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NO_x Removal by Selective Noncatalytic Reduction with Urea Solution in a Fluidized Bed Reactor

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Abstract–A fluidized bed reactor has been developed to overcome the plugging problem of urea injection by employing a sparger rather than nozzles in the SNCR process for simultaneous removal of SO_2 and NO_x. In a developed fluidized bed reactor, the optimum temperature to remove NO_x is shifted to lower values, the reaction temperature window is widened with the presence of CO in flue gas, and NO conversion is higher than that in a flow reactor. The optimum amount of urea injection in the reactor is found to be above 1.2 based on the normalized stoichiometric molar ratio (NSR) with respect to NO conversion. In the simultaneous removal of SO_2/NO, conversions of SO_2 and NO reach 80-90%, nearly the same values for the individual removal of SO_2 and NO above 850 °C.

Key words : NO_x Removal, Urea, Selective Noncatalytic Reduction (SNCR), Nozzle, Fluidized Bed

INTRODUCTION

Numerous studies have been reported for cost-effective NO_x reduction from stationary combustion sources. These technologies include selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR). In these processes, a chemical agent is injected into flue gas stream. SCR processes, which can achieve NO_x removal at lower temperatures, are more complicated, expensive and require higher upstream pressures than SNCR processes. Also, the SNCR process is a useful method for NO_x reduction by injecting amines (-NH-) or cyanides (-CN-) containing selective reducing agents such as NH_3, urea, cyanuric acid and ammonium sulfate into flue gas. This process could rapidly and effectively reduce NO to N_2 and N_2O at 1,073-1,373 K [Gullett et al., 1994]. It has been reported that injection of some additives together with the reducing agent in SNCR processes can lower and widen the optimum reaction temperature window for NO_x reduction [Lee and Kim, 1996; Lim et al., 1997; Leckener et al., 1991; Duo et al., 1992]. On the other hand, SNCR processes have some drawbacks to overcome difficulties of reaction temperature control, nozzle plugging due to injection of reducing agent and formation of ammonium salt by the reaction of reducing agent (NH radicals) with SO_2 in flue gas.

Therefore, in the present study, a simple sparger was installed in a fluidized bed reactor to eliminate nozzle plugging due to the injection of urea solution in the reactor to remove SO_2 and NO_x simultaneously. The effects of reaction temperature, normalized stoichiometric molar ratio (NSR), O_2 concentration, gas flow rate and SO_2 on NO reduction have been determined in a fluidized bed reactor.

EXPERIMENTAL

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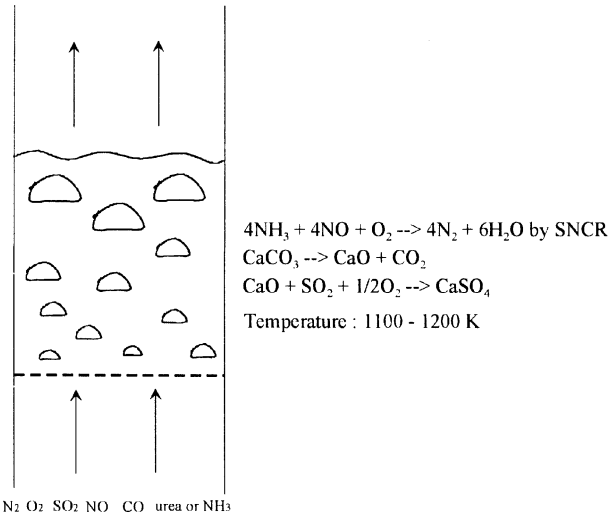

Fig. 1. Reaction scheme of SO_x/NO_x removal in a fluidized bed.

The reaction scheme of SO_x/NO_x removal in a fluidized bed reactor is shown in Fig. 1. NO in flue gas and NH radicals produced from evaporation of urea solution were mixed and reacted through a distributor and the bubbling fluidized bed with violent solid mixing. The reactor was operated at 1,100-1,200 K where NO can be reduced by the injected of NH radicals and gaseous additive (CO) and SO_2 can also react with the calcined lime to produce $CaSO_4$. The multiple reactions such as NO reduction, calcination of limestone and sulfation of calcined CaO with SO_2 take place in the bubbling fluidized bed.

