Technical Note

NO removal by reducing agents and additives in the selective non-catalytic reduction (SNCR) process

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Abstract

The effect of the additives on the selective non-catalytic reduction (SNCR) reaction has been determined in a three-stage laboratory scale reactor. The optimum reaction temperature is lowered and the reaction temperature window is widened with increasing concentrations of the gas additives (CO, CH₄). The optimum reaction temperature is lowered and the maximum NO removal efficiency decreases with increasing the concentration of alcohol additives (CH₃OH, C₂H₅OH). The addition of phenol lowers the optimum reaction temperature about 100–150 °C similar to that of the toluene addition. The volatile organic compounds (VOCs: C₆H₅OH, C₇H₈) can be utilized in the SNCR process to enhance NO reduction and remove at the same time. A previously proposed simple kinetic model can successfully apply the NO reduction by NH₃ and the present additives.

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1. Introduction

The rapid industrialization brought severe air pollution problems (SOₓ, NOₓ) caused by combustion processes in industries and transportation engines (car, train, aircraft). Because of these air pollution problems, air quality has become worse and worse so that the air pollution control regulations became stringent accordingly. Therefore, new technologies should be developed to reduce the pollutants within the regulation limit from combustion processes.

Numerous studies have been reported for cost-effective NOₓ reduction from stationary combustion sources. These technologies include selective catalytic reduction and selective non-catalytic reduction (SNCR). The SNCR process is a useful method for NOₓ reduction by injecting amines (–NH–) or cyanides (–CN–) containing selective reducing agents such as NH₃, urea and cyannic acid into the flue gases (Rota and Zanoelo, 2003; Lee et al., 2005). This process could reduce nitric oxides to nitrogen and water rapidly and effectively at rather higher (1073–1373 K) temperatures (Gullett et al., 1994). It has been reported that injection of some additives together with the reducing agents in SNCR processes can lower and widen the optimum reaction temperature window for NOₓ reduction (Leckner et al., 1991; Duo et al., 1992; Lee and Kim, 1996; Lim et al., 1997).

In the present study, the effects of the additives and reaction temperatures in the SNCR process were determined in the lab-scale reactor.

2. Experimental

Experiments were carried out in a laboratory scale reactor (0.05-m ID × 0.72-m height) that has three-stages with a plenum chamber (0.05-m ID × 177-mm height) at the bottom of the reactor as shown in Fig. 1. A perforated gas distributor, with 19 holes drilled 2 mm in diameter holes on a triangle grid, separates the main column and the plenum. The α-alumina particles (3 mm in diameter) were added...
as packing media in each section of the reactor to increase the gas mixing through the distributor and the packing. The experimental apparatus consists of three sections: feeding system of the reducing agents and additives, a reactor and a gas analyzer. The reactor wall was insulated by Fiberfrax to prevent heat loss. The reactor temperature was measured by two K-type thermocouples in each stage of the reactor and one in the plenum chamber. The total flow rate through the reactor was maintained at \( 47 \text{ l min}^{-1} \) (residence time = 1.4 s) and the reaction temperatures were varied in the range of 973–1323 K. The inlet concentration of NO into the reactor was 300 ppm and that of O\(_2\) and H\(_2\)O were 3 vol.\% and 5 vol.\%, respectively. The gas flow was controlled by a flow meter (Mathexon Co.) and the liquid flow was controlled by Masterflex pump. The normalized stoichiometric ratio (NSR) of the reducing agent ([NH\(_3\)]/[NO]) was 2.0 which is the optimum point in the present experimental conditions. The NSR ([additives]/[NO]) of additives (CO, CH\(_4\), CH\(_3\)OH and C\(_2\)H\(_5\)OH) was varied from 1.0 to 3.0 and that of C\(_6\)H\(_5\)OH and C\(_7\)H\(_8\) additives was varied from 0.5 to 1.5. The concentrations of NO and NH\(_3\) were continuously measured by ND-IR type gas analyzers (Chung Eng. Co., Korea, Siemens Co., Germany) and those of toluene and phenol were measured by gas chromatography analyzer (GC, HP-5890). The measured concentrations of NO and NH\(_3\) over 30 min were averaged by more than 5 times within 10% error bound.

