KINETICS OF NO\textsubscript{x} REDUCTION BY UREA SOLUTION IN A PILOT SCALE REACTOR

JUNG BIN LEE** and SANG DONG KIM
Department of Chemical Engineering and Energy & Environment Research Center, Korea Advanced Institute of Science and Technology, TaeJon, 305-701, Korea

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The effects of urea molar ratio (1.0 - 2.6), reaction temperature and additives on NO reduction in flue gas have been determined in a pilot-scale flow reactor. A kinetic model is proposed for NO reduction rate with -NH and -CN in selective reducing agents (urea, cyanuric acid, ammonia). Two primary reactions can be expressed kinetically in the \text{DeNO\textsubscript{x}} process as:

\[
\begin{align*}
\text{N.S. (nitrogenous species)} + \text{O}_{2} (\text{oxidants}) & \rightarrow \text{NO} + \cdots (k_{1} \text{ rate constant for NO formation}) \\
\text{N.S.} + \text{NO} & \rightarrow \text{N}_{2} + \cdots (k_{2} \text{ rate constant for NO reduction})
\end{align*}
\]

in which the rate constants of \(k_{1}\) and \(k_{2}\) in the model are determined from the experimental data in the temperature range 1173 K - 1373 K as:

\[
\begin{align*}
k_{1} &= 4.01 \times 10^{11} \exp \left( - \frac{267}{RT} \right) \\
k_{2} &= 7.24 \times 10^{9} \exp \left( - \frac{230}{RT} \right)
\end{align*}
\]

The proposed model can predict the lowered activation energies caused by the addition of different species and molar ratio to NO.

Introduction

Numerous studies have been reported for cost-effective NO\textsubscript{x} reduction from fossil- and waste-fueled stationary combustion sources. Combustion modifications such as low NO\textsubscript{x} burner, flue gas recirculation and over fire air feeding are effective, yet only permit NO\textsubscript{x} reduction normally in the range of 20 - 50\% for liquid or solid fueled boilers. Recently, selective catalyst reduction (SCR) system is required for further NO\textsubscript{x} reduction to comply with the environmental air pollution regulation. However, SCR entails substantial capital and operating costs associated with the reactor construction, catalyst replacement, pressure drop through the system, and ammonia consumption. On the other hand, selective non-catalyst reduction (SNCR) is a useful method for NO\textsubscript{x} reduction by injecting amines (-NH\textsubscript{2}) or cyanides (-CN)- containing selective reducing agents such as (NH\textsubscript{3}, urea, cyanuric acid, and ammonium sulfate with air) into flue gas. This process could rapidly and efficiently reduce nitric oxide (NO) to N\textsubscript{2} and water at 1073 - 1373 K, the restrictive temperature window (Gullet et al., 1994). Numerous studies have been carried out to reduce NO with different reducing agents in a variety of flow reactors and the different approaches have been made to develop kinetic models of SNCR process. Although their experimental reactors are different each other, the obtained results are not greatly different with the same reducing agents. However, the difference in their kinetic models is the selection of the representative reactions for model analyses among the 150 chain radical reactions for NO reduction in the ammonia process (Duo et al., 1992; Fenimore, 1980; Hemberger et al., 1994; Lyon, 1976; VanDooren et al., 1994).

In the present study, the effects of urea molar ratio, reaction temperature and additives of liquid (CH\textsubscript{3}OH, \text{C}_{2}H\text{O}_{2}H) or gas (CO, \text{C}_{2}H\text{H}_{6}) to urea solution on NO reduction in flue gas have been determined in a pilot-scale flow reactor. A kinetic model for the overall NO reduction rate with -NH and -CN containing selective reducing agents is proposed for engineering application.

1. Urea/NO Reaction Mechanism

In the urea process, the urea solution injected into flue gas may initiate a sequence of reactions that convert NO to N\textsubscript{2}. At a sufficiently high temperature (\(\approx 793\) K), urea decomposes to HOCN and NH\textsubscript{3} in gas phase and initiates a sequence of NO removal reactions.

