

Kinetic Modeling of Complex Gas Phase Reactive Systems with Participation of Condensed Disperse Phase on the Example of Soot and Metal Clusters Formation in Shock Tubes

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Abstract

The kinetics of formation of microparticles in high-temperature reacting gas-phase systems is of practical importance, and computer modeling is a valuable and unique instrument which may reveal the detailed mechanism of cluster and microparticle growth from the gas phase and may help to optimize the real technological processes. In the current work we present some results of kinetic calculations of soot formation processes and nucleation, growth, coagulation and thermal decomposition of iron clusters and microparticles. The comparison with the experimental results was carried out.

Introduction

The used Galerkin method is based on an error-controlled expansion of the size distribution function into orthogonal polynomials $l_k(S; \rho)$ of a discrete variable, i. e. the chain length S , with $\Psi(S; \rho)$ as a weight function and $a_k(t; \rho)$ as time-depending coefficients with a time-depending parameter ρ [1]:

$$P(S; t) := \Psi(S; \rho) \cdot \sum_{k=0}^{\infty} a_k(t; \rho) l_k(S; \rho) \quad , \quad S = 1, 2, \dots$$

The first program to implement the analytical and numerical prerequisite of this method, in combination with the solution of the chemical elementary reactions, has been the software package MACRON [2]. An adapted version was used for performing simulations of homogeneous combustion processes. We extended MACRON to cope with several specific polymerization steps, e. g. those required by the growth reactions (HACA [8]) of the soot particles.

Modeling of metal cluster formation

The MACRON package was successfully used to model the process of iron atom vapor condensation during thermal decomposition of $\text{Fe}(\text{CO})_5$ behind shock waves [3, 4]. A self-consistent kinetic scheme for description of thermal decomposition of $\text{Fe}(\text{CO})_5$, different reactions with participation of $\text{Fe}(\text{CO})_n$ ($n = 1 - 4$) fragments, nucleation of Fe atoms and $\text{Fe}(\text{CO})_n$ ($n = 1 - 4$) fragments, growth, coagulation, and fragmentation of iron clusters and microparticles, and, finally, their thermal decomposition was constructed. The rate constants growth and thermal decomposition of iron clusters and microparticles were obtained based on the approach of the RRKM theory, when iron clusters and microparticles are considered as large molecules [5].

The size distributions of iron clusters and microparticles were calculated for various conditions (Fig. 1). Based on the Mie theory ($\lambda \gg$ the mean particle diameter), for the sufficiently diluted systems, so that the multiple scattering may be neglected and the scattering-absorbing particles are randomly positioned, we calculated the absorption of monochromatic laser radiation ($\lambda = 632.8$ nm) and performed some comparisons with the results of the experimental measurements (Figs. 3, 4). Based on the experimentally measured time dependence of light absorption by the ensemble of iron microparticles during their thermal decomposition behind reflected shock wave, we performed the reconstruction of

their size distribution at the moment of the beginning of their thermal decomposition. The results of reconstruction and numerical calculation are presented in Fig. 2.

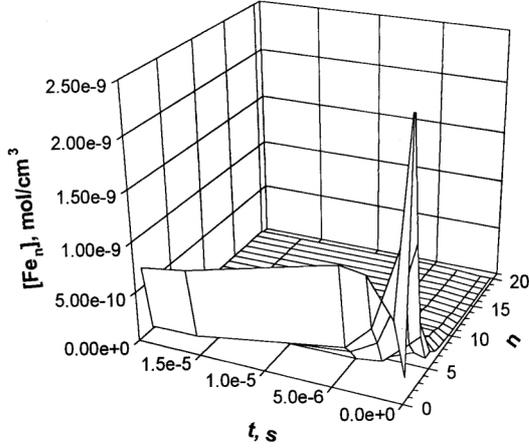


Figure 1: The time evolution of the size distribution of small iron clusters for the following initial conditions: $[\text{Fe}(\text{CO})_5] = 1.55 \cdot 10^{-9} \text{ mol/cm}^3$, $[\text{Ar}] = 3.63 \cdot 10^{-6} \text{ mol/cm}^3$, $T_g = 1380 \text{ K}$.