3. Result and discussion

The effect of reaction temperature on NO reduction with a variation of [CO]/[NO] is shown in Fig. 2a. The optimum reaction temperature is lowered and the reaction temperature window is widened with increasing CO concentration as reported by Caton and Siebers (1989). The effect of CO addition to flue gas on NO conversion can be explained by CO oxidation in the presence of water vapor. Oxidation of CO in the presence of water vapor increases the supplies of OH and O at lower temperatures by the reactions of

\[
\begin{align*}
H + O_2 & \rightleftharpoons OH + O \\
O + H_2O & \rightleftharpoons OH + OH
\end{align*}
\]

and coupled with the following reaction as of the CO oxidation mechanism.

\[
OH + CO \rightleftharpoons H + CO_2
\]

The availability of OH- and O-atoms shifts NO reduction to lower temperatures that results in lowering the optimum reaction temperature (Suhlmann and Rotzoll, 1993; Alzuet et al., 1997).

The effect of reaction temperature on the NO reduction with a variation of [CH\(_4\)]/[NO] is shown in Fig. 2b. The optimum reaction temperature is lowered and the reaction temperature window is widened with increasing CH\(_4\) concentration. The addition of hydrocarbon widens the reaction temperature window and shifts the reaction temperature to lower points through reactions (4) and (6). However, the maximum NO removal efficiency decreases with increasing the hydrocarbon concentration by the oxidation mechanism of reaction (7) (Lodder and Lefers, 1985; Jodal et al., 1992; Lim et al., 1997).

\[
\begin{align*}
CH_4 + NO & \rightarrow HCN + O \rightarrow HNCO \\
HNCO + OH & \rightarrow NCO + H_2O \\
NCO + NO & \rightarrow N_2 + CO_2 \\
NCO + O & \rightarrow NO + CO
\end{align*}
\]

As can be seen in Fig. 3, the addition of liquid additives (CH\(_3\)OH, C\(_2\)H\(_5\)OH) does not provide wider reaction temperature window compared to that of the gas additives.
The optimum reaction temperature is shifted a little to lower temperature than that of the reducing agents only. However, NO removal efficiency at the optimum temperature decreases with increasing the concentrations of liquid additives (Evans et al., 1992; Lee and Kim, 1996).

In the present study, phenol (C₆H₅OH) and toluene (C₇H₈) were employed as the additives in the SNCR process. As can be seen in Fig. 4a, the optimum reaction temperature is shifted to lower temperature with an addition of phenol to the feed stream. At higher temperature above 700°C, phenol is decomposed into CHᵢ and OH radical. CHᵢ radical promotes NO reduction through reactions (4) and (6) as in case of CH₄. The supplies of OH radical concentration increase NH₂ radical concentrations through reaction (9) and NH₂ radicals promote NO reduction through reactions (10) and (11) (Teixeira et al., 1991; Chen et al., 1993; Rota et al., 2002).

\[
\text{C}_6\text{H}_5\text{OH} + \text{O}_2 \rightarrow \text{CH}_i + \text{OH} + \text{CO}_2 + \text{H}_2\text{O} \quad (8)
\]
\[
\text{NH}_3 + \text{OH} \rightarrow \text{NH}_2 + \text{H}_2\text{O} \quad (9)
\]
\[
\text{NH}_2 + \text{NO} \rightarrow \text{NNH} + \text{OH} \rightarrow \text{N}_2 + \text{H}_2\text{O} \quad (10)
\]
\[
\text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H} + \text{OH} \quad (11)
\]

As shown in Fig. 4b, an addition of toluene to the main stream also promotes NO reduction. The maximum NO removal efficiency decreases somewhat compared to phenol at the same molar ratio. Phenol and toluene were not detected in the outlet gases by gas chromatography analyzer. Therefore, it can be claimed that the volatile organic
compounds (VOCs) such as phenol and toluene can promote NO reduction and these pollutants can be removed at the same time.

