

Role of Oxygen in NO Reduction by Carbon

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Introduction

The reduction of nitrogen oxide by carbon has been widely studied during the last decade. Recently, we found the accumulation of a large amount of nitrogen-containing species on carbon surface, C(N), during C-NO reaction¹, and concluded that N₂ is mainly formed by the reaction between these surface species and gaseous NO².

As coal combustion occurs in the presence of a large amount of oxygen, a particular attention should be paid to the role of oxygen on this reaction. However, few papers were dedicated to the mechanism of NO reduction in the presence of oxygen,³⁻⁶ and it is not yet well understood. There are many possible explanations for the enhancement effect by O₂ for the production of N₂ from C-NO reaction. The present work was undertaken to identify the role of oxygen on the formation and consumption of surface C(N) species during C-NO reaction.

Experimental

Samples

Phenol formaldehyde resin (PF) char was used as ¹²C source. ¹³C and ¹⁵N¹⁸O were purchased from Isotec Inc.

Isothermal reactions and transient kinetics

C-NO reaction was carried out in a fixed bed reactor at atmospheric pressure. In a typical experiment, carbon was first activated with 5% O₂ at 600 °C for 20 min, and then the sample was heated to 950 °C for 30 min in He to remove surface oxygen species. The sample weight at this stage was ca. 160 mg. Isothermal reaction was achieved by flowing 0.05 % NO diluted in He in the presence of 0 - 0.4 % O₂. Gas flow was controlled at 200 ml/min. Transient kinetic was performed by switching feed gas from ¹⁵N¹⁸O/¹⁸O₂ to ¹⁴N¹⁶O/¹⁶O₂. Gaseous products were analyzed by mass spectrometry and gas chromatography.

Results and Discussion

Reaction profile

Figure 1 shows the mass balance for C-NO reaction without and with 0.2 % O₂. The formation of N₂ and N₂O was observed, but their sum was much less than the NO con-

sumed. This suggests the accumulation of nitrogen on carbon, indicated as N(C(N)) in Figure 1. In the initial 5 min, consumed N was transformed mainly to C(N) with some N₂ and a trace amount of N₂O. Interestingly, the accumulation rate was independent of O₂ concentration in this region (Figure 2). From this result, it can be said that the role of O₂ may

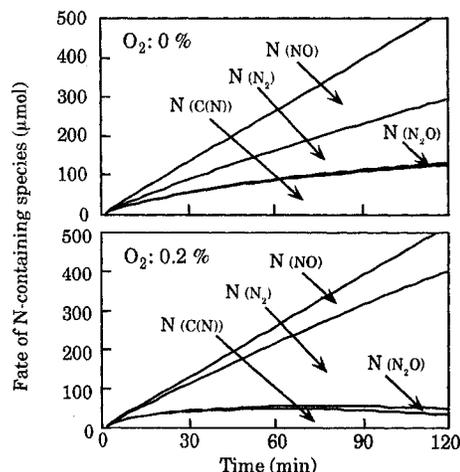


Figure 1. Fate of nitrogen-containing species during NO reduction by carbon in the absence and presence of O₂.

Carbon: PF char (ca. 160 mg); NO feed rate: 4.4 µmol·min⁻¹; Reaction temperature: 850°C.

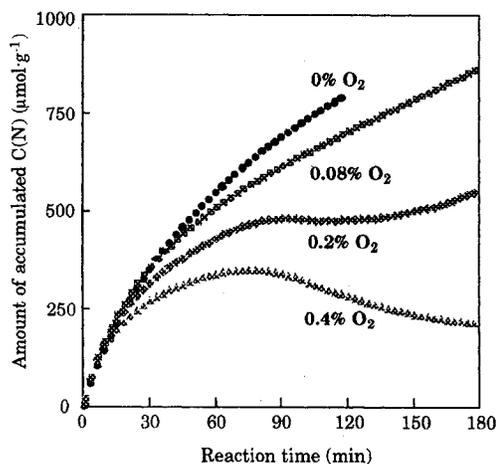


Figure 2. Variation of C(N) accumulated in PF char during the reaction. NO concentration: 0.05 % (feed rate: 4.4 µmol·min⁻¹); O₂ concentration: 0 - 0.4 %.

not be the activation of carbon for C(N) formation. In the later stage, less accumulation was seen with more O₂ feed. In the presence of 0.4 % O₂, the removal of C(N) was faster than accumulation after 80 min.

