

Selective Non-Catalytic Removal of NO₂ by Ammonia: Experimental and Numerical Results

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Abstract

For further understandings of the exhaust gas chemistry related to both NO and NO₂, results from model calculations were compared to results from experiments on the SNCR of NO₂ by NH₃ for temperatures of 800–1300 K. In general, NO₂ removal was a strong function of temperature and gas composition. The presence of ammonia promoted the NO₂ removal which was converted mostly to NO and to a lesser degree to N₂O. At higher temperatures, the formed NO further reacts to form N₂, resulting in up to 80–90% conversions from the initial NO₂ and NH₃. The effect of carbon monoxide on the amount of NO₂ removal was modest, but caused the temperature for the zero ammonia slip, minimum NO concentration and maximum N₂ formation to shift to lower values.

Introduction

The emission of pollutant gases (*e. g.*, NO, NO₂, N₂O, and CO) from combustion devices is of concern due to their noxious roles to the global environment [1, 2]. Among the pollutants, the nitric oxides (NO_x = NO + NO₂) are two of the major ones produced by combustion processes involving exothermic reactions with air [2].

Of a number of available NO_x removal processes, selective non-catalytic removal (SNCR) of NO_x by the injection of ammonia (NH₃) into the exhaust gas stream (Thermal DeNO_x [3]) has been reported to be effective for NO_x control. Although the SNCR of nitric oxide (NO) using ammonia has been extensively investigated, the SNCR of nitrogen dioxide (NO₂) using ammonia has not been studied to a similar degree.

In 1995, Glarborg *et al.* [4] reported an important study closely related to this topic. They used a system of NH₃/NO₂ (but no O₂ or H₂O). Their contribution was to identify two important product channels of the NH₂+NO₂ reaction, namely:



They suggested that the former was dominant at high temperatures, while the latter dominated at lower temperatures. Motivated by those results, Miller and Glarborg [5, 6] included the NO₂ forming mechanism, NNH+O₂=N₂+HO₂ and NO+HO₂=NO₂+OH in their study of the NO removal by ammonia.

To further the understanding of NO₂ chemistry in different operating conditions, including O₂ and/or CO, a kinetic model has been devised based on the latest work of Miller and Glarborg [6]. In this study, experimental results from the systems of NO₂/O₂, NO₂/NH₃/O₂ and NO₂/NH₃/O₂/CO are compared with the corresponding

results from the model predictions for the NO₂ removal pathways and for the effects of carbon monoxide.

Experiment

The flow reactor and the setup of the experiments are described in detail elsewhere (Gentemann and Caton [7]). For completeness, a brief overview of the experiments is provided next. A quartz-tube reactor (inside diameter of 1.8 cm) designed for obtaining plug flow was placed in a three zone electrically heated furnace to provide a uniformly heated length of about 45 cm. The temperature of the gases in the reactor was within ±5% of the temperature set-point as measured by a thermocouple.

The total flow rate of the simulated gas stream, containing the reactants and balance nitrogen, was 1100 sccm (standard cubic centimeters per minute at 0°C and 1 atm) and was kept constant for all experiments. Thus, the residence time in the reactor varied with temperature and was estimated to be between 1.3 sec (at 1300 K) and 2.1 sec (at 800 K).

The product gas from the reactor is diluted by 5000 sccm of nitrogen at the outlet of the reactor to avoid any water condensation. The species concentrations from the product gas, that is, NO₂, NO, N₂O, NH₃, CO and CO₂, are analyzed with an FTIR (Fourier Transform Infra-Red) spectrometer.

Numerical Work

Computations were completed using the Chemkin chemical kinetics package [8] for plug flow in conjunction with the thermodynamic data base [9] associated with Chemkin. The chemical reaction mechanism used in the current analysis is based on the previous work for the

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thermal DeNO_x process by Miller and Glarborg [6], in which a reaction subset of moist CO oxidation, including the reaction $\text{CO} + \text{NO}_2 = \text{CO}_2 + \text{NO}$, was adopted from the works of Mueller *et al.* [11]. In addition, for completion of the mechanism, the reaction subsets related to the species HCO, NCO and HNCO were also taken from the works of Glarborg *et al.* [12], and Bowman [10]. On account of limited space, it is not possible to list the complete mechanism, which involves 30 species and approximately 180 reactions. Upon request, the full listing of reactions and rate coefficients can be obtained from the authors.

The NO₂ sensitivities of participating reactions were calculated through the sensitivity analysis using the Senkin code [13], in which the linear sensitivity coefficients, ω_{ij} , were defined,

$$\omega_{ij}(t) = \frac{a_j}{X_{i,max}} \frac{\partial X_i}{\partial a_j}(t),$$

where t is time, X_i is the mole fraction of species i (*i. e.*, NO₂ for the current study), $X_{i,max}$ is the maximum mole fraction of species i , and a_j is the extra parameter of reaction j , which is normally $a_j = 1$, except for the pressure-dependent reactions [13].

Results and Discussion

From the experiments of Gentemann and Caton [7] on the NO₂ removal, including NO₂, O₂, CO and balance N₂ as simulated exhaust gas species, three sets were chosen to study the ammonia and carbon monoxide (CO) effects on the SNCR of NO₂ in terms of detailed mechanisms. Table 1 lists the initial gas composition of each set. For ease of discussion, they are categorized as (1) Case with no Ammonia for Set 1 (NO₂/O₂) and (2) Cases with Ammonia for both Set 2a (NO₂/O₂/NH₃) and 2b (NO₂/O₂/NH₃/CO)

Table 1. Initial Conditions For Selected Sets

Set	NO ₂	O ₂	NH ₃	CO
1	420 ppm	0.73%	0	0
2a	420 ppm	0.73%	760 ppm	0
2b	420 ppm	0.73%	760 ppm	900 ppm

(1) Case with no Ammonia (Set 1)

For Set 1 (NO₂/O₂), figure 1 shows the resultant concentrations of NO₂ (circular symbols) and NO (triangles) as a function of temperature for the experiments (upper plot) and for the model calculations (lower plot). Only insignificant amounts of N₂O were found for these conditions from both the experiments (less than 4 ppm) and model calculations (less than 1 ppm).

In general, the removal of NO₂ gradually increases (*i. e.*, the concentration of NO₂ gradually decreases) as temperature increases, while the production of NO increases as temperature increases. The model predictions capture these behaviors, except for the quantitative dis-

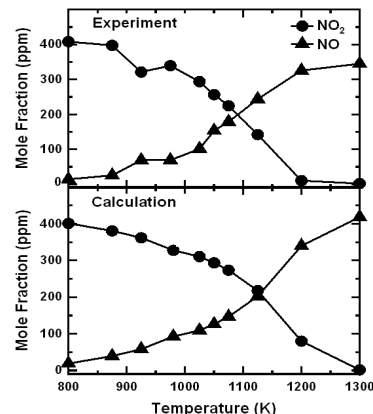


Figure 1. Comparisons of Experiments and Calculations for the NO₂ and NO Concentration from Set 1 (NO₂/O₂).

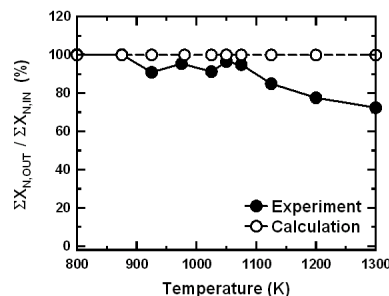


Figure 2. Comparisons of Experiments and Calculations for the Nitrogen Atom Balance from Set 1 (NO₂/O₂).

agreement on the removal of NO₂ and the production of NO at temperatures above 1200 K.