It has been known that the total reaction mechanism of SNCR process is described by the following two reactions as

\[
\begin{align*}
NH_3 + NO + 1/4O_2 & \rightarrow N_2 + 3/2H_2O \quad (12) \\
NH_3 + 5/4O_2 & \rightarrow NO + 3/2H_2O \quad (13)
\end{align*}
\]

The total reaction mechanism of NO reduction using reducing agents is described by the two primary reactions (Duo et al., 1992; Lee and Kim, 1996) as

\[
N.S. + O_x \rightarrow NO + \ldots \quad (14)
\]

\[
N.S. + NO \rightarrow N_2 + \ldots \quad (15)
\]

\(k_f\): rate constant for NO formation

\(k_r\): rate constant for NO reduction.

In Eqs. (14) and (15), N.S. is nitrogenous species leading to formation or reduction of NO and \(O_x\) is an oxidant.

It was assumed that the reverse reactions (Eqs. (14) and (15)) do not occur and oxygen is present in great excess so that \(O_2\) concentration can be constant during the reaction. Thus, the rate expression for NO and N.S. can be expressed as

\[
\begin{align*}
\frac{d[NO]}{dt} &= k_f[N.S.] - k_r[N.S.][NO] \quad (16) \\
\frac{d[N.S.]}{dt} &= -k_f[N.S.] - k_r[N.S.][NO] \quad (17)
\end{align*}
\]

with the following initial conditions:

\[
[NO] = [NO]_i, \quad [N.H_3] = [N.H_3]_i \quad \text{at} \ t = 0 \quad (18)
\]
It was assumed that the present experiments may take place in an isothermal flow condition. In Eqs. (16) and (17), the values of $k_f$ and $k_r$ were obtained by numerical integrator (IMSL, International Mathematical and Statistical Library) with the variation of NO and NH$_3$ concentrations as a function of time from Fig. 5. The value of $k_f$ and $k_r$ were estimated from the Arrhenius plot of the four different temperatures from Fig. 5. The plots for $\ln k_f$ and $\ln k_r$ versus $1/T$ approximately obey a linear relation and the relationships between $k_f$ or $k_r$ and reaction temperature ($T$) can be represented with the following equations:

$$\ln k_f = 29.550 - 3.247 \times 10^4 / T$$

$$\ln k_r = 28.771 - 2.818 \times 10^4 / T$$

Therefore, the activation energies and the pre-exponential factors of NO formation and NO reduction are found to be $270$ kJ mol$^{-1}$ at $6.81 \times 10^{12}$ and $234$ kJ mol$^{-1}$ at $3.17 \times 10^{12}$, respectively.

The activation energies ($E_f$, $E_r$) are lowered by the additives that can be predicted by the model Eqs. (21) and (22) and the predicted values of $E_{fa}$ and $E_{ra}$ with the additives (CO, CH$_4$, CH$_3$OH, C$_2$H$_5$OH) are listed in Table 1.

The comparison of the experimental and calculated NO reductions with the gas and liquid additives is shown in Fig. 6. The calculated conversion from the kinetic model predicts the experimental data very well. Therefore, the NO reduction by NH$_3$ and the additives can be predicted by the simple kinetic model of Lee and Kim (1996) in the present system.

4. Conclusions

The NO removal characteristics with NH$_3$ and the additives in SNCR process have been determined in the three-stage laboratory scale reactor. The addition of CO and CH$_4$ lowers the optimum reaction temperature and widens the optimum temperature window. The liquid additives (CH$_3$OH, C$_2$H$_5$OH) do not provide wider reaction temperature window. At higher temperatures above 700°C, the addition of phenol and toluene lowers the optimum reaction temperature about 100–150°C by their decomposition and they can be removed with NO in the SNCR process simultaneously. The NO reduction by NH$_3$ and the additives in the present study can be predicted successfully by the simple kinetic model of the present author (Lee and Kim, 1996).

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