Experiments were carried out in a fluidized bed reactor (0.15 m-ID×2.5 m-high) having a bubble cap type distributor as shown in Fig. 2. The experimental apparatus consisted of three sections: a gas feeding system, a reactor and a gas analyzer. Simulated flue gas was introduced in the reactor through flow meters. An electric heater was installed to preheat the simulated

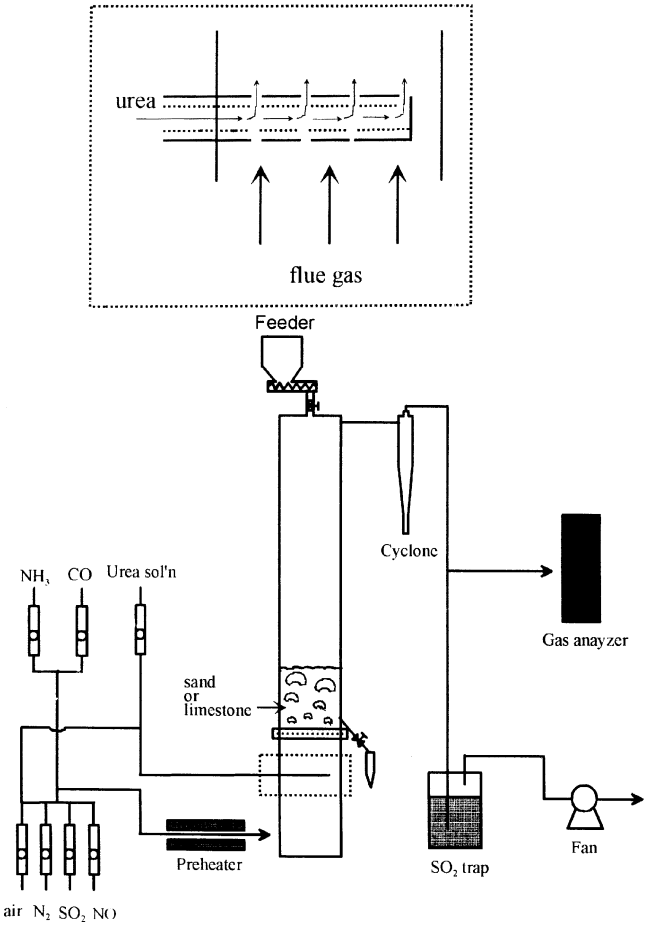

Fig. 2. Experimental apparatus (fluidized bed reactor).

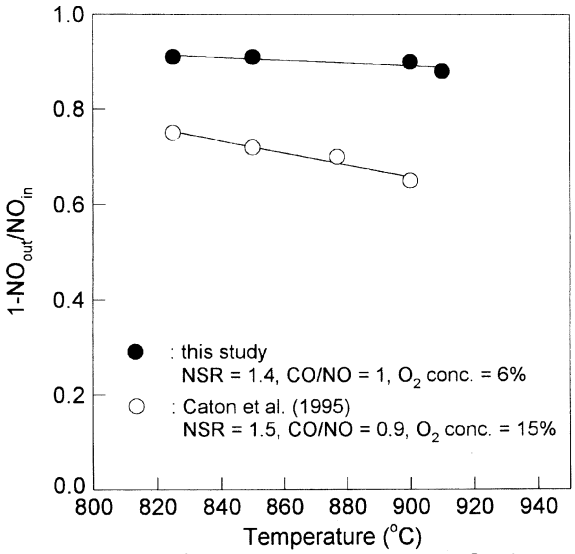

Fig. 3. Effect of reaction temperature on NO reduction using NH_3 as a reducing agent.