Figure 2 shows the normalized nitrogen (N) atom balances, including NO, NO₂ and N₂O, which is calculated by

$$\frac{\sum X_{N,OUT}}{\sum X_{N,IN}} = \frac{(X_{NO} + X_{NO_2} + 2 \cdot X_{N_2O})_{OUT}}{(X_{NO_2})_{IN}}.$$

By examining the experimental results (filled symbols), it can be noted that there are deficits of the N-atom balance. The deficits increase with increasing temperature and reach a value of about 30% at 1300 K (*i. e.*, the N-atom balance is about 70% at 1300 K). This result suggests that, along with the major production of NO from the removed NO₂, the probable formation of molecular nitrogen (N₂), undetectable by the FTIR, may have taken place. On the other hand, such deficits are not predicted in the model calculation, in which the N-atom balance yields about 100% over the whole temperature range. Therefore, it can be reasoned that the observed disagreement of the NO₂ and NO concentrations in the model calculation may be caused by missing or weakly presented reaction mechanism(s), responsible for the direct or indirect conversions of NO₂ to N₂.

In Figure 3, five reactions showing significant NO₂ sensitivities at 1100 K are presented, while others than those reactions have exhibited negligible NO₂ sensitivi-

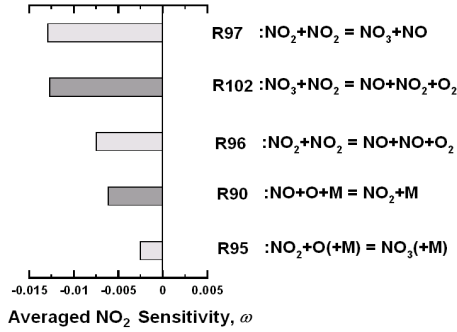
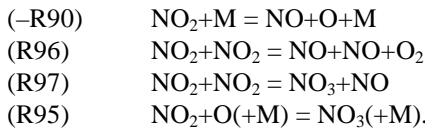
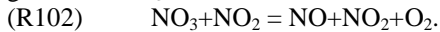


Figure 3. Averaged NO_2 Sensitivity Coefficients of Reactions at 1100 K for Set 1 (NO_2/O_2).

ties. The reaction numbers are assigned according to their appearance in the authors' reaction mechanisms. The averaged NO_2 sensitivity coefficients for the participating reactions, ranked by the absolute magnitudes over the entire residence time, have been calculated through sensitivity analysis. A negative sensitivity coefficient for a reaction indicates that the resulting concentration of NO_2 will be decreased if its reaction rate increases. It can be seen that the removal of NO_2 is responsible for the direct production of NO and the intermediate NO_3 , along with O and O_2 via



The generated NO_3 is converted further to NO via



In other words, it can be identified that the NO_2 removals are mainly achieved through the conversions to NO by the dissociation and association of NO_2 itself.

(2) Cases with Ammonia (Set 2a and 2b)

In this section, the results from Set 2a ($\text{NO}_2/\text{O}_2/\text{NH}_3$) and Set 2b ($\text{NO}_2/\text{O}_2/\text{NH}_3/\text{CO}$) are discussed. In Figure 4, for both experiments (upper plot) and calculations (lower plot), the concentrations of NO_2 and NO are plotted as functions of temperature. In this figure, the filled symbols and solid lines represent Set 2a with no CO , while the empty symbols and broken lines are for Set 2b with 900 ppm CO .

Observations for the NO_2 concentrations (circular symbols), with and without CO , indicate that the participation of ammonia (NH_3) leads to significant NO_2 removal even at the lower temperatures. For example, at 800 K, about 400 ppm NO_2 exists for Case 1, but only about 100 ppm NO_2 for Case 2. Increasing temperature results in a further decreased NO_2 concentration up to almost complete removal at higher temperatures (*i. e.*, above 1075 K for the experiment and above 1125 K for the calculations). The effects of CO on NO_2 removal seem to be mixed for the experimental results. This may be considered that the changes on NO_2 brought by CO addi-