It has been reported (Caton and Siebers, 1989) that urea \([\text{(NH\textsubscript{2})\text{CO}}]\) decomposed into equal amounts of NH\textsubscript{3} and HNCO.

\[
\text{(NH\textsubscript{2})\text{CO} \longrightarrow NH\textsubscript{3} + HNCO (1)}
\]
The most important reaction path in NH₃ reaction with OH, O and H has been presented by Miller and Bowman (1989). Ammonia is converted to NH₃ primarily by the reaction with OH in the presence of water.

$$\text{NH}_3 + \text{OH}^- \longrightarrow \text{NH}_2^- + \text{H}_2\text{O}$$  (2)

and by the reaction with O in the absence of water.

$$\text{NH}_3 + \text{O}^2- \longrightarrow \text{NH}_3^- + \text{OH}^-$$  (3)

For self-sustaining the NH₂-NO reaction, OH must be directly or indirectly regenerated to proceed the conversion of NH₃ to NH₂. This regeneration is accomplished by the reactions (4) and (5).

$$\text{NH}_2^- + \text{NO} \longrightarrow \text{NNH}^- + \text{OH}^-$$  (4)

$$\text{NNH}^- + \text{NO} \longrightarrow \text{N}_2 + \text{HNO}^-$$  (5)

If the chain termination process does not interrupt the branching reaction sequence at the majority of reaction time, then the overall reaction is self-sustaining. The important chain termination reactions in the present mechanism are reactions (6)-(8) as shown below.

$$\text{NH}_2^- + \text{NO} \longrightarrow \text{N}_2 + \text{H}_2\text{O}$$  (6)

$$\text{NH}_2^- + \text{HNO}^- \longrightarrow \text{NH}_3 + \text{NO}$$  (7)

$$\text{OH}^- + \text{HNO}^- \longrightarrow \text{H}_2\text{O} + \text{NO}$$  (8)

The reaction kinetics on the HNCO process are not well understood compared to those of the NH₃ process. Perry and Siebers (1986) proposed the following mechanism to describe the HNCO process in which isocyanuric acid initiates reactions (9) and (10) and products of intermediates and reaction sequence are reactions (11) and (13).

$$\text{HNCO} \longrightarrow \text{NH}^- + \text{CO}^-$$  (9)

$$\text{NH}^- + \text{NO} \longrightarrow \text{N}_2\text{O} + \text{H}^-$$  (10)

$$\text{HNCO} + \text{H}^- \longrightarrow \text{NH}_2^- + \text{CO}^-$$  (11)

$$\text{NH}_2^- + \text{NO} \longrightarrow \text{N}_2 + \text{H}_2\text{O}$$  (12)

$$\text{NH}_2^- + \text{NO} \longrightarrow \text{NNH}^- + \text{OH}^-$$  (13)

Reactions (10), (12) and (13) contribute to NO removal (Mertrens et al., 1988; Traffic et al., 1988) and reaction (10) can explain the high levels of N₂O observed in a previous study (Caton and Siebers, 1989).

Since the complicated paths of NO reduction are unclear at the present time, the primary NO removal paths in the urea process can be only estimated by a hybrid of HNCO and NH₃ process (Caton and Siebers, 1989). Hence, it appears that the reaction mechanism of gas-phase urea-NO-O₂ comprises several reactions that are important in the NH₃ process since the comprised reactions in the HNCO process are also important in the NH₃ process (Miller and Bowman, 1989).

2. Experimental

Experiments were carried out in a pilot scale flow reactor of 0.20 m in diameter and 6.0 m high with a cylindrical LPG gas fired (30 kW) furnace attached at the bottom of the reactor as shown in Fig. 1. The main section of the reactor was constructed from the stainless steel tube with an internal diameter of 0.20 m. The reactor wall was insulated by fiberfrax (carbon-resistant materials) to prevent heat loss to surroundings so that a nearly constant temperature gradient can be attained. The flow rate of flue gas in the reactor was varied from 50 to 100 Nm³/hr. Eight sampling ports were mounted at 0.5 m height intervals along the reactor axis and radially spaced about 0.1 m. To measure temperatures at the urea injection point, axial and radial directions in the reactor, eight K-type thermocouples were mounted along the axial and radial locations in the reactor with a variation of thermal load in the furnace. The desired amount of NO was added at the bottom of the reactor. The oxygen concentration was also controlled by varying the relative amounts of air and LPG. Air was introduced into the reactor through two atomizing nozzles (0.4 mm-ID) at the middle of lower combustion tunnel. To prevent reactions of urea solution and the additives before injecting into flue gas, a water-cooled injection tube was employed. Also, a perforated distributor plate (200 holes of 2 mm-ID) was installed at the bottom of the reactor to maintain uniform fluid velocity and NO concentration in the reactor.