flue gas (400 ppm NO, 400 ppm CO, 5% O_2, balanced N_2). Urea solution was injected through a sparger by pressure instead of atomizing nozzles to eliminate nozzle plugging. A cyclone was installed at the outlet of the reactor. The outlet concentration of flue gas was measured by a Non-dispersed Infrared (ND-IR) type gas analyzer with a vacuum pump. The particle size of the bed material (sand or limestone), which was introduced into reactor through a screw feeder, was 500 μm and the static bed height was 0.15 m from the distributor. The flow rate of the simulated flue gas was 2 U_{mf} of the bed material. The inlet concentrations of NO and CO as an additive in the reactor were 400 ppm in 6% O_2 condition, respectively. After the reactor reached steady state, urea solution (5% w/w) was introduced into the reactor through a sparger. During the experiments, the molar ratio of urea solution to NO was varied from 0.5 to 2.5. The concentrations of outlet gases were measured by ND-IR gas analyzer and recorded on a personal computer.

RESULTS AND DISCUSSION

Carbon monoxide (CO) is produced by insufficient combustion due to oxygen deficiency in a fuel-rich region. It has been reported that the optimum temperature is shifted to lower values and reaction temperature window is widened by the presence of CO in flue gas [Caton and Siebers, 1989]. Also, the presence of acalcium-based sorbent such as limestone during combustion increases NO_x emission [Leckner and Amand, 1987; Kiil et al., 1996]. Therefore, CO as an additive and sand as the bed material, which is inert to the reaction with NH_2 radical, were used to lower the reaction temperature and to enhance gas mixing between NO and the reducing agents.

The effect of temperature on NO conversion with NH_3 as a reducing agent is shown in Fig. 3. As can be seen, NO conversion reaches 90% since flue gas is well mixed through a preheater, a distributor and in the bed of sand particles. 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 $H+O_2 \leftrightarrow OH+O$ and $O+H_2O \leftrightarrow OH+OH$ coupled with the reaction of $OH+CO \leftrightarrow H+CO_2$ as in the CO oxidation mechanism. The availability of OH and O-atoms at lower temperatures shifts both NO reductions, which results in lowering the optimum reaction temperature [Suhlmann and Rotzoll, 1993]. As can be seen in Fig. 3, NO conversion in the present study is higher than that of Caton et al. [1995] in the O_2 rich condition (15%). The difference in NO conversion may result from the more active oxidation to NO of NH_2 radicals in the O_2 rich condition.

The effect of NSR on NO conversion in the different reactors with different gas mixing intensity is shown in Fig. 4. It has been reported that NO conversion in SNCR is affected by the degree of gas mixing and geometry of reactors [Φstberg et al., 1997]. NO conversions in flow reactor with a distributor and nozzles in the present study and that of Jϕdal et al. [1990] were measured in the CO-free condition at 950 °C. As can be seen in Fig. 4, NO conversion increases with NSR up to 1.2 and remains constant with a further increase in NSR in the present fluidized bed reactor. However, NO conversions in the flow reactors remain constant at an NSR value above 1.5. This finding may indicate gas mixing in the developed fluidized bed reactor is superior compared to a conventional flow reactor.

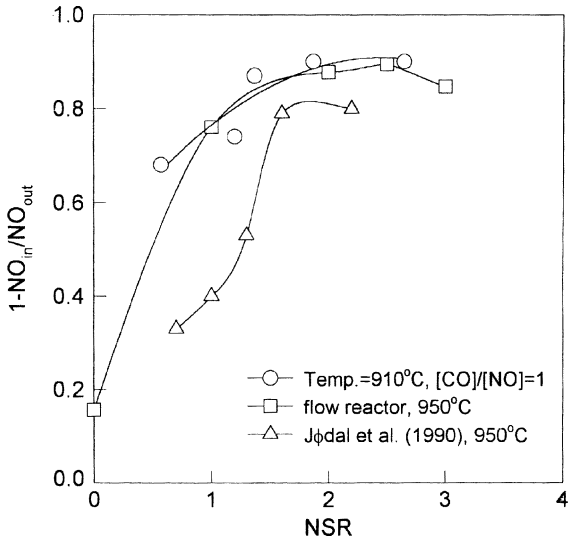

Fig. 4. Effect of normalized stoichiometric ratio (NSR) on NO reduction using urea solution as a reducing agent.

