

SUPPRESSION OF NITROGEN OXIDES EMISSION BY CARBONACEOUS REDUCTANT

Akira Tomita

Institute for Chemical Reaction Science, Tohoku University,
Sendai, 980-8577, Japan.

Keywords: Coal Combustion, NO_x , Surface Complexes

Abstract

For several decades many attempts have been made to suppress the NO_x emission from coal-fired power plant. In order to meet a more stringent environmental regulation in future, it is necessary to develop new technologies. In this paper, the effective measures achieved so far will be summarized and then the unsolved problems will be discussed. Among them, the understanding of the heterogeneous reactions, where char surface is involved, is not enough. Thus we have investigated the heterogeneous reactions of the NO_x formation and destruction over char surface. The formation of NO during coal char combustion was examined by paying attention to the role of surface nitrogen species on char. The reactions of model carbon with NO as well as N_2O were also examined both experimentally and theoretically.

The Present State of the Art

In the 21st century, we may have to use more coal to meet the increasing energy demand, but unfortunately the use of coal results in many pollution problems. NO_x is the cause of acid rain, photochemical smog and greenhouse effect. N_2O is another important greenhouse gas and contributes to ozone depletion. The suppression of these gases is one of the most urgent subjects for us. Without any measures coal-fired power plant may emit NO_x of more than 700 ppm. Thanks to many efforts in the last 25 years, emission was reduced to a considerable extent. As primary measures, low NO_x burners, air staging (overfire air), fuel staging (reburning), flue gas recirculation and others were developed (Fig. 1), and selective catalytic reduction (SCR) or selective non-catalytic reduction are widely used as secondary measures [1]. Simply speaking, the purpose of these technologies is either to decrease NO_x formation by moderating combustion temperature or to enhance the reduction of NO_x once formed. Main reducing agents in furnace are hydrocarbon radicals and coal char, while NH_3 and urea are used to reduce NO_x in flue gas.

The present state of the art can be summarized as follows. Primary measures achieve 30-70% reduction in NO_x when applied separately. Higher reductions, up to 90%, can be achieved with their combination. Therefore, the reduction to 150-200 ppm level is easily achieved in advanced coal-fired power stations without SCR unit. If these primary measures are combined with SCR, the emission level can be suppressed to as low as 50-70 ppm. The most recent study even claims the success of designing a burner to reduce the NO_x level below 100 ppm, by keeping the amount of unburnt carbon at 3%. In Japan, legislation to limit NO_x emissions was enforced in 1970's, with more stringent standards in 1987. Occasionally even severer regulation is enforced by regional authority. Most frequently used primary measures are the combination of low NO_x burner and air staging. Sometimes flue gas recirculation or reburning is used in addition. SCR unit is also installed in many plants. The situations in other countries are quite different. For example, common power plants in the US use only low NO_x burners and the NO_x emission level is around 240 ppm.

These technologies became possible only through a fundamental understanding of the formation and destruction mechanisms that affect the overall NO_x emission. It can be said that the principal mechanisms have been identified in most cases. The formation of thermal NO_x , Zeldovich NO_x , is initiated by the reaction between O radical with N_2 in air. Another source of thermal NO_x is known as prompt NO_x , where hydrocarbon radicals assist the decomposition of N_2 leading to the NO_x formation. The most important contribution to the overall NO_x emission in coal-fired plant comes from fuel nitrogen. About 75-90% of NO_x is due to this source when low NO_x burner is used. The fate of fuel nitrogen is illustrated in Fig. 2. The volatile nitrogen and char nitrogen are oxidized to NO, and the NO is reduced by various reductants including char. The formation of NO_x from coal nitrogen is quite complex and not yet fully understood. The reduction of NO_x over char surface takes place to a significant extent. However, the contribution of this reaction on the overall NO_x reduction is not yet clear. The reaction mechanism, especially in high temperature zone, is also not well understood.