N₂ and N₂O formation

Figure 3 shows N₂ formation rate with different O₂ concentrations. The rate sharply increased in the very initial stage for all the cases, and the rate appeared independent of O₂ concentration. Since CO concentration at this stage strongly depends on O₂ concentration, the following possibility for the role of O₂ can be ruled out: more O₂ produces more CO, which then accelerates the homogeneous reduction of NO. In the later stage, a higher formation rate is achieved when more O₂ is present in the feed gas. N₂ formation is clearly enhanced by O₂. In our previous work, we observed that PF char containing some C(N) mainly produced N₂ instead of NO upon the reaction with O₂ at 600 °C⁵. It seems reasonable to assume that the principal role of O₂ is to remove C(N) from carbon surface.

N₂O formation rate is much smaller than that of N₂. In contrast with the rapid increase of N₂ formation rate in the initial stage, N₂O formation rate monotonously increased with time, implying that the mechanism of these reactions is not the same.

Transient kinetics

Figure 4 shows the result of transient kinetics with PF char (¹²C). N₂ production as determined by GC was rarely affected by gas switching. Main products in the second stage, ¹⁵N₂ and C¹⁸O, have the same m/e of 30. Immediately after the gas switching, a great amount of m/e 29 (¹⁴N¹⁵N) was observed, which might be formed via eq 1.



The most probable role of O₂ may be the removal of C(N). The nascent NO produced by the C(N)-O₂ reaction will be easily converted to N₂ via eq 1. It is interesting to check whether ¹⁴N₂ was produced from C(¹⁴N) accumulated in the first stage. Transient kinetics using ¹³C clearly indicated that a small portion of N₂ comes from the recombination of C(N). Such observation is very similar to those observed in the absence of O₂².

Conclusion

The initial step of NO reduction by carbon is the NO adsorption onto carbon surface to form C(N) and C(O). These surface species are removed by both O₂ and NO, forming N₂ and N₂O. In the presence of O₂, more N₂ was produced in

spite of less C(N) accumulation. It was suggested that the role of oxygen is likely to enhance the removal of C(N) from the surface.

References

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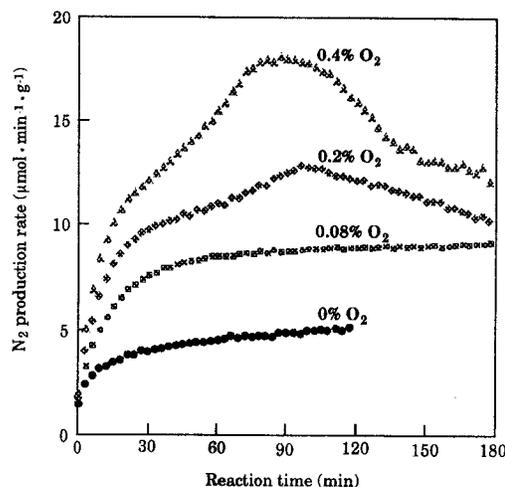


Figure 3. Variation of N₂ formation rate per remaining mass unit of PF char during the reduction of NO. NO concentration : 0.05 % (feed rate: 4.4 μmol · min⁻¹); O₂ concentration: 0 - 0.4 %; Temperature: 850 °C.

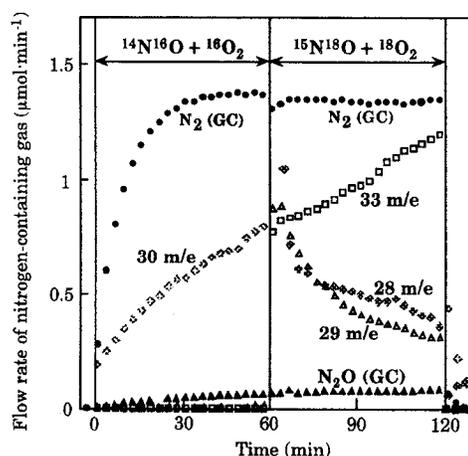


Figure 4. Gas evolution profile obtained by switching the reactant gas from ¹⁴N¹⁶O/¹⁶O₂ to ¹⁵N¹⁸O/¹⁸O₂. Carbon: PF char; NO: 0.05 %; O₂: 0.2 %; Temperature: 850 °C.