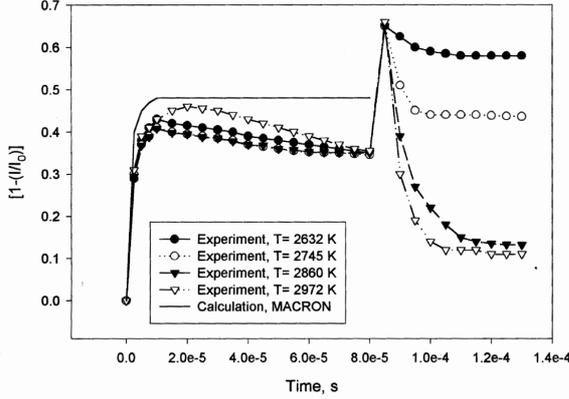


Figure 3: The experimentally measured time dependences of absorption of a He-Ne laser radiation ($\lambda = 632.8 \text{ nm}$) during the growth of iron clusters and microparticles behind incident shock waves (from $t = 0$ to $85 \mu\text{s}$) ($T_2 = 1300 - 1400 \text{ K}$, $P_2 = 5.0 - 5.5 \text{ bar}$, $[\text{Fe}(\text{CO})_5] = 4000 \text{ ppm}$ in Ar) and their thermal decomposition behind reflected shock waves ($t > 85 \mu\text{s}$) ($T_5 = 2600 - 3000 \text{ K}$, $P_2 = 24 - 25 \text{ bar}$). The solid line represents the results of calculation by the MACRON package.

The detailed calculations of the kinetics of iron clusters and microparticles in the gas and condensed phases allow us to divide the contribution of metal clusters (the gas phase) and microparticles (the condensed phase) into the experimentally measured signal of absorption of laser radiation. It is possible to calculate the contribution of each individual metal cluster (from $n = 2$ to $n = n^*$, where n^* is the boundary value after which the particles are considered as being belonged to the ensemble described by the discrete Galerkin method (the condensed phase)) into the absorption signal as a function of time. In the future, from the comparison of the experimentally measured and calculated absorption signals this permits one to clear up the question from which number of atoms in cluster (n) such a particle exhibits the optical properties fulfilled the Mie theory.

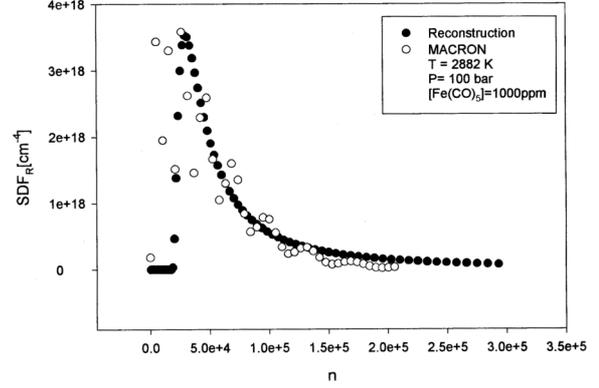


Figure 2: The calculated size distribution function of iron microparticles (the MACRON package) and reconstructed size distribution function obtained from the experimentally measured time dependence of light absorption ($\lambda = 632.8 \text{ nm}$) of the ensemble of iron microparticles during their thermal decomposition behind reflected shock wave.

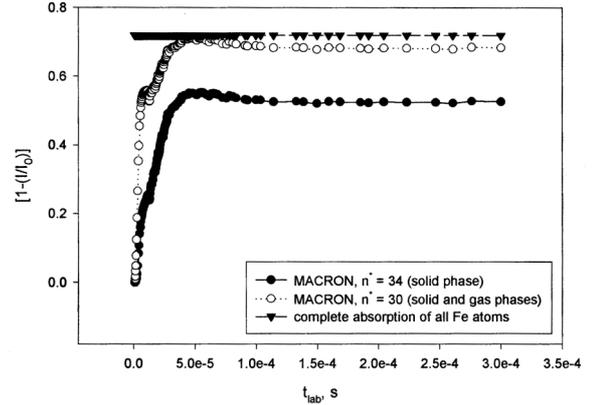
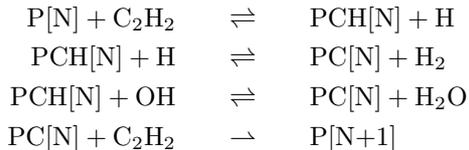


Figure 4: The calculated time dependences of light absorption ($\lambda = 632.8 \text{ nm}$) by the ensemble of iron clusters and microparticles for the conditions behind incident shock wave (Fig. 2) for different boundary values of the number of iron atoms in the absorbing particle. The upper curve represents the maximum allowed level of light absorption if all iron atoms in the system would be incorporated into the absorbing particles.

