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Modeling nitrogen chemistry in combustion

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ABSTRACT

Understanding of the chemical processes that govern formation and destruction of nitrogen oxides (NO_x) in combustion processes continues to be a challenge. Even though this area has been the subject of extensive research over the last four decades, there are still unresolved issues that may limit the accuracy of engineering calculations and thereby the potential of primary measures for NO_x control. In this review our current understanding of the mechanisms that are responsible for combustion-generated nitrogen-containing air pollutants is discussed. The thermochemistry of the relevant nitrogen compounds is updated, using the Active Thermochemical Tables (ATcT) approach. Rate parameters for the key gas-phase reactions of the nitrogen species are surveyed, based on available information from experiments and high-level theory. The mechanisms for thermal and prompt-NO, for fuel-NO, and NO formation via NNH or N_2O are discussed, along with the chemistry of NO removal processes such as reburning and Selective Non-Catalytic Reduction of NO. Each subset of the mechanism is evaluated against experimental data and the accuracy of modeling predictions is discussed.

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1. Introduction

Emission of oxides of nitrogen from combustion and high temperature industrial processes continues to be an environmental concern. Nitrogen oxides, collectively termed NO_x, are formed in essentially all combustion processes, mostly as nitric oxide (NO) with smaller amounts of nitrogen dioxide (NO_2) and nitrous oxide (N_2O). Nitric oxide is subsequently oxidized to NO_2 in the atmosphere. Nitric oxide and nitrogen dioxide are acid rain precursors and participate in the generation of photochemical smog, while nitrous oxide is a greenhouse gas.

Several separate mechanisms have been identified that can lead to formation of nitrogen oxides in significant quantities. These mechanisms involve either fixation of the molecular nitrogen contained in the combustion air or oxidation of organic nitrogen chemically bound in the fuel. Fig. 1 provides an overview of the most important sources of NO in combustion.

For gaseous fuels with no or negligible amounts of fuel-bound nitrogen (e.g., natural gas), as well as for fuels with a low nitrogen content (oil, woody biomass, plastic waste), formation of NO arises from fixation of N_2 in the combustion air. Homogeneous mechanisms for fixation of N_2 involve the attack of reactive radicals (O, CH_n, H) on the triple bond in molecular nitrogen [1–4]. These reactions form either NO or a reactive nitrogen intermediate (N_2O, cyanides, NNH) that may subsequently be oxidized to NO. For fuels with a considerable content of organically bound nitrogen, i.e., most solid fuels, oxidation of fuel-bound nitrogen constitutes the dominant source of nitrogen oxides. Here, formation of NO will depend on the partitioning of fuel-N between volatiles and char. The chemistry of the volatile nitrogen is complicated, since it may involve oxidation of tar-N, soot-N, cyclic compounds, and light species such as HCN and NH_3. Volatile-N from coal is mostly released with tar, emerging subsequently mainly as HCN, while for biomass and low rank coals, significant amounts of NH_3 may be released directly from the solid matrix during devolatilization [3].

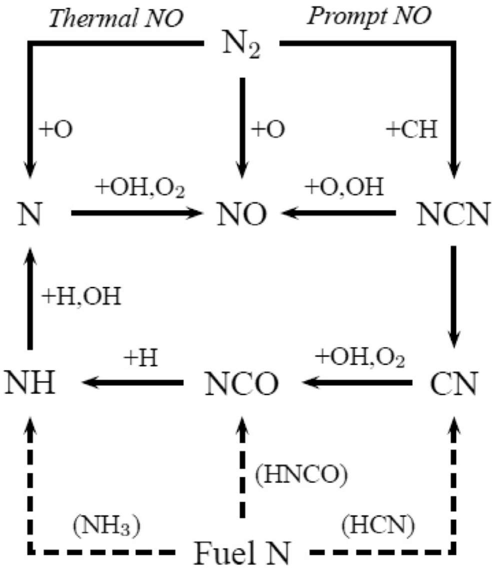

Fig. 1. Simplified reaction path diagram illustrating the major steps in the formation of thermal NO, prompt NO, and fuel NO. Recycling of NO to N_2 through reaction with atomic nitrogen or to cyanides through reaction with hydrocarbon radicals is not shown.

A large amount of work has been devoted to improve the understanding of NO_x formation mechanisms in combustion and to develop control strategies to reduce emissions [1–3,5,6]. Restrictions on NO_x emissions that used to apply only to large combustion systems such as power plants are now implemented on ever smaller scales: they continue to be a driving force for research and development in many industrial high temperature processes. In large power plants and for certain engines, emissions are typically controlled by catalytic flue gas cleaning. However, this technology can be challenging to use for fuels such as biomass and waste due to poisoning issues or undesirable due to comparatively high costs. For this reason there is still an incentive to control NO_x emissions by primary means or by in-situ techniques such as Selective Non-Catalytic Reduction (SNCR) or reburning. To achieve this aim, it is important to have access to reliable and versatile chemical kinetic models for formation and consumption of NO in high temperature processes. The use of detailed reaction mechanisms together with engineering models such as Computational Fluid Dynamics (CFD) has, with the strongly enhanced computational power now available, become an important tool in designing low-NO_x combustion systems.

The objective of the present work is to establish and evaluate a state-of-the-art, non-optimized chemical kinetic model for homogeneous nitrogen chemistry in combustion. It is based on the work on nitrogen chemistry reported over the last decades, drawing also on recent advances in the knowledge of thermochemistry and reaction rates from theoretical work. The different mechanisms for formation and consumption of NO are discussed and the key reaction steps are evaluated. Different subsets of the model are validated against experimental data and the predictive capability of the mechanism is assessed.

To limit the scope of the review, we emphasize nitrogen chemistry in combustion of light hydrocarbons, mostly CH_4, and/or light fuel-nitrogen species (HCN, NH_3, HNCO) at atmospheric or sub-atmospheric pressure. Oxidation of heterocyclic nitrogen compounds, which may be formed in combustion of more complex fuels, or of energetic materials such as nitroalkanes is not addressed in the current work. Furthermore, we focus on experimental conditions