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Modeling study of hydrogen production via partial oxidation of H₂S–H₂O blend

V.A. Savelieva, N.S. Titova, A.M. Starik*

Central Institute of Aviation Motors, Scientific Educational Centre “Physical and Chemical Kinetics and Combustion”, Aviamotornaya st. 2, Moscow, 111116 Russia

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ABSTRACT

Kinetic analysis of the thermal partial oxidation in the H₂S–H₂O–O₂(air) mixture in a flow reactor with given length is conducted numerically on the basis of developed reaction mechanism. This mechanism incorporates the reaction paths typical both for the H₂S pyrolysis and for the H₂S oxidation and describes with reasonable accuracy a large set of experimental data. The computations have demonstrated that addition of H₂O to the fuel-rich H₂S–O₂(air) mixture allows one to increase the relative yield of H₂ in the conversion products. At identical fractions of H₂S and H₂O in the H₂S–H₂O blend the increase in the H₂ relative yield can amount to a factor of 1.5. Though the addition of H₂O to H₂S leads to the delay of the conversion of H₂S, nevertheless, at initial temperature ($T_0 = 1000$ K) it is possible to occur the conversion process in a shot flow reactor of 1 m length at atmospheric pressure. It has been shown that the formation of additional amount of H₂ in the conversion products upon the H₂O admixture to H₂S is caused by the increase of the role of reaction $H_2O + H = OH + H_2$. The growth in the initial temperature of the H₂S–H₂O–O₂(air) mixture increases the absolute concentration of H₂ in the conversion products and its relative yield.

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Introduction

Nowadays, hydrogen is considered as a very promising fuel possessing high burning rate, rather light ignition and great mass heating value [1]. The other important issue is that burning of hydrogen provides much more friendly environment combustion exhaust compared to that of hydrocarbons and other fossil fuels. For past years, a number of different approaches were proposed to produce hydrogen. Among them there are partial oxidation, steam and dry conversion of hydrocarbons [2,3], coal gasification [4], electrolyze of H₂O molecules [5] and oxidation of Al particles in H₂O environment

[6,7]. One of the perspective way to enhance the conversion of hydrocarbons to synthesis gas (syngas) enriched by hydrogen is the usage of thermally non-equilibrium plasma comprising excited oxygen molecules or highly reactive atoms and radicals [3,8]. However, all these approaches are based on reforming of substances that serves as traditional fuels.

A very interesting alternative way to produce hydrogen or syngas is the usage of biofuels or chemical substances identified as ecologically harmful gases, such as H₂S, CH₂O and other organic species. Hydrogen sulfide H₂S is produced in different natural processes, upon refining of heavy oil, bitumen and coal. As well, it is constituent of associated petroleum gas. Hydrogen sulfide is a strongly toxic and corrosive

* Corresponding author.

E-mail address: star@ciam.ru (A.M. Starik).<http://dx.doi.org/10.1016/j.ijhydene.2017.03.155>

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gas [9]. Therefore, the problem of its utilization is currently under the extensive attention [10]. In this point of view, a few approaches were proposed. One of them is well-known Claus process [11–13] that is based on the two-steps oxidation of H₂S: the thermal step



and the catalytic step



Sulfur and water vapor are the products of this process.

The other approach, studied both experimentally [14,15] and numerically [16–20], is the thermal decomposition of H₂S, which produces hydrogen and molecular sulfur in line with following global reaction:



However, the reaction R3 is endothermic, and a fairly large heat is required to supply to the system. Therefore, decomposition of H₂S occurs at rather high temperature and its conversion does not exceed 50% even at temperature $T \sim 1600$ K [21]. For low-temperature decomposition of H₂S with high H₂ yield, the catalysts should be used [22–26].

Another approach concerns the steam reformation of hydrogen sulfide, which is also highly endothermic reaction. The possibility of such process has been demonstrated experimentally [27], although the conversion level of H₂S did not reach the equilibrium value. However, the usage of molybdenum as a catalyst increased the conversion over non-catalytic case. Arrhenius parameters for both thermal and steam reformation of hydrogen sulfide were derived.