Regulations for NO_x and N_2O will become more and more stringent in near future. Without knowing the detailed mechanism of the reactions occurring during coal combustion, it would be difficult to meet such regulations. The formation of NO_x from fuel nitrogen and the decomposition of NO_x over char surface should be elucidated. The N_2O formation and destruction mechanism is also important to find out the best way to reduce it. At present, there is no regulation on N_2O emission, but about 50 ppm of

N₂O is emitted from fluidized bed coal combustor.

The Scope of this Paper

Among all reactions occurring in coal-fired combustion system, the least clear parts are the char-related reactions. Formation of NO_x from char and the reduction of NO_x over char surface are understood only superficially. Therefore in order to get a clearer picture of these reactions, we have investigated the mechanism of C-NO_x reaction. For the purpose of simplification, we used PF char (phenol formaldehyde resin char) as a model of coal char. This does not have inherent nitrogen before the reaction. We have studied the reaction of PF char with NO, the reaction of PF char with N₂O, as well as the NO_x formation from coal char combustion. The computer simulation studies have also been carried out for these systems. In this presentation we would like to summarize our results and discuss the future direction related to this field.

The most unique feature of our study is that we have paid a special attention to the role of surface nitrogen species on char. Boldly speaking, combustion people are only interested in the formation of NO_x but not necessarily in the N₂ formation. This was deduced from the fact that many studies have used air as oxidizing gas. This is simply because air is used in practical combustion systems. Thus the formation of N₂ has been neglected and, as a result, the nitrogen mass balance has not been obtained. On the contrary, we are interested in the overall reaction pathways including the formation of N₂. Thus we used O₂-He mixture instead of O₂-N₂ mixture for the coal char combustion, and NO-He mixture for the study of C-NO reaction. Thus we could establish the accurate nitrogen mass balance. Through this attempt, the amount of nitrogen species on carbon surface during the reaction could be quantitatively determined. It is well known that such surface species play an important role in many carbon gasification reactions.

Reaction of PF Char with NO

We have studied the C-NO reaction from various aspects, and have made several new findings in these studies [2-5]. First, the accurate mass balance clearly showed the presence of nitrogen accumulated on carbon surface. Many studies had noticed the presence of such surface nitrogen species, but there had been neither direct evidence nor quantitative data. Not only from the mass balance, but also from the XPS analysis the presence of surface nitrogen species was confirmed very clearly. The reaction can be described as



where C(·), C(N) and C(O) denote the surface free site, nitrogen and oxygen complexes, respectively. Then, the N₂ formation mechanism from C-NO reaction was identified in step response experiments using isotope gases. The reactant gas was switched from ¹⁴N¹⁶O to ¹⁵N¹⁸O during the reaction with PF char, and the product gases were analyzed (Fig. 3). The appearance of ¹⁴N¹⁵N immediately after the introduction of ¹⁵N¹⁸O strongly suggested that the main route for N₂ formation is as eq 2.



This holds true in a wide range of temperature from 600 to 1000 °C. This study presented the elementary reaction step of N₂ formation for the first time. Before this study, it was thought rather ambiguously that N₂ is formed from two C(N) species.

Effect of O₂ on the Reaction of C-NO

In the coal combustion system, the NO reduction by char takes place more or less in the presence of O₂. The effect of O₂ on the C-NO reaction is very remarkable. For example, N₂ formation rate is significantly increased by the presence of O₂, and N₂O formation is greatly affected by O₂. Even though the reasons for these observations are not known, there has been almost no systematic study on the C-NO-O₂ system. We carried out step response experiments in the presence of O₂, and it was found that the main N₂ formation path is similar to eq 2 [6]. As for the N₂O formation during the C-NO reaction, many studies reported that there is no N₂O formation in the absence of O₂ [7]. On the contrary, we observed some N₂O formation in the absence of O₂. This finding is practically not so important, but from a fundamental point of view this is important for identifying the true reaction mechanism. We need to revise the former explanation for this reaction.

