Ignition delays in methane–oxygen mixture in the presence of small amount of iron or carbon nanoparticles

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Abstract. The influence of small additions (0.3–2 ppm) of iron or carbon nanoparticles on ignition delay times in stoichiometric mixture of 20% (methane + oxygen) diluted in argon was investigated. The experiments were performed in 50 mm diameter shock tube behind reflected shock waves. The nanoparticles were synthesized in pyrolysis of 0.5–1% Fe(CO)5 and 1–2% of C6H6 diluted in argon in the experiment before the ignition test. The residual nanoparticles were pulled into the flow behind incident and reflected shock wave from the shock tube walls and their volume fraction was measured by laser light extinction at the wavelength 633 nm. Additions of 0.3–2 ppm of iron nanoparticles to stoichiometric methane–oxygen mixture resulted in twofold decrease of ignition delays at temperatures below 1400 K relatively to calculated and experimental data for the mixture without nanoparticle addition. At additions of 0.4–1 ppm of carbon nanoparticles to stoichiometric methane–oxygen mixture a weak decrease of ignition delay relatively to the calculated data for the mixture without additives of carbon nanoparticles was observed.

1. Introduction
The possible contribution of coal dust to the explosions in the underground coal mines has been known for nearly two centuries. Since that time there have been a large number of studies of the dangers of coal dust, their properties and how they affect the risk of explosions, and the various methods of eliminating or reducing the hazards of explosions. Coal dust explosions occur when fine coal particles become airborne and are ignited by some means. In a coal mine, the precursor to explosion is usually the ignition of a quantity of methane. Methane/air mixtures are explosive in the range from 5 to 15% methane, with the most violent explosions resulting from a 9.5% methane concentration. The minimum energy required to ignite a cloud of coal dust is 0.03 J. This is about 100 times as much energy as is required to ignite a methane/air mixture. Most authors agree that coal dust greater than 850 microns in size do not contribute to explosions [1]. What will occur if the particle size is around 10–20 nm? Which substances will ignite the first, nanoparticle dust or methane with oxygen? The answer on these questions is the goal of present study.

Passive explosion barriers are the most common at explosion quenching. One of the possibilities is the inert dust (stone or rock dust). A marked suppression and inhibition of highly exothermic chemical reactions is indicated when finely divided particulate matter of special...
physical structure is present in small or even trace amounts. Usually the particulate matter has a composition or makeup which optimizes the combination of properties of density, heat capacity, heats of fusion and vaporization, thermal conductivity, exothermic heat of formation and particle size. Specifically, the particulate matter is structurally skeletonized for porosity and its surface is distinguished by a high incidence of peaks, edges, pores and cavities. Numerous materials, organic and inorganic, may comprise the particulate matter, e.g. boron, boric acid, boron carbide, lithium oxide, lithium hydroxide, lithium carbide, lithium nitride, lithium fluoride and particularly the inorganic compounds of such elements as magnesium, aluminum, potassium, calcium, titanium, vanadium, chromium, manganese, nickel and zinc and related organometallic compounds. The iron and iron oxide nanoparticles are the materials which have unknown effect on combustion [2]. In this study we try to answer on the question—is the iron nanoparticles prevent ethane/oxygen ignition or not?

Thus, the goal of this work is investigation of influence of small additions of iron and carbon nanoparticles on the ignition of methane/oxygen stoichiometric mixture diluted in argon.

2. Experimental

The experiments were performed behind the reflected shock waves in a conventional stainless steel diaphragm type shock tube with an inner diameter of 50 mm. The optical access to the measurement section was given by four quartz glass windows of 6 mm in a diameter, mounted perpendicular to each other at the distance of 45 mm from the end flange. The scheme of the experimental section of the shock tube and diagnostics used is shown in figure 1. The shock tube was cleaned and evacuated down to the pressure of $2 \times 10^{-2}$ mbar by a fore-vacuum pump before every run. The experiments to measure the ignition delays in 20% methane–oxygen mixture in argon were carried out behind the reflected shock wave. The carbon nanoparticles were synthesized in pyrolysis of 1–2% of C₆H₆ in the mixture with argon behind the reflected shock waves at the temperatures of $T_5 = 1900–2100$ K and pressures of 5–6 bar. According to the study [3] the carbon nanoparticle size formed under these conditions measured by laser induced incandescence (LII) was found to be 8–13 nm. The iron nanoparticles were synthesized

Figure 1. Experimental setup.
in pyrolysis of 0.5–1% of Fe(CO)$_5$ in the mixture with argon at the temperatures behind the incident shock waves of $T_2 = 700–900$ K and pressures of 1.3–1.7 bar. In work [4] the iron particle sizes formed in that range of parameters were evaluated by LII measurements as 7–11 nm.

After the first shock tube run for nanoparticle formation the shock tube was not cleaned (excepting the windows) and the low pressure section of the shock tube was filled with stoicheometric mixture of 20% of methane + oxygen in argon and second shock tube run was performed. The incident and reflected shock waves lifted up the nanoparticles from the shock tube walls to the stream and volume fraction of condensed phase was registered by means of laser extinction on the wavelength of 633 nanometers. The volume fraction of condensed nanoparticles often used in the analysis of results of extinction measurements is determined as [5]:

$$f_v = -\frac{\ln(I/I_0)\lambda}{6\pi E(m)\lambda l}$$

(1)

In this equation, $I_0$ and $I$ are the incoming and transmitted laser light intensities respectively, $l$ is the optical path length, $\lambda$ is a diagnostic wavelength, $E(m)\lambda$ is the refractive index function of particle material at a diagnostic wavelength. Note, that for evaluation of the value of refractive index function $E(m)\lambda$ is required that is a priory unknown and in general is dependent on the diagnostic wavelength [6] and the particle size [7]. The value of $E(m)\lambda$ for $f_v$ evaluation was chosen as 0.3 and 0.2 for carbon and iron nanoparticles respectively using recommendation from the study [7].

