

Ignition Delay Times of Dual-Fuel Mixtures of Silane/Hydrogen at High and Low Temperatures

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1 Introduction

Silane is one of the most widely used silicon source gas in the semiconductor industry, it has potential for unpredictable ignition [1, 2] and can be ignited at fairly low temperatures [3]. Recently, silane considered as the initiator of hydrogen ignition which used as fuel in the supersonic engines. Let's consider briefly the numerical calculations of hydrogen oxidation in the presence of silane [4-6].

Thus, in papers [4, 5] on the basis of developed detailed chemical kinetics models of the silane oxidation, taking into account the 78 and 90 reactions, respectively, the ignition delay times of the mixtures silane / hydrogen / oxygen / nitrogen were calculated. In the papers the effect of the silane addition to a mixture of hydrogen / oxygen / nitrogen on the ignition delay times at temperatures ranging from 800 to 1250K and pressures ranging from 0.5 to 1.35 atm was studied. For these purposes series of calculations of ignition delay times of hydrogen-silane mixtures with oxidizer in the range of mixture compounds from pure hydrogen / oxygen / nitrogen mixture to pure silane / oxygen / nitrogen mixture were performed. Calculations have shown that the addition of small amount of silane (to 20%) in mixture of hydrogen / oxygen / nitrogen greatly decreases the ignition delay times of mixtures. Further increase in the amount of silane in the mixture (from 20% to 100%) only slightly changes the ignition delay times.

In [6] the model of chemical kinetics of the hydrogen / silane / oxygen / nitrogen mixtures oxidation, taking into account the 134 elementary chemical reactions, was developed. Based on this model qualitatively shown that the addition of silane in the mixture decreases the ignition delay times of the mixture of hydrogen / oxygen / nitrogen.

In this study, we carried out similar calculations of ignition delay times of the hydrogen / silane / air mixtures based on previously used detailed kinetics model [7] in a wider range of the thermodynamic parameters of the mixture.

2 Physical and mathematical formulation of the problem

Let's consider the problem of ignition of hydrogen / silane / air mixture behind the front of the reflected shock wave (SW). Since the flow behind the reflected SW front is motionless, then the physical and

mathematical model describing this process reduced to equation for the mixture temperature, closed by the equations of state and the equations of detailed chemical kinetics [3, 7].

To describe the kinetics of ignition and combustion of the hydrogen / silane / air mixture we use slightly modified detailed kinetic scheme [8], which consists of 140 reactions for twenty five components. Modifications of the kinetics model, the thermodynamic and kinetic constants are described in detail in our previous works [3, 7]. Note, that using this kinetics model we described the detonation wave structure, the ignition delay times of silane / hydrogen / oxygen / nitrogen mixtures and ignition limits of silane / oxygen and silane / air mixtures [3, 7, 9].

There are several criteria to determine the ignition delay times [3, 10]. Earlier, in [3, 10] it was shown that different ignition criteria give very close results to each other both for hydrogen / oxygen / argon mixture and for silane / hydrogen / oxygen / nitrogen / argon mixtures. Therefore, in this study to determine the ignition delay time we choose one of the criteria: the time of mixture temperature maximization -

$$\max\left(\frac{dT}{dt}\right).$$

3 The calculation results

Let's consider the effect of silane concentration in hydrogen-air mixtures at temperatures ranging from 1200 K to 2500 K on the ignition delay times of the mixture. Thus, in papers [4, 5] it has been shown that the addition of silane in concentrations greater than 20% at temperatures ranging from 800 K to 1200 K insignificantly affects to ignition delay times of hydrogen-air mixture. Fig. 1 shows the dependence of the ignition delay time of the hydrogen / silane / air mixture on the composition of the fuels (hydrogen and silane): on the top abscissa axis - the ratio of the mass concentration of hydrogen in the mixture to a mass concentration of hydrogen in a stoichiometric hydrogen-air mixture; on the bottom abscissa axis - the ratio of the mass concentration of silane in the mixture to a mass concentration of silane in the stoichiometric silane-air mixture. It is evident that for all temperatures, the addition a small amount of silane in hydrogen-air mixture results in a significant decrease (in 3 times) in ignition delay times of the mixture. A further increase of the silane concentration in the mixture leads to a monotonic decrease of the ignition delay times at temperatures up to about 2200 K, and at temperatures of more than 2200 K the dependencies tends to the asymptotic value corresponding to the ignition delay times of stoichiometric silane-air mixture. Thus, at high temperatures (more than 2200K) the presence of hydrogen in the mixture does not affects to the ignition delay times.

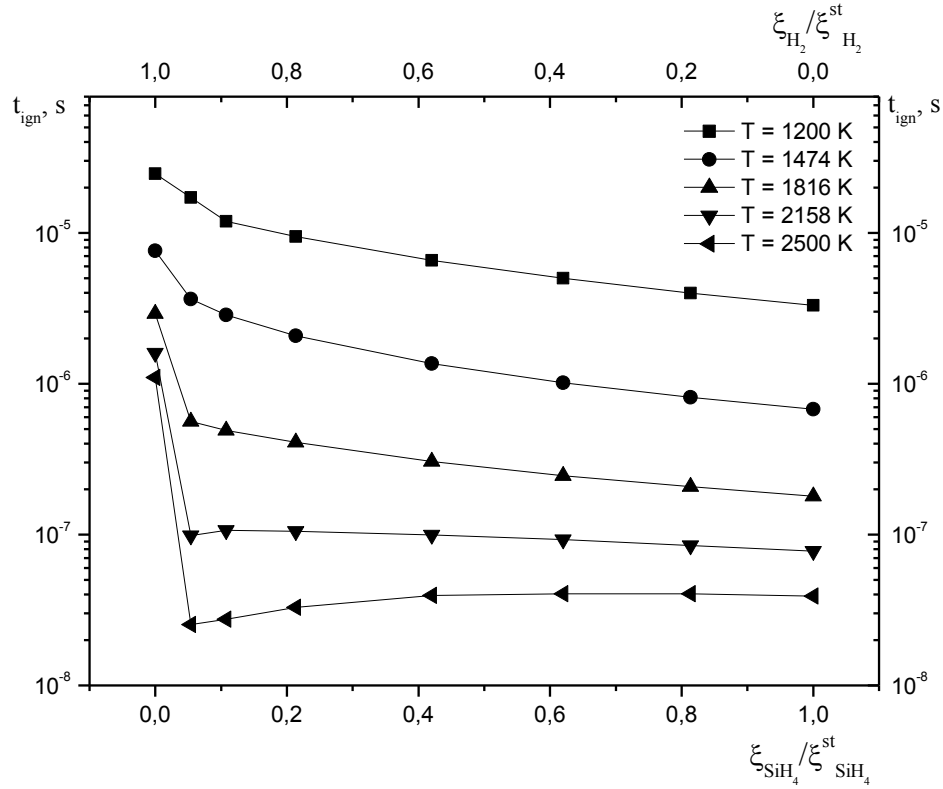


Figure 1. The dependence of the ignition delay times of hydrogen / silane / air mixtures on concentrations of fuels (hydrogen and silane).

Moreover, calculations at low temperatures (ranging from 800K to 1200K) were carried out. Fig. 2 shows the dependences of the ignition delay times of silane/hydrogen/air mixtures on concentrations of fuels (hydrogen and silane) calculated in these work as well as the calculations of Jachimowski and McLain [4] and experiments of Slack and Grillo [11]. It is seen that in whole temperature range the addition of small amount of silane (about 20%) in the hydrogen/air mixture results in a significant decreasing of the ignition delay times of the mixtures both in our calculations and calculations carried out by Jachimowski and McLain (1983).

Besides that, we see in whole temperature range satisfactory agreement between our calculations and calculations carried out in [4] at high concentrations of silane (higher than 20%) in the mixture. But at concentrations of silane less than 20% and temperatures less than 1000 K we have a significant discrepancy between our data and data of Jachimowski and McLain [4]. However, it is clear that our calculations in these parameters gives values closer to the experimental data of Slack and Grillo [11] compared with data of Jachimowski and McLain [4].

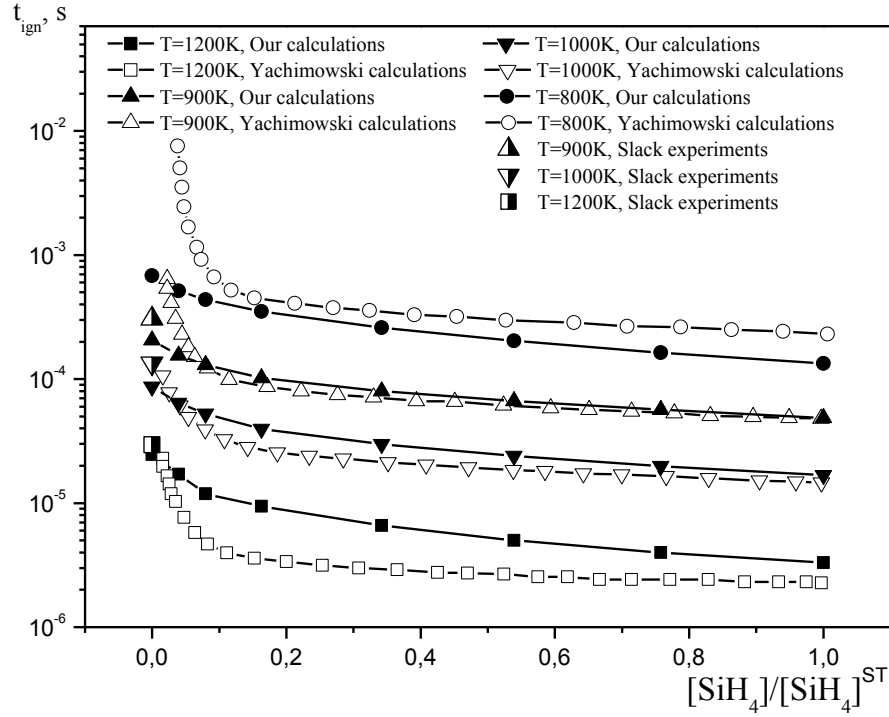


Figure 2. The dependence of the ignition delay times of hydrogen / silane / air mixtures on concentrations of fuels (hydrogen and silane). Comparison with calculations of Jachimowski and McLain (1983) and experiments of Slack and Grillo (1977).

It is known that the dependence of the ignition delay time of mono-fuel mixtures on temperature can be described by the standard Arrhenius formula [7, 10]. Thus, in the variables $\left(\ln(t_{ign}), \frac{1}{T}\right)$ these

dependencies represents a straight line: $\ln(t_{ign}) = A + \frac{E}{RT}$. In the case of dual-fuel mixtures such relations

with a constant activation energy may not be performed. For example, in [12] similar approximation formula for mixtures of methane / hydrogen / air within the Arrhenius model, but with the assumption that the activation energy depends on fuel concentration in the mixture ξ_{fuel} , were constructed. It made it possible to describe the experimentally observed ignition delay times of the mixtures. Therefore, it seems appropriate to build the logarithm of the ignition delay time $\ln(t_{ign})$ of hydrogen / silane / air mixture on the reverse temperature $1/T$. Such dependencies were constructed at several areas of ignition:

1. In area of high silane concentrations ($\xi_{SiH_4} / \xi_{SiH_4}^{st} \in [0.6, 1]$) in which the dependences represent a straight line with different inclination angle:

$$\ln(t_{ign}) = -20.69307 + 0.969545 \cdot \left(\frac{10^4}{T}\right)^{1.03243} - 0.4715 \left(\frac{\xi_{SiH_4}}{\xi_{SiH_4}^{st}}\right)^{1.77025};$$

2. In area of average silane concentrations ($\xi_{SiH_4} / \xi_{SiH_4}^{st} \in [0.2, 0.6]$) in which the dependences are non-linear:

$$\ln(t_{ign}) = -115.07446 + 85.59464 \cdot \left(\frac{10^4}{T}\right)^{0.09579} + 43.01449 \cdot \left(\frac{\xi_{SiH_4}}{\xi_{SiH_4}^{st}}\right)^{0.51673} - 37.41786 \cdot \left(\frac{10^4}{T}\right)^{0.09579} \cdot \left(\frac{\xi_{SiH_4}}{\xi_{SiH_4}^{st}}\right)^{0.51673};$$

