

## ACTIVATED CARBONS FOR THE REMOVAL OF NITRIC OXIDES

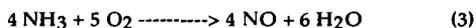
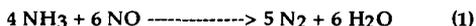
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### INTRODUCTION

Nitrogen oxide (NO<sub>x</sub>) emissions from stationary and mobile sources are precursors to acid precipitation, are important in the formation of ozone during interaction with hydrocarbons, and have been implicated as intermediates in greenhouse gas formation. The amount of NO<sub>x</sub> emitted is distributed nearly equally between transportation, industry and power generation (1). For stationary sources, the recent Title III federal legislation will restrict NO<sub>x</sub> emissions to levels of approximately 0.45 lb/MM Btu. As a result, it is anticipated that many coal fired power sources will be required to install some type of post combustion clean-up equipment to reduce NO<sub>x</sub> emissions.

One of the commercially available technologies that has been used to control NO<sub>x</sub> is selective catalytic reduction (SCR) using NH<sub>3</sub> as a reductant over oxide supported catalysts. It is called selective because with O<sub>2</sub> in the combustion flue gas, the following reactions are possible:



Reactions (1) and (2) are desired where as nonselective Reaction (3) would cause NO to be produced.

Currently, SCR technology using metal oxide catalysts has an optimum reaction temperature between 350-450°C. This range places restrictions on locating the catalyst bed for flue gas treatment in coal fired units. For example, if the catalyst bed is placed before the particulate and the sulfur oxide clean-up equipment, the flue gas temperature would be within the desired range but the catalyst life would be reduced because of high concentrations of particulates and catalyst poisons (2,3). If the catalyst bed is placed after the clean-up equipment, an additional source of heating is required to reheat the flue gas to a desired temperature.

To investigate catalysts for alternative lower temperature NO<sub>x</sub> decomposition, we have initiated studies on the use of activated carbons and their modification. To date, these studies have concentrated on commercially available carbons and on comparisons with commercially available V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>.

## EXPERIMENTAL

A schematic diagram of the overall experimental setup is presented in Figure 1. Gas flow rates were controlled by Tylan model FC-280 mass flow controllers. Each stream was filtered through a 0.5 micron sintered metal filter before entering the flow controller. After passing through a block valve and a check valve, the gases entered the mixing chamber which was made up of a 2.54 cm od stainless steel pipe filled with 3 mm glass balls. This arrangement allowed a thorough mixing of gases before entering the reactor vessel. The reactor vessel was a 1.9 cm od stainless steel tube with a 1.22 cm id and was 30.45 cm in length. The catalyst bed was sandwiched between glass wool plugs which were supported by 3 mm glass beads. The reactor was enclosed in a tube furnace. After passing through the reactor, the product stream was analyzed by a non-dispersive infrared CO<sub>2</sub> detector, a chemiluminescence NO/NO<sub>x</sub> detector and mass spectrometer.

Four commercial samples, originating from three different precursors have been obtained for this investigation. Their origins and surface areas are presented in Table I. Three of these samples (labelled SP1, SP2 and SP3) will be discussed here. They were used in a powdered form (50 - 100 mesh) and have characteristics shown Table II.

In the test runs, the temperature was varied from 100-300°C, the total gas flow rate was 1000 SCCM, and the catalyst weight was 3 g. An emphasis was placed on using the conditions similar to that of flue gas generated from power plants; hence, the NO and NH<sub>3</sub> concentrations were 700 ppm and O<sub>2</sub> was 4%. Prior to each test run, samples were heated for four hours at 300°C under a helium flow. For comparisons, a commercially prepared V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst was tested under the same conditions.

The pH of the samples was obtained using a standard procedure in which 3 g of the sample was mixed with 60 ml of distilled water and heated at 100°C for three minutes. The solution was then filtered, allowed to cool to room temperature, and its pH was measured.

## RESULTS AND DISCUSSION

Figure 2 shows the NO conversion for the three samples as a function of temperature. SP1, which was produced from coal, had the highest activity and SP3, which was produced from peat, had the lowest activity. All samples showed a decrease in activity between 120°C and 200°C.

The NO conversion did not correlate with BET surface area, as shown in Figure 3. SP1 showed the highest activity but had the lowest surface area. Similarly, there was no correlation between pore volume and activity. Rather, NO conversion activity correlated inversely with pH and ash content, as displayed in Figure 4 and Figure 5. SP1, which had the lowest pH, showed the highest activity. This trend implies that a more acidic surface would maximize activity. The inverse correlation obtained for activity and ash contents of the samples might complement the inverse correlation between pH and activity. However, the mineralogy of the carbons have not been examined to define the influence of the ash on pH.

