

NO_x reduction by hydrazine in a pilot-scale reactor

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Abstract

The effects of the hydrazine molar ratio, reaction temperature and addition of CO on the NO_x reduction in flue gas containing 12% oxygen were determined in a pilot-scale flow reactor. The optimum reaction temperature and molar ratio for maximum NO_x reduction were found to be about 873 K and 4.0, respectively. With CO, hydrazine provides a wider temperature window for effective NO_x reduction. The proposed model predicts the reduction of NO reasonably well at high oxygen content. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: NO_x reduction; Kinetics; Additives; Hydrazine

1. Introduction

It has long been known that NO can be reduced homogeneously to N₂ and H₂O by NH₃ at relatively low oxygen concentrations (less than 5%) over the temperature range 1073–1323 K [1,2]. Other nitrogen-containing compounds, such as urea [3] and cyanic acid (CA) [4], have been investigated as reductants of NO_x. However, they require a higher temperature range for effective NO reduction. During boiler operation at varying loads and in many existing boilers, the injection space for NH₃, urea and CA solutions is not available in the temperature range 1073–1323 K; moreover, NO reduction is often desirable at lower temperatures [5].

The addition of small amounts of additives, such as hydrocarbons and amines, to this process makes it possible to shift the effective temperature to below about 1023 K [6]. From a practical viewpoint, a further reduction in temperature is desirable without the addition of additives, but little is known about the successful replacement of NH₃, urea and CA. On a laboratory scale, the N₂H₄–NO_x–O₂ reaction has been studied by Azuhata et al. [7]. However, little information is available on the applicability of N₂H₄ as a reductant of NO. In addition, the distribution of even a small amount of aqueous solution in a gas stream is very difficult in a large reactor [8]. Nevertheless, the use of an authentic flue gas from gas combustion makes the results obtained more meaningful for the estima-

tion of NO_x reduction in a full-scale plant. Hydrazine should be used as an NO_x abatement agent with complete conversion, otherwise it may cause safety concerns in a real combustor.

In this study, the effects of the hydrazine molar ratio (1.0–4.0), reaction temperature and addition of CO on the reduction of NO_x in flue gas containing 12% O₂ were determined in a pilot-scale flow reactor. Moreover, the effect of CO addition in the case of hydrazine, NH₃ and CA was determined. A kinetic model for the overall NO reduction rate, with hydrazine as a selective reducing agent, is proposed for engineering applications.

2. Experimental details

The experimental procedure was similar to that described in a previous study of NO reduction by urea solution [9]. Briefly, the hydrazine solution was sprayed onto the stream of combustion products through two atomizing nozzles (internal diameter (i.d.), 0.4 mm) in a pilot-scale flow reactor (i.d., 0.20 m; height, 6.0 m) as shown in Fig. 1. The mean droplet size of the hydrazine solution through the nozzles was approximately 50 μm in diameter. The reactor wall was insulated by fiberfrax (Carborundum resistant materials) to prevent heat loss to the surroundings, so that a nearly constant temperature gradient could be attained. The total flow rate of the flue gas was varied from 54 to 108 Nm³ h⁻¹, and the oxygen concentration was varied in the range 11.5–12%. The flue gas contained less than 10 ppm of CO, 10% of H₂O and 7.5% of CO₂. Eight sampling ports were mounted at 0.5 m

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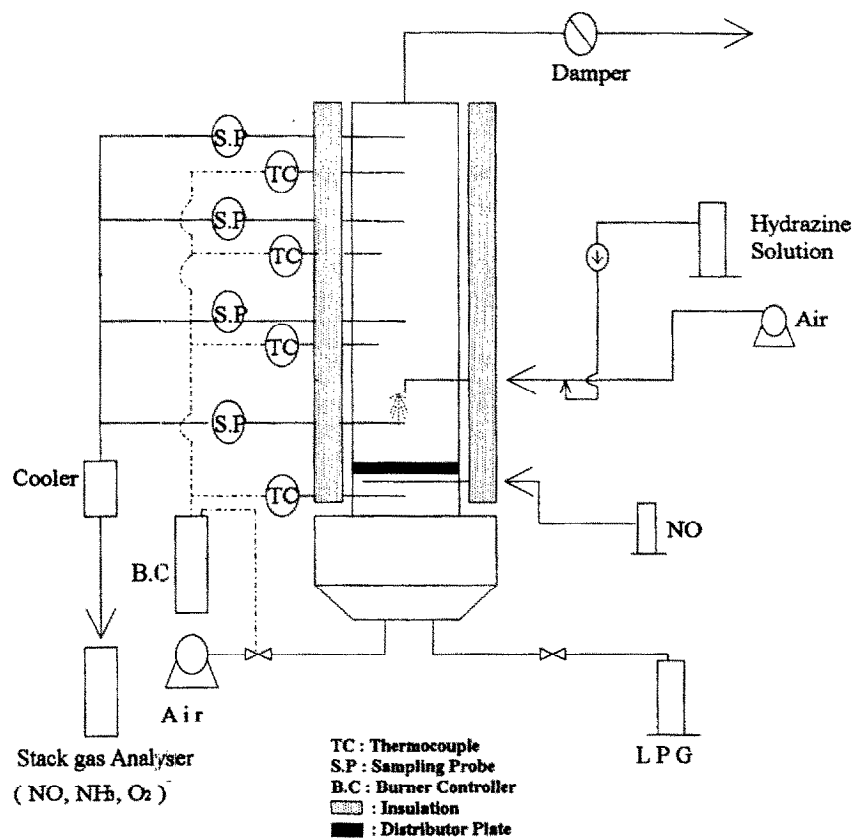


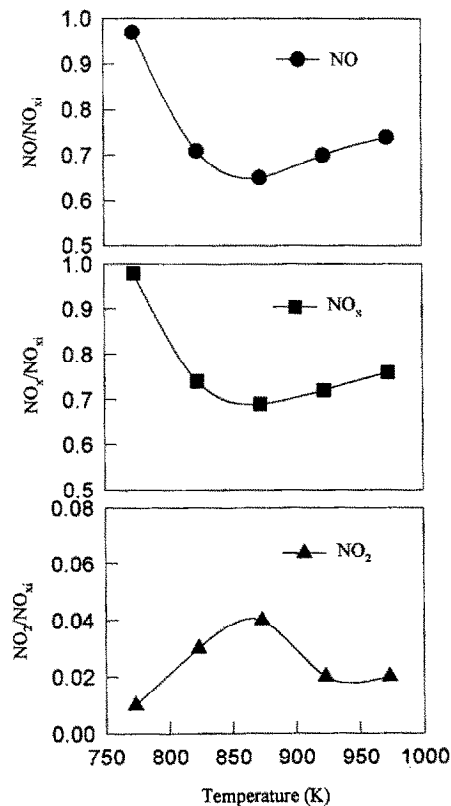
Fig. 1. The experimental apparatus.

height intervals along the reactor axis, and radially spaced by about 0.1 m. To measure the temperatures at the hydrazine injection point and at axial and radial directions in the reactor, eight K-type thermocouples were mounted along the axial and radial locations as a function of the variation in the thermal load in the furnace. The inlet concentration of NO in the reactor was varied from 200 to 300 ppm, and the outlet concentration of NO was measured in the injection temperature range 773–973 K at 50 K intervals. During the experiments, the molar ratio of hydrazine solution (10% w/w) to NO varied from 1.0 to 5.0. The sampled gas from the sampling probe was passed through a cooler for the removal of water, and sent to a stack gas analyser (ND-IR type, Chung Eng. Instrument, System CX-8AN) to measure the concentrations of NO, NH₃ and O₂ to within $\pm 5\%$. In addition to the direct measurement, a number of samples were taken in a tedlar bag, and were analysed using tube detectors (Gastec, Japan) to verify the direct measurements of the NO₂ concentration. The results obtained from the two methods exhibited good agreement.

