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Features of low-temperature oxidation of hydrogen in the medium of nitrogen, carbon dioxide, and water vapor at elevated pressures

Anatoly A. Vostrikov, Oxana N. Fedyaeva*, Andrey V. Shishkin, Daniil S. Tretyakov, Mikhail Y. Sokol

Kutateladze Institute of Thermophysics SB RAS, 1, Acad. Lavrentiev Av., Novosibirsk, Russia

ARTICLE INFO

Article history:

Received 6 March 2018

Received in revised form

6 April 2018

Accepted 14 April 2018

Available online xxx

Keywords:

Hydrogen

Self-ignition

Explosion

Nitrogen

Carbon dioxide

Water vapor

ABSTRACT

The article discusses novel research results on combustion features of high-density H_2/O_2 mixtures ($\rho_{H_2} = 0.70\text{--}1.89\text{ mol/dm}^3$, $\rho_{O_2} = 0.32\text{--}0.81\text{ mol/dm}^3$) diluted with nitrogen, carbon dioxide, or water vapor (from 46 to 76% mol.) at the uniform heating (1 K/min) of tubular reactor. Based on time dependencies of temperature increment in the reaction mixtures caused by the heat release during oxidation of H_2 , it is found that the self-ignition temperature of $H_2/O_2/N_2$ and $H_2/O_2/H_2O$ mixtures is by $\approx 30\text{ K}$ lower than that of the $H_2/O_2/CO_2$ mixture. Unlike combustion of H_2 in the N_2 medium, in the CO_2 and H_2O media a chain-thermal explosion is observed at a certain concentration of reagents. The influencing mechanisms of diluents on the H_2 oxidation dynamics, as well as the contribution of homogeneous and heterogeneous reactions in the heat release are revealed. It is established that high heat capacity of $H_2/O_2/CO_2$ mixture, chemical interaction between its components, and presence of CO_2 molecules adsorbed on the reactor inner surface, are the factors determining the H_2 oxidation dynamics in CO_2 medium. At oxidation of H_2 in the H_2O medium, the process takes place against the background of water evaporation and, as a consequence, is characterized by increased heat capacity and thermal conductivity of the $H_2/O_2/H_2O$ reaction mixture.

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Introduction

Combustion of fossil fuels and organic wastes directly in the heat carrier (water vapor and supercritical water) increases energy efficiency and ecological cleanness of heat and electric energy production [1–3]. The positive ecological effect when using supercritical water (SCW: $T_c = 647\text{ K}$, $P_c = 22.1\text{ MPa}$) for fuel and waste conversion is due to the ability of SCW to dissolve organic substances and gases [4,5], remove CO_2 in

liquid form due to the high pressure of reactants [6,7] and low process temperature ($\leq 1073\text{ K}$) preventing the formation of oxides NO_x , SO_2 , and soot [8–10]. Hydrogen and methane are the main combustible products of SCW gasification of fuels and wastes [11–16]. It is obvious that in order to develop new technologies based on combustion of different types of fuels in high-density water vapor or SCW, it is necessary to identify combustion features of individual compounds, including H_2 and CH_4 , in these media. Earlier we have studied the

* Corresponding author.

E-mail address: fedyaeva@itp.nsc.ru (O.N. Fedyaeva).

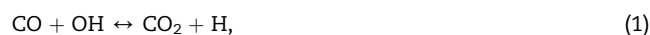
<https://doi.org/10.1016/j.ijhydene.2018.04.105>

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Nomenclature			
<i>Roman Symbols</i>		λ	thermal conductivity, W/m·K
C	heat capacity, J/K	ν	vibrational frequency, cm^{-1}
E	energy, J/mol	ρ	density, mol/dm^3
J	flow, molecules/ $\text{cm}^2 \cdot \text{s}$	σ	standard deviation
N	density, molecules/ cm^3	τ	time, s
P	pressure, MPa	φ	fuel-equivalence ratio
q	heating rate, K/min	<i>Superscript</i>	
Q	heat release, J	*	parameter of self-ignition
R	universal gas constant, J/mol·K	+	to the surface
S	area, K·min	–	from the surface
SCW	supercritical water	<i>Subscript</i>	
t	time, min	a	adsorption
T	temperature, K	ad	adiabatic
v	velocity, cm^2/s	c	critical
x	molar fraction, % mol.	d	diluent
y	mass fraction, % wt.	ex	explosion
<i>Greek Symbols</i>		ev	evaporation
Δ	increment	in	internal thermocouple
ε	stoichiometric coefficient	out	outer thermocouple
θ	number of molecules, molecules/ cm^2	ox	oxidation
		v	isochoric