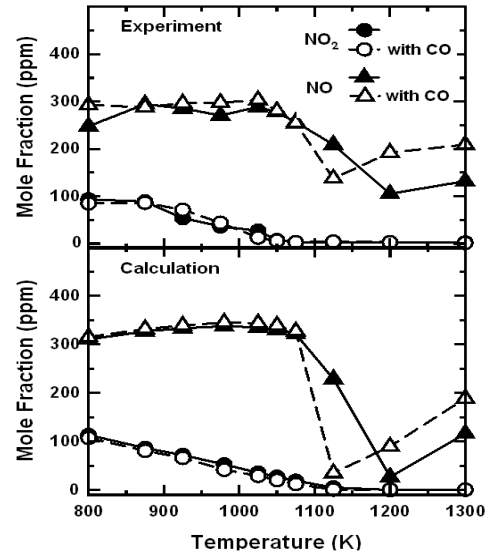


Figure 4. Comparisons of Experiments and Calculations from Set 2a ($\text{NO}_2/\text{O}_2/\text{NH}_3$) and Set 2b ($\text{NO}_2/\text{O}_2/\text{NH}_3/\text{CO}$) for NO_2 and NO concentration.

tion are less than the uncertainty for the experiments. On the other hand, the model predicts a slight enhancement of the NO_2 removal with the presence of CO .

Despite some quantitative discrepancies, the NO behaviors (triangular symbols) for these temperatures are predicted fairly well by the model calculations. That is, corresponding to the removal of NO_2 , significant amounts of NO appear at the lower temperatures. In detail, the NO concentrations are roughly constant up to an intermediate temperature, starting to decrease rather rapidly to the minimum at a greater temperature, and then gradually increase. The intermediate temperatures of major changes are around 1050 K with and without CO for both studies, while the temperature for the minimum NO concentrations are shifted to lower by the presence of CO (*i. e.*, from 1200 K with no CO to 1125 K with CO).

These behaviors of NO were not reported in the previous study of Glarborg *et al.* [4] for the NH_3/NO_2 ratio of about 1.9 (= 542 ppm/225 ppm) with no O_2 that was similar to the current NH_3/NO_2 ratio of about 1.8 (= 760 ppm/420 ppm) but with O_2 . Rather, in their study, the NO concentration increased with increasing temperature, beginning with the slow production of NO at the lower temperatures. However, for the current conditions, the behaviors of the formed NO for these temperatures (with and without CO) resemble those of the conventional SNCR of NO using ammonia as shown in Figure 5 [14]. Although the absolute quantitative comparison is impossible due to the different initial compositions, the similarities cannot be overlooked. Thus, it can be implied that the NO removal mechanisms on the $\text{NH}_3/\text{NO}/\text{O}_2$ system may be an important part of the current NO_2 removal sequence.

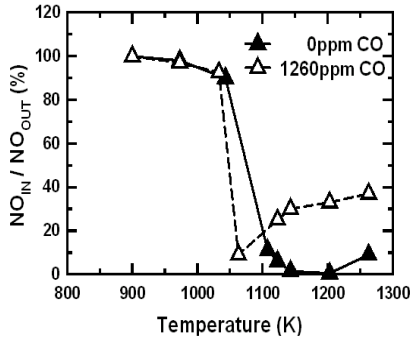


Figure 5. Normalized NO Concentration for the SNCR of NO using NH_3 [14]: Initial Conditions of 330 ppm NO, 760 ppm NH_3 , 4.5% H_2O , 1.9% O_2 , and Specified CO for the residence time of 0.64 sec at 1340 K.

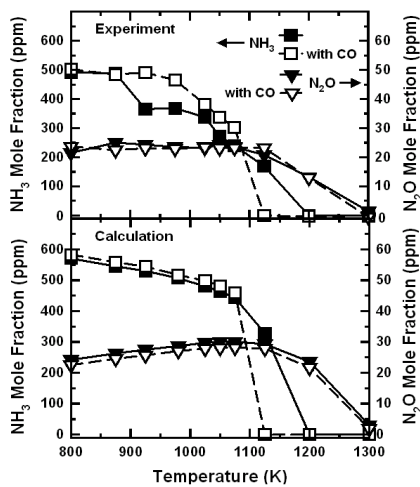


Figure 6. Comparisons of Experiments and Calculations from Set 2a ($\text{NO}_2/\text{O}_2/\text{NH}_3$) and Set 2b ($\text{NO}_2/\text{O}_2/\text{NH}_3/\text{CO}$) for the NH_3 and N_2O Concentrations.