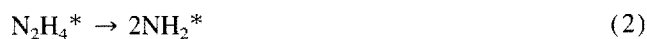
3. Results and discussion

3.1. Effect of the reaction temperature on NO_x reduction

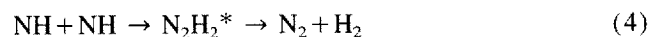
The effect of the reaction temperature on the N₂H₄–NO reaction was determined at 12% (w/w) O₂, as shown in Fig. 2, for NO, NO₂ and NO_x (NO + NO₂) at an initial molar

Fig. 2. The variation of NO, NO₂ and NO_x with reaction temperature.

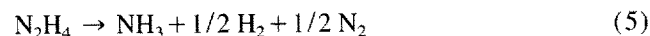
ratio (N_2H_4/NO) of unity. Significant NO reduction begins to occur at about 823 K, and reaches a maximum value at about 873 K. At temperatures above 873 K, NO reduction decreases with a further increase in reaction temperature. A peculiar finding is that the temperature window for effective NO reduction coincides with that of the formation of NO_2 . As can be seen, the temperature at which maximum NO reduction (823 K) is obtained exhibits a maximum NO_2/NO_x mole fraction. This result can be easily understood from the kinetic data of thermal decomposition of N_2H_4 obtained by Desen [10]. The primary reaction in the dissociation of hydrazine is assumed to be the rupture of the N–N bond to give an NH_2 radical. The rate constants for the disappearance of hydrazine are those of a unimolecular reaction as



where, in the second-order region, the collisional activation (Eq. (1)) is the rate-controlling step. At higher temperatures, the results are consistent with the very simple reaction scheme of reactions (1) and (2), followed by the radical–radical reaction



The global mechanism is as follows



The most important reaction pathways in the reaction of NH_3 with OH, O and H have been presented by Miller and Bowman [11]. At temperatures below approximately 1000 K, the hydrogen abstraction reaction between hydroxyl (OH) and NH_3 is too slow, and there is insufficient hydroxyl present initially in the reaction sequence leading to and originating from NO reduction. Therefore, the chain-terminating reaction dominates over the chain-branching reaction. These effects lead to $NH_3 \rightarrow NH_2$ conversion, which is insufficient to produce any significant amount of NO reduction. However, in the N_2H_4 –NO– O_2 reaction, chain-branching from the NH_2 +NO reaction sequence no longer occurs, because hydrogen (H_2) is produced during the decomposition of hydrazine (N_2H_4). Hence, it can be assumed that the effect of N_2H_4 on NO reduction is the same as that of the addition of H_2 to NH_3 . Consequently, NO reduction in a lower reaction temperature window may be due to the large increase in OH concentration from the reaction sequence: $OH + H_2 \leftrightarrow H_2O + H$; $H + O_2 \leftrightarrow OH + O$; $O + H_2O \leftrightarrow OH + OH$ [12,13]. Although the complicated pathways of NO reduction are unclear at present, it is assumed that the mechanism of the gas-phase N_2H_4 –NO– O_2 system comprises several reactions that are important in the NH_3 – H_2 –NO– O_2 system.

The degree of maximum NO reduction increases with increasing initial molar ratio of N_2H_4 to NO_x ; however, the conversion of NO_2/NO_x is almost independent of the initial molar ratio of N_2H_4 to NO_x as can be seen in Fig. 3.