The conversion of H₂S–CH₄ mixture for hydrogen production is also attractive. Karan and Behie [28] have studied the reaction between H₂S and CH₄ in a high temperature flow reactor focusing on the CS₂ formation. They concluded that H₂S thermal decomposition was the rate-limiting step and the H₂S consumption in the CH₄–H₂S mixture proceeds at a rate of H₂S thermal decomposition. The production of hydrogen from CH₄–H₂S has been fully analyzed in Ref. [29]. On the base of thermochemical equilibrium calculations the authors of that work identified the conditions at which the reaction of methane with hydrogen sulfide must produce mostly hydrogen and carbon disulfide without solid carbon as by-product. The energy required for the H₂S–CH₄ reformation was estimated. The experimental study of hydrogen production from the reaction between hydrogen sulphide and methane has been carried out in Ref. [30] with the use of a thermal non-catalytic and MoS₂ catalytic tubular reactor. The catalytic reaction rate appeared to be much greater than the thermal one, but due to the catalyst deactivation in operation process, the reaction rate decreased. The effect of catalysts composition on the rate of CH₄–H₂S mixture conversion has been studied in Refs. [31,32]. In Ref. [33] the amounts of hydrogen produced in a laboratory-scale reactor from H₂S–CH₄ mixture diluted by nitrogen at temperatures of 1273–1673 K were presented. The experimental results demonstrated the possibility of ~95% hydrogen recovery from the mixture of hydrogen sulfide and methane. The temperature and the residence time required to reach asymptotic

steady state value was depicted. The experimental observation was supported by numerical simulation.

The effect of hydrogen sulfide on steam reforming of methane has been studied both experimentally and theoretically in Ref. [34]. It was shown that even very small amount of hydrogen sulfide decreased the catalyst activity and reduced drastically the reforming of methane.

The production of H₂ from acid gas (H₂S and CO₂) in industrial Sulfur Recovery Units has been studied numerically in Ref. [35]. The standard operation conditions of SRU appeared to lead to very low H₂ yield (3%). It was shown that the change of operation conditions such as the extent of H₂S oxidation and feed preheating could increase H₂ yield from 3% to 38% without changing the composition of the acid gas stream.

Because the pure conversion of H₂S requires a lot of energy cost or very expensive catalysts, another approach of H₂ production from H₂S seems to be promising. As the reaction R1 proceeds with energy release, therefore, the combination of the processes of H₂S oxidation and its thermal decomposition can produce hydrogen with rather high energetic efficiency without catalysis [20,36]. It was shown that the addition of small amount of oxygen in the inlet H₂S gas stream could significantly enhance the production of hydrogen. The optimal operating conditions for high H₂S conversion and good H₂ yield were identified [36]. In particular, the O₂/H₂S ratio equal to 0.2, the temperature equal to 1100 °C and a residence time of 150 ms allowed to obtain H₂S conversion of about 60% and H₂ yield of 20%.

The other interesting issue concerns the investigation of the possibility of the increase of H₂ relative yield upon the partial oxidation of hydrogen sulfide due to addition of water vapor to the fuel-rich H₂S–O₂(air) mixture. As was demonstrated numerically [3], the admixture of H₂O to the fuel-rich CH₄–O₂ mixture at $T = 1200$ K, $P = 1$ atm and $\phi = 4$ allows one to increase the relative (in respect to used CH₄) yield of H₂ in the products of methane conversion. In order to gain an insight in the kinetic features of the processes of the H₂S conversion to hydrogen upon the partial oxidation in the H₂S–H₂O–O₂ (air) system, the detailed reaction mechanism with rather high prediction ability should be developed. However, today, the kinetic data for such a system are rather scarce.

The purpose of the present work is to analyze numerically the possibility of the H₂ production via non-catalytic partial oxidation of H₂S in the H₂S–H₂O–O₂(air) mixture and to clarify the principal mechanisms responsible for the growth of H₂ relative yield on the basis of the detailed kinetic model of H₂S decomposition and oxidation.

Kinetic model

Nowadays, a few reaction mechanisms of hydrogen sulfide pyrolysis and combustion were developed [19,20,35,37–40]. Some of them reproduces a wide set of experimental data both on ignition delay and on velocity of flame propagation for the stoichiometric and fuel-rich H₂S–O₂ (air) mixtures with reasonable accuracy. In the present work, the reaction mechanism of hydrogen sulfide oxidation, developed in Ref. [40], was taken as the basic one. This mechanism

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