3. In area of small silane concentrations ($\xi_{SiH_4} / \xi_{SiH_4}^{st} \in [0, 0.2]$) in which a very significant change of ignition delay times at high temperatures (30 times) and small change (2 times) at low temperatures are observed:

$$\ln(t_{ign}) = 80204 \cdot \frac{1 - 0.884 \cdot (x - 1.625y)}{1 + 1765 \cdot (x - 20.2y) + 484 \cdot (x^2 + 273y^2)}, \text{ where } x = \frac{10^4}{T}, y = \frac{\xi_{SiH_4}}{\xi_{SiH_4}^{st}}.$$

4 Conclusions

Physical and mathematical model and mathematical technology to describe the ignition and combustion of silane in the reflected shock wave, based on the detailed kinetics of the oxidation of silane, is proposed. Based on this model the ignition delay times of dual-fuel silane/hydrogen/air mixtures at high and low temperatures were calculated. It was revealed the effect of fuel concentration on the ignition process. It were defined:

- in all considered temperature range (from 800 K to 2500 K), addition a small amount of silane (up to 20%) in the hydrogen-air mixture results in a significant decrease (in 3 times) of ignition delay time of the mixture;
- the addition of more than 20% of the silane results in a slight decreasing of the delay ignition time of hydrogen-air mixture, i.e. the presence of hydrogen in such mixtures has no effect on the ignition delay times.

It was shown that for dual-fuel silane/hydrogen/air mixtures, there are three areas of ignition: 1. The area in which the activation energy depends on the concentration of the silane (at silane concentrations 60 - 100%); 2. The area in which the activation energy is a function of the mixture components concentration and the mixture temperature (at silane concentrations 20 - 60%); 3. The area in which a very significant change of ignition delay times at high temperatures (30 times) and small change (2 times) at low temperatures are observed (at silane concentrations 0 - 20%). It was determined the dependencies of ignition delay time of the mixtures on temperature and silane concentrations for all three areas by the approximation of the data obtained by detailed kinetics.

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References

- [1] Chen JR, Tsai HY, Chen SK, Pan HR, Hu SC, Shen CC, Kuan CM, Lee YC, Wu CC. (2006). Analysis of a silane explosion in a photovoltaic fabricant plant. *Process Safety Progress*. 25 : 237.
- [2] Chang YY, Peng DJ, Wu HC, Tsaur CC, Shen CC, Tsai HY, Chen JR. (2007). Revising of a silane explosion in a photovoltaic fabrication plant. *Process Safety Progress*. 26 : 155.
- [3] Tropin DA, Fedorov AV. (2016). Calculation of ignition limits of silane-oxygen and silane-air mixtures. *Combustion, Explosion and Shock Waves*. 1 : 46.
- [4] Jachimowski CJ, McLain AG. (1983). A Chemical Kinetic Mechanism for the Ignition of Silane/Hydrogen Mixtures. NASA Technical Paper 2129.
- [5] Chinitz W. (1985). Theoretical Studies of the Ignition and Combustion of Silane-Hydrogen-Air Mixtures. NASA Contractor Report 3876.
- [6] Golovitchev VI, Bruno C. (1998). Numerical Study of the Ignition of Silane/Hydrogen Mixtures. *Journal of Propulsion and Power*. 1 : 92.
- [7] Tropin DA, Fedorov AV. (2015). Physicomathematical modeling of ignition and combustion of silane in transient and reflected shock waves. *Combustion, Explosion and Shock Waves*. 4 : 431.
- [8] Britten JA, Tong J, Westbrook CK. (1990). A Numerical Study of Silane Combustion. Twenty-Third Symposium (International) on Combustion, The Combustion Institute. 195.
- [9] Fomin PA, Fedorov AV, Chen JR. (2016). Calculation of detonation characteristics of silane-air mixtures. *Proceedings of 11th International Symposium on Hazards, Prevention and Mitigation of Industrial Explosions (11th ISHPMIE)*. 74.
- [10] Fedorov AV, Fomin PA, Fomin VM, Tropin DA, Chen JR. (2012). Mathematical Analysis of Detonation Suppression by Inert Particles. Kao Tech Publishing (ISBN 978-986-88423-0-4).
- [11] Slack M, Grillo A. (1977). Investigation of hydrogen-air ignition sensitized by nitric oxide and by nitrogen dioxide. NASA Contractor Report 2896.
- [12] Cheng RK, Oppenheim AK. (1984). Autoignition in methane-hydrogen mixtures. *Combustion and Flame*. 58 : 125.