To examine further whether pH affects activity, SP3 was washed with distilled water for 24 hrs to reduce its pH from 9.55 to 8.23. This washing increased its activity at temperatures above 100°C (see Figure 6); no increase occurred at 100°C. This may imply that two conversion mechanisms are operative. One dominant at low temperatures and the other prevalent at higher temperatures.

The oxygen content of the carbons also was observed to correlate with activity. For example, as shown in Figure 7, SP1, which had the highest oxygen content, showed the highest activity. Hence, oxygen plays an important role in NO conversion. Perhaps, the amount of oxygen in the sample indicates the presence of acidic surface oxides, which decrease the sample's pH. SP1, which had the highest oxygen content, also had the lowest pH.

SP1 was also tested for the nonselective formation of NO by reacting  $\text{NH}_3$  with  $\text{O}_2$  in the absence of reactant NO (Reaction (3)). NO was not formed, thus suggesting that activated carbons promote NO reduction. In absence of reactant or gas phase oxygen, NO conversion was negligible.

A comparison of NO conversion activity for SP1 and  $\text{V}_2\text{O}_5/\text{TiO}_2$  is shown in Figure 8. At low temperatures around 100°C, SP1 proved to be a better catalyst than  $\text{V}_2\text{O}_5/\text{TiO}_2$ . However, at temperatures higher than 150°C,  $\text{V}_2\text{O}_5/\text{TiO}_2$  was more active than SP1.

SP3, which had shown the lowest activity, was further treated with sulfuric acid. Initial results have shown that its activity increased considerably. This could probably be due to the oxidation of the surface thus creating acidic functional groups on the surface. This possibility is under further investigation.

## CONCLUSIONS

Activated carbons are potentially good catalysts for NO reduction. Low pH, activated carbons have higher activity for NO reduction implying that activated carbons which are acidic in nature are better catalysts for NO reduction. A higher oxygen content in the activated carbons increases their activity, whereas gas phase oxygen

is needed for NO conversion. Activated carbons can have a higher activity than  $V_2O_5/TiO_2$  at low temperatures around  $100^\circ C$ .

#### REFERENCES

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**TABLE I. SAMPLE'S BET SURFACE AREA**

SAMPLE	PRECURSOR	BET SURFACE AREA m <sup>2</sup> /g
SP1	Coal	466
SP2	Peat	1110
SP3	Coconut Shell	739
SP4	Peat	791

**TABLE II. ULTIMATE AND PROXIMATE ANALYSIS**

SAMPLE	C%	O%	H%	N%	S%	ASH %
SP1	91.54	4.77	0.47	1.17	0.70	2.05
SP2	91.55	3.87	0.17	0.54	0.46	3.44
SP3	91.54	2.55	0.46	0.51	0.02	4.92