Simulation of C-NO Reaction by Molecular Orbital Theory

The chemisorption of NO molecule on carbon surface and the subsequent decomposition of the surface species were simulated by an *ab initio* molecular orbital theory (MO) [8]. For simplicity, single layer of polyaromatic compounds was employed as a model for carbon. The MO calculation of the system including both the model carbon and NO molecule was made, and its geometrical parameters were optimized. The adsorption of NO on carbon edge sites resulted in the formation of several types of stable NO containing complexes, C(NO). To elucidate the N₂ formation route from the

surface nitrogen complexes, one more molecule of NO was put on the N atom of the C(NO) species. The MO calculation predicted the formation of six-member ring complex including NNO bonding. The bond population analysis predicted that N₂ desorption from such complex is very probable. The N-O bond is so weak as seen in Fig. 4 that C(NN) complex will be formed. The C-N bond in the resultant species is much weaker than N-N bond, and it can be easily dissociated to release N₂ molecule. This reaction scheme is exactly the same as eq 2, which was experimentally implied.

Reaction of PF Char with N₂O

Compared with the reaction with NO, the reduction of N₂O by carbon and the formation of N₂O from coal char are investigated to lesser extent. These reactions are not important at high temperature combustion, but very important for low temperature process like fluidized bed combustion.

In the case of the reduction of N₂O by carbon, it has been assumed that N₂ is produced from N₂O without any bond breaking between two nitrogen atoms, although there was no direct evidence. We have carried out a step response experiment, and found the reaction mechanism being eq 3 as was expected. There is little N=N splitting during C-N₂O reaction [9].



In MO simulation study, the calculation predicted the release of N₂ and the formation of C(O) when N₂O was put on the carbon edge [8]. This is again in agreement with the experimental observation.

NO_x Formation from Coal Char Combustion

As a result of recent development in low NO_x burner, the contribution of coal nitrogen to NO emission is of significant importance. In particular, the char nitrogen is the major contributor to the overall NO emissions. Therefore many studies have been carried out in relation to this reaction, and the importance of secondary reactions is suggested [10]. However, few researchers have shown an interest in the quantitative analysis of secondary reactions. We have carried out the reaction of coal char with O₂ in a fixed-bed reactor until the complete conversion of char, and established the mass balance. Fig. 5 shows the result of isothermal reaction at 850 °C with different bed heights. Several common features are noteworthy; (1) as a total, the major product was N₂, followed by NO, with a very small amount of N₂O, (2) the ratio of NO/N₂ was very small at the beginning but became almost unity at the final stage of reaction, and (3) the ratio decreased with increasing bed height. All of these observations can be explained if the occurrence of secondary reaction on char surface is assumed. We would like to emphasize again the important role of surface nitrogen species in this reaction. NO is expected to be the primary nitrogen-containing product from char combustion. NO thus produced would react with the char in the downstream to produce C(N), which then react with another NO to produce N₂ as in eq 2. If the remaining char became less and less, NO would escape from the bed without being converted to N₂. Thus the fractional conversion of char nitrogen to NO increased with char burn-off. This is in contrast with the observation by De Soete who reported that the fractional conversion of char nitrogen to NO was approximately proportional to the carbon burn-off [11]. This is probably due to the difference in reactor type, but further work is required.

Future Subjects

We now realize that we do not know much about the char-related NO_x reactions. We have to further investigate what actually happens in combustor. Especially the reaction behavior of char rapidly heated to high temperature should be explored. Through these studies, we may be able to design a better combustor with a lower NO_x emission.

