Soot Formation in Shock Tube Methane Pyrolysis and Oxidation of Rich Methane/Oxygen Mixtures

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1 Introduction

Methane is a fuel, which is widely used in many practical applications because it is a major component of the natural gas. Combustion products of methane have the highest H_2O/CO_2 ratio due to the highest H/C ratio in methane. Methane is traditionally considered to be among the least polluting fuels available possessing the longest ignition delay time. However, even in nonsooting methane flames the concentration of PAH molecules may be considerable. This means that under particular conditions soot can also be formed during methane combustion.

Another interesting aspect of methane oxidation is the synthesis gas production. Partial oxidation of methane in the gas phase is a convenient way to produce synthesis gas with a required H_2/CO ratio. The gas phase methane conversion occurs owing to the energy release in the reacting mixture due to the partial oxidation of methane by oxygen. Noncatalytic partial oxidation of methane occurs only at high temperatures. Under conditions, which provide the highest H_2 and CO yields, the soot formation becomes a serious undesirable factor influencing the whole process.

The main goal of the current work is further development of a detailed kinetic model of soot formation proposed in [1, 2]. The kinetic model should describe the ignition delay times of different methane/oxygen mixtures within a wide range of temperatures and pressures and should predict soot formation both in methane pyrolysis and rich oxidation of methane/oxygen mixtures.

2 The kinetic model

The kinetic model of soot formation developed consists of the gas phase reaction mechanism, which describes the pyrolysis and oxidation of the parent hydrocarbons, in particular methane, and the formation and growth of PAHs through different reaction pathways up to coronene. The formation, growth, oxidation and coagulation of soot precursors and soot particles are described within the framework of a discrete Galerkin technique [3].

The gas-phase reaction mechanism is based on the reaction sequence of PAH formation in laminar premixed acetylene and ethylene flames (HACA). Several additional channels of PAH formation and growth (up to coronene) and a comprehensive set of reactions of C_3-, C_5-, and C_7-hydrocarbons were also added in the kinetic

mechanism. Thus, several pathways of PAH formation and growth are incorporated in the reaction mechanism: (1) the alternating H-abstraction/C_2H_2-addition (HACA) route, resulting in a successive growth of PAHs, (2) the combination reactions of phenyl with C_6H_6, (3) the cyclopentadienyl recombination, and (4) the ring closure reactions of aliphatic hydrocarbons.

Due to the importance of alkylperoxy chemistry in the low to medium temperature range, the reactions related to the formation of methylperoxy (CH_3O_2), ethylperoxy ($C_2H_5O_2$), and propylperoxy ($C_3H_7O_2$) were added to describe the ignition delay time of CH_4/O_2 mixtures [4].

Thus, the modified gas-phase reaction mechanism of the model consists of 2683 direct and reverse reactions between 266 different species, where the rate coefficients of some important reactions have pressure dependence.

Soot precursors are formed by radical-molecule reactions of different PAHs starting from phenylacetylene and ace- and ethynylnapthalene up to coronene and radical-radical reactions (from cyclopentaphenanthrene up to coronene radicals). These reactions result in the formation of polyaromatic molecules containing from 16 to 48 carbon atoms, which are stabilized by the formation of the new chemical bonds. Soot precursors are activated in reactions with H and OH radicals. They are deactivated in reactions with H, H_2 and H_2O. Soot precursors grow in reactions with C_2H_2, C_4H_2, and C_6H_2, whose concentrations are rather high in pyrolysis and oxidation of aliphatic and aromatic hydrocarbons, and in reactions with polyaromatic molecules and radicals, and in coagulation. Soot precursors are oxidized by O and OH radicals. They are transformed into soot particles in the reactions of internal conversion, in which the number of active sites in the reacting system is preserved. Soot particles with active sites grow in the reactions with C_2H_2, C_4H_2, C_6H_2 and PAH molecules and radicals. All types of soot particles participate in coagulation. Oxidation of soot particles is described by reactions with O and OH radicals.

