Investigations of available experimental and modeling data on the oxidative coupling and partial oxidation of methane

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Abstract
Large amount of experimental data, related to measurements of oxidative coupling and partial oxidation of methane in stirred and flow reactors were collected in which distributions of C_2 and partially oxygenated products were determined. Several detailed reaction mechanisms published for the description of these processes were also gathered. Some of these mechanisms were developed primarily for the modeling of ultra-rich combustion of methane, while others were developed for a wider range of conditions. Simulations using all these reaction mechanisms were carried out at the conditions of all collected experimental data. A large part of the experimental data could be described well using one or another reaction mechanism. In general, the modern comprehensive mechanisms performed better compared to the specialized mechanisms. However, there is not a single published mechanism that is able to reproduce all these experimental data. Some other experiments reported a slow conversion from methane to oxygenates and higher hydrocarbons, which could not be described by any of the investigated mechanisms. This behavior of the models might indicate a fundamental lack of understanding of the main reaction pathways, or an incomplete description of the physical-chemical phenomena that occur during the experiments (*e.g.* heat loss, radical recombination at walls). Simple models for taking into account the effect of the reactor wall were investigated, but a good reproduction of these "problematic" experiments could not be achieved.

Introduction

The partial oxidation and oxidative coupling of methane can be used for large scale production of higher hydrocarbons and oxygenates from natural gas. Utilization of such technologies could be of great industrial importance if sufficiently high yield and selectivity were achieved for the more valuable products. Both partial oxidation and ultra-rich combustion of natural gas produces a series of chemicals, and the product spectrum can be controlled by the type of the reactor and the operating conditions, like temperature, pressure, gas mixture composition, and residence time.

The chemistry involved in these complex processes can be described with detailed kinetic models, which can be used to predict the optimal conditions for the conversion of natural gas. The present work aims to provide an overview of the currently available detailed reaction mechanisms that could be used for the simulation of the partial oxidation or oxidative coupling of methane, and the available experimental data from the literature that can be used for the validation of these mechanisms.

Testing of detailed kinetic mechanisms should be based on experiments that are well characterized and also relevant to the conditions at which the models are to be used. The most commonly used validation targets in combustion chemistry are the ignition delay and laminar flame speed measurements, but these experiments are not relevant to the study of the partial oxidation (POX) or oxidative coupling of methane (OCM) since these do not provide information about the distributions of the products. Also, it is extremely difficult or impossible to carry out ignition or flame studies at ultra-rich (say, $\varphi > 4$) conditions.

The most valuable types of data for the study of POX or OCM are experiments where the product distributions are measured in reactors that can be modeled as a homogenous reactor, such as plug-flow reactors or well-stirred reactors. However, in several experimental studies the authors call the attention to the possibility of significant wall reactions.

An overview of the literature indicated, that there is not a consensus which experimental data can be described by spatially homogeneous simulations and which reaction mechanisms are appropriate for the description of the chemistry of POX and OCM systems. Therefore, in this work we report about the testing of many reaction mechanisms against large number of experimental data.

Experimental data were collected from 13 publications, which are summarized in Table 1. These experiments investigated the conversion of methane into higher hydrocarbons and oxygenated products at various temperatures, pressures, and equivalence ratios. Some experiments also investigated the effects of the addition of nitrogen oxides (NO_x), ethane and water on the product distributions.

17 detailed kinetic mechanisms were collected from the literature. Some of these mechanisms were originally developed for modeling the oxidative coupling or partial oxidation of methane, while others were elaborated for the description of the oxidation of methane or higher hydrocarbons mostly near stoichiometric conditions. The mechanisms are summarized in Table 2. The table contains the sizