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Influence of oxygen on soot formation during acetylene pyrolysis

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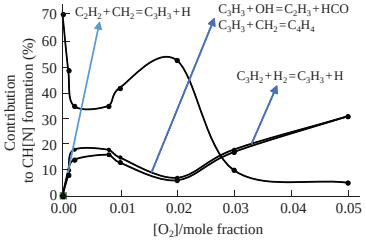
Kinetic modeling of pyrolysis of acetylene diluted with argon showed a strong influence of small additives of oxygen on the routes of formation of soot nuclei. The influence of oxygen on various channels of formation and consumption of propargyl radicals C_3H_3, which are important precursors of soot formation, as well as the fundamental possibility of controlling the process of soot formation and its properties are considered.



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A deep understanding of the mechanism of soot formation during burning of hydrocarbons is still one of the most difficult problems of combustion science.[1,2] In addition, the control of the formation of carbon particles and their properties is of primary importance not only for the suppression of undesirable soot formation during combustion and thermal decomposition of hydrocarbons, but also for the synthesis of highly specific carbon nanomaterials.[3] An important aspect of the kinetics of acetylene pyrolysis is the effect of chemically active additives and impurities on the pyrolysis process itself and the formation of solid carbon nanoparticles.[4] In this work, the effect of small oxygen additives on the formation of soot during oxidative pyrolysis of acetylene was investigated by kinetic modeling.

The process of oxidative pyrolysis of acetylene in a mixture with argon was simulated using a unified kinetic model of soot formation, which was previously successfully used to describe experiments on soot formation during pyrolysis and oxidation in a shock tube of various hydrocarbons such as methane, ethane, ethylene, acetylene, benzene, and toluene.[5] The contributions of different soot particle nucleation channels at different oxygen concentrations in the acetylene–argon mixture were compared. The model used described the soot nucleation not only from polyaromatic structures,[6] but also from polyyne-like structures formed from C_8H_4 fragments. It can be noted that fragments of C_8H_4 of various isomeric structures were found experimentally in the flames of various hydrocarbons.[7] According to our model, these C_8H_4 fragments can lead to the formation of soot nuclei and, thus, open the way for their formation from aliphatic hydrocarbons without intermediate formation of the first aromatic ring.[5]

The reactions of formation of soot nuclei from particles with polyaromatic and polyyne-like structure in the gas phase lead to the formation of soot nuclei that belong to the ensemble of heterogeneous particles. Thereafter, they can react with components from the gas phase in surface growth and oxidation reactions, and can be activated or inactivated. However, all nucleation reactions in the model are considered irreversible, since the detailed balancing principle does not apply to these reactions. Unlike reactions in the gas phase, the kinetics of changes in the ensembles of heterogeneous particles (activated and inactivated nuclei and soot particles) is described in the model using the formalism of the discrete Galerkin method, Schulz–Flory weight functions and orthogonal Laguerre polynomials with a discrete variable.[5]

In our model of soot formation, we consider particles in the gas phase formed as a result of pyrolysis or oxidation of the parent hydrocarbon (or a mixture of various hydrocarbons), and three ensembles of so-called heterogeneous particles that can react with each other (coagulation processes) and with gas phase particles (activation and inactivation processes, surface growth processes leading to particle mass growth and oxidation reducing particle mass). The transition from the gas phase to the ensemble of heterogeneous particles occurs only in the reactions of the formation of soot nuclei. There are many such reactions in the model, and they involve various polyaromatic particles, the concentration of which is quite high, and particles with a polyyne-like structure, which are especially important for describing soot formation during acetylene pyrolysis, when the formation of polyaromatic structures is hampered.

All kinetic calculations were carried out at constant density using the MACRON software package.[8] It was postulated that surface growth reactions of soot particle nuclei occur at active sites that appear when hydrogen atoms on the ‘surface’ are consumed as a result of their interaction with hydrogen atoms from the gas phase. Thus, the model considers two ensembles of nuclei: with and without active sites, which are described as ‘macromolecules’ containing N monomers (C[N] and CH[N], respectively).

