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Combustion of lean methane–air mixtures in monolith beds: Kinetic studies in low and high temperatures

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HIGHLIGHTS

- Kinetics studies of thermal methane combustion in monolith bed were investigated.
- Kinetic experiments were carried out in low and high temperature.
- Temperature, size and type of monolith's surface influence on reaction mechanism.
- Thermal combustion in monolith consists of two types: heterogeneous and homogeneous.

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ABSTRACT

The paper summarizes results of Gosiewski et al. (2009), Pawlaczyk and Gosiewski (2013) and Pawlaczyk (2013) kinetic studies of non-catalytic (thermal) combustion of lean methane–air mixtures, carried out in a low and high temperature, in monolith bed and compared with similar results for a free space. The study reveals an influence of size, type of monolith's surface and temperature in combustion zone on the reaction mechanism and its kinetics. It was formulated a hypothesis that the share of combustion type: heterogeneous with surface effect (on the monolith's wall) and homogeneous (in the free space) depends on the temperature in the combustion zone. The appropriate kinetic equations were estimated. Moreover the paper presents corrected values of kinetic parameters which in contrast to Gosiewski et al. (2009) and Pawlaczyk and Gosiewski (2013) were estimated using concentrations of components related to actual gas volume in the combustion zone.

1. Introduction

This paper comprises a summary of the previous works [1–3] where successively non-catalytic (also named as thermal) combustion of lean methane–air mixtures was investigated. After the first part of studies [1], where a three global reaction models were taken into account, the experimental values of reaction rates were in a relatively good agreement with that calculated by the Arrhenius type of the reaction rate equation with the parameters estimated solely on the base of the conducted experiments. Unfortunately, when these parameters were applied in the mathematical model [4] of the TFRR (Thermal Flow Reversal Reactor) it occurred that the parameters given in [1] simulate real processes sufficiently well in a relatively low range of temperatures (LT – approximately below 700 °C). This was important for further usefulness of the model. Initiation of the reactions was very well reproduced in the model, while in higher temperatures the calculated reaction rates were obviously underestimated. Therefore, in the next parts of studies [2,3] range of temperatures in experiments has been extended towards higher temperatures (HT). Basically, it was possible by reducing the residence time in the experimental combustion zone. However, as it turned out, the kinetic equation parameters obtained in HT range poorly estimate reaction initiation in the LT range. Therefore, an algorithm combining the LT and HT parameters was proposed [2]. The compliance of the model with larger scale TFRR was quite satisfactory [4], only when this algorithm was implemented. Moreover, in [3] a hypothesis about different reaction mechanisms in LT and HT was formulated. This hypothesis will be discussed in more detail further in this paper.

On the other hand, in the both works [1,2] for the reaction rate equations, the gas volume recalculated for the STP (standard temperature and pressure) was used to calculate reagents concentrations, instead of the commonly used gas volume in the actual conditions. This article brings together all current results of the topic, unifying them with necessary corrections.

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Nomenclature

a_j	exponent for concentration term in the kinetic equation (1), –
b	exponent for temperature in the kinetic equation (1), –
C_i	concentration of i-th component, mol m^{-3}
E_j	activation energy for the j-th reaction, J mol^{-1}
k_j	reaction rate constant of the j-th reaction, $mol^{(1-a)}$ $m^{-3(1-a)}$ s^{-1}
$k_{0,j}$, $k_{0,l}$	pre-exponential factor in the kinetic equation, $mol^{(1-a)}$ $m^{-3(1-a)}$ s^{-1}
n_i	molar flow rate of i-th component, mol s^{-1}
R	universal gas constant, J mol^{-1} K^{-1}
$r_{\mathrm{hom},j}$	reaction rate of the j-th reaction, mol $m^{-3}_{\mathrm{monolith}}$ s^{-1}
t	time, s
T	temperature, K or °C
V	monolith volume, m^{-3}
V_M	molar gas volume, $m^3_{(STP)}$ mol^{-1}
x_i	volume fraction of i-component, –
Δ_{C_j}	average absolute relative error for the outlet concentration of the j-th reaction, %
Δ_{r_j}	average absolute relative error for the reaction rate of the j-th reaction, %
$\Delta^{calc}_{r_j}$	average absolute relative differences value of calculated reaction rates, ‰
ε	void fraction, m^3 $m^{-3}_{\mathrm{monolith}}$

Acronyms

FS	experiments in free space
HT	high temperature experiments
LT	low temperature experiments
MA38	experiments in monolith A in reactor with a diameter of 38 mm
MB38	experiments in monolith B in reactor with a diameter of 38 mm
MB65	experiments in monolith B in reactor with a diameter of 65 mm
TFRR	Thermal Flow Reversal Reactor
STP	standard temperature and pressure
VAM	Ventilation Air Methane

Subscripts and superscripts

actual	actual value
av	average value
calc	calculated value
i	i-th component
j	j-th reaction
in, *out*	inlet, outlet
l	consecutive number of experiment at given temperature
meas	measured value
p	product

Combustion of lean gas fuel in a mixture with air combined with reaction heat recovery is a significant challenge for scientists. Coal mining is an important anthropogenic source of methane emissions. The total amount of methane released from the coal-seams of Polish mines in 2013 year was about 847.8 million m^3. 67% (571.2 million m^3) of this amount was emitted as VAM (Ventilation Air Methane) to the atmosphere. Annual global emission of methane is estimated about 18–20 $MtCH_4$ $year^{-1}$. Main problem with VAM abatement consists in low methane concentrations in the mixtures, which vary depending on coal mine location, for example [5]: Poland – average about 0.3 wt.% (0.55 vol.%); China – average 0.46 vol.% (from 0.3 to 0.6 vol.%); Australia average about 0.4 vol.%.

Due to low concentration of VAM, one of the most reasonable options seems to be the autothermal combustion of CH_4 in the TFRR. Thus the results of the kinetic studies were to be used in mathematical simulations of such reactors. Knowledge of the global reaction models and kinetics of the combustion is crucial in design works and simulation studies.

2. Mechanisms of methane combustion

Homogeneous oxidation of methane is a free-radical process. A lot of mechanisms describing kinetics of methane combustion reaction are given in the literature. There are elementary mechanisms which may consist of several hundred radical reactions and global mechanisms [6–9] without radical reactions, limited to two or three reactions [10,11]. The usefulness of elementary mechanisms that could seem to be more precise than global one, from numerical point of view is not useful and doubtful. Comparison of kinetic parameters presented in [12] for chosen combustion reactions, obtained by software as GRI-mech or CHEMKIN, shows that parameters of the same radical reactions differ significantly. Authors emphasize that available elementary mechanisms must be verified on the basis of experimental studies, some authors probably neglect this. Moreover, direction of the free chain radical reaction might depend on the geometry of space or vessel where the reaction is occurred [13]. Problem of a practical application of available elementary and complex combustion mechanisms is often caused by lack of information which of these models should be applied in a given case.

Computer thermal reversed flow reactor model simulations [14] with use of several kinetic models [15–17] revealed large differences in the simulation results (i.e. in the ignition temperature and simulated maximum reactor temperature). Necessity of conducting own kinetic experiments appeared after detailed literature studies and unsuccessful attempts to apply of the available kinetic description in simulations of TFRR. Due to rather complex mathematical model of the reversal reactor, it was assumed that description of thermal methane combustion kinetics should be based upon a simple single-step scheme leading directly to CO_2 and H_2O or on a two-stage global reaction model with CO as the sole intermediate product.

The successive kinetic studies of thermal methane combustion were carried out in [1,3,14,18] for:

- ceramic pelletized bed,
- monolith bed with narrow channels and high geometric surface area (called as Monolith A),
- monolith bed with wider channels and lower than Monolith A geometric surface area (called as Monolith B),
- free space.

The experiments revealed that the obtained kinetic description of the non-catalytic combustion differs significantly depending on environment in which the oxidation occurs.

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