocarbon. The efficiency order of reductant was acetone > 2-propanol > isobutanol > ethyl ether > propene, ethanol > methanol. The major NO reduction product was N₂ with >99% selectivity. Acetone was the most active reductant for NO selective reduction in the presence of O₂ and H₂O over the 5%Cu-2%Ag/C catalyst at 150 °C. The NO conversion with acetone was 35% with 3,000 h⁻¹ space velocity after 5 h on stream. Interestingly, the NO conversion without any reductant was higher than the conversion using propene, ethanol, or methanol as reductant. The results suggest

that propene, ethanol, and methanol inhibit the direct reduction of NO with carbon which is known as catalyzed by Cu in the presence of O₂.

The necessity of oxygen to promote the reduction of NO by acetone is shown in Figure 1. The NO conversion was low in the beginning and decreased to ~10% after 20 min on stream for the reaction without the presence of O₂. With 1% of O₂, NO conversion was high and slowly decreased to a steady level. With O₂ concentration of 4%, the reduction activity followed the same trend except with higher NO conversion. This shows that the reaction of NO directly with acetone is not significant in comparison with the NO selective reduction in the presence of O₂. Under the reaction conditions, the fast decrease of NO conversion during the first hour is not due to the NO adsorption on carbons since the conversion is also low in the absence of O₂. It is also unlikely that the decrease of NO conversion is caused by the adsorption of NO₂ since NO₂ decomposes quickly to NO on the surface of carbons.

Effect of H₂O and SO₂. Most literature shows an inhibiting effect of H₂O on NO reduction over various catalysts, e.g., Cu-ZrO₂ [4] and Co-ZSM-5 [1]. In contrast, results on 5%Cu-2%Ag/C showed that H₂O had no effect on NO reduction. The conversion of NO with 8% H₂O or without H₂O was essentially the same. Probably the highly hydrophobic property of carbon material surface prevents the interference of H₂O. SO₂, on the other hand, has a large negative effect on NO selective reduction with acetone. As shown in Figure 2, the catalyst deactivated very fast with 0.1% of SO₂. It is suspected that the presence of SO₂ poisons the metals by the formation of metal sulfates which deactivate the NO reduction activity.

Effect of Metals. Carbon alone is known as a catalyst for the selective reduction of NO with ammonia [5]. Figure 3 shows the NO conversion versus time for the carbon alone and for the 5%Cu-2%Ag/C catalyst. The enhancing effect of Cu+Ag on the activity of active carbon for NO conversion can be clearly seen with acetone as a reductant. The NO conversion decreased rapidly on active carbon alone (without Cu+Ag) with acetone in the presence of O₂ and H₂O. NO conversion was negligible after 1 h of reaction. On the other hand, the NO conversion over 5%Cu-2%Ag/C slowly decreased to 35% after 5 h. The results show that acetone in the absence of oxygen is not an effective reductant for NO reduction and it suggests that the function of Cu+Ag is to promote the oxidation of acetone for the selective reduction of NO. All experiments, with one exception, over 5%Cu-2%Ag/C in the presence of O₂ showed nearly 100% N₂ selectivity, i.e., no N₂O was formed. The only exception was the NO reduction with acetone in the absence of O₂, which showed >80% N₂O selectivity, suggesting that the NO reduction pathway in the presence of O₂ is different from the pathway in the absence of O₂. The formation of N₂O is probably from the direct reaction between NO and acetone or from the disproportionation of NO [6]. The high selectivity of the 5%Cu-2%Ag/C catalyst may be related to low catalyst activity for the activation of molecular oxygen, as observed on some solid acid catalysts [7]. Other metals supported carbon catalysts, such as Pt and Pd, were also tested for NO selective reduction with acetone. However, the NO reduction activity over Pt and Pd supported catalysts was much lower than the activity with Cu+Ag. Besides lower NO reduction activity with Pt and Pd, lower selectivity to N₂ was also noticed.

NO Oxidation

Active Carbon Fibers vs Active Carbon. Both the activated carbon fibers (ACFs) and PCB active carbon showed high NO oxidation activities at low temperature. The results are summarized in Table 2. At 30 °C with 400 ppm NO, 4% O₂, and balance He, NO conversions are 90% and 82% over ACF and active carbon, respectively. The activity, however, decreases with the temperature. At 75 °C, the NO oxidation conversion decreased to 51% and 42% on active carbon fibers and active carbon, respectively. Negligible oxidation was observed at 120 °C. This is consistent with results reported by Machida et al. [8]. The oxidation activity of both active carbon fibers and active carbon are interesting. Figure 4 shows the NO_x concentration versus time during NO oxidation reaction over active carbon at 30 °C. In the beginning, the adsorption of NO_x is severe. The concentration of NO increased with time and no NO₂ was detected for the first 7 h. After 7 h, NO₂ adsorption sites were saturated and as a result NO₂ breakthrough was observed. This suggests that NO₂ is adsorbed more strongly than NO on carbon materials.

