

Kinetic modeling of non-hydrocarbon/nitric oxide interactions in a flow reactor above 1,400 K

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Abstract—The reduction of nitric oxide by reaction with non-hydrocarbon fuels under reducing conditions at comparatively higher temperature has been studied with a detailed chemical kinetic model. The reaction mechanism consists of 337 elementary reactions between 65 chemical species based on the newest rate coefficients. The experimental data were adopted from previous work. Analyses by comparing existing experimental data with the modeling predictions of this kinetic mechanism indicate that, at comparatively high temperature, apart from the reaction path $\text{NO} \rightarrow \text{HNO} \rightarrow \text{NH} \rightarrow \text{N}_2$, $\text{NO} + \text{N} \rightarrow \text{N}_2$ is also prominent. In the presence of CO, NO is partly converted to N by reaction with CO. Based on present model, the reduction of NO at high temperature, which was usually underestimated by previous work, can be improved to some extent.

Key words: Nitric Oxide, Rate Coefficient, Non-hydrocarbon, Reburn, Reaction Mechanism

INTRODUCTION

Nitrogen oxides, also known as NO_x, are important and problematic contaminants produced in combustion processes. Several techniques have been developed to reduce the NO_x emissions in coal combustion systems. Nowadays, reburning is shown as one of the most efficient and attractive NO_x reduction techniques. Reburning is a chemically complex process in which nitric oxide is abated by using fuel as a reducing agent. Over the years a significant amount of work has been devoted to improve the understanding of NO_x reduction by the hydrocarbon radicals, both experimentally and theoretically [1-7]. The ability of non-hydrocarbon fuels such as hydrogen and carbon monoxide has been proven to be 20-30%, both experimentally and with detailed reaction mechanisms [8,9]. The experimental work includes studies in pilot-scale experiments (CTT) and flow reactors.

The reaction mechanism for non-hydrocarbon/NO interactions [9] is fairly well established. Conversion of NO to N₂ proceeds primarily through the sequence $\text{H} + \text{NO} \rightleftharpoons \text{HNO} \rightleftharpoons \text{NH} \rightleftharpoons \text{N}_2$. The modeling predictions are in qualitative agreement with the experimental results, but tend to underestimate the reduction of NO. Based on the work of Miller et al. and Glarborg et al., Sun et al. [10] established a reaction mechanism (200 elementary reactions between 46 chemical species) used for coal-gas reburn. Recent work, however, suggests that there were a number of elementary reactions from previous work used for conditions under 1,400 K, which is not of interest for reburning. The accuracy of prediction models was affected accordingly. Little work has focused on the impact of the reaction rate coefficients of different temperature range on the reburning mechanism.

To take advantage of the ability of non-hydrocarbon fuels such as CO and H₂ to reduce NO_x, the reaction mechanism for non-hydrocarbon/NO interactions was modified. The objective of this work is to obtain a better understanding of reburn chemistry based on the newest database, under reducing conditions at comparatively higher temperatures, by means of a detailed kinetic modeling study. Experimental data were drawn mainly from the flow reactor experiments of Glarborg et al., who investigated the reduction of NO using carbon monoxide and hydrogen as reburn fuels under fuel-rich conditions. The flow reactor systems as well as the experimental procedures are described in detail elsewhere [11,12].

REACTION MECHANISM

The experimental data of Glarborg et al. [9] were conducted in different flow reactors. Both flow reactors were designed to obtain a good plug flow approximation.

A model for NO reduction in the presence of hydrogen, carbon monoxide and methane was established in the present work with 337 elementary reactions between 65 chemical species. This mechanism was evaluated carefully against flow reactor experiments on interactions between non-hydrocarbon and NO. It can be used for NO reduction by non-hydrocarbon fuels at high temperature. With a few exceptions [5,13] thermodynamic data were drawn from the Sandia Thermodynamic Database [14].

The reaction mechanism includes a C1/C2/cyanide species subset adopted from Glarborg et al. [5] together with a subset describing the H/N/O chemistry and H₂/CO/O₂ subset. The H/N/O subset was drawn mainly from previous work [9] on reduction of NO by non-hydrocarbon fuels. Interactions between hydrogen, carbon monoxide and oxygen are described by reactions in the H₂/CO/O₂ subset, much of which was adopted from Miller and co-workers [15]. In the present work, a number of rate constants were updated compared to the previous mechanism, and these are discussed below. All calculations in the present work were performed using the Chemkin

