Reduced Kinetic Mechanism of a Selective Non-Catalytic Process with Urea as Reducing Agent

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***Abstract*—A detailed kinetic mechanism consisting of 116 reactions and 26 species was obtained based on the NOxOUT mechanism proposed by Rota and the mechanism developed by Miller et al. The kinetic mechanism proposed in this contribution is suggested as a model of SNCR process using urea as reducing agent. The mechanism was validated with experimental data reported by Gentemann and Caton for various CO concentrations; good agreement of the detailed model with experimental data was obtained. The detailed mechanism was reduced to 44 reactions and 23 species. Agreement between the detailed and reduced kinetic mechanisms was good for the range of conditions of SNCR studied. The new reduced mechanism has been incorporated into CFD simulation in order to validate, the reduced reaction mechanism compares well the seven-step mechanism reported by Nguyen.**

I. INTRODUCTION

The rapid industrialization has had a significant negative effect on air quality. Therefore, more stricte mission standards have fostered the development of technologies for control of emissions. Among them, selective non-catalytic reduction (SNCR) is a cost-effective post-combustion technology for controlling emissions of nitrogen oxides (NOx). SNCR consists in the controlled injection of a reducing agent, such as ammonia or urea, into the flue gas. Use of urea has been widely accepted due to its easier and safer handling. The relatively narrow temperature window over which significant NOx reduction can be attained depends on parameters such as composition of the flue gas (NOx, CO, H_2O and O_2), and reductant/NO molar ratio (or NSR) [1, 2].

Computational Fluid Dynamics (CFD) techniques have been used to simulate SNCR processes in order to gain a better understanding of the process as well as to obtain the best operating conditions. However, CFD simulations can be easily overwhelmed because kinetic models may involve hundreds of species and reactions[3].Moreover, coupling of turbulence and heat transfer phenomena with the detailed chemistry is very demanding on computer time and memory. Several authors have reported various reduced kinetic models for NOx reduction [3–6]; these models have been widely adopted in CFD modeling.

The main objectives of this work are: (1) to develop a detailed mechanism based on kinetic mechanism reported in the literature and validate it with experimental data for SNCR process, (2) to reduce the detailed kinetic mechanism, and (3) compare the results of the reduced kinetic mechanism and of the detailed kinetic mechanism (4) evaluate its performance in CFD simulations.

II. DEVELOPMENT OF THE DETAILED MECHANISM

The detailed mechanism was based on the mechanism of Miller and Bowman [7]for NOx reduction using NH_3, and the mechanism of Rota et al.[8]with urea, ammonia and isocyanic acid as reducing agents some elementary reactions related to SNCR process were chosen from the Miller and Rota mechanisms.

Kinetic mechanism of 116 reactions and 26 species was determined. The results of the model were compared with experimental data (Table 1) reported by Gentemann[9], using four different CO concentrations..

TABLE I.
EXPERIMENTAL CONDITIONS OF GENTEMANN REPORT FOR SNCR PROCESS WITH UREA [9]

Experimental conditions			
Temperature range	800-1300 K	Nitric oxide	330
Residence time	1.3-2.1 sec	Urea	0-900 ppm
Total reactor flow	1100 sccm	Oxygen	5%
ID reactor	1.8 cm	Carbon monoxide	0,100,600,900 ppm
Length	30.48 cm	Nitrogen	Balance

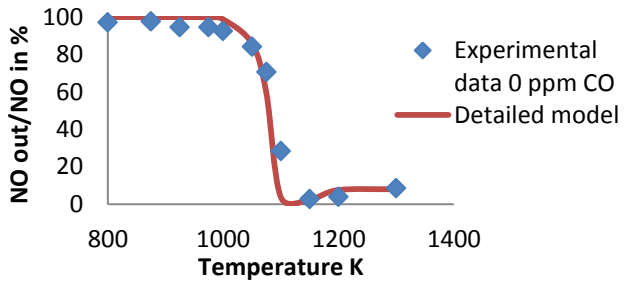

Figure 1. Nitric oxide reduction as a function of reactor temperature for 0 ppm carbon monoxide and for 5% oxygen.