The inlet concentration of NO in the reactor was varied between 250 and 350 ppm and the outlet concentration of NO was measured at the injection temperature range from 700 K to 1373 K at 50 K intervals. During the experiments, the molar ratio of urea solution (5% w/w) to NO was varied from 1.0 to 2.5 and that of oxygen was varied in the range of 3 to 5%. To determine the effect of additives on NO reduction, the additive was sprayed into the stream of combustion products together with the urea solution through two atomizing nozzles (0.4 mm-ID). The mean droplet size was approximately 50 μm in diameter. The sampled gas from the sampling probe was passed through a cooler for removal of water and
sent to a stack gas analyzer to measure concentrations of NO, NH₃ and O₂.

3. Results and Discussion

3.1 Proposed reaction mechanism

A simple reaction kinetic model of the urea process is proposed for two major reaction paths: one is the NO reduction and the other is NO formation. In general, the overall reactions of NO reduction with the selective reducing agents containing -NH and -CN can be described as two primary reactions as:

\[
\frac{d[NO]}{dt} = k_r [N.S.] - k_i [N.S.][NO] \quad (16)
\]

\[
\frac{d[N.S.]}{dt} = k_r [N.S.] - k_i [N.S.][NO] \quad (17)
\]

with the following initial conditions:

\[
[NO] = [NO]_i, \quad [N.S.] = [N.S.]_i \quad t = 0 \quad (18)
\]

In the above rate expressions, the non-uniform temperature profile in the present pilot scale reactor may be considered by coupling Eqs. (16) and (17) with \(dT/dt = \) constant. However, \(dT/dt = \) constant term is not needed in the present model since the reaction time is very short and most of the reaction takes place at a nearly constant injection temperature. Therefore, it can be assumed that the present experiments may take place in an isothermal flow condition.

To develop a simple and quantitative reaction rate equation for the urea process, since urea (\(NH_2CONH_2\)) based chemicals decomposes into \(NH_3\) and HOCN per mole of urea, it is assumed that molar fraction of urea to two moles of NO is same as the molar fraction of \(NH_3\) to NO or HOCN to NO. Also, the nitrogenous species of urea may be expressed in terms of \(NH_3\) by multiplying molecular weight of ammonia by urea concentration and then dividing by
the molecular weight of urea. Then, Eqs. (16) to (18) may be expressed as:

\[
\frac{d[NO]}{dt} = k_t \left[ \frac{NH_3}{NO} \right] \left[ \frac{NH_3}{NH_3} \right]
\]

\[
- k_t \left[ \frac{NH_3}{NO} \right] \left[ \frac{NO}{NH_3} \right] \left[ \frac{NH_3}{NH_3} \right]
\]

\[
\frac{d[N.S.]}{dt} = -k_t \left[ \frac{NH_3}{NH_3} \right] - k_t \left[ \frac{NO}{NO} \right] \left[ \frac{NH_3}{NH_3} \right] \left[ \frac{NO}{NO} \right]
\]

(19)

with the following initial conditions

\[
\left[ \frac{NO}{NO} \right] = 1, \quad \left[ \frac{NH_3}{NH_3} \right] = 1, \quad t = 0
\]

(21)

The nonlinear differential equations of (19) and (20) can be solved by adjusting two parameters \((k_t, k_i)\) by using the Runge-Kutta-Verner method.

### 3.2 Estimation of amounts of NO and NH₃ with time in urea process

To model the urea process, a relationship between the time required to complete the reaction (urea+NO) and reaction temperature in the present experimental conditions has to be determined. The relationship between the time required to complete reaction and reaction temperature with the measured concentration of NO and NH₃ at a normalized stoichiometric ratio (NSR) of 1.0 is found to be \(T = 0.65 - 4.02 \times 10^{-4} T\) as shown in Fig. 2.

The calculated fractions of NO and NH₃ as a function of reaction time at the injection or reaction temperature of 1173–1373 K are shown in Fig. 3. At the higher temperatures, the NO and NH₃ fractions sharply decrease up to reaction time of 0.05 s and thereafter it remains constant. The calculated values agree well with the experimental values since the conversions of NO and NH₃ are constant after the calculated reaction time of \(T = 0.65 - 4.02 \times 10^{-4} T\). Whereas, the agreement between the model and experimental data becomes poorer with decreasing reaction temperature with wide fluctuation of NH₃ concentration since the NO reduction is limited principally by the rates of chain termination reactions (6)-(8) that compete with the branching sequence reactions (4) and (5). As temperature increases, an increase in chain-carrier concentration becomes so rapid that reaction (3) eventually begins to compete favorably with reactions (4) and (6) for NH₂ in the absence of water. Reaction (2) followed by reaction NH₃+HNO——NH₃+NO and OH+HNO——H₂O+NO leads to NO formation (Miller and Bowman, 1989).