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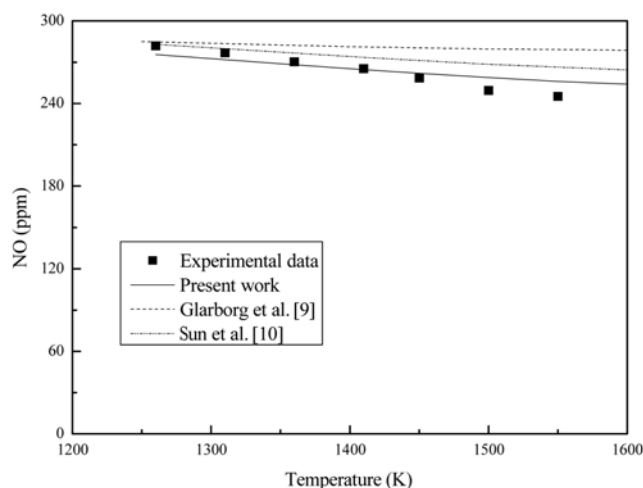


Fig. 2. Reduction of NO by H₂ in the fast-mixing flow reactor. Comparison between experimental data (symbols) and model predictions (lines) as a function of temperature. The inlet condition is shown as set 1 in Table 2.

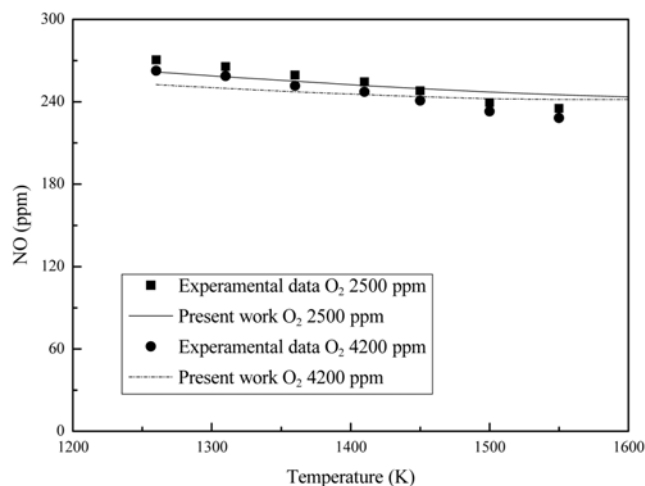


Fig. 3. Reduction of NO by H₂ in the fast-mixing flow reactor. Comparison between experimental data (symbols) and model predictions (lines) as a function of temperature. The inlet conditions are shown as sets 2 and 3 in Table 2.

Fig. 2 shows a comparison of model predictions with experimental data. Compared with other model predictions, the present model predictions are close to the experimental data between wide temperature ranges. The discrepancy of the experimental data and prediction is less than 4% at temperatures of 1,400 K and higher. We also made some calculations based on the modification of the mechanism from previous work (Sun et al. [10]) with the old rate coefficients. These prediction results are not very representative. It indicates that based on the newest rate coefficient the present model is applicable and reasonable.

The present modeling prediction of NO reduction by H₂ for different oxygen concentration as a function of temperature is shown in Fig. 3. Comparing the model predictions with experimental data, the NO reduction of experimental data is not sensitive to oxygen concentration. However, with the increase of temperature, the abil-

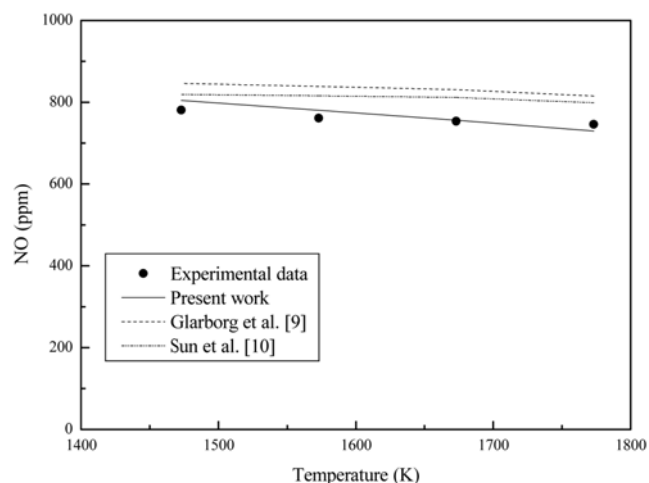


Fig. 4. Reduction of NO by CO in the premixed flow reactor. Comparison between experimental data (symbols) and model predictions (lines) as a function of temperature. The inlet condition is shown in set 4 in Table 2.

ity of NO reduction of prediction results gradually increases.

Figs. 4 and 5 show results of CO as reburn fuel in the premixed flow reactor. In Fig. 4, compared with experimental data, although other model predictions are seen to be in qualitative agreement with the flow reactor results, the present model predictions are consistent with the experimental results between 1,473 and 1,773 K. It solves the problem of underestimating the removal of NO at higher temperature.