The ignition delays of methane–oxygen mixture were measured as the time from moment of passing of the reflected shock wave throughout the measurement section of the shock tube until the sharp growth of radiation in the OH radical band (306 nm) registered by photomultiplier

**Figure 2.** The time profiles of iron particles volume fraction (upper plot), OH radical emission (middle plot), and pressure transducer signal (lower plot) at ignition of 20% stoichiometric methane–oxygen mixture diluted by argon behind the reflected shock wave.
Figure 3. The temperature dependence of the ignition delays in a stoichiometric mixture of 20% (CH\textsubscript{4} + O\textsubscript{2}) diluted by argon with additives of iron nanoparticles: 1—experiment in the methane–oxygen mixture without additives [8]; 2—calculations for the methane–oxygen mixture without additives [8]; 3—experimental data with the addition of 0.8–2 ppm of iron nanoparticles; 4—experimental data with the addition of 0.3–0.5 ppm of iron nanoparticles; 5—approximation of the experimental data with iron nanoparticle additions.

with narrow band pass optical filter. In figure 2 the example of iron particle volume fraction profile, a signal of OH emission behind reflected shock wave and a signal of pressure transducer in the measurement plane obtained in the 20% methane–oxygen mixture in argon are presented. In the experiments the temperature behind the reflected shock waves was varied in the range of 1300–1900 K at the pressure of 4–6 bar. The volume fraction of the condensed particles pulled into the flow from the walls of the shock tube was varied in the range of 0.3–2 ppm depending on composition of the mixture for synthesis of nanoparticles, a type of nanoparticles (iron/carbon) and the temperature of their formation. The temperatures \( T_2 \), \( T_5 \) and the pressure \( P_2 \), \( P_5 \) behind the incident and reflected shock waves were determined based on the measured incident shock wave velocity by applying one-dimensional gas-dynamic theory with the assumption of “frozen” reaction conditions. An inaccuracy of the temperature \( T_5 \) calculation affected by an uncertainty of incident shock wave velocity, measured by three pressure transducers, was about 1–1.5% for all range of experiments.

3. Results and discussion
The dependences of ignition delays of stoichiometric mixture in 20% methane + oxygen diluted by argon on the temperature behind reflected shock wave in the presence of 0.3–2 ppm of iron and carbon nanoparticles are presented in figures 3 and 4. The investigated temperature range was 1300–1900 K and pressure was varied in the range of 4–6 bar. The experimental data on the ignition delays of methane–oxygen mixture in the presence of iron and carbon nanoparticles are compared with the experimental data and calculated data of ignition delays in nanoparticle free stoichiometric 20% methane–oxygen mixture obtained using the software package CHEMKIN II and the kinetic schemes of combustion of methane GRI-3 in the same range of temperatures and pressures, reported in [8]. From figure 3 one can see that iron nanoparticles additions
Figure 4. The temperature dependence of the ignition delays of a stoichiometric mixture of 20% \((\text{CH}_4 + \text{O}_2)\) diluted by argon with additives of carbon nanoparticles: 1—experiment in the methane–oxygen mixture without additives \([8]\); 2—calculations for the methane–oxygen mixture without additives \([8]\); 3—experimental data with the addition of 0.8–1 ppm of carbon nanoparticles; 4—experimental data with the addition of 0.4–0.5 ppm of carbon nanoparticles; 5—approximation of the experimental data with carbon nanoparticle additions.

to methane–oxygen mixture resulted in more than twofold decrease of ignition delays at the temperatures lower 1400 K relatively to calculated data for pure methane–oxygen mixture. For the other hand, it was found that the iron nanoparticles additions in the range of 0.4–1 ppm do not influence on ignition delay measurements results.

In contrast to figure 3, figure 4 shows that additions of carbon nanoparticles resulted in a weak influence on ignition of the methane–oxygen mixture diluted with argon in the investigated range of temperature and pressure. One can see that ignition delays with the carbon nanoparticle additions have a small difference from the experimental data in the mixture without these additions. One can suppose that iron nanoparticles increase the concentration of active radicals on their surface during decomposition of \(\text{CH}_4\) and \(\text{O}_2\) molecules. This effect is similar to that reported in \([9]\), where the decrease of ignition delays in stoichiometric methane–air mixture explained by early ignition of micron sized iron nanoparticles was observed. Evidently, such an effect does not take place for carbon nanoparticles, therefore the influence of the investigated carbon nanoparticles additives on ignition of methane–oxygen mixture is negligible.

4. Conclusions

The ignition delay times in 20% stoichiometric methane–oxygen mixture in argon with additives of iron or carbon nanoparticles were measured behind reflected shock wave in the shock tube. The experimental data obtained were compared with experiments and calculations for the stoichiometric methane–oxygen mixture diluted in argon without any additions. Additions of 0.3–2 ppm of iron nanoparticles to stoichiometric methane–oxygen mixture resulted in twofold decrease of ignition delays at temperatures below 1400 K relatively to calculated and experimental data for the mixture without nanoparticles. At additions of 0.4–1 ppm of carbon nanoparticles to stoichiometric methane–oxygen mixture the insignificant decrease of ignition delays in the mixture with carbon nanoparticles was seen.
delay relatively to the calculated data for the mixture without additives of carbon nanoparticles was observed.

Acknowledgments
This work was supported by the Russian Science Foundation (project No. 14-19-00025).

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