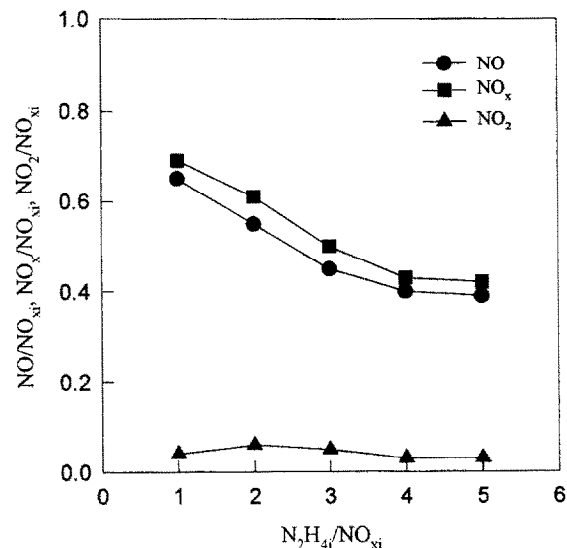
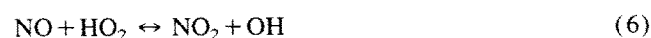


Fig. 3. The relationship between the variations in NO, NO_x , and NO_2 and the initial molar ratio of N_2H_4 to NO_{xi} .

There are three plausible reaction pathways for the formation of NO_2 . The first is NO – O_2 . However, this reaction can be ruled out, because it was verified experimentally that the direct oxidation of NO by O_2 does not occur under the present experiment conditions. The second possibility is the oxidation of N_2H_4 by O_2 , and the third is the oxidation of an intermediate product formed from the oxidation of N_2H_4 by O_2 . Although it is difficult to predict NO_2 formation and the overall reaction mechanism for the experimental conditions used, it can be assumed from the experimental data that hydrazine is not the main source of NO_2 formation.

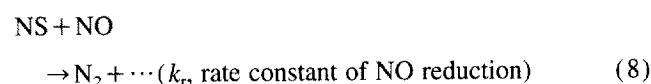
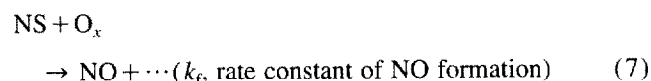
Miller and Bowman [11] reported that the formation of NO_2 usually indicates the presence of HO_2 , which is known to convert NO rapidly to NO_2 by the following reaction



In most combustion systems, this reaction constitutes the only important source of NO_2 .

3.2. Proposed reaction mechanism

A simple kinetic model of the N_2H_4 –NO– O_2 system is proposed for the two major reaction paths described previously [9]



In Eqs. (7) and (8), NS is the nitrogenous species (NH_3 , NH_2 , NNH , HNO), leading to the formation or reduction of NO, and O_x is the oxidant.

Simple and quantitative reaction rate equations for Eqs. (7) and (8) for the N_2H_4 –NO– O_2 system are given below

(Eqs.(9)–(11)), because one molecule of hydrazine (N_2H_4) yields one molecule of NH_3

$$\frac{d[NO]}{dt} = k_f \left[\frac{NH_{3i}}{NO_i} \right] \left[\frac{NH_3}{NH_{3i}} \right] - k_r [NH_{3i}] \left[\frac{NH_3}{NH_{3i}} \right] \left[\frac{NO}{NO_i} \right] \quad (9)$$

$$\frac{d[NS]}{dt} = -k_f \left[\frac{NH_3}{NH_{3i}} \right] - k_r [NO_i] \left[\frac{NH_3}{NH_{3i}} \right] \left[\frac{NO}{NO_i} \right] \quad (10)$$

with the following initial conditions

$$\left[\frac{NO}{NO_i} \right] = 1, \left[\frac{NH_3}{NH_{3i}} \right] = 1, t = 0 \quad (11)$$

The non-linear differential equations (Eqs. (9) and (11)) can be solved by adjusting two parameters (k_f , k_r) using the Runge–Kutta–Verner method.

3.3. Estimation of the amounts of NO and NH_3 as a function of the reaction time

The relationship between the time required to complete the reaction and the reaction temperature for measured concentrations of NO and NH_3 at a normalized stoichiometric ratio (NSR) of unity is $\tau = 0.65 - 4.02 \times 10^{-4} T$ as shown in Fig. 4.

