

Soot Formation in Isothermic Pyrolysis of Mixtures of Various Hydrocarbons

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Abstract—Soot formation upon the pyrolysis of binary and ternary mixtures of various hydrocarbons is studied. The experimental values of the specific surface areas S_{sp} of soot particles are compared to the calculated values obtained assuming that any of the hydrocarbons in the mixture are inhibitors. Analysis of the results obtained for the mixtures containing acetylene shows that, when the acetylene concentration is higher than a certain value, the nuclei of soot particles are formed from acetylene, whereas other hydrocarbons participate in

INTRODUCTION

We have found that soot formation in the pyrolysis of binary hydrocarbon mixtures is inhibited [1–4]. The inhibition is due to the existence of a single inhibitor/hydrocarbon that forms the nuclei of soot particles and prevents the formation of particles from the other hydrocarbon, which is consumed for the particle growth only.

We showed in [1] for a benzene–acetylene mixture that the number of soot particles that formed in a wide range of the component ratios was equal to the number of particles formed during the pyrolysis of an acetylene–helium mixture in which the concentration of acetylene was equal to its concentration in the mixture with benzene. We concluded that the nuclei of soot were formed only from acetylene molecules, and benzene molecules were consumed for the particle growth only. Together with the consideration of geometry, this fact was used to derive equation (1) for the specific surface area of soot obtained by the pyrolysis of a mixture of hydrocarbons when the particles were formed from

one hydrocarbon only:

$$S_{sp} = S_1 / (1 + m_2/m_1)^{1/3}, \quad (1)$$

where S_{sp} is the specific surface area of the soot from a hydrocarbon mixture, S_1 is the specific surface area of the soot from the inhibiting hydrocarbon, and m_1 and m_2 are the weights of the soot particles from the inhibiting and inhibited hydrocarbons, respectively.

For the calculation using equation (1), we accepted the following values of S_1 : (1) 21, 25, and 34 m²/g for acetylene pyrolysis at 1200, 1250, and 1300°C, respectively, and (2) 21, 72, and 70 m²/g for the pyrolysis of benzene [5], naphthalene, and anthracene [6] at 1200°C, respectively.

Equation (1) agrees well with experiment [1] and it was used to analyze the experimental findings [2, 3]. If this equation applied to a hydrocarbon from the mixture gives a result that coincides with the experiment, then this hydrocarbon is an inhibitor (i.e., forms the particles). Therefore, we apply this equation to analyze the results in this work.

Table 1. Specific surface area and yield of soot formed by pyrolysis of acetylene–benzene–naphthalene–helium and acetylene–benzene–anthracene–helium mixtures ($T = 1200^\circ\text{C}$)

Composition of hydrocarbon mixture	Concentration of naphthalene or anthracene, wt %	Yield of soot, wt %	Specific surface area of soot, m ² /g				
			experiment	additive value	calculation by equation (1)*		
					benzene	naphthalene or anthracene	anthracene
Acetylene–benzene–naphthalene–helium	2.0	33.0	10.6	21.8	20.2	20.1	9.0
	16.0	33.7	11.5	27.4	18.2	38.6	9.5
Acetylene–benzene–anthracene–helium	0.9	35.2	9.4	21.4	20.0	15.4	9.0
	1.75	34.1	12.7	21.7	19.9	18.2	9.0

* Calculation assuming that soot nuclei are formed from benzene, naphthalene or anthracene, and acetylene, respectively.

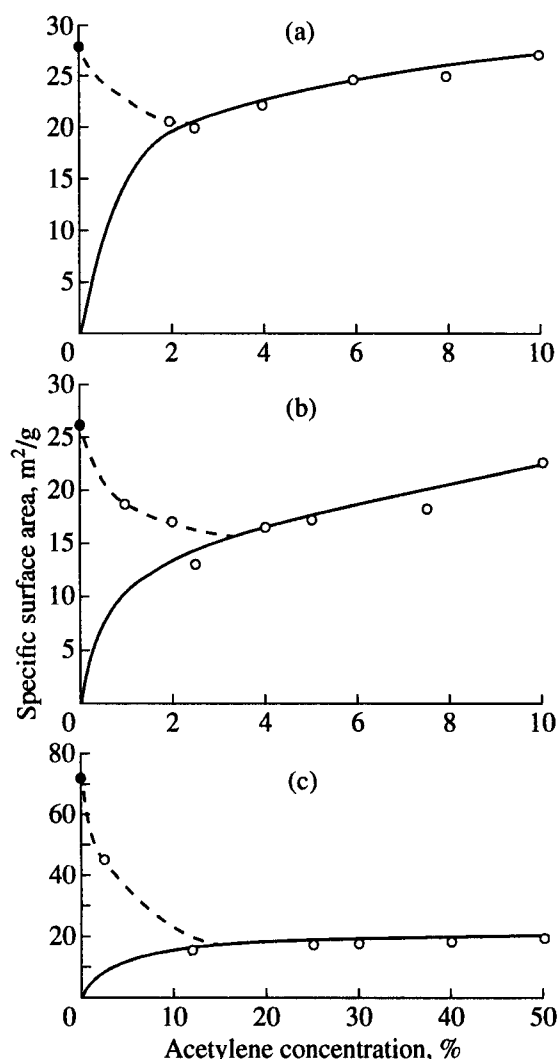


Fig. 1. Specific surface area of soot formed by the pyrolysis of a hydrocarbon mixture at different acetylene concentrations: (a) ethylene-acetylene mixture, ethylene concentration 11%, $T = 1300^{\circ}\text{C}$; (b) hexane-acetylene mixture, hexane concentration 4%, $T = 1250^{\circ}\text{C}$; and (c) naphthalene-acetylene mixture, naphthalene concentration 1%, $T = 1200^{\circ}\text{C}$. Points correspond to the experiment, and curves correspond to calculation by equation (1).

This work was aimed at studying the soot formation in the pyrolysis of the mixtures of hydrocarbons of different classes.

EXPERIMENTAL

The procedure for the measurement of soot formation was the same as in [1]. A quartz tube with a diameter of 20 mm heated in an electric furnace was used as a reactor. Measurements were performed at a constant temperature, which was provided by the introduction of a mixture of gases in the zone of constant temperature via two channels in an allund tube with a diameter of 1 mm. The soot was captured in a bag filter and partially deposited on the reactor walls. The soot deposited

on the walls at a temperature lower than 800°C had the same specific surface area as that captured in the filter. This soot was removed from the walls and weighed together with the soot from the filter. The specific surface area of the soot was measured by the thermal desorption of argon. The following hydrocarbon mixtures were studied: acetylene-ethylene, acetylene-hexane, acetylene-naphthalene, acetylene-benzene-naphthalene, acetylene-benzene-anthracene, benzene-naphthalene, and benzene-anthracene.

RESULTS AND DISCUSSION

Figure 1 presents the results on the first three mixtures. Tables 1 and 2 summarize other findings.

The specific surface areas of the soot obtained from ethylene, hexane, and naphthalene, respectively, at the temperature of the experiment are shown in Fig. 1 by solid dots on the ordinate axis. These data are taken from [5-7]. The curves correspond to calculation by equation (1), assuming that acetylene is the inhibiting hydrocarbon.

Since the yields of the soot (in % of the hydrocarbon introduced into the reaction zone) for acetylene, ethylene, naphthalene, and their binary mixtures slightly differed, the m_2/m_1 parameter in equation (1) was set equal to the product of the ratios of the carbon content in hydrocarbon molecules to their concentrations in the reacting mixture. For example, for the ethylene (11%)-acetylene (2%) mixture,

$$\frac{m_2}{m_1} = \frac{211}{22} = 5.5.$$

Analysis of the data presented in Fig. 1 shows that, in all cases, the experimental points for the hydrocarbon mixture under study at the acetylene concentration higher than some value correspond well to the curve calculated by equation (1). For ethylene and hexane, this concentration is 2-3%, and that for naphthalene is 12%. At a lower acetylene concentration, the experimental points approach the specific surface area of the second component in the mixture.