Effect of Pretreatment. Three different pretreatments were tested to increase the NO oxidation activity of active carbons including heat treatment at 800 °C in N₂, reduction with H₂ at 800 °C, and oxidation using HNO₃. The results are shown in Table 3. None of the pretreatments increased NO oxidation at 120 °C. As reported by Machida et al. [8], the heat treatment increased the oxidation activity of active carbon fibers for NO to NO₂ in the presence of H₂O. It is speculated that the increased oxidation activity of fibers is from the formation unsaturation of carbon surface by the liberation of CO and CO₂ with the heat treatment in N₂. The removal

of the oxygen functional group, which increases the hydrophobic nature of the carbon, also contributes to the increase in NO oxidation activity of carbons in the presence of H₂O. However, as shown in Table 3, the heat treatment actually slightly decreased the oxidation activity of the PCB active carbon at 75 °C. The NO oxidation activity decreased from 42% to 35% at 75 °C after the heat treatment.

It was reported that H₂ reduction at high temperature was able to reduce the oxygenated functional groups on carbons [9]. The active carbon pretreated with H₂ was then tested for NO oxidation. The activity, also shown in Table 3, was negligible at 120 °C. The oxidation activity at 75 °C was close to the activity after the heat treatment and was lower than the catalyst without pretreatment. Both heat treatment and H₂ reduction treatment were intended to remove the oxygenated functional groups on carbon and to improve the oxidation activity. However, the results showed a negative effect on NO oxidation to NO₂. The results of active carbon for NO oxidation after the HNO₃ treatment are also included in Table 3. The activity was negligible at 120 °C and was only 28% at 75 °C.

All pretreatments resulted in some negative change of the activity of activated carbons for NO oxidation, indicating that the functional groups alone do not play the major role in the NO oxidation reaction. It is possible that the cooperative relationship between oxygenated functional groups and nonoxygenated functional groups is important for NO oxidation to NO₂.

Effects of SO₂ and H₂O. The effect of SO₂ on NO oxidation activity over heat-treated PCB active carbons was studied by adding 0.1% SO₂ to the inlet gas. The results are also shown in Table 3. The NO oxidation activity was negligible in the presence of SO₂ over the catalyst at 120 °C. When the reaction temperature was further decreased to 75 °C, no oxidation activity was observed as compared to 35% NO oxidation conversion in the absence of SO₂. The result suggests that the presence of SO₂ poisoned the oxidation activity of carbon catalysts, which is similar to the results reported in the literature [10-12]. The competitive adsorption of NO and SO₂ on carbon surfaces is possibly the cause.

We also tested the combined effect of SO₂ and H₂O on the active carbon for NO oxidation. As reported earlier [13], SO₂ greatly promotes the NO oxidation reaction in the presence of H₂O over Co/Al₂O₃. However, the NO oxidation activity was negligible over the active carbon in the presence of SO₂ and H₂O at 120 °C.

Active Carbon Supported Catalysts. Five percent cobalt oxide and 1% iron oxide supported on active carbons were tested for NO oxidation. The results are summarized in Table 4 to compare with the NO oxidation activity of unsupported active carbon. Again, both active carbon-supported catalysts showed negligible activity at 120 °C. It is believed that the decomposition activity of carbons for NO₂ to NO is too fast at 120 °C to be overcome by the oxidation activity of metal oxides. The activities at 75 °C were obtained followed by the tests at 120 °C. The NO oxidation activities were 26% and 24% over 1% iron oxide/A.C. and 5% cobalt oxide/A.C., respectively. The activities of active carbon-supported catalysts were lower than the unsupported catalyst at 75 °C.

CONCLUSIONS

Acetone was the most active reductant for NO selective reduction over 5%Cu-2%Ag/C among the hydrocarbons tested. Acetone, oxygen, and carbon-supported Cu+Ag catalyst are all required to maintain high NO conversion and high N₂ selectivity at these low temperatures. Although 35% NO conversion is relatively high at 150 °C in the presence of O₂ and H₂O, further improvement is needed for the process to be competitive with other processes. The NO reduction activity of Cu-Ag/carbon with acetone was also greatly decreased by the presence of 0.1% SO₂, which may be present even downstream of some flue gas desulfurization systems.

Both active carbon fibers and active carbon are active for NO oxidation to NO₂ at low temperature. At 30 °C and 0.01 g-min/cm³ space velocity, the NO conversions to NO₂ were 90% and 82% on active carbon fibers and active carbon, respectively. However, the activity decreased with the temperature, becoming negligible at 120 °C on both active carbon fibers and active carbon. Different treatments (heat treatment at 800 °C, reduction in H₂, and oxidation with HNO₃) and additional metals did not improve the NO oxidation activities of carbons at 120 °C. With the addition of 0.1% SO₂, the NO oxidation activity of activated carbon was poisoned and the conversion was negligible at 75 °C.

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Table 1. NO Selective Reduction by Hydrocarbons over 5% Cu-2% Ag/C (1,000 ppm NO, 4% O₂, and 8% H₂O, 3,000 h⁻¹, 150 °C)^a

Reductant	NO	
	Conversion (%)	N ₂ Selectivity (%)
0.13% acetone	35	>99
0.13% 2-propanol	31	>99
0.10% isobutanol	25	>99
0.08% ethyl ether ^b	18	>99
0.20% ethanol	<10	>99
0.11% propene	<10	>99
0.40% methanol	negligible	>99
none	11	>99

^a All catalysts subjected to He treatment at 400 °C for 1 h before reaction. The conversion and selectivity was taken after 5 h on stream.