The calculated fractions of NO and NH_3 as a function of the reaction time for injection or reaction temperatures in the range 773–973 K are shown in Fig. 5. At higher temperatures, the NO and NH_3 fractions decrease sharply up to a reaction time of 0.1 s. Thereafter, the fraction of NO remains constant and that of NH_3 approaches zero. At lower temperatures, the fractions of NO and NH_3 decrease with reaction time, and the agreement between the model and the experimental data becomes poorer with a wide fluctuation of NH_3 concentration.

The rate constants of NO formation (k_f) and NO reduction (k_r) are determined from an Arrhenius plot ($\ln k_f$ and $\ln k_r$

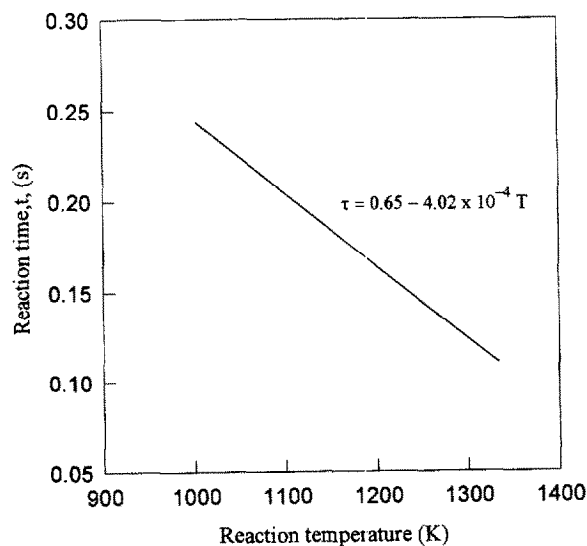


Fig. 4. The relationship between the time required to complete the reaction and the reaction temperature.

vs. $1/T$) at reaction temperatures in the range 773–973 K at atmospheric pressure in the presence of approximately 12% O_2 .

The relationships between k_f and k_r and the reaction temperature (T) can be represented by the straight lines in Fig. 6 with the following equations,

$$\ln k_f = 19.09 - 1.63 \times 10^4 / T \quad (12)$$

$$\ln k_r = 16.32 - 1.30 \times 10^4 / T \quad (13)$$

The parameters k_{f0} , k_{r0} , E_f and E_r can be determined from Eqs. (12) and (13) as

$$k_{f0} = 19.45 \times 10^7 \text{ s}^{-1} \text{ and } E_f = -135 \text{ KJ mol}^{-1} \quad (14)$$

$$k_{r0} = 12.24 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ and } E_r = -108 \text{ KJ mol}^{-1} \quad (15)$$

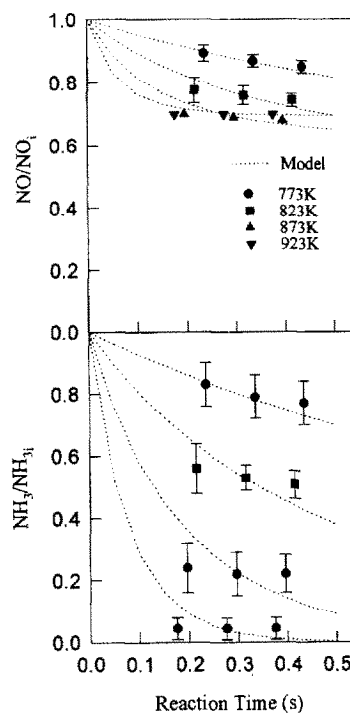


Fig. 5. Comparison of the experimental and calculated fractions of NO and NH_3 .