In Figure 6, the behaviors of N_2O and NH_3 are compared between experiments (upper plot) and calculations, and between the cases with no CO (filled symbols) and with CO. Similar to the NO concentrations, the major change on NH_3 (square symbols) concentrations occur at about 1050 K, from which they rapidly decrease to zero (zero ammonia slip) at a higher temperature. This temperature for the zero ammonia slip coincides with that for the minimum NO concentration and shifts depending on the presence of CO, (*i. e.*, from 1200 K with no CO to 1125 K with CO). Also, the NH_3 reduction below 1050 K is somewhat suppressed by the presence of CO.

Unlike the previous NO_2 removal with no NH_3 , relatively significant amounts of N_2O (triangular symbols) have been formed. N_2O concentrations are about constant (*i. e.*, about 25-30 ppm) below 1125 K, and then decrease close to zero at 1300 K. Although the CO effects on the N_2O concentrations are not strong, the presence of CO slightly suppresses the N_2O production overall by both studies.

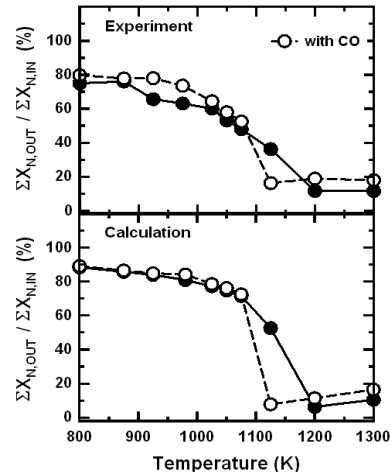


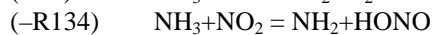
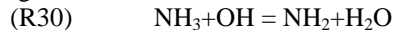
Figure 7. Comparisons of Experiments and Calculations from Set 2a ($\text{NO}_2/\text{O}_2/\text{NH}_3$) and Set 2b ($\text{NO}_2/\text{O}_2/\text{NH}_3/\text{CO}$) for the Nitrogen Atom Balances.

For the experiments (upper plot) and calculations, Figure 7 shows the normalized N-atom balances, including the detectable nitrogen species NO_2 , NH_3 , NO , and N_2O , which are calculated by

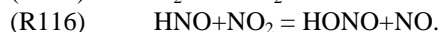
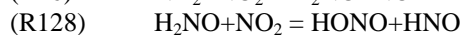
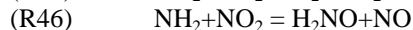
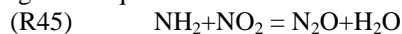
$$\frac{\sum X_{N,OUT}}{\sum X_{N,IN}} = \frac{(X_{NO} + 2 \cdot X_{N_2O} + X_{NO_2} + X_{NH_3})_{OUT}}{(X_{NO_2} + X_{NH_3})_{IN}}$$

In general, the N-atom balances decrease with increasing temperature, and minimized at the same temperatures where the zero ammonia slip and minimum NO concentrations take place depending on the presence of CO. Thus, it can be predicted by both studies that, starting from 10 to 20%, the maximum 80 to 90% of conversions of the NO_2/NH_3 system to N_2 can be achieved.

Equivalent to the initial conditions of Set 2a ($\text{NO}_2/\text{O}_2/\text{NH}_3$), Figure 8 shows the averaged NO_2 sensitivities at 1100 K for the top 15 reactions (as determined by the absolute magnitudes among all the reactions). The NO_2 removal process using ammonia involves more chain reactions compared to Set 1 (NO_2/O_2). The reactions are initiated by the generation of the amine radical (NH_2) through reactions,



Glarborg *et al.* [4] reported that the reaction (-R134) served as an important initiation step, and was sensitive only at lower temperatures. For the current conditions, however, the sensitivity analysis consistently indicates that the NO_2 and thus NH_2 behaviors are sensitive to the rate coefficient of this reaction as high as 1100 K. As identified in their study [4], the next steps take place through the sequence of reactions:



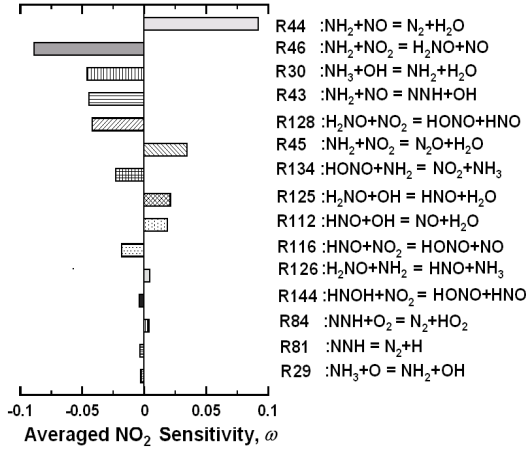


Figure 8. Averaged NO₂ Sensitivity Coefficients of Reactions at 1100 K for Set 2a (NO₂/O₂/NH₃).

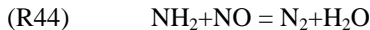
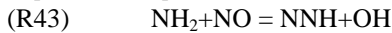
The reaction (R45), a branch of the NH₂+NO₂ reaction, is found to be responsible for N₂O formations in the process of NO₂ removal by ammonia. The other branch, the reaction (R46), generates NO with H₂NO that further forms NO through the reactions (R128 and 116), say,



in which another two reactions shown in Figure 8, (R125) H₂NO+OH=HNO+H₂O and (R112) HNO+OH=NO+H₂O, also participate in that sequence by generating either HNO or NO.

The reaction, (R45) NH₂+NO₂=N₂O+H₂O, has a positive sensitivity coefficient although it contributes to the removal of NO₂. This is because it plays the role of a chain termination without generating a radical or an equivalent that can induce a further propagation of the reactions in the process. Hence, the NO₂ removal will, in effect, be impeded when its reaction rates are increased for the same conditions. Some others (*e. g.*, (R112), and (R125)) have positive sensitivities because they are competing for the important radicals (*e. g.*, OH) in the process.

The following sequences are the removal processes of the formed NO through the NH₂+NO reaction that is a crucial step in the conventional SNCR of NO using ammonia [5, 6, 10, 12], via



in which some of the formed NO in the process is converted to N₂ by the reaction (R44), while the rest of the NO contributes to the production of the NNH radical by the reaction (R43), which further reacts to N₂ through the reactions,



Sensitivities of these two reactions become significant at higher temperatures where less NO concentrations are found. Therefore, the formed NO is converted to N₂ via

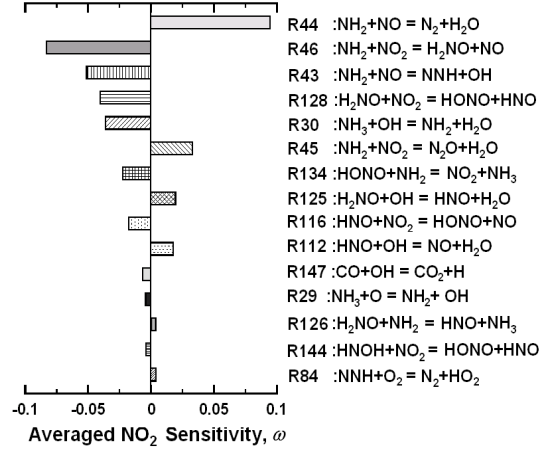
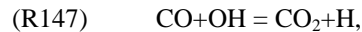


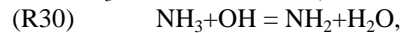
Figure 9. Averaged NO₂ Sensitivity Coefficients of Reactions at 1100 K for Set 2b (NO₂/O₂/NH₃/CO).

which resulted in the maximum 80-90% conversions from the initial NO₂/NH₃ concentrations. The sensitivity analyses at 1250 K (not shown here due to the space limitations) indicate that the reaction, HNO+M = H+NO+M can be responsible for the increase of the NO concentrations at the higher temperatures after passing their minimum.