^b The concentration of ethyl ether was limited by its solubility in water.

Table 3. NO Oxidation to NO₂ over PCB Active Carbon (A.C.)

PCB A.C.	Temperature	
	120 °C	75 °C
Fresh	negligible	42%
Heat treatment	negligible	35%
H ₂ reduction	negligible	31%
HNO ₃ oxidation	negligible	28%
With 0.1% SO ₂	negligible	negligible
With 0.1% SO ₂ + 10% H ₂ O	negligible	not available

Note: Activities at 120 °C were obtained after 24 h on stream and the activities at 75 °C were obtained after 24 h at 120 °C and 40 h at 75 °C. Reaction conditions: 400 ppm NO, 4% O₂, and balance He; 400 cm³/min over 4.0 g of catalysts.

Table 2. NO Oxidation to NO₂ over Active Carbon Fibers (ACF) and PCB Active Carbon (A.C.)

Carbon	Temperature		
	30 °C	75 °C	120 °C
ACF	90%	51%	negligible
PCB A.C.	82%	42%	negligible

Note: Activities were obtained after 40 h on stream. Reaction conditions: 400 ppm NO, 4% O₂, and balance He; 400 cm³/min over 4.0 g of catalysts.

Table 4. NO Oxidation to NO₂ over PCB Active Carbon (A.C.) and Active Carbon-Supported Catalysts

Catalyst	Temperature	
	120 °C	75 °C
Fresh A.C.	negligible	42%
1% iron oxide A.C.	negligible	26%
5% cobalt oxide A.C.	negligible	24%

Note: Activities at 120 °C were obtained after 24 h on stream and the activities at 75 °C were obtained after 24 h at 120 °C and 40 h at 75 °C. Reaction conditions: 400 ppm NO, 4% O₂, and balance He; 400 cm³/min over 4.0 g of catalysts.

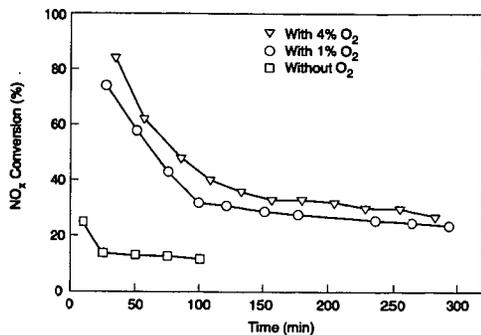


Figure 1. NO conversion over 5% Cu-2% Ag/C as function of time with different O₂ concentration. Reaction conditions: 0.1% NO, 0.13% acetone, 8% H₂O at 150 °C with 3,000 h⁻¹ space velocity.

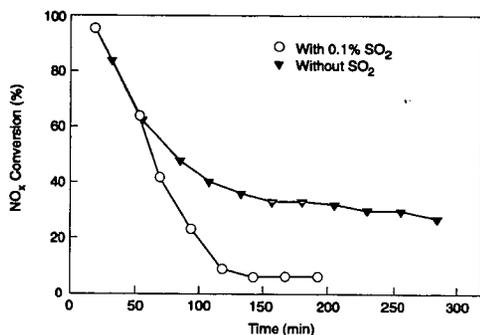


Figure 2. The effect of SO₂ on NO reduction with acetone over a Cu supported carbon catalyst at 150 °C; 0.1% NO, 0.13% acetone, 4% O₂ and 8% H₂O; 3,000 h⁻¹.

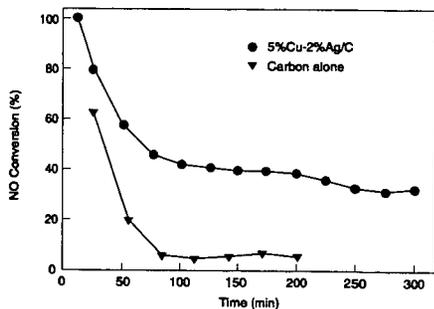


Figure 3. NO conversion versus time over 5% Cu-2% Ag/C and carbon only. Reaction conditions: 1,000 ppm NO, 8% H₂O, 3,000 h⁻¹, 150 °C.

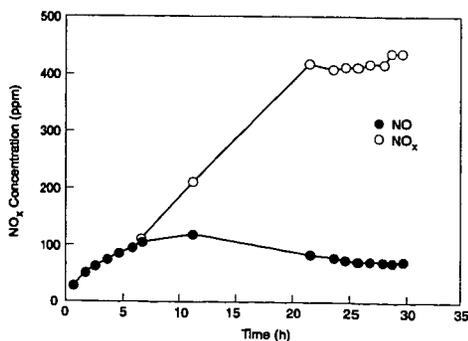


Figure 4. NO and NO_x concentrations as function of time during NO oxidation over activated carbon at 30 °C; 400 ppm NO, 4% O₂, and balance He; 400 cm³/min over 4.0 g of catalysts.

STATE OF NO_x OVER PITCH BASED ACTIVE CARBON FIBER AT THE INITIAL STAGE OF NO-NH₃ REACTION

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KEYWORDS : NO reduction, Pitch based ACF, Initial stage of NO-NH₃ reaction

INTRODUCTION

Removal of NO in the atmosphere as well as the flue gas is still an objective to increase the efficiency. The present authors have reported a significant catalytic activity of pitch based active carbon fiber for the reductive[1,2] and oxidative[3] removal of NO at room temperature, especially after the ACF was heat-treated at a proper temperature [4,5]. The problem to be solved is the inhibition of humidity above 70% relative humidity (rh). [6,7]. Hence the enhancement of the activity in the humid area is the major target to be explored.