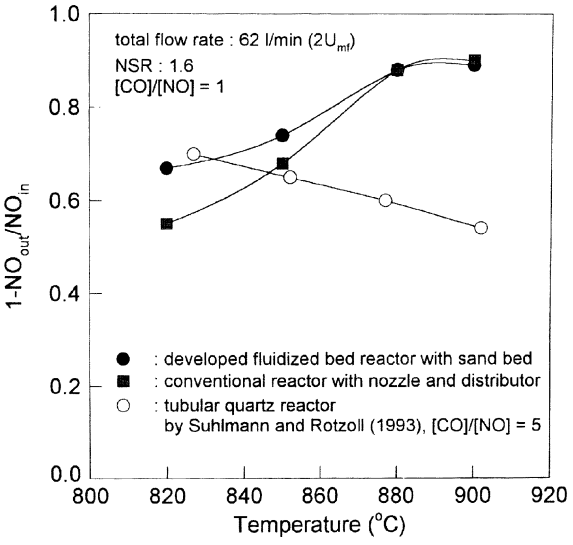

Fig. 5. Comparison of NO reductions in flow reactors and a developed fluidized bed reactor.

As can be seen in Fig. 5, NO conversion in the present fluidized bed of sand particles with a sparger is higher than that of a conventional flow reactor with nozzles and a distributor at lower temperatures (<850 °C) since gas mixing is enhanced by solid mixing in the bubbling fluidized bed. However, NO conversions in two different reactors are nearly the same at a reaction temperature above 880 °C since SNCR has a very fast radical reaction which exhibits the optimum conversion at that temperature range. A gas distributor in a conventional flow reactor provides good gas mixing that produces higher NO conversion in the present fluidized bed reactor compared to that in a tubular quartz reactor [Suhlmann and Rotzoll, 1993]. With increasing reaction temperature in a tubular quartz reactor, NO conversion decreases since the reaction path is altered by the excess CO [Suhlmann and Rotzoll, 1993]. Therefore, it can be claimed that the fluidized bed reactor with a sparger for urea

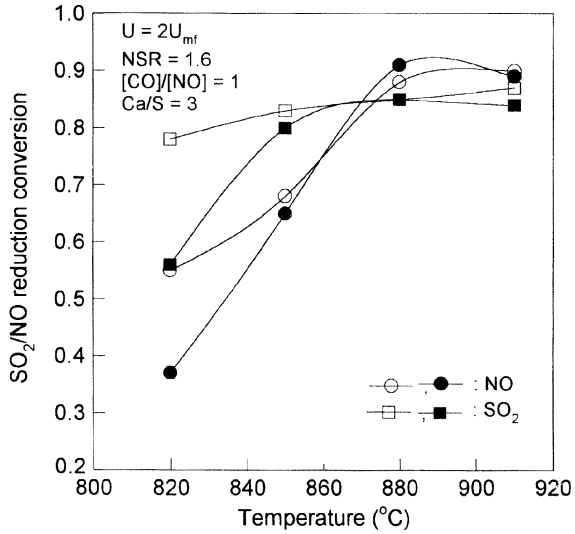

Fig. 6. Effect of temperature on SO_2/NO reduction in a developed reactor; open symbol: individual removal, closed symbol: simultaneous removal.

injection system is an effective means for reduction of NO_x in SNCR process.

