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Experimental study and detailed kinetic modeling of the effect of exhaust gas on fuel combustion: mutual sensitization of the oxidation of nitric oxide and methane over extended temperature and pressure ranges

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Abstract

New experimental results were obtained for the mutual sensitization of the oxidation of NO and methane in a fused silica jet-stirred reactor operating at 1–10 atm, over the temperature range 800–1150 K. Probe sampling followed by on-line FTIR analyses and off-line GC-TCD/FID analyses allowed the measurement of concentration profiles for the reactants, stable intermediates, and final products. Detailed chemical kinetic modeling of the experiments was performed. An overall reasonable agreement between the present data and modeling was obtained, whereas previously published models failed to properly represent these new data. According to the proposed model, the mutual sensitization of the oxidation of methane and NO proceeds through the NO to NO_2 conversion by HO_2 and CH_3O_2. The modeling showed that at 1–10 atm, the conversion of NO to NO_2 by CH_3O_2, is more important at low temperatures (800 K) than at higher temperatures (850–900 K), where the reaction of NO with HO_2 dominates the production of NO_2. The NO to NO_2 conversion is enhanced by the production of HO_2 and CH_3O_2 radicals from the oxidation of the fuel. The production of OH resulting from the oxidation of NO promotes the oxidation of the fuel: $NO + HO_2 \rightleftarrows OH + NO_2$ is followed by $OH + CH_4 \rightleftarrows CH_3$. At low temperature, the reaction further proceeds via $CH_3 + O_2 \rightleftarrows CH_3O_2$, $CH_3O_2 + NO \rightleftarrows CH_3O + NO_2$. At higher temperatures, the production of CH_3O involves NO_2: $CH_3 + NO_2 \rightleftarrows CH_3O$. The sequence is followed by $CH_3O \rightleftarrows CH_2O + H$, $CH_2O + OH \rightleftarrows HCO$, $HCO + O_2 \rightleftarrows HO_2$, and $H + O_2 \rightleftarrows HO_2$. $\rightleftarrows CH_2O + H$, $CH_2O + OH \rightleftarrows HCO$, $HCO + O_2 \rightleftarrows HO_2$, and $H + O_2 \rightleftarrows HO_2$.

Keywords: NO_x; Methane; JSR; Kinetic modeling; Ignition

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1. Introduction

The kinetic interactions between nitric oxide (NO) and fuels have been studied previously, showing that the ignition of simple fuels is promoted by nitrogen oxides [1,2]. This can be viewed as a mutual sensitization: the oxidation of the fuel is promoted by NO_x and the oxidation of NO into NO_2 is promoted by hydrocarbons. Kinetic studies have mainly been performed in tubular flow reactors (FR), investigating the promoting effect of NO on the oxidation of hydrogen [3], methane to *n*-pentane [4–13], while other studies concentrated on the promotion of the NO to NO_2 conversion by simple hydrocarbons [11,14–16]. Kinetic modeling was previously presented [4,5,11, 13,17]. Bendtsen et al. [5] reported that a previous model [4] failed to represent their data, whereas theirs overestimated the reactivity of the system at low temperature. The most recent models [11,13,17] looked to be the most advanced since they had been applied to a wide range of fuels (C_1–C_3 [17] and C_1 to C_5 [11,13]) oxidized at 1 atm in FR. However, controversial results regarding the reaction yielding mutual NO–hydrocarbon sensitized oxidation were reported: according to these models, sensitization is due to either HO_2 or CH_3O_2 reactions with NO. This issue needed to be clarified since taking into account this chemistry is of importance in several practical systems, among which are (i) the NO–NO_2 conversion by hydrocarbons in recent NO_x-reduction strategies, (ii) the modeling of combustion in engines using exhaust-gas recirculation (EGR) such as Diesel and, more importantly, in HCCI engines. HCCI engines can run with purified biogas (methane) or natural gas. A variable fraction of the exhaust gas is reinjected in the engine, reducing the combustion temperature and in turn the emission of NO, by slowing down the importance of the thermal–NO mechanism. The other effect of EGR is the reduction of ignition delays in the engine by an NO-promoted oxidation of the fuel. It is well known that the firing of HCCI engines is critically controlled by the kinetics of the ignition of the fuel. It is thus of major importance to take into account the promoting effect of NO on this process to better control the ignition in such engines. However, no kinetic data was available for the promotion of methane oxidation by NO under high-pressure conditions, and most of the data were obtained in FR, where back-mixing is minimal, whereas it is important in practical systems.

Therefore, a series of experiments was performed at 1 to 10 atm to evaluate the kinetics of the NO-sensitized oxidation of methane and higher hydrocarbons using a jet-stirred reactor (JSR), where back-mixing is important. The new data involving methane were used to validate a detailed chemical kinetic reaction mechanism and clarify the relative importance of the reactions of NO with HO_2 and RO_2 in the NO-sensitized oxidation of methane.

2. Experimental

A spherical fused silica jet-stirred reactor was used [18]. It was located inside a regulated electrical resistance system of ≈1.5 kW, surrounded by insulating material and a pressure-resistant jacket allowing operation up to 10 atm. Methane (99.9995% pure), NO (>99.995% pure), and oxygen (99.995% pure) flow rates were measured and regulated by thermal mass-flow controllers. These gases were diluted by a flow of nitrogen (<50 ppm of O_2 and H_2O; <1000 ppm of Ar; <5 ppm of H_2) and mixed at the entrance of the injectors after preheating. Residence time distribution studies showed that the reactor is operating under macro-mixing conditions: a perfectly stirred reactor model could thus be used. As previously [7,9], good thermal homogeneity was measured along the vertical axis of the reactor by thermocouple measurements (Pt/Pt–Rh 10%, 0.1-mm-diameter located inside a thin-wall fused-silica tube, <0.5 mm, to prevent catalytic reactions on the metallic wires). Typical temperature changes of <8 K along the vertical axis of the reactor were measured in the present work. Because of the high degree of dilution, the temperature rise due to the reaction was generally <30 K. Low-pressure samples of the reacting mixtures have been taken by sonic sampling and collected in 1-L Pyrex bulbs at ca. 30 Torr for immediate gas chromatography (GC) analyses as in [7,9]. On-line Fourier transform infrared (FTIR) analyses of the reacting gases were also performed. The present analytical system allowed the measurement of methane, ethane, ethylene, acetylene, H_2, O_2, H_2O, NO, NO_2, N_2O, CO, CH_2O, and CO_2. As previously [7,9], very good agreement between the GC and FTIR analyses was found for the compounds measured by both techniques (methane, CO, CO_2). Carbon balance was checked for every sample and found good within <5%. The mole fractions of NO and NO_2 were determined to within ±5–20 ppm.

3. Chemical kinetic modeling

We used the PSR computer code [19] for the JSR modeling. Senkin [20] was used for modeling FR experiments. The base set of the proposed reaction mechanism is the kinetic scheme developed for the mutual oxidation of NO and ethane [7] or DME [9] and that used to model NO reburning by C_1 to