In the present study, adsorption and reduction of NO over pitch based active carbon fiber (ACF) was analyzed especially at the initial stage of NO-NH₃ reaction where the high rate of NO removal was observed over the ACF in the humid air, although the activity decreased gradually to the stationary level. The analyses of NO adsorption and reduction over the ACF may suggest plausible ways how to maintain or regenerate such an activity for more efficient process of NO removal.

EXPERIMENTAL

The ACF examined in the present study was a pitch based active carbon fiber supplied by Osaka Gas Co. (OG-8A, surface area 800m²/g). The ACF was heat-treated at 850°C to develop the highest activity for NO reduction with NH₃ (OG-8A-H850).

The reactivity and adsorption of NO-NH₃ (200 and 300ppm respectively in air) was studied by a conventional flow reactor at 25 to 70°C. The ACF of 0.5g (8cm length) was packed in the reactor. The flow rate of the total gas was fixed at 100 ml/min. Humidity of air was controlled by feeding H₂O in the reactor.

By analyzing the outlet NO and NH₃ concentrations by NO_x meters (NH₃ was oxidized before the analysis), the removal and desorption of NO were quantified to calculate the adsorption and the reduction of NO.

The desorption of NO and NH₃ adsorbed on the ACF during the NO-NH₃ reaction and their single flow was performed by program heating up to 300°C the ACF bed in the flowing He of 100ml. The heating rate was 3.3°C/min.

RESULTS

Removal of NO in the reactor with NH₃ over OG-8A-H850

Figure 1 illustrates the removal of NO in the presence of NH₃ in dry and humid (80%rh) air over OG-8A-H850 at 25 to 70°C by W/F : 5x10⁻³g·min/ml. NO was completely removed for initial 20min at 25°C in dry air and then its removal decreased gradually for 120min to give a stationary removal of 98%. The higher temperature shortened the periods of complete removal and gradual reduction, reducing the stationary removal. Thus the stationary removal obtained at 40, 55 and 70 was 85, 75 and 50%, respectively.

Relative humidity of 80% eliminated the period of complete removal under the present conditions and reduced the stationary removal to 20, 60, 50 and 40%, respectively, at 25, 40, 55 and 70°C. It should be noted that an intermediate temperature of 40°C allowed the largest removal of NO in humid air of 80%rh, being very contrast to the reaction in dry air.

Adsorption of NO and NH₃ at the early stage of the reaction

Figure 2 illustrates the temperature programmed desorption of adsorbed NO and NH₃ over OG-8A-H850 after for the NO-NH₃ reaction at 25°C for 3h.

NO started to desorb at 30°C, slowly up to 60°C, after which the desorption became may rapid to reach a maximum at 80°C. Further heating provide another maximum at 180°C. The total amount of desorbed NO was 7x10⁻²mmol/g ACF.

Ammonium started to desorb immediately after the switch of carrier gas and increased rapidly its concentration to the maximum at 40°C. The second maximum of small concentration was found at 230°C.

Figure 3 summarizes the amounts of adsorbed NO after 3h reaction at several reaction temperatures, as measured by the procedure described in Figure 2. The amount under dry conditions decreased monotonously at higher temperatures. In contrast, the amount at 80%rh showed the maximum at 40°C where the inhibition of H₂O may be reduced.

The conversion of NO by 3h shown in Figure 1 includes the amounts of reduced as well as adsorbed NO. The amounts of reduced NO thus calculated are plotted also in Figure 3. The amount of NO by 3h under dry conditions was much the same up to 55°C, then decreased sharply. Hence the conversion decreasing at the higher reaction temperature shown Figure 1 decreases reduction of NO reduction as well as adsorption.

In contrast, the amount of NO reduction was much higher at 40 - 70°C than at 25°C in humid air. Inhibition by H₂O on reduction and adsorption of NO is reduced at higher temperature where the adsorption of H₂O is minimized.

Figure 4 shows the adsorption amount of NO alone over OG-8A-H850 for 3h where adsorption appeared saturated. The amount of NO adsorption were very similar to those during NO-NH₃ in the same temperature range, indicating that the adsorption of NO is saturated regardless of NH₃ presence.

Reactivity of NO adsorbed during the NO-NH₃ reaction

Figure 5 illustrates the desorption profiles of NO during the NO-NH₃ reaction over OG-8A-H850 after the reaction with 300ppm NH₃ alone for 3h at 25 - 55°C. Desorption amount of NO was markedly reduced by the reaction with NH₃. NO desorbing at the lower temperature was reduced more readily by the reaction. The higher temperature reduced more NO of desorption.

DISCUSSION

The present study focussed the early stage of NO-NH₃ reaction over a pitch based active carbon fiber of fairly large surface heat-treated at 850°C. At the initial stage, NO was completely removed by adsorption and reduction over the ACF. The adsorption took place rapidly to contribute principally to the removal at the very initial stage, however its contribution decreases as the progress of run because the adsorption approaches the saturation. After the saturation of the adsorption, the NO removal becomes stationary. Although humidity reduces both adsorption and reduction, the situation of the NO removal over the ACF was basically common.