### 3.3 Determination of the rate constants \((k_t, k_i)\)

The rate constants of NO formation \((k_t)\) and NO
reduction \( (k_c) \) are determined at the reaction temperature in the range of 1173–1373 K and atmospheric pressure with about 4% O\(_2\). From the Arrhenius plot \( (\ln k_f \text{ and } \ln k_r \text{ vs } 1/T) \) in Fig. 4, temperature dependence of the reaction rate coefficient can be derived as:

\[
k_f = k_{f0} \exp \left(-\frac{E_f}{RT}\right)
\]
\[
k_r = k_{r0} \exp \left(-\frac{E_r}{RT}\right)
\]

where \( k_{f0} \) and \( k_{r0} \) are the pre-exponential factors and \( E_f \) and \( E_r \) are activation energies.

The relationships between \( k_f \) or \( k_r \) and reaction temperature (T) can be represented by straight lines in Fig. 4 with the following equations.

\[
\ln k_f = 27.717 - 3.207 \times 10^4 / T
\]
\[
\ln k_r = 25.005 - 2.765 \times 10^4 / T
\]

The parameters of \( k_{f0}, k_{r0}, E_f \) and \( E_r \) in Eqs (22) and (23) can be determined from Eqs. (24) and (25) as:

\[
k_{f0} = 4.01 \times 10^{11} \text{ and } E_f = -267
\]
\[
k_{r0} = 7.24 \times 10^{10} \text{ and } E_r = -230
\]

3.4 Prediction of NO and NH\(_3\) conversion at different molar ratio of Urea/NO

To verify the present kinetic model, the calculated NO and NH\(_3\) conversion data from the model are compared with the experimental data from the present and previous studies (Jørgensen et al., 1990; Lin et al., 1991; Arand et al., 1980).

The effect of reaction temperature on the fractional conversions of NO and NH\(_3\) is shown in Fig. 5 as a function of reaction temperature and the normalized stoichiometric molar ratio of urea to NO (NSR \( \approx \) 1.0, 1.5 and 2.0) with the data of previous studies (Jørgensen et al., 1990; Lin et al., 1991; Arand et al. 1980). As can be seen, the conversions of NO and NH\(_3\) in the different reactors are similar at the same molar ratio to NO and the best agreement between the data from the model and experiment is observed at NSR \( \approx \) 1.0. The agreements with the experiment data at NSR \( \approx \) 1.5 and 2.0 are not as good as for the experimental data at NSR \( \approx \) 1.0 due to the possible uncertainty in the correlated equation between the time required to complete reaction and reaction temperature as well as uncertainties in the other rate parameters such as droplet size of urea solution or the overall mixing behavior (Görner and Eppler, 1989).

At the molar ratio above 2.0, further NO reduction can not be achieved and NH\(_3\) emission increases slightly at the optimum reaction temperature.

3.5 Effect of additives to urea solution on NO reduction

A disadvantage of the SNCR process would be the narrow temperature range for effective NO reduction. In the boiler operation with varying load, many existing boilers do not have enough space to inject urea solution at the effective temperature range and NO reduction is often desirable at lower tem-
temperatures. Addition of small amounts of additives to urea solution makes it possible to decrease the optimum reduction temperature. Therefore, the effect of additives [CO, C\textsubscript{3}H\textsubscript{8}, CH\textsubscript{3}OH(MeOH), C\textsubscript{2}H\textsubscript{5}OH(EtOH)] to urea solution on the NO reduction has been determined with the proposed kinetic model. The gas additive of CO or C\textsubscript{3}H\textsubscript{8} was injected into the carrier gas for spraying urea solution. The amounts of gas additives were varied from 1.0 to 4.0 of the relative molar ratio to NO and the molar ratio urea to NO is constant at 2.0. It has been found that CO additive provides wider temperature window (1073 K - 1373 K) for optimum NO reduction than that (1173 K - 1373 K) of urea solution only (Fig. 6).