combustion of CH_4 in water vapor, nitrogen, and SCW in autoclave and flow regimes [17]. It was shown that the self-ignition temperature of methane in the water vapor is lower than that in the nitrogen, and it decreases with an increase in the concentration of CH_4 . Self-sustaining combustion of methane in counter jets of CH_4 and O_2 in an upward concurrent flow of SCW takes place only at $T > 700$ K.

A large number of papers have been devoted to the study of the mechanisms and combustion kinetics of H_2 . The obtained results have been considered in a recent review [18]. Here we will focus only on the effects associated with diluting the H_2/O_2 mixture with nitrogen, carbon dioxide, water vapor, or supercritical water. Rudy et al. [19] in the study of spontaneous ignition of H_2/N_2 mixture during its high-pressure (4.3–15.9 MPa) release into air showed that N_2 may increase the initial pressure necessary to self-ignite the mixture as much as by 2.1 or 2.8 times for 5 and 10% mol. N_2 , respectively. Based on the calculations of the adiabatic flame temperature, Piqueras et al. [20] revealed that in the high-pressure region, CO_2 inhibits the ignition of H_2 to a greater extent than N_2 does (the lower flammability limit for the $\text{H}_2/\text{O}_2/\text{CO}_2$ and $\text{H}_2/\text{O}_2/\text{N}_2$ mixtures at 20 MPa amounts to 7–9 and 6% mol. H_2 , respectively). Qiao et al. [21] investigated by experimental and numerical methods the effect of diluents on the velocity of $\text{H}_2/\text{O}_2/\text{N}_2$ flames (300 K, 0.05–0.10 MPa) and showed that dilutions provided greater reductions of the laminar combustion velocity in the order He, Ar, N_2 , and CO_2 . According to the authors [21], this order reflects their increased capacities either to quench the reaction zone by increased specific heats or to reduce flame velocities by reduced transport rates. As factors determining the difference in combustion rate of H_2 in N_2 and CO_2 media, Liu et al. [22] highlight the possible direct chemical effect of CO_2 due to the reaction



as well as the enhanced radiation transfer by CO_2 as compared with N_2 .

Liu et al. [23] studied the effect of water vapor concentration ($\leq 30\%$ mol.) on H_2 /air flame propagation (323–423 K, 0.1 MPa) and revealed that the average flame propagation rate increases with increase in the concentration of H_2 and the initial temperature, though decreases with increase in the concentration of water vapor. The authors [23] explained the latter effect by the decrease of the air content in the mixture (as a consequence, a decrease in the frequency of effective collisions between O_2 and H_2 molecules) and a decrease in the flame temperature due to the high heat capacity of water vapor. Wang et al. [24], when studying the effect of water vapor ($\leq 70\%$ mol.) on the H_2/CO mixture flammability limits, identified the main factors corresponding to different concentrations of water vapor. The effects of water vapor on promoting heat absorption and chain-terminating reactions, mainly, the reaction



play the key role, when $[\text{H}_2\text{O}] < 30\%$ mol. However, at $[\text{H}_2\text{O}] = 30\text{--}60\%$ mol. this effect becomes less significant. When $[\text{H}_2\text{O}] > 60\%$ mol., the dilution effect of water becomes apparent, i.e. the lower flammability limit increases with the increasing $[\text{H}_2\text{O}]$. Holgate and Tester [25,26], when studying mechanisms and kinetics of H_2 oxidation in supercritical water with strong dilution ($x_{\text{H}_2\text{O}} = 99.4\text{--}99.8\%$ mol., 678–873 K, 24.6 MPa), found that rate of the branching reaction.



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