61. NO REDUCTION WITH CARBON
- FORMATION RATE OF N₂ AND N₂O -

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SYNOPSIS

NO reduction by carbon is investigated in the presence and absence of O₂. N₂ and N₂O formation are evidenced in both. N₂ formation mechanism is proposed, which take the presence of nitrogen containing surface compound into account. O₂ is found to increase NO reduction by removing nitrogen containing complexes from the carbon surface.

INTRODUCTION

With the increasing awareness of environmental problems as acid rains and photochemical smog, many attempts have been done to reduce nitrogen oxides emission from power plants and diesel engines. One way would be the use of carbon particles, often emitted at the same time as reducing agent. There is a general agreement that NO adsorbs dissociatively on the carbon surface as the first reaction step [1]. It results in the formation of oxygen and nitrogen containing surfaces species. The role of oxygen containing complexes, C(O), was carefully investigated. In a previous study, the reaction of bulk NO with nitrogen incorporated on carbon surface, C(N), was evidenced by the use of labeled reactants.

\[ \text{C( )} + \text{NO} \rightarrow \text{C(N)} + \text{C(O)} \]  \hspace{1cm} [1]

This study investigates further the behavior of C(N), based upon detailed mass balance, during NO reduction by carbon.

EXPERIMENTAL

Phenol formaldehyde resin (PF) char was used as carbon source throughout this study. Its preparation was described in details in a recent publication. In a typical experiment, about 200 mg of PF char was placed in a fixed bed reactor under He flow and then heat-treated at 950 °C for 30 min immediately before the following activation. Activation was achieved at 600 °C, under flowing 5% O₂ diluted in He for 20 min, resulting in about 20% burn-off. Samples were got rid of oxygen containing surfaces complexes by heating up to 950 °C for 30 min immediately before reaction. The concentration of reactant gas was normally around 535 ppm of NO diluted in He, alone or in the presence of O₂.

Gases emitted during experiments were identified and quantified simultaneously by a mass spectrometer (MS: Anelva AQA 200) and gas chromatography (GC: Area M200). For GC analysis, MS5 and PPQ columns were used for the separation of O₂, N₂ and CO and for CO₂ and N₂O respectively. GC was calibrated by using commercially available standard gases diluted in He. Ar was used as internal standard for quantitative MS analysis.
RESULTS AND DISCUSSION

Reduction of NO at 850 °C.

Gas evolution profiles presented in Figure 1 were obtained during the isothermal reduction of about 535 ppm NO over PF char, at 850 °C. As expected\textsuperscript{1,2,3}, CO represents the main contribution whether O\textsubscript{2} is present or not. CO\textsubscript{2} is present in lower concentration. Residual NO is present in both cases but a greater part is consumed in the presence of oxygen. The main nitrogen containing product is N\textsubscript{2}. Its concentration rapidly increases in the initial stage and reaches 100 ppm after 100 min when NO is flown alone and 200 ppm when 0.2% O\textsubscript{2} is added to the feeding mixture. N\textsubscript{2}O is detected as well, in low concentration. N\textsubscript{2}O concentration increases steadily with time and did not appear to level-off during experiments. When O\textsubscript{2} is added, N\textsubscript{2}O production is enhanced as well as N\textsubscript{2}. Whether O\textsubscript{2} is present or not, nitrogen unbalance appears, indicating that some nitrogen is accumulating on the PF char surface during experiment.

![Figure 1](https://example.com/figure1.png)

Figure 1. NO, N\textsubscript{2} and N\textsubscript{2}O evolution profile during the reduction of 535 ppm NO over PF char at 850 °C. I refers to curves obtained without O\textsubscript{2} while II were obtained in the presence of 0.2% O\textsubscript{2}.

Formation of Nitrogen-Containing Surface Compounds.

An estimate of the nitrogen accumulated on PF char (C(N)) was done in the presence of O\textsubscript{2} as well as in its absence and represented in Figure 2. Curve a represents the nitrogen concentration in PF char in the absence of
O₂ while curves b and c correspond respectively to a presence of 0.1 and 0.2 % oxygen in the reactant gas. For the shortest reaction time, no difference appears; the three curves follow the same evolution. For longer reaction times, the slope of the three curves decreases, indicating a lower accumulation rate. In the presence of oxygen, smaller amount of nitrogen are present on the carbon surface. This behavior may have two explanations. One is the occupation of reactive sites by O₂ and the second is the removal of C(N) from the surface by O₂. The negative slope obtained for the highest oxygen concentration favors the second.

Figure 2. Nitrogen accumulation into PF char during NO reduction at 850 °C. (a) Without O₂, (b) with 0.1 % O₂, (c) with 0.2 % O₂.

Figure 3. Influence of C(N) concentration in PF char on N₂ formation rate during NO reduction by PF char at 850 °C. (a) without O₂, (b) with 0.1% O₂, (c) with 0.2% O₂.
Mechanism of $N_2$ and $N_2O$ formation.

The relationship between $N_2$ formation rate and C(N) concentration shown in Figure 3 is not straightforward. However, a general trend is the increase of $N_2$ formation rate with the amount of C(N). Therefore reaction [2] would be the main reaction route.

In the presence of O$_2$, reaction [3] has been reported$^{3,4}$ to occur during the combustion of nitrogen-containing PF char. Due to this reaction, the amount of C(N) decreases with time in the presence of O$_2$ as is seen in Figure 2. $N_2$ formation rate per unit amount of C(N), the slope of the curve in Figure 3, is a function of O$_2$ concentration. NO concentration is appreciably lower in the presence of O$_2$ (Figure 1). Thus reaction [2] alone can not explain the results in Figure 3. NO reduction by CO is likely to increase the reaction rate in the presence of O$_2$.

$$\text{C(N) + NO} \rightarrow \text{C(O) or CO + N}_2$$ \hspace{1cm} [2]

$$\text{C(N) + O}_2 \rightarrow \text{C(O) or CO + NO + C( )}$$ \hspace{1cm} [3]

$N_2O$ formation rate presented in Figure 1 is too small to propose a detailed formation mechanism. However, it is noteworthy that some $N_2O$ was produced in the absence of O$_2$ (Figure 1), since it is generally accepted that $N_2O$ formation was observed only in the presence of O$_2$.\(^5\) A mechanism similar to $N_2$ formation (reaction[4]) would be postulated for the $N_2O$ formation in the absence of O$_2$. Since the $N_2O$ formation rate is larger in the presence of O$_2$ as shown in Figure 1, some other mechanism like reaction [5] should be taken into consideration.

$$\text{C(N) + NO} \rightarrow \text{C( ) + N}_2O$$ \hspace{1cm} [4]

$$\text{C(N) + NO + O}_2 \rightarrow \text{C( ) + N}_2O + \text{CO}_2$$ \hspace{1cm} [5]

CONCLUSION

Oxygen removes some C(N) from the carbon surface, providing reactive sites for further NO reaction, increasing $N_2$ and $N_2O$ production rate.

The formation of C(N) was proposed to explain the $N_2$ and $N_2O$ formation mechanism in the course of NO reduction by the carbon. This step is confirmed by thorough nitrogen mass balance established during the reaction. C(N) appeared to be the precursor of both $N_2$ and $N_2O$, though the reaction mechanism is not exactly the first order in C(N) as suggested by [2].

REFERENCES