Sulfur dioxide (SO_2) reacts rapidly with CaO (calcined limestone) to produce $CaSO_4$ at the temperature range of 800-1,000 °C that coincides with the optimum temperature range for NO removal by SNCR in the present study. Therefore, simultaneous removal of SO_2 and NO was carried out in the bed of limestone ($CaCO_3$) particles instead of sand particles. At a reaction temperature above 800 °C, limestone particles are calcined very rapidly to produce CO_2 and lime (CaO) that reacts with SO_2 in flue gas to form $CaSO_4$ since calcination is much faster than sulfation. Also, CO_2 is evolved through bubbles, and then the gas-solid reaction between SO_2, O_2 and CaO proceeds. At the same time, NO is removed by NH radicals from the decomposition of urea solution.

The effects of reaction temperature on the individual and simultaneous removals of SO_2/NO are shown in Fig. 6. Simultaneous removal of SO_2 and NO is significantly lower than that of the individual removal of SO_2 or NO at 820 °C. Lower NO conversion may result from active oxidation of NH_3 to NO on the calcined limestone [Wallman and Carlsson, 1993] and lower SO_2 conversion may be due to the inhibition of SO_2 adsorption by NH_3 on calcined limestone at 820 °C. However, it has been reported that oxidation of NH_3 to NO decreases due to the reduction of NH_3 adsorption onto the calcined limestone at higher temperatures [Wallman and Carlsson, 1993]. Also, Lin et al. [1993] reported that sulfation of limestone can reduce oxidation of NH_3 due to the decrease of NH_3 adsorption onto limestone by pore plugging. In the present simultaneous SO_2 and NO removal process, the amount of sulfates in the calcined limestone gradually increases with reaction time. As a result, conversions of SO_2 and NO in the simultaneous removal reach 80-90%, which agrees reasonably well with the individual removal of SO_2 and NO. Therefore, it can be claimed that the higher sulfation conversion of calcined limestone has to be maintained for efficient removal of SO_2 and NO.

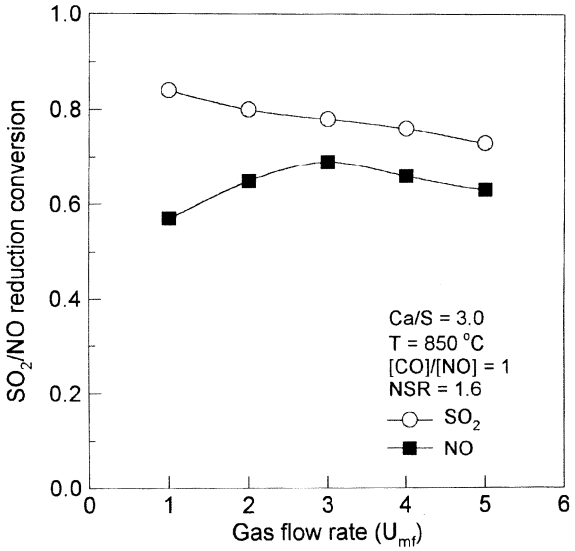

Fig. 7. Effect of gas flow rate on SO_2/NO reduction in a developed reactor.

The effect of gas flow rate on conversions of SO_2 and NO at 850 °C is shown in Fig. 7. As can be seen, SO_2 conversion decreases with increasing gas flow rate due to bypassing of SO_2 to the freeboard region through bubbles. On the other hand, NO conversion exhibits a maximum value at 3 U_{mf}. Therefore, it can be concluded that the developed fluidized bed reactor with a sparger for urea injection in the SNCR process is an effective tool for removing NO and SO_2 from flue gas.

CONCLUSIONS

The deNO_x characteristics by SNCR have been determined in a fluidized bed reactor with a sparger for urea injection. The optimum temperature is shifted to lower values and the window of the reaction temperature is widened by the presence of CO in the flue gas. The optimum amount of urea to be injected is found to be an NSR value above 1.2 with respect to NO conversion. NO conversion in the developed fluidized bed is higher than that in a flow reactor. In simultaneous removal of SO_2/NO, conversions of SO_2 and NO are nearly the same as in the case of the individual removal of SO_2 and NO above 850 °C. The developed fluidized bed in the present study is an effective reactor for removing SO_2 and NO.

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