The higher reaction temperature reduces the adsorption of NO to decrease its reduction in dry air as previously reported and hence NO removal decreases. In contrast, the higher reaction temperature up to 40°C increased both adsorption and reduction in humid air because the inhibition of H₂O due to its adsorption decreases markedly up to 40°C. A particular temperature of 40°C allows the highest removal by compromising adsorptions of NO and H₂O.

The adsorbed NO at the early stage stayed unreduced while NO and NH₃ are fed. However NH₃ alone can reduce NO, the higher temperature up to 45°C accelerating the reduction. It should be noted that two adsorbed species of NO are present on the ACF, of which desorption temperatures are very different and that the NO species desorbing at the lower temperature is more reactive with NH₃. It is also worthwhile to note that the stationary reduction of NO does not appear to reflect such adsorbed species. More details of NO adsorbed species are of value to be analyzed. The lower stationary removal of NO in humid air is a task to be overcome for the practical application. The removal of NO at early stage which includes both adsorption and reduction can be applied for the complete removal where the regeneration of adsorption ability by reducing adsorbed NO and NO removal can be practically cycled. The optimization is the next target of the study.

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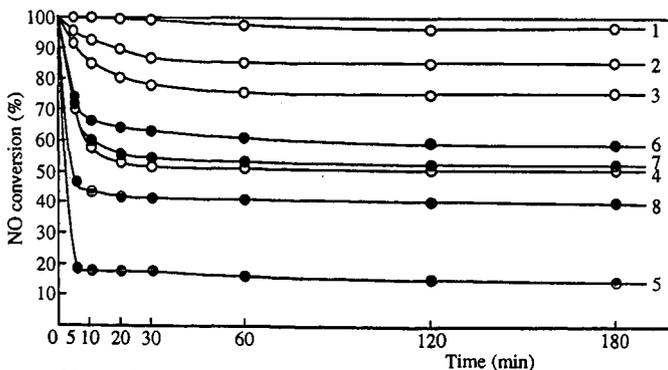


Fig.1 NO-NH₃ reaction profile over ACF OG-8A-H850 in dry and wet air
 NO : NH₃ = 1:1.5 (NO = 200ppm), O₂ = 10%, N₂ balance
 W/F = 5 × 10⁻³ g · min · ml⁻¹, W = 0.5g, Time : 180min
 Dry (r.h. = 0%) : ○ 1. 25°C, 2. 40°C, 3. 55°C, 4. 70°C
 Wet (r.h. = 80%) : ● 5. 25°C, 6. 40°C, 7. 55°C, 8. 70°C

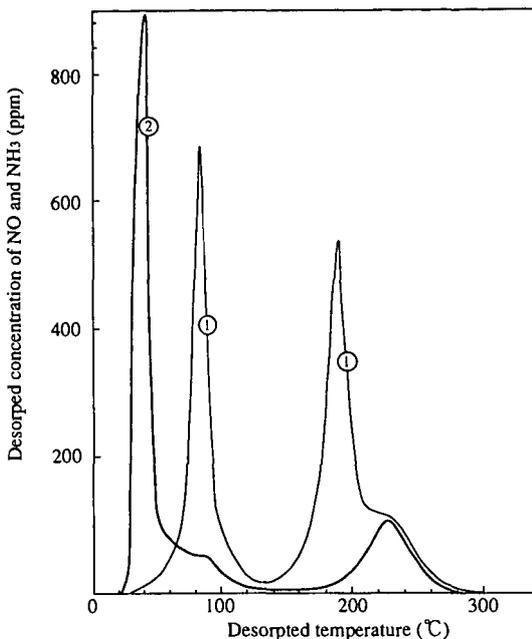


Fig.2 Desorption profile of NO and NH₃ after NO-NH₃ reaction over OG-8A-H850

Reaction : NO : NH₃ = 1 : 1.5 (NO = 200 ppm), O₂ = 10%, N₂ balance
 W = 0.5g, W/F = 5 × 10⁻³ g · min · ml⁻¹, Temp. = 25°C
 r.h = 0%, Time = 180 min
 Desorption : Flow gas (He) = 100 ml/min, Temp. : 25 - 300°C
 H.R. = 3.3°C/min
 ○ 1 NO, ○ 2 NH₃

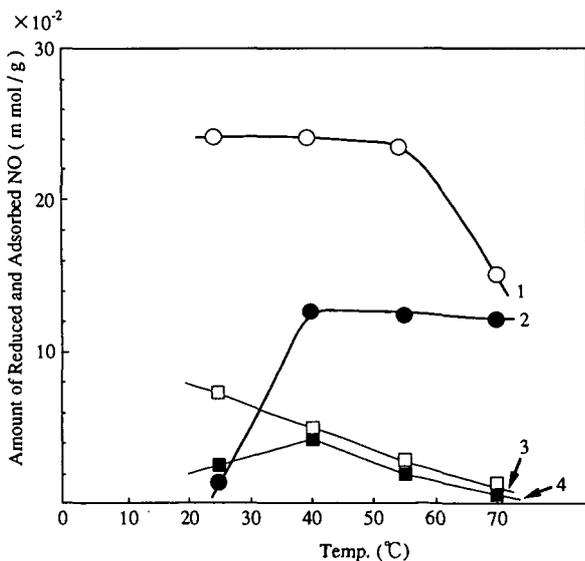


Fig. 3 NO reduction and adsorption over OG-8A-H850

NO : NH₃ = 1 : 1.5 (NO = 200 ppm), N₂ balance, O₂ = 10%
 W/F = 5 × 10⁻³ g · min · ml⁻¹, W = 0.5, F = 100 ml/min, Time : 180min
 ○ : 1. Reduction (Dry, rh = 0%) □ : 3. Adsorption (Dry, rh = 0%)
 ● : 2. (Wet, rh = 80%) ■ : 4. (Wet, rh = 80%)