3 Results and discussion

The results of calculations were compared with the experimental chromatographic measurements of the concentrations of the main gas phase products [5] (Fig. 1) and the induction time and soot yield (Fig. 2) determined by the cw-laser extinction technique [6] in shock tube pyrolysis of different CH_4/Ar mixtures.
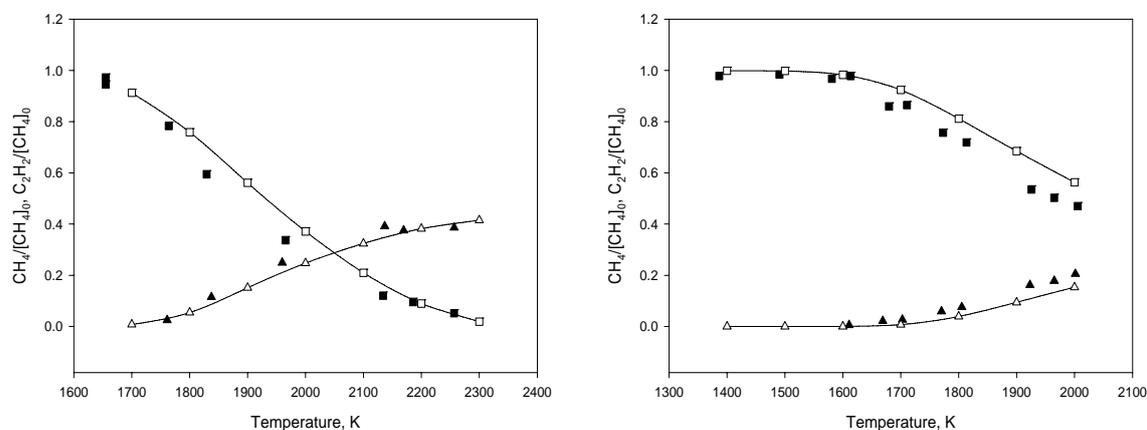
Fig. 1. Product distribution in shock tube pyrolysis of $0.02CH_4 + 0.98Ar$ (left) and $0.05CH_4 + 0.95Ar$ (right) mixtures. Closed squares and triangles correspond to the methane and acetylene concentrations, respectively, experimentally measured in [5]. Open symbols designate the results of our calculations (p_{50} = 3.0 bar, the effective reaction times are: 1940, 1780, 1620, 1460, 1300, 1140, and 1000 μs at 1600, 1700, 1800, 1900, 2000, 2100, and 2200 K, respectively, for the $0.02CH_4 + 0.98Ar$ mixture and 2050, 1900, 1700, 1620, 1440, 1240, and 1060 μs at 1400, 1500, 1600, 1700, 1800, 1900, and 200 K, respectively, for the $0.05CH_4 + 0.95Ar$ mixture.
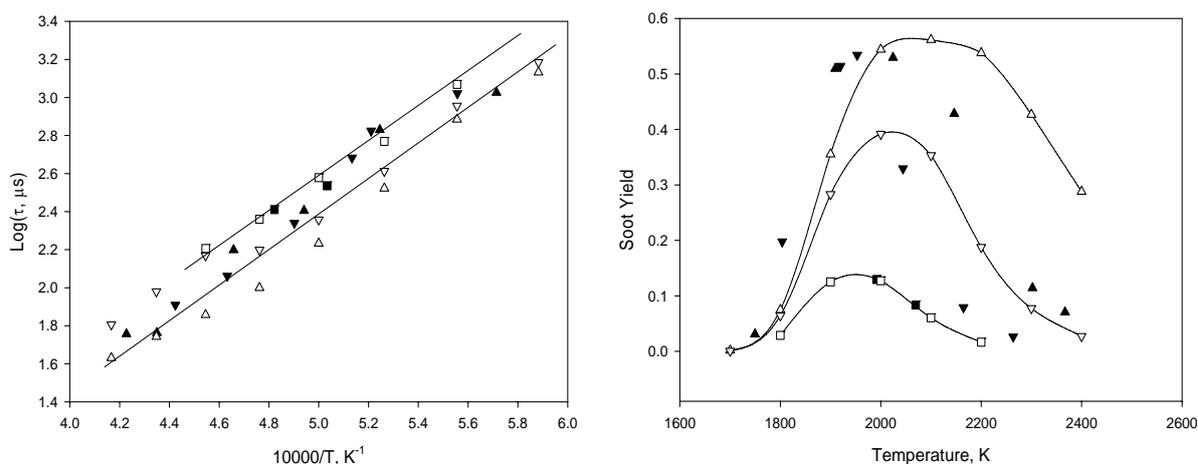
Fig. 2. Temperature dependences of the induction time (left) and the soot yield (right) in shock tube pyrolysis of different methane/Ar mixtures: (triangles up) p_{50} = 55 bar, $[C]_0$ = 6.4 mol/m^3, (triangles down) p_{50} = 55 bar, $[C]_0$ = 3.4 mol/m^3, (squares) p_{50} = 55 bar, $[C]_0$ = 1.7 mol/m^3. Closed symbols designate the results of experiments [6] and open symbols designate the results of our calculations.
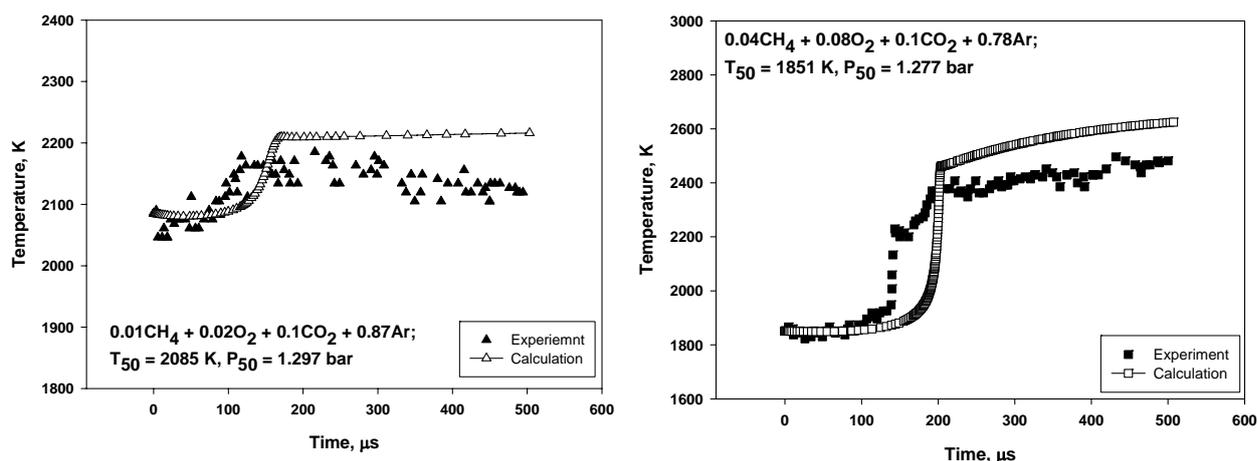
Fig. 3. Time dependences of the temperature behind reflected shock wave for different $CH_4/O_2/CO_2/Ar$ mixtures and the initial reflected shock conditions. Open symbols and lines designate the results of our constant density calculations, closed symbols the experimental measurements carried out in [7].