Fig. 5 shows results of NO reduction at different stoichiometry (excess air ratio), respectively, 0.1, 0.4, 0.5 and 0.8. Consistent with the results of Fig. 4 the reduction of NO by CO is seen to increase with temperature except that in Fig. 5(d), little effect of temperature is observed. At the stoichiometry=0.1, the prediction results overestimate the NO reduction, especially at 1,773 K. However, at the stoichiometry=0.5, both the present work and Glarborg et al. [9] underestimate the removal of NO observed experimentally. Compared with prediction results of Glarborg et al. [9], the present model improves the accuracy of prediction.

In summary, the present model results indicate that an NO reduction potential of hydrogen and carbon monoxide increases slightly with temperature, consistent with the flow reactor results of Glarborg et al. [9].

Sensitivity analysis was also made, and the sensitivity coefficients for NO for the conditions of Fig. 2 at 1,600 K and the conditions of Fig. 4 at 1,773 K are plotted in Fig. 6 and Fig. 7. The NO sensitivity profiles show the most important reaction channels for NO reduction.

Fig. 6 shows that large positive sensitivities occur for reaction (51), $\text{HNO} + \text{H} \rightleftharpoons \text{NO} + \text{H}_2$, and for reaction (113). Large negative sensitivities arise for reaction (104). The most important reaction paths in NO reduction by H₂ or CO have many common features, as shown in Fig. 7.

CONCLUSION

Non-hydrocarbon /nitric oxide interactions above 1,400 K under

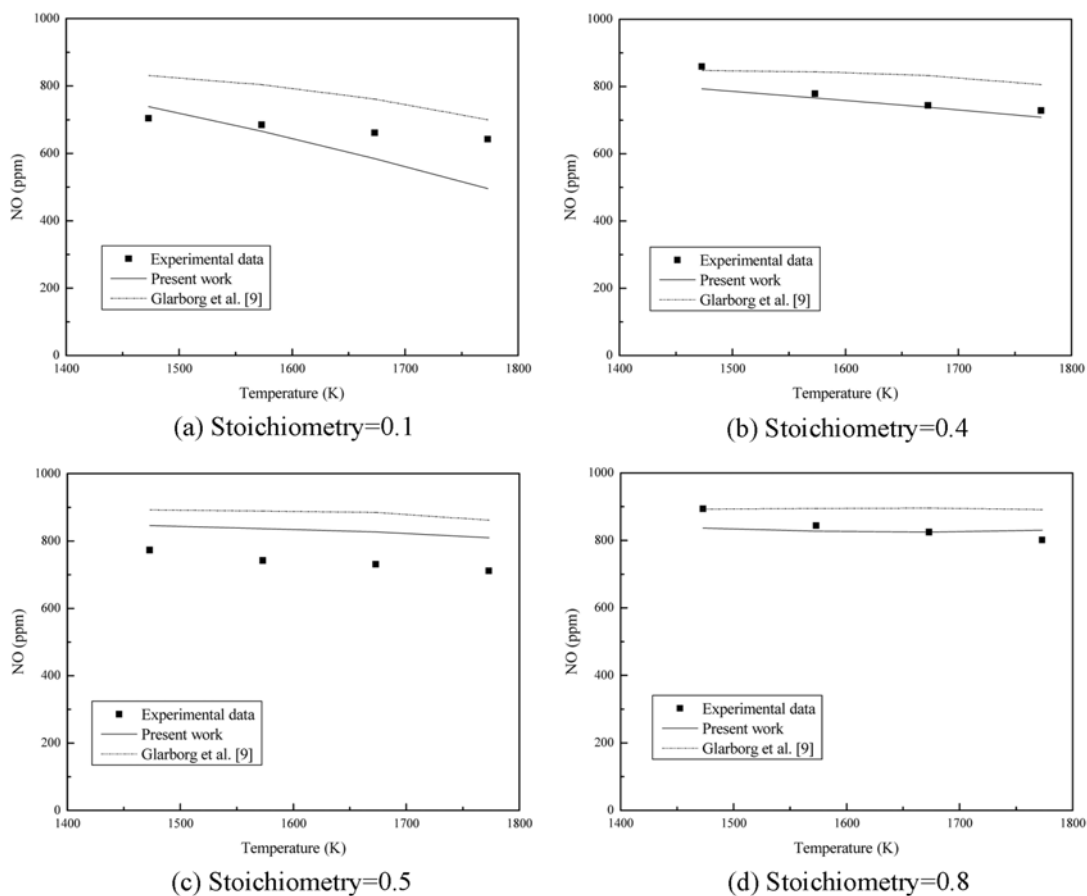


Fig. 5. Reduction of NO by CO in the premixed flow reactor. Comparison between experimental data (symbols) and model predictions (lines) as a function of temperature. The inlet conditions are shown in sets 5-8 in Table 2.