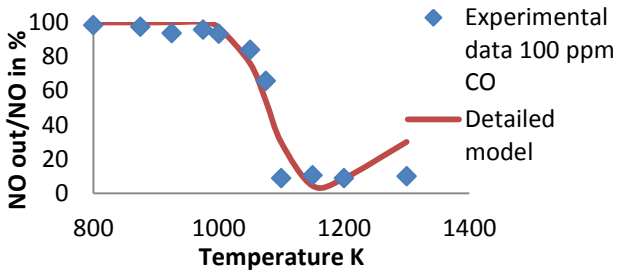

Figure 2. Nitric oxide reduction as a function of reactor temperature for 100 ppm carbon monoxide and for 5% oxygen.

As presented in the above Figures 1 and 2, the simulated data of NO reduction using the detailed mechanism show good agreement, both qualitatively and quantitatively, with the experimental data of Gentemann[9].

III. Development of Reduced Mechanism

A new reduced chemical kinetic model was developed through a sensitivity analysis of the detailed mechanism. The reduced mechanism includes 44 reactions and 23 species. Deviation between results of the detailed and reduced kinetic mechanisms was very small for the concentration of the more important species. For instance, a low Residual Square Sum (RSS) value and a high Determination Coefficient (r^2) of 0.98 were obtained when comparing the two mechanisms (see Figures 3 and 4).

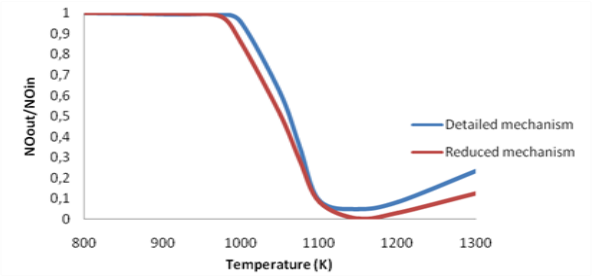

Figure 3. Comparison between detailed kinetic mechanism and reduced kinetic mechanism in NO reduction

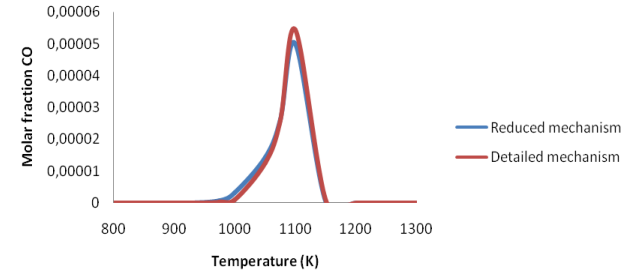

Figure 4.Carbon monoxide concentration as a function of the temperature using detailed kinetic mechanism and reduced kinetic mechanism

The reduced kinetic mechanism was incorporated into a CFD model without excessive computational load into the simulation (less than two times that of a reduced mechanism with 7 reactions and 13 species). The reduced reaction mechanism compares well a seven-step mechanism for an isothermal reactor at 940ºC, Figure 5.

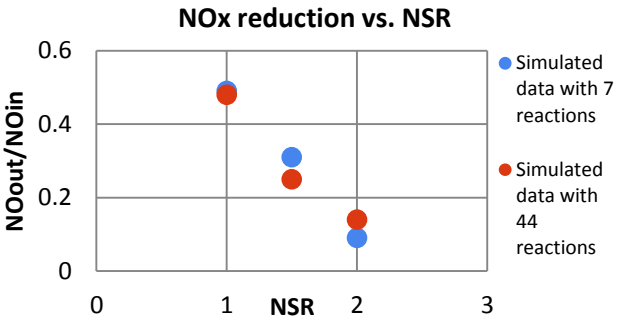

Figure 5. Comparison of simulations results using mechanism reported by Nguyen and mechanism proposed in this work. Inlet conditions: 400ppm NO, 5%v/v H_2O, 12%v/v O_2 and balance N_2.

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