Modeling of soot formation

The process of hydrocarbon combustion will produce soot, under sufficiently rich conditions, in addition to the main products CO/CO_2 and $\text{H}_2/\text{H}_2\text{O}$. The formation and output of soot is not desired in most combustion systems because of reduced combustor lifetimes, increased fuel consumption, and environmental and health hazards. Future regulations will further decrease limiting values and thus require additional investigations to reduce soot formation. To simulate the soot formation in combustion systems we present a suitable chemical mechanism describing the gas phase, containing many elementary reactions up to three-aromatic fused rings [6, 7]. Characteristic steps are: the formation of the resonantly stabilized propargyl (H_2CCCH), by acetylene (C_2H_2) in reaction with methylene (CH_2) and ketyl (HCCO), and also by H abstraction starting from propene (C_3H_6) via allyl (C_3H_5) and propyne (C_3H_4). The formation of the first aromatic ring (phenyl) is modeled by combination of two H_2CCCH molecules in addition to the reaction of C_2H_2 with the two isomers H_2CCCCH or HCCHCCH . Further one-ring species built up directly by nonaromatic molecules are benzyl ($\text{C}_6\text{H}_5\text{CH}_2$) and o-xylol ($\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3$). The further growth up to the three-aromatic fused ring molecules, namely acenaphthylene and phenanthrene, in the gas phase is mainly modeled by two different growth mechanisms: The hydrogen abstraction induced acetylene growth (HACA) [8] and the competing combination reactions involving the resonantly stabilized cyclopentadienyl radical [9].

Additionally, the soot chemistry, consisting of macromolecular reactions and different polymer species, is handled by the discrete Galerkin technique. The three-aromatic fused rings from the gas phase are taken to build up the nuclei of soot particles. The growth of the soot particles is described by the HACA mechanism



and by coagulation reactions. Macromolecular oxidation reactions are not necessary in the present case. The described method yields the size distributions $P(S)$, $PCH(S)$, and $PCH(S)$ for the different polymer types. They give the mean chain length as the first statistical moment, plus the number density to calculate diameter, yield, and volume fraction of the soot particles.

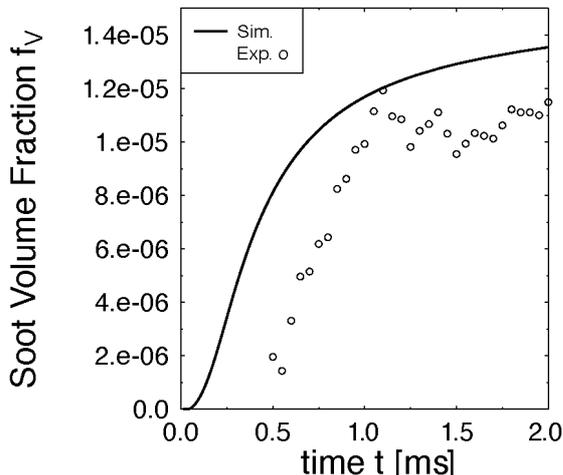


Figure 5: Simulated and experimental soot volume fraction f_V over time for a 0.66% n-heptane, 1.44% O_2 and 97.90% Ar ($\Phi = 5.0$) mixture under shock tube conditions [10]. Initial temperature and pressure were 1750 K and 25 bar, correspondingly.

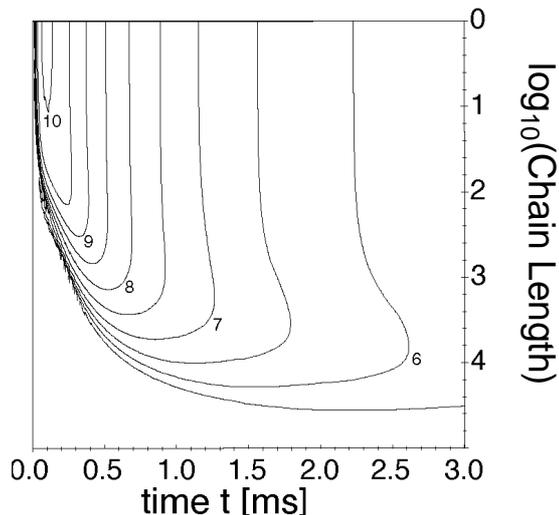


Figure 6: Contour plot of the chain length distribution of soot particles $P(S)$ over time under the same shock tube conditions as in Fig. 5. The numbers near the contour lines indicate the value of $\log_{10}(P(S)[1/\text{cm}^3])$.

We applied this to simulate soot formation for an n-heptane-filled shock tube at initial temperature and pressure of 1750 K and 25 bar, respectively, with an equivalence ratio of $\Phi = 5.0$ [10]. As may be

seen from Fig. 5, the soot volume fraction f_V is in a good agreement with the experiment. Especially the shape of the curve corresponds very well to the experimental data points. The simulated soot induction time resulting from f_V is too small because of a deviating definition of the minimum size of a soot particle by Kellerer et al. [10]. The maximum of the size distribution of the soot particles (Fig.6) moves to larger chain length with increasing time, as to be expected.

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