The optimum temperature window shifted to lower reaction temperatures about 50 K with increasing the molar ratio of CO/NO, but NO reduction is about 15% lower than that of urea solution only at the optimum reaction temperature. Thus, the urea process is proven to be more effective in CO rich environment due to reburning of CO in flue gas which may extend to lower temperature range for NO reduction (Suhlmann and Rotzoll, 1993) (Fig. 7).

Compared to CO additive, C\textsubscript{3}H\textsubscript{8} gas additive provides wider window reaction temperature (1023 K - 1373 K) at C\textsubscript{3}H\textsubscript{8}/NO molar ratio of 2.0. In this case, the degree of NO reduction is about 15\% lower than that of urea solution only at the optimum reaction temperature. With a further increase in molar ratio of C\textsubscript{3}H\textsubscript{8}/NO to 4.0, the reaction temperature window can not be widened compared to that with the molar ratio of 2.0 and NO reduction decreases about 20\% at the optimum reaction temperature.

In case of liquid additives of CH\textsubscript{3}OH (MeOH) or C\textsubscript{2}H\textsubscript{5}OH (EtOH), the additive into urea solution was sprayed into the stream of combustion products. The molar ratio of urea/NO was held at 2.0 and the molar ratios of MeOH/NO and EtOH/NO were held constant at 0.5. These liquid additives do not provide wider reaction temperature window compared to that of the gas additives (CO, C\textsubscript{3}H\textsubscript{8}) as can be seen in Fig. 8. The optimum temperature window is shifted to lower temperature about 50 K than that with urea solution only (Evans and Seeker, 1993), but NO reduction decreases at the optimum reaction temperature in the case of gas additives. The NO reduction with a wider reaction temperature window may be due to the acceleration of NO reduction and NO formation by urea solution with the addition of additives (Duo et al., 1992). Hence, the nitrogenous intermediate radicals (NH\textsubscript{3}, NH\textsubscript{2}, NNH, HNO) are produced from conversion of urea and consequent reduction and formation of NO at lower temperatures as in the case.
Table 1  Activation energy lowered by additives at the molar ratio of urea/NO=2.0

<table>
<thead>
<tr>
<th>Additive</th>
<th>Molar ratio to NO</th>
<th>$E_\text{f}$ (kJ/mol)</th>
<th>$E_\text{r}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>2.0</td>
<td>242</td>
<td>211</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>232</td>
<td>202</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>2.0 and 4.0</td>
<td>237</td>
<td>205</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>257</td>
<td>227</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>0.5</td>
<td>252</td>
<td>220</td>
</tr>
</tbody>
</table>

of this study.

The activation energies of NO formation ($E_\text{f}$) and reduction ($E_\text{r}$) with the additives can be predicted by the presented model and the predicted values of $E_\text{f}$ and $E_\text{r}$ with the additives of CH₃OH, CO, MeOH and EtOH are listed in Table 1.

Conclusion

The effects of reaction temperature, molar ratio of urea to NO and additives on NO reduction by using urea solution have been determined in a pilot scale reactor. The optimum reaction temperature and the molar ratio for maximum NO reduction are found to be about 1273 K and 2.0, respectively. Ammonia emission is not observed at an optimum temperature, but the emission becomes significant at the molar ratio greater than 2.0. Among the tested liquid or gas additives, CO gas additive is the most effective one for NO reduction with wider temperature window.

A simple kinetic model is proposed based on the two main reactions for the urea process. The model can successfully predict NO and NH₃ concentrations with urea solution and the additive to urea solution in a pilot-scale reactor.

Nomenclature

- $E_\text{f}$: activation energy of rate constant $k_\text{f}$ [kJ/mol]
- $E_\text{r}$: activation energy of rate constant $k_\text{r}$ [kJ/mol]
- $k_\text{f}$: rate constant of NO formation [s⁻¹]
- $k_\text{r}$: rate constant of NO reduction [m³/mol s]
- NH₃: NH₃ concentration corresponding to urea molar ratio to NO [ppm]
- NH₃: NH₃ concentration at the sampling probe [ppm]
- NO: NO concentration at the reactor inlet [ppm]
- NO: NO concentration at the sampling probe [ppm]
- NSR: normalized stoichiometric ratio [urea/NO]
- $R$: gas constant, 8.314×10⁻⁵ [kJ/mol K]
- $t$: reaction time [s]
- $T$: injection or reaction temperature of urea solution in the reactor [K]
- $\tau$: time required to complete reaction between urea and NO [s]

Literature Cited