Analysis of the relative contribution of various reactions in the gas phase to the formation of ensembles of activated and inactivated precursors (nuclei) of soot particles C[N] and CH[N] were carried out in order to qualitatively determine the relative contribution of polyyne-like and polyaromatic nucleation channels to this process. This is necessary to understand the

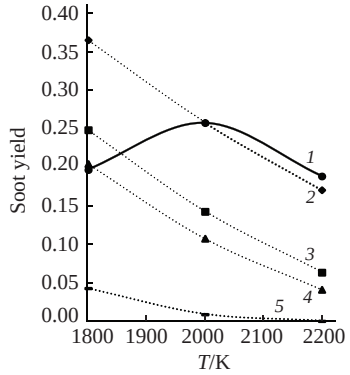

Figure 1 Temperature dependence of the soot yield during acetylene pyrolysis ($[C_2H_2]$ = 0.05 mole fractions) diluted with argon at different amounts of oxygen (% mole fractions): *1* – 0% O_2, *2* – 0.1% O_2, *3* – 0.8% O_2, *4* – 1.0% O_2, *5* – 2.0% O_2. *P* = 4.5 bar.

relative contribution of each of the channels to the formation of the entire set of activated and inactivated soot nuclei particles C[N] and CH[N]. This makes it possible to compare the nucleation processes with the other processes involved in the formation of soot nuclei, such as growth, coagulation, oxidation, activation, and inactivation.

Kinetic simulations show (Figure 1) that in the absence of oxygen, the temperature dependence of the soot yield has a typical bell-shaped appearance with a maximum of ~0.25 at *T* = 2000 K. With an increase in oxygen content and temperature, the soot yield decreases. However, it is worth noting that at *T* = 1800 K, the addition of a small amount of oxygen in the range x_{O_2} = 0.001–0.01 mole fractions results in the increase in the soot yield compared to the case of oxygen-free pyrolysis. The acceleration of soot formation by small oxygen additives at relatively low temperatures is primarily due to the fact that the presence of O_2 contributes to the formation of hydrocarbon radicals.[3,4] Temperature increase due to the additional heat release may also contribute to intensify soot formation.[9]

Analysis of the relative contribution of various reactions to the formation of CH[N] showed that under the conditions studied, the only reactions involved in the formation of the first soot nuclei CH[1] were the association of C_8H_4 fragments [reaction (1)] and reactions involving structures with one aromatic ring [reactions (2) and (3)]:

$$C_8H_4 + C_8H_4 \rightarrow CH[1], \quad (1)$$

$$A_1C_2H + A_1C_2H^* \rightarrow CH[1] + H, \quad (2)$$

$$A_1C_2H + A_1C_2H\text{-} \rightarrow CH[1] + H, \quad (3)$$

where A_1 is an aromatic molecule consisting of one benzene ring, *i.e.* a benzene molecule, A_i is an aromatic molecule consisting of i condensed aromatic rings, A_i- is an aromatic radical formed by the abstraction of an H atom from A_i molecule, A_1C_2H- is an aromatic radical with a side chain formed by the hydrogen atom H abstraction from A_1, $A_1C_2H^*$ is a radical formed by the addition of the C_2H_2 molecule to the A_1- radical.[6]

The influence of reaction (1) on the formation of CH[N] increases with temperature, namely, if at *T* = 1800 K it decreases from 58% in the absence of oxygen to 2% at $[O_2]$ = 0.05 mole fractions, at *T* = 2200 K, we observe a decrease from 76 to 16% with a similar change in oxygen content. On the other hand, the influence of temperature on the behavior of reactions (2) and (3) seems less obvious: in the temperature range *T* = 1800–2000 K, the temperature practically does not change their behavior.

Due to the key role of the propargyl radical C_3H_3 in the formation of the first aromatic ring and, consequently, the emergence of an aromatic pathway for the formation of soot particle nuclei, an analysis of various reaction routes and their contribution to the formation and consumption of propargyl radicals was carried out. In parallel with the analysis of reactions of formation and consumption of propargyl radicals C_3H_3, the contribution of reactions (2) and (3) to the formation of CH[N] was analyzed depending on the amount of oxygen in the mixture. Figure 2 shows the presence of the maxima of the contribution of reactions (2) and (3) and the minimum of the contribution of reaction (1) to the formation of CH[N] on the temperature dependence of the formation of CH[N] at $[O_2] < 0.01$ mole fractions.