The results obtained suggest that, in the mixtures under study, acetylene is an inhibitor, and the inhibition has a mechanism observed during the pyrolysis of the acetylene-benzene mixture [1].

The data on soot formation from the acetylene-benzene-naphthalene, acetylene-benzene-anthracene, benzene-naphthalene, and benzene-anthracene mixtures are presented in Tables 1 and 2. These tables contain the data for the additive specific surface areas and the results of calculation of the specific surface area, assuming that any of the hydrocarbons in those mixtures is an inhibitor. Analysis of the results obtained for the acetylene-containing mixtures (Table 1) shows an agreement between the experiment and the calculation under the assumption that the mixture is inhibited by

Table 2. Specific surface area and yield of soot formed by pyrolysis of benzene–naphthalene–helium and benzene–anthracene–helium mixtures ($T = 1200^{\circ}\text{C}$)

Composition of hydrocarbon mixture	Concentration of naphthalene or anthracene in benzene, wt %	Yield of soot, wt %	Specific surface area of soot, m^2/g			
			experiment	additive value	calculation by equation (1)*	
					benzene	naphthalene or anthracene
Benzene–naphthalene–helium	15.0	33.0	6.6	32.6	19.8	38.2
	20.0	30.0	7.2	36.0	19.4	41.5
	30.0	32.0	9.1	42.2	18.5	49.0
Benzene–anthracene–helium	2.25	32.0	3.9	23.6	20.7	25.5
	4.5	32.0	5.2	26.0	20.6	26.4

* Calculation assuming that soot nuclei are formed from benzene, naphthalene, or anthracene, respectively.

acetylene. The mechanism of this inhibition is the same as that observed for the acetylene–benzene system.

For the naphthalene–benzene and anthracene–benzene mixtures (Table 2), the experiment shows intensive inhibition, because the specific surface area of soot from these hydrocarbon mixtures is very low compared to that for the starting hydrocarbons. Calculation by equation (1), assuming that the particle is formed from benzene or naphthalene and anthracene, gives much higher values of the specific surface area. Therefore, the mechanism of this inhibition differs from that for the acetylene-containing mixtures.

a result, the particles are formed from both hydrocarbons. When the acetylene concentration approaches zero, soot particles are formed from the second hydrocarbon only. Therefore, in all cases, the dependence of the specific surface area of soot from a hydrocarbon mixture as a function of the acetylene concentration has a minimum. A similar situation is also observed for the inhibition of methane by benzene [2] and of benzene by xylene [3]. A minimum was observed for a $\text{CH}_4\text{--CCl}_4$ mixture in [8]. It should also be noted that pronounced inhibition in the benzene–naphthalene and benzene–anthracene mixtures does not obey the mechanism of pyrolysis for acetylene-containing mixtures.

CONCLUSION

The results obtained in this work show that many mixtures of hydrocarbons inhibit soot formation. It is noteworthy that acetylene is a versatile inhibitor, because it is capable of soot formation in mixtures with paraffins, olefins, and aromatic and polyaromatic hydrocarbons. The satisfactory agreement of the experimental points with the calculation by equation (1) shows that, in all cases, the nuclei of the particles are formed from acetylene, and other hydrocarbons are consumed for the particle growth only. At low acetylene concentrations, the experimental points diverge from the curve plotted by equation (1), approaching the specific surface area of the soot obtained from the second hydrocarbon. Therefore, we may conclude that, at the acetylene concentration lower than some value, there is no complete cessation of the formation of the soot particle nuclei from the inhibited hydrocarbon. As

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