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Soot Formation in the Isothermal Pyrolysis of a Mixture of Acetylene with Diacetylene

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Abstract—Soot formation from acetylene–diacetylene mixtures was experimentally studied under isothermal conditions. It was found that new soot particles were formed only from diacetylene, whereas acetylene was consumed only in particle growth. Thus, diacetylene exhibited a higher activity in the formation of new soot particles, as compared with acetylene, which is a soot-forming agent in mixtures with other hydrocarbons.

INTRODUCTION

The results of studies on soot formation in the isothermal pyrolysis of hydrocarbons, which were performed at the All-Russia Research Institute of Natural Gas and Gas Technologies (VNIIGAZ) up to 1998, were surveyed in review [1]. In the course of these studies, it was found that soot formed in the pyrolysis of hydrocarbon mixtures exhibited a specific surface area that is significantly different from that calculated using an additivity assumption, that is, assuming that particles are formed independently from each hydrocarbon.

This effect was found for the first time in an acetylene–benzene mixture [2, 3] and referred to as the inhibition of soot formation. The inhibition consists in that soot particles are formed from only one (inhibiting) hydrocarbon, whereas the other hydrocarbon (or hydrocarbons) is consumed only in particle growth. On this basis, Eq. (1) was derived for calculating the specific surface area of soot formed from a hydrocarbon mixture. This equation was found to be very convenient for solving the question of which hydrocarbon in the mixture is inhibiting. It was also applied to analyze the results of this study.

$$S_{\mathrm{m}} = \frac{S_{\mathrm{i}}}{(1 + m_2/m_1)^{1/3}}, \qquad (1)$$

where S_{m} is the specific surface area of soot formed in a hydrocarbon mixture, m^2/g; S_{i} is the specific surface area of soot formed from an inhibiting hydrocarbon, m^2/g; m_1 is the weight of soot formed from the inhibiting hydrocarbon; and m_2 is the weight of soot formed from the inhibited hydrocarbon.

These values were calculated from the yield of soot and the percent concentration of a hydrocarbon in the mixture.

Previously, soot formation was studied in acetylene–methane mixtures [4] and in the mixtures of acetylene with ethylene, hexane, or naphthalene, as well as in acetylene mixtures with benzene–naphthalene and benzene–anthracene [5].

An analysis of data obtained in these studies demonstrated that acetylene can inhibit soot formation in mixtures with paraffinic, olefinic, aromatic, and polyaromatic hydrocarbons. In all cases, the mechanism of inhibition was no different from that observed in acetylene–benzene mixtures. In all cases, the specific surface area of soot obtained from a mixture can be calculated using Eq. (1).

In this work, we studied soot formation from a diacetylene–acetylene mixture. Data on soot formation in the isothermal pyrolysis of diacetylene were reported elsewhere [6].

The experimental technique used in this study was analogous to that described in the publications cited above. To provide isothermal pyrolysis, a mixture of acetylene with helium was supplied to a constant-temperature zone (1200°C) via two channels of an alundum tube 1 mm in diameter. The flow rate of a gas mixture was 2 l/min. The diacetylene content of the mixture with helium was 4%, and the acetylene content was 2.5–12.5%. To remove volatile products, the resulting soot was held at 900°C for 30 min. The specific surface area was measured by the adsorption of argon at liquid-nitrogen temperature.

The figure illustrates the results. Curves *1* and *2* were calculated using Eq. (1). Diacetylene or acetylene was taken as an inhibiting hydrocarbon for curve *1* or *2*, respectively. In this case, the specific surface areas of soot prepared at 1200°C from acetylene and diacetylene were taken as equal to 20 and 100 m^2/g, respectively.

The arrangement of experimental points by curve *1* clearly indicates that in the test mixture of hydrocarbons diacetylene was an inhibiting hydrocarbon. Consequently, soot particles were formed from diacetylene. This result is of interest because acetylene was an inhibiting hydrocarbon in all of the previously studied

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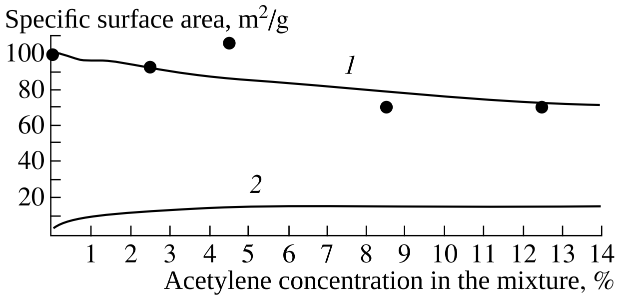

Specific surface area of soot formed in the isothermal pyrolysis of a helium–diacetylene–acetylene mixture as a function of acetylene concentration. Points indicate experimental data; curves *1* and *2* were calculated by Eq. (1) on the assumption that (*1*) diacetylene or (*2*) acetylene is an inhibitor.

acetylene-containing mixtures, which were free of diacetylene. Thus, diacetylene exhibited a higher activity in the formation of soot particles compared to acetylene. These data can be considered as corroboration of the polyyne model proposed by Krestinin [7–9].

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