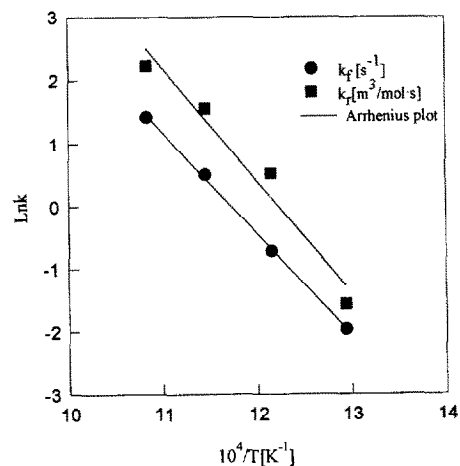


Fig. 6. The Arrhenius plot of the calculated rate constants k_f and k_r .

These activation energies are lower than those of the urea process ($E_r = -267 \text{ kJ mol}^{-1}$ and $E_r = -230 \text{ kJ mol}^{-1}$). This difference in activation energy leads to the initiation of the reaction at lower temperatures with hydrazine.

3.4. Prediction of NO reduction at different $N_2H_4/NO_{x,i}$ molar ratios

To verify the present kinetic model, the calculated NO and NH_3 conversion data from the model were compared with the experimental data at different initial hydrazine/NO molar ratios. A comparison between the experimental data and the model predictions for the fractional conversions of NO is shown in Fig. 7 as a function of the reaction temperature and the normalized stoichiometric initial molar ratio of hydrazine to NO (NSR $\approx 1.0, 2.0, 3.0$ and 4.0). As can be seen, the model predicts the experimental data reasonably well at 12% O_2 ; however, it overestimates the NO conversion in the lower temperature range at higher NSR values. Therefore, a re-evaluation of the parameters in this model is required, with special emphasis on NO reduction at lower temperatures.

3.5. Effect of the addition of CO on NO reduction by N_2H_4 , NH_3 and CA

The behaviour of hydrazine is compared with that of NH_3 and CA at a high oxygen content (about 12% O_2). The experimental data presented by Caton and Siebers [4] at $NH_3/NO = 2.3$, $CA/NO = 1.4$ and $CO/NO = 3.8$ were selected for the NH_3 and CA processes. In addition, $N_2H_4/NO = 4.0$ and $CO/NO = 4.0$ were selected for comparison purposes.

The effect of the addition of CO on the reduction of NO and the reaction temperature windows obtained with NH_3 , CA and N_2H_4 are compared in Figs. 8 and 9, respectively.

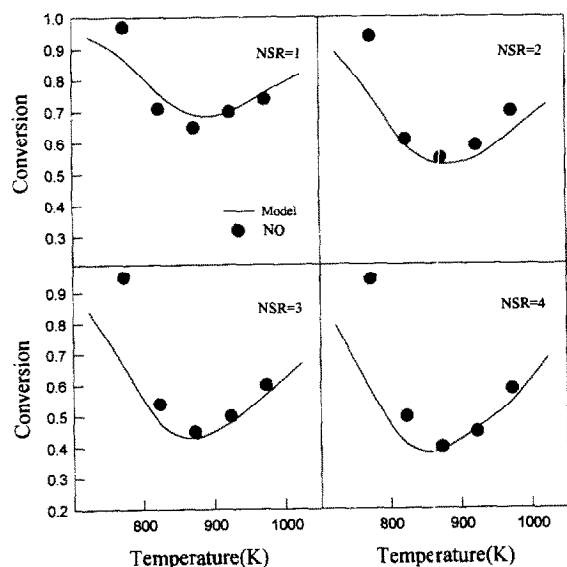


Fig. 7. Comparison of the experimental and calculated fractions of NO as a function of temperature at different NSR values.

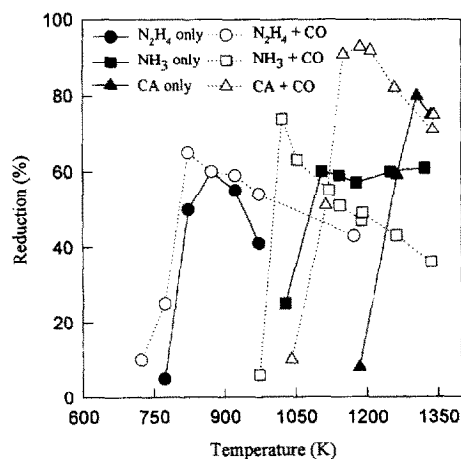


Fig. 8. Effect of the addition of CO on NO reduction with NH_3 , CA and N_2H_4 .