For CH_4/O_2 mixtures, all calculations were carried out for nonisothermal conditions, when the density is constant (Fig. 3).

As can be seen from Fig. 4, the kinetic model can describe quantitatively the behavior of the ignition delay time for the rich CH_4/O_2 mixture (φ = 3) within a wide pressure range (up to p_{50} = 260 bar). It can describe also the promoting effect of the C_2H_6 and C_3H_8 additives. Our calculations demonstrate a pronounced increase of the soot yield with the increase of the equivalent ratio φ of a CH_4/O_2 mixture (Fig. 4). At the same time, the temperature rise during the autoignition of the rich CH4/O2 mixture decreases with the increase of the equivalent ratio. As a result, the induction time of soot formation becomes longer and the soot yield decreases at a fixed reaction time.
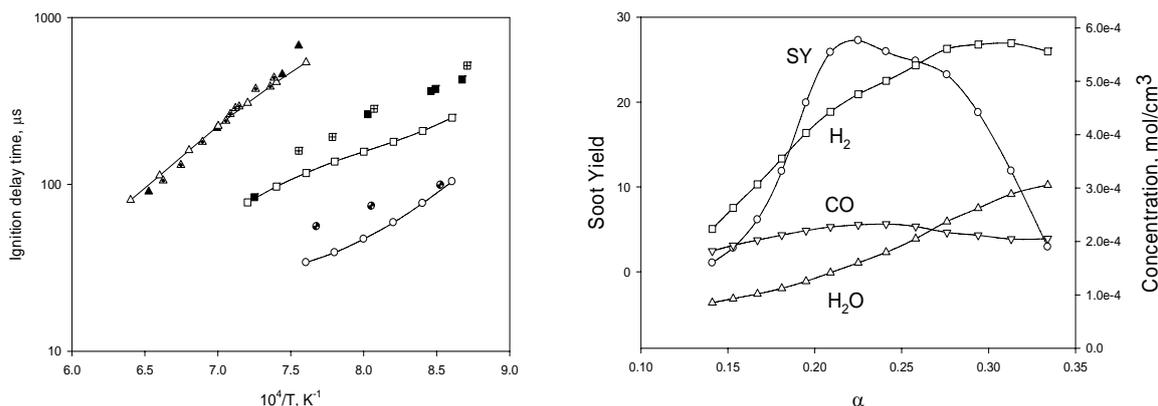
Fig. 4. Temperature dependences of the ignition delay times (left) for the $0.2CH_4 + 0.133O_2 + 0.667Ar$ ($\varphi = 3$) mixture at various pressures (($\blacktriangle$) $p_{50} = 40$ bar, ($\blacksquare$) $p_{50} = 115$ bar, ($\bullet$) $p_{50} = 260$ bar) and dependences of the H_2, CO, H_2O concentrations and soot yield (right) for various CH_4/O_2/He mixtures (various $\alpha = 1/\varphi$ values, $\tau_{reac} = 650$ μs) for $p_{50} = 90$ bar. Closed symbols designate the results of experiments [8] and open symbols designate the results of our calculations.

4 Conclusions

The new detailed kinetic model of soot formation in shock tube methane pyrolysis and oxidation is proposed. The model is based on the comprehensive kinetic model of PAH formation and growth, which incorporates several pathways such as the alternating H-abstraction/C_2H_2 addition (HACA) route, resulting in a successive growth of PAHs, the combination reactions of phenyl with C_6H_6, the cyclopentadienyl recombination, the ring closure reactions of aliphatic hydrocarbons, and the combination reaction of resonantly stabilized propargyl radicals. The new pathways of PAH formation introduced into the gas-phase kinetic mechanism of the soot formation model and the new concepts of soot nucleation and soot surface growth implemented in the new model made it possible to demonstrate a decisive role of PAHs in the soot inception and soot growth and to improve considerably the agreement between the results of calculations and experimental measurements.

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