Figure 9 shows the NO₂ sensitivities for Set 2b (NO₂/O₂/NH₃/CO) at 1100K, for the same temperature used in Figure 8 for Set 2a (with no CO). Since the presence of CO has brought about only slight changes in the relative concentrations of species (refer to Figure 4 and 6), the NO₂ sensitivities in the participating reactions for Set 2b do not differ too much from Figure 8 for the case with no CO. One of the differences is the participation of the reaction between CO and OH,



which may cause a slightly negative influence on the removal of NH₃ due to the reaction,



by competing for the chain carrier, OH. Thus, the reduction of NH₃, subsequently the reduction of the formed NO, and the formation of N₂O may be slightly impeded by the presence of CO as shown in the regions below the temperature, at which the major changes occur (*i. e.*, below about 1050 K in Figure 4 and 6). The reason for the temperature shifts by CO addition (in the minimal NO and NH₃ concentrations) cannot be determined directly with the current sensitivity analysis. However, the study of Brouwer and Heap [15] reported that one of the reasons for the temperature shifts is the increase of the local temperatures due to the exothermicity of the reaction, (R147) CO+OH.

For reference, the reaction of CO+NO₂=CO₂+NO, with the rate of $k=9.03 \times 10^{13} \times e^{-33800/RT}$ (cc/gmol-s) from Mueller *et al.* [11], was included in the current model, to account for the direct interaction between CO and NO₂ in the NO₂ removal process. However, relatively insignificant NO₂ sensitivities were assigned to the CO+NO₂ re-

action (*i.e.*, it was ranked 26th at 1100 K, and thus, is not shown in Figure 9). Therefore, it can be noted that for the model calculation the participation of this reaction in the presence of CO barely influenced the NO₂ removal and its concentration when compared to the case without CO.

Conclusions

This investigation considered the removal of NO₂ in a SNCR process using ammonia (NH₃) including the systems of NO₂/O₂, NO₂/O₂/NH₃ and NO₂/O₂/NH₃/CO. The results from both the experiments and the model calculations (including the sensitivity analysis) lead to the following conclusions:

- (1) For the NO₂/O₂ system (case with no ammonia), NO₂ was primarily converted to NO by the self-destruction and self-combination of NO₂ without forming N₂O.
- (2) For the NO₂/O₂ system, the experiments indicated that a maximum of 30% of the NO₂ was removed possibly converted to N₂ which was not predicted by the current model.
- (3) For the systems of NO₂/O₂/NH₃ and NO₂/O₂/NH₃/CO (cases with ammonia), the NO₂ removal was significantly promoted by the injection of ammonia.
- (4) The removed NO₂ was converted mostly to NO and to a lesser degree to N₂O. The two routes of chain sequence that were responsible were,
 - (a) $\text{NO}_2 \xrightarrow{+\text{NH}_2} \text{N}_2\text{O}$,
 - (b) $\text{NO}_2 \xrightarrow{+\text{NH}_2} \text{H}_2\text{NO} \rightarrow \text{HNO/HONO} \rightarrow \text{NO}$.
- (5) The sequence for the conversion of the formed NO to N₂ exhibited the global characteristics similar to the conventional SNCR of NO using ammonia via
 - (a) $\text{NO} \xrightarrow{+\text{NH}_2} \text{N}_2$,
 - (b) $\text{NO} \xrightarrow{+\text{NH}_2} \text{NNH} \rightarrow \text{N}_2$.
- (6) At higher temperatures, the conversion to N₂ from the initial NO₂ and NH₃ concentrations was observed both experimentally and numerically to be up to 80–90%.
- (7) For the NO₂/O₂/NH₃/CO system, the participation of CO barely affected the major species concentrations, relative to the NO₂/O₂/NH₃ system. Rather, the temperature, at which the minimal NO and NH₃ concentrations (and thus the maximum N₂ formation) were found, was lowered by the CO addition.

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