Under these conditions, as in the case of the introduction of other additives during pyrolysis of acetylene diluted with argon,[10] the aromatic route arises due to the formation of the propargyl radicals C_3H_3. This may explain the greater role of reactions (2) and (3) compared to reaction (1). However, it is worth noting that at a certain oxygen concentration ($[O_2]$ ~0.01–0.02 mole fractions) the contribution of reactions (2) and (3) decreases. This may be due to reactions of withdrawal of propargyl radicals competing with the reactions (4) and (5) of their consumption on the formation of the first aromatic ring:

$$C_3H_3 + OH = C_2H_3 + HCO, \quad (4)$$

$$C_3H_3 + CH_2 = C_4H_4 + H. \quad (5)$$

Thus, the minimum contribution of the aromatic pathway to the formation of soot particle nuclei, which is provided by reactions (2) and (3), at *T* = 1800–2000 K corresponds to the oxygen concentration $[O_2]$ ~0.02 mole fractions. With a further increase in oxygen concentration, the contribution of the aromatic pathway to the formation of CH[N] nuclei compared with the polyyne-like pathway increases again, which may be due to the appearance of an additional channel (6) for the formation of C_3H_3:

$$C_3H_2 + H_2 = C_3H_3 + H. \quad (6)$$

In particular, at *T* = 2000 K the contribution of reaction (6) to the formation of propargyl radicals changes from 24 to 66% with

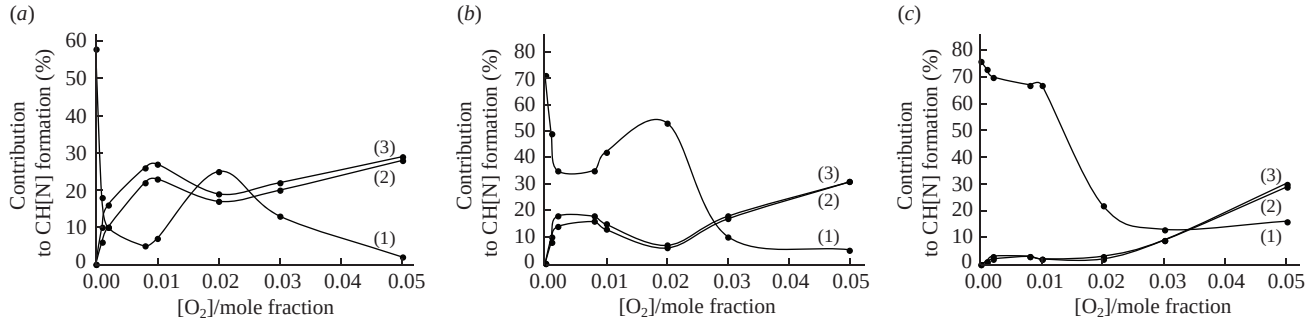

Figure 2 Contribution of reactions (1), (2) and (3) to the formation of CH[N] during pyrolysis of acetylene ($[C_2H_2]$ = 0.05 mole fractions) diluted with argon depending on the oxygen content at *P* = 4.5 bar and (*a*) at *T* = 1800 K, (*b*) at *T* = 2000 K, (*c*) at *T* = 2200 K.

an increase in oxygen concentration x_{O_2} from 0.02 to 0.03 mole fractions.

To conclude, oxygen additives seem to have different effects on the soot yield depending on their concentration and pyrolysis temperature, namely, low temperatures and oxygen concentrations favour increase in the soot yield. The change in oxygen concentration seems to affect the ratio of soot generation routes due to the change in the ratio of the contribution of competing reactions of formation and consumption of propargyl C_3H_3 radicals. Based on the conducted study of the effect of oxygen on various routes of soot formation, one may conclude that it is possible to control the process of soot formation in combustion processes within certain limits due to variation of oxygen concentration. By changing the ratio between polyyne-like and aromatic pathways of soot nucleation due to oxygen additives, it is possible to change to a certain extent the properties of carbon black obtained by acetylene pyrolysis.

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