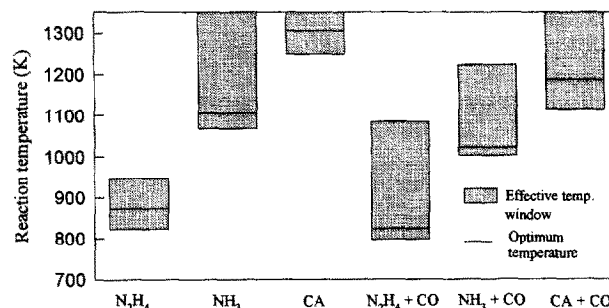


Fig. 9. Effect of the addition of CO on the effective temperature window (more than 60% reduction of NO_x) with NH_3 , CA and N_2H_4 .

The behaviour of hydrazine in the presence of 12% O_2 is most effective with respect to the shift of the effective temperature window to lower temperatures for more than 60% reduction of NO. However, the maximum NO reduction is somewhat lower and the effective temperature window is narrower than those in the NH_3 process. The problem of the narrow range of the temperature window (800–970 K) can be resolved by the addition of CO to N_2H_4 . CO provides a wider temperature window (780–1173 K) with significant NO reduction as can be seen in Fig. 9. The effect of the addition of CO to hydrazine solution on the reduction of NO can be explained by CO oxidation in the presence of water. The oxidation of CO increases the supply of OH and O at lower temperatures via the reactions $H + O_2 \leftrightarrow OH + O$ and $O + H_2O \leftrightarrow OH + OH$, coupled with the reaction $OH + CO \leftrightarrow H + CO_2$ in the CO oxidation mechanism [4]. Consequently, the availability of OH and O atoms leads to NO reduction over a wider reaction temperature window.

4. Conclusions

The effects of the reaction temperature and molar ratio of hydrazine to NO_x on the reduction of nitric oxide using hydra-

zine solution were determined in a pilot-scale reactor. The optimum reaction temperature and molar ratio for maximum NO reduction are found to be about 873 K and 4.0, respectively. Ammonia emission is negligible in the optimum temperature range, but becomes significant at lower temperatures. Hence, hydrazine has the greatest effect on the effective temperature window at lower temperatures. With the addition of CO, hydrazine provides a wider temperature window for effective NO reduction. Nitrogenous species and NO are mainly oxidized to NO₂ at the optimum temperature, and the temperature window of NO₂ formation coincides with that of NO reduction.

A simple kinetic model is proposed on the basis of the two main reactions for the N₂H₄–NO–O₂ system. The proposed model reasonably predicts the reduction of NO at high oxygen content (12% O₂).

Appendix A. Nomenclature

E_f	Activation energy of rate constant k_f (kJ mol ⁻¹)
E_r	Activation energy of rate constant k_r (kJ mol ⁻¹)
k_f	Rate constant of NO formation (s ⁻¹)
k_r	Rate constant of NO reduction (m ³ mol ⁻¹ s ⁻¹)
NH _{3<i>f</i>}	NH ₃ concentration corresponding to hydrazine/ NO _i molar ratio (mol m ⁻³)
NH ₃	NH ₃ concentration at the sampling probe (mol m ⁻³)
NO _i	NO concentration at the reactor inlet (mol m ⁻³)
NO	NO concentration at the sampling probe (mol m ⁻³)
NSR	normalized stoichiometric ratio (urea/NO _i)
R	Gas constant, 8.314×10^{-3} (kJ mol ⁻¹ K ⁻¹)
t	Reaction time (s)
T	Injection or reaction temperature of urea solution in the reactor (K)
τ	Time required to complete reaction between urea and NO (s)

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