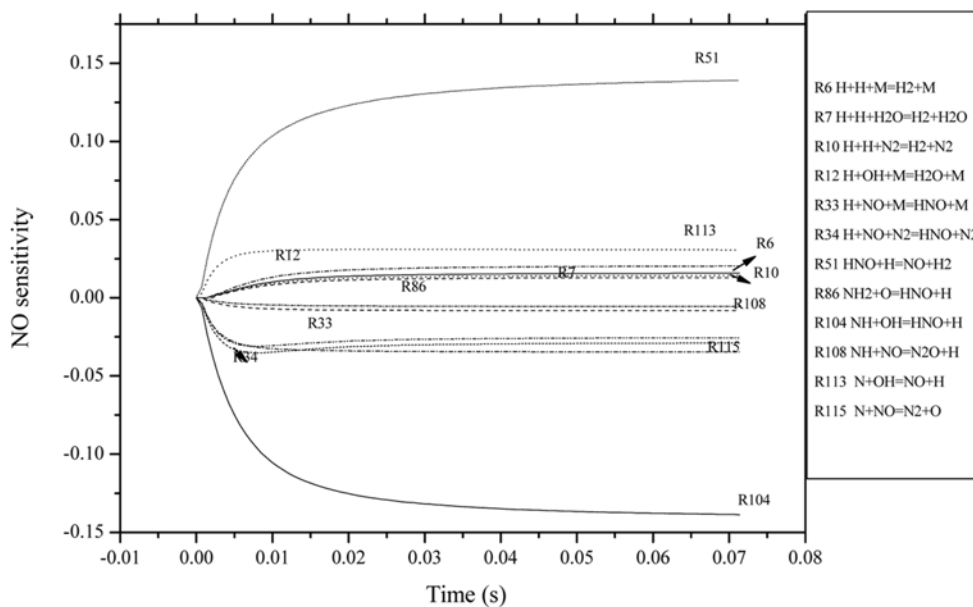


Fig. 6. Sensitivity plot of selected reactions for NO for the reduction of NO by H_2 at $T=1,600$ K.

reducing conditions were analyzed with a detailed chemical kinetic model. The experimental data were adopted from previous work. The chemical kinetic model is an update of the Miller-Bowman and

Glarborg mechanisms, in which a large fraction of the rate coefficients were updated according to recent work on specific reactions. In addition, some reactions were revised and extended. The model

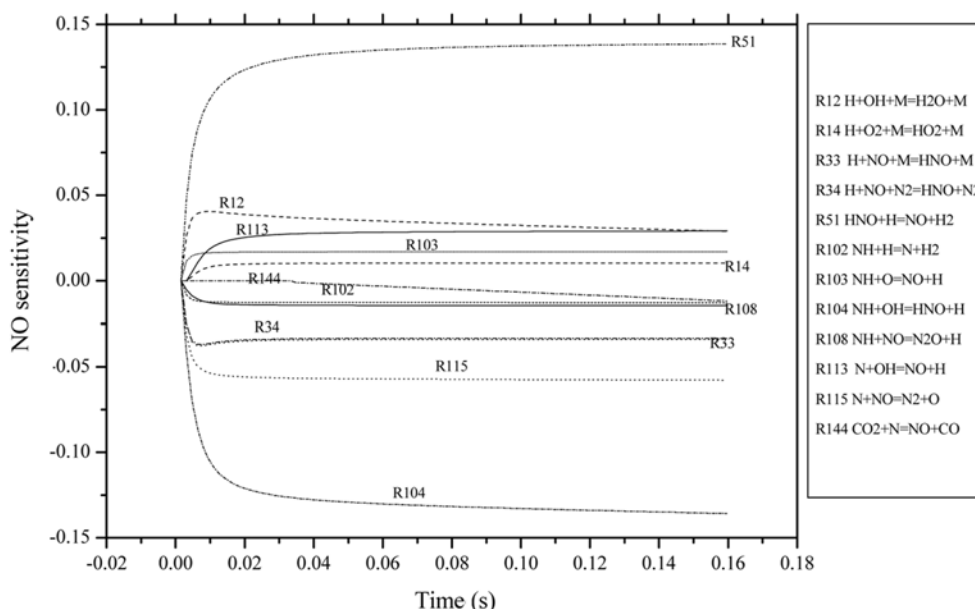


Fig. 7. Sensitivity plot of selected reactions for NO for the reduction of NO by CO at T=1,773 K.

predictions indicate that, at comparatively higher temperature, both the reaction path $\text{NO} \rightarrow \text{HNO} \rightarrow \text{NH} \rightarrow \text{N}_2$ and $\text{NO} + \text{N} \rightarrow \text{N}_2$ are prominent. In the presence of CO, NO is partly converted to N by reaction with CO. With the present mechanism, the results of NO reduction by H_2 and CO at high temperature can be improved to some extent.

It is unlikely that the mechanism presented here is the final word on the subject. However, future modifications are more likely to be quantitative rather than qualitative. We hope that the present article will be a useful point for future discussions of reburn.

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