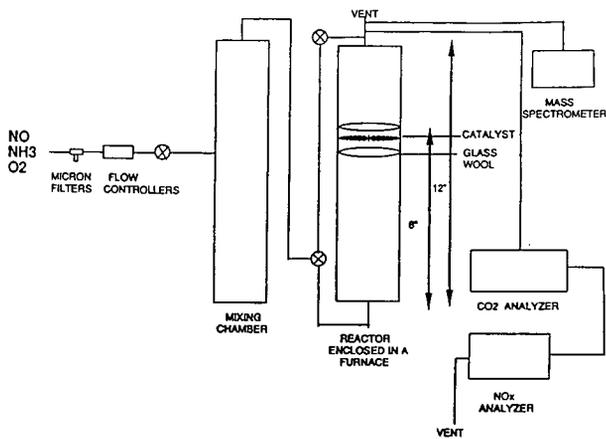


FIGURE 1. PROCESS FLOW DIAGRAM

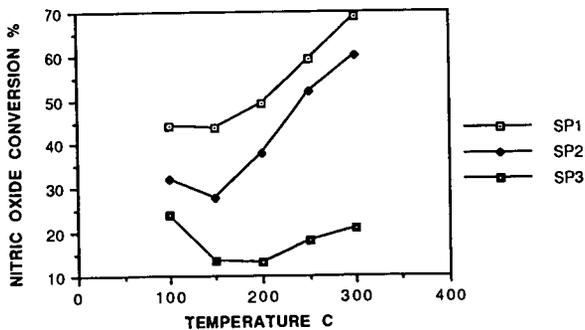


FIGURE 2. NO CONVERSION AT VARIOUS TEMPERATURES

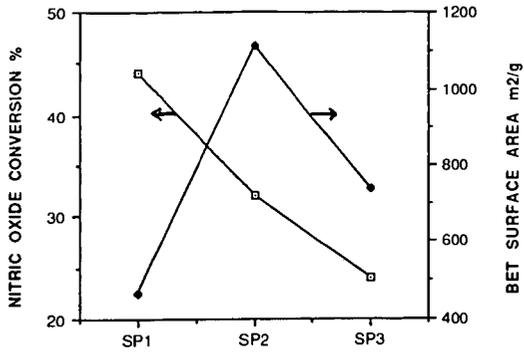


FIGURE 3. ACTIVITY (100C) VS BET SURFACE AREA

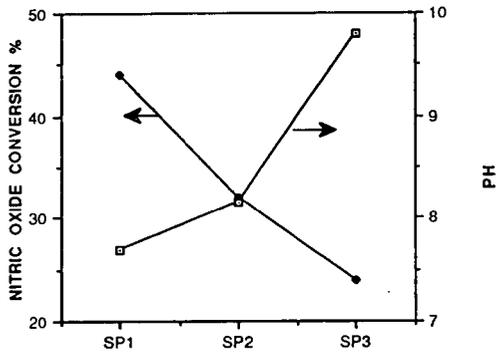


FIGURE 4. ACTIVITY (100 C) VS pH

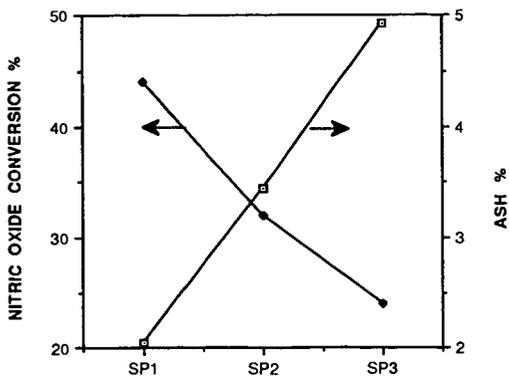


FIGURE 5. ACTIVITY (100C) VS ASH CONTENT

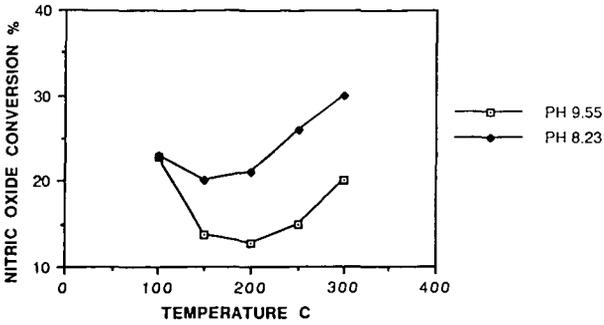


FIGURE 6. EFFECT OF pH ON THE ACTIVITY

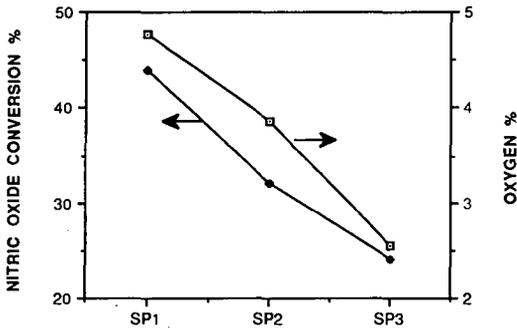


FIGURE 7. ACTIVITY (100 C) VS OXYGEN CONTENT

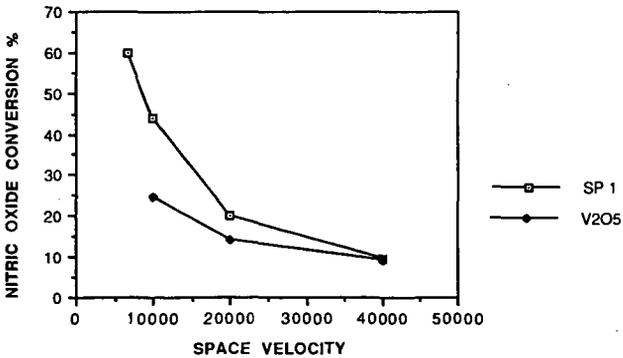


FIGURE 8. COMPARISON OF SP 1 AND V2O5/TiO2 (100C)