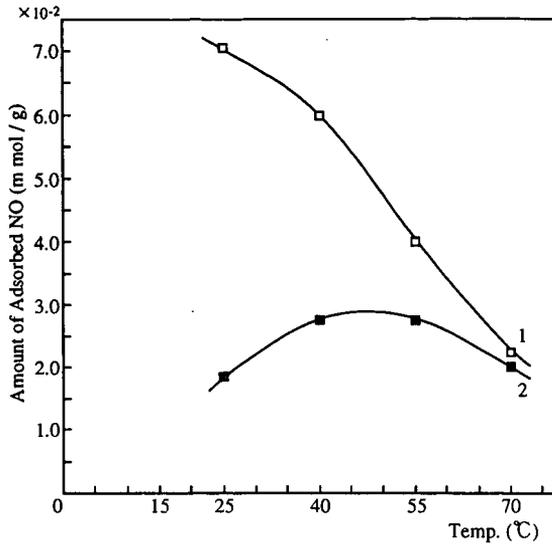


Fig. 4 Adsorption amount of NO alone over OG-8A-H850

NO : 300ppm, W/F = $5 \times 10^{-3} \text{ g} \cdot \text{min} \cdot \text{ml}^{-1}$, W = 0.5g, Time : 180min
 1 : Dry (r.h. = 0%), 2 : Wet (r.h. = 80%)

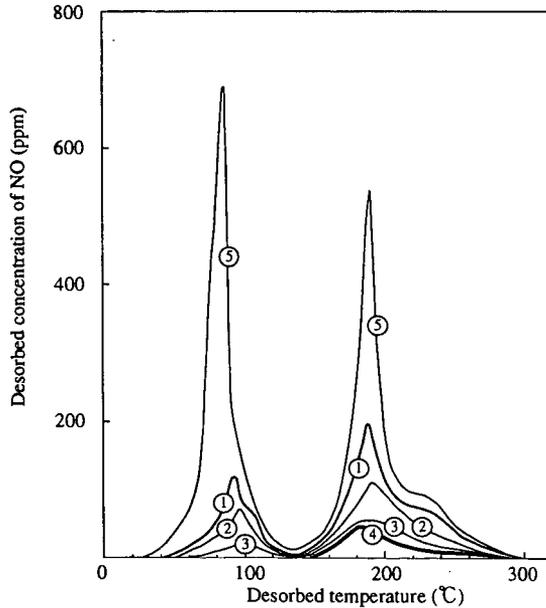


Fig.5 Desorption after regeneration with NH_3 of adsorbed NO during NO- NH_3 reaction

ACF : OG-8A-H850 (Pitch based)
 Reaction : NO : NH_3 = 1 : 1.5 (NO = 200ppm), O_2 = 10%, N_2 balance,
 W / F = $5 \times 10^{-3} \text{ g} \cdot \text{min} \cdot \text{ml}^{-1}$, r.h. = 0%, Time : 180min
 Regeneration : NH_3 = 300 ppm, O_2 = 10%, N_2 balance
 W/F = $5 \times 10^{-3} \text{ g} \cdot \text{min} \cdot \text{ml}^{-1}$, W = 0.5g
 r.h = 0%, Temp. : 25 - 55°C, Time : 180min
 Desorption : Flow gas (He) = 100 ml/min, Temp. : 25 - 300°C, H.R. = 3.3°C/min
 ① Regen. Temp. = 25°C ④ Regen. Temp. = 55°C
 ② " " = 35°C ⑤ Non-Regen.
 ③ " " = 45°C

EFFECT OF PRESSURE ON THE HEATS OF SORPTION AND DESORPTION OF O₂, NO AND N₂, ON AN ACTIVE CARBON AND A CARBON MOLECULAR SIEVE

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Keywords: carbon molecular sieve : pressure : heat of adsorption.

Introduction

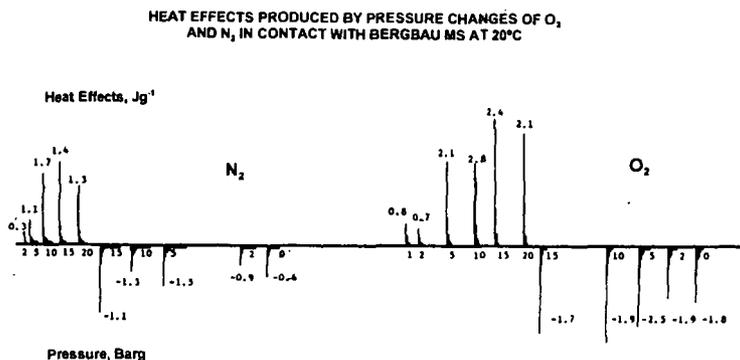
Pressure swing adsorption techniques with the use of carbon molecular sieves (CMS) are now all established for the separation of individual components of gas mixtures. One important example of such a separation is the isolation of pure oxygen and nitrogen from air. Recently K.M. Thomas, M.L. Sykes and H. Chagger have shown that the heat evolution which accompanies the adsorption of O₂ and N₂ on various CMS's from a stream of helium, takes place at rates which are closely similar to the heats of adsorption, with nitrogen adsorbing much more slowly than oxygen (1). The work was carried out at room temperature and at atmospheric pressures. Pressure swing separation processes which are used industrially, employ adsorption pressures that can vary from atmospheric pressure to 20 barg. The application of pressure increases the adsorption of individual components of gas mixtures and generates heat evolution due not only to adsorption of the first layer of molecules, but also to the pore filling phenomena which densify the gas contained in micropores. The heats evolved or absorbed during pressure swing operations are important parameters which affect the efficiency of gas separation operations as indicated recently by Sircar (2). But so far experimental determination of the heats of pore filling and gas adsorption on molecular sieves have not received much attention. This work was carried out, therefore, to determine experimentally the effect of pressure on heat evolution during adsorption of O₂ and N₂ on a commercial molecular sieve and an active carbon using a Microscal Flow Microcalorimeter (FMC) modified for use at high pressures under static conditions.

The pressures of oxygen and nitrogen in contact with the adsorbent were increased in steps from 1 to 20 barg and decreased back to atmospheric pressures and the resulting heats of sorption determined together with the duration of each heat effect. A limited amount of work was also carried out on nitric oxide.

Experimental

A schematic diagram of Microscal's Flow Microcalorimeter (FMC) which can be used under static conditions at pressures up to 50 barg is shown in Figure 1. In the procedure used, the calorimetric cell which had a volume of 0.17 cc was filled with accurately weighed adsorbent, with outlet tube in position, and the cell closed by a tightly fitting stainless steel inlet tube. The inlet tube is connected to a gas cylinder via a Druck pressure regulator capable of increasing or decreasing the gas pressure inside the cell in steps determined by the operator. The heat effects produced by the increasing or decreasing pressures are measured by the thermistors and calibration is effected by generating heat effects inside the cell electrically, as described previously for a Flow Microcalorimeter (3). The cell in the high pressure instrument is made from MACOR (glass reinforced with mica flakes) giving high temperature and pressure capability and very low time constant. With the inlet open and the outlet tube closed, the pressure was changed in a stepwise fashion resulting in the generation of heat effects. A typical record of one such measurement series is shown in Figure 2 for O₂ and N₂ adsorbed sequentially on a 0.095 g sample of Bergbau molecular sieve. The carbon adsorbents used in this study were Chemviron BPL active carbon and a commercial sample of a Bergbau molecular sieve. Gases were Aldrich materials with purities exceeding 99%. All the work was carried out at 20°C ± 1°C.

Figure 2



Results and discussions

A plot of differential heat effects represented in Figure 2 for the adsorption of O₂ and N₂ on the carbon molecular sieve is shown in Figure 3. There is a clear difference between the two gases with the ratio of the heats for O₂ and N₂ diminishing as the pressure increases. This suggests that the efficiency of gas separation would be somewhat higher for pressure swings of 0 - 2 barg than it would be for the swings of 18 - 20 barg, notwithstanding the greater amounts of gas throughput at the higher pressures. The heat effects plotted in Figure 3 do not take into account the rates of heat evolution which are very different for O₂ and N₂, as illustrated by the heat evolution peaks shown in Figure 4. It appears, however, that the differences in the rates of heat evolution under a pressure swing regime are smaller than those reported by K.M. Thomas et al for the adsorption at atmospheric pressure (1).

Figure 3

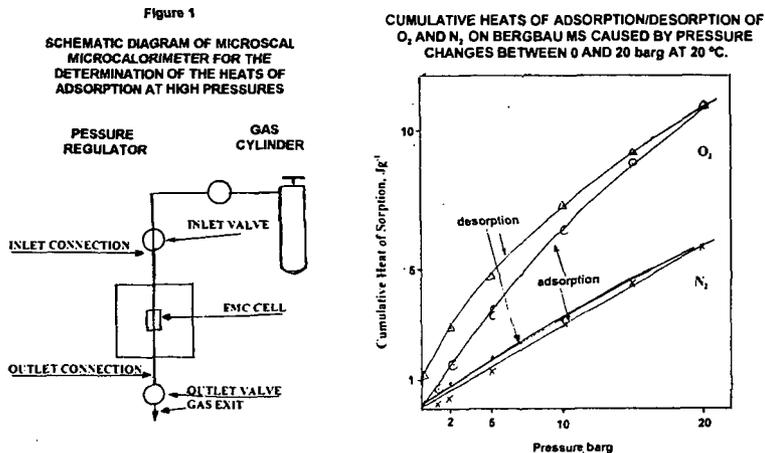
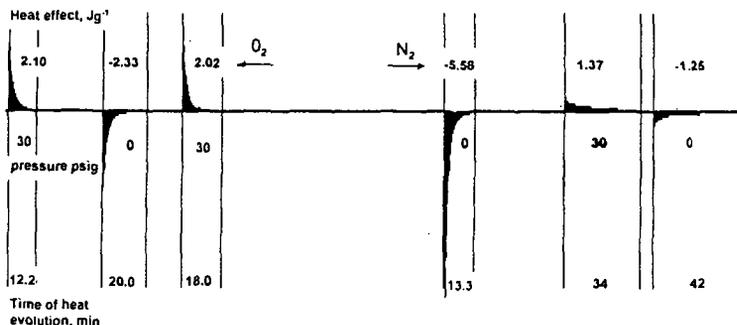


Figure 4

EVOLUTION AND ABSORPTION OF HEAT DURING A
PRESSURE SWING OPERATION WITH O₂ AND N₂
ON BERGBAU CARBON MOLECULAR SIEVE



The differences between the heats adsorptions of O₂ and N₂ on CMS and active carbon BPL are shown in Figure 5 for pressure changes between 0 and 2 barg. As can be seen, the active carbon, as expected, shows very different behaviour from the CMS and gives slightly higher heats of adsorption for O₂ than for N₂. The active carbon does not show any significant difference between the rates of heat evolution. However, for CMS it is evident that the periods of heat evolution for N₂ are longer than they are for O₂. If it is assumed that the rates of heat evolution are directly related to the rates of adsorption, the differences between the rates can be used to optimise the gas separation efficiency over the whole range of the pressures investigated.

A brief investigation of the effect of pressure on the heat of adsorption of NO shows that this gas is very strongly adsorbed on both carbons and that the adsorption that occurs initially at low pressures is to a large extent irreversible. However, after saturation of the surface sites on the carbon with the chemisorbed NO, the additional more weakly adsorbed gas gives much higher increases in the heats of adsorption to those shown by nitrogen or oxygen. This is shown in Figure 6 in which the heats of adsorption after the initial contact of NO with the carbon molecular sieve are monitored during pressure changes between 0 and 2 barg. The first adsorption cycle gives a higher heat of adsorption than the following two cycles for which the heats of adsorption continue to be higher than the heats of desorption. The rates of heat evolution for NO are even slower than those shown by N₂, indicating that even the weaker more reversible adsorption of NO is still much stronger than that of N₂ and O₂. The rates of heat evolution are also relatively low for NO indicating a difficulty that the molecule has in entering and leaving the micropores modified by chemisorption after several cycles of NO adsorption. The subsequent adsorption cycles of O₂ give much higher heats of adsorption and are of longer duration than those obtained on CMS before contact with NO. Clearly the interaction of CMS surface within the pores with NO changes fundamentally the nature of the interaction between the O₂ molecules and the micropores in the CMS.

Figure 5

EFFECT OF PRESSURE ON THE HEAT OF ADSORPTION OF O₂ AND N₂ ON CHEMIVRON BPL AND BERGBAU MS

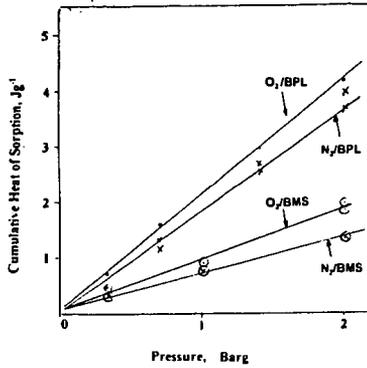
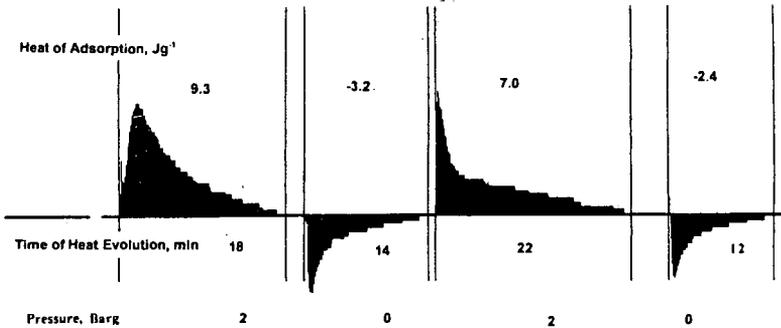


Figure 6

EFFECT OF PRESSURE CHANGES ON THE HEAT EVOLUTION OF NO IN CONTACT WITH BERGBAU MOLECULAR SIEVE AFTER INITIAL IRREVERSIBLE ADSORPTION



Conclusions

The heats of adsorption and desorption of O₂ and N₂ change significantly when the pressure is varied between 0 and 20 barg at room temperature. The changes are much greater for O₂ than for N₂ on carbon molecular sieve, but this effect is not observed for a typical active carbon which adsorbs both O₂ and N₂ with similar intensity and similar rates of adsorption. The work indicates that apart from the sieving action the pore filling mechanism may play an important role in the separation of gases on carbon molecular sieves. The adsorption of NO on microporous carbons is very intense and is partly irreversible. NO modifies the nature of the adsorbing sites in the carbon molecular sieve investigated and makes the adsorption of O₂ on such a modified adsorbent much stronger and apparently more extensive.

References

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