References

- [1] S. C. Mitchell, "NO_x in pulverised coal combustion", IEA Coal Research (1998).
- [2] T. Suzuki, T. Kyotani and A. Tomita, *Ind. Eng. Chem. Res.*, **33**, 2840 (1994).
- [3] Ph. Chambriion, H. Orikasa, T. Suzuki, T. Kyotani and A. Tomita, *Fuel*, **76**, 493 (1997).
- [4] Ph. Chambriion, T. Suzuki, Z.-G. Zhang, T. Kyotani and A. Tomita, *Energy Fuels*, **11**, 681 (1997).
- [5] Ph. Chambriion, T. Kyotani and A. Tomita, *Energy Fuels*, **12**, 416 (1998).
- [6] Ph. Chambriion, T. Kyotani and A. Tomita, *Twenty-Seventh Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1998, pp. 3053.
- [7] G. F. Kramer and A. F. Sarofim, *Combust. Flame*, **97**, 118 (1994).
- [8] T. Kyotani and A. Tomita, *J. Phys. Chem.*, **107**, 3434 (1999).
- [9] K. Noda, Ph. Chambriion, T. Kyotani and A. Tomita, *Energy Fuels*, **13**, 941 (1999).
- [10] K. M. Thomas, *Fuel*, **76**, 457 (1997).
- [11] G. G. De Soete, *Twenty-Third Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1990, pp. 1257.

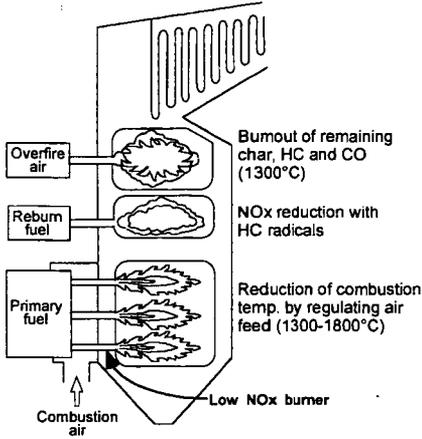


Figure 1. Advanced utility boiler with various measures for NO_x reduction.

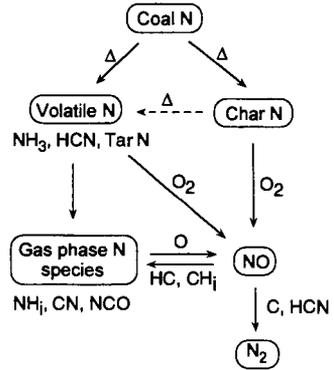


Figure 2. Reaction pathways to the formation of NO and N_2 from coal nitrogen.

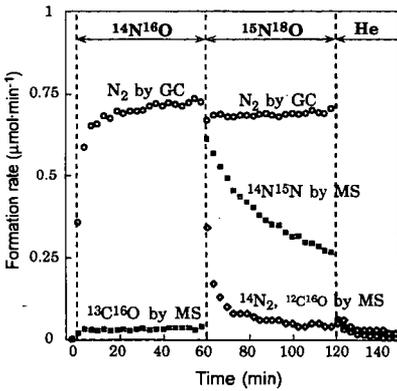


Figure 3. N_2 evolution profile during a step response experiment for C-NO reaction at 850°C .

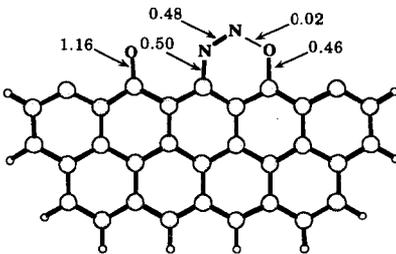


Figure 4. Stable structure of carbon with two NO molecules, suggested by MO simulation. Numbers indicate parameter of bond strength.

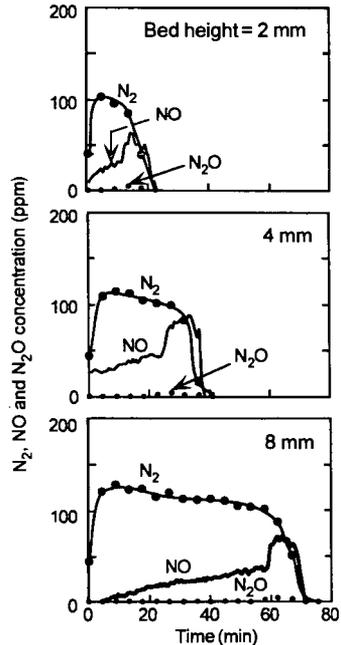


Figure 5. Effect of bed height on the gas evolution during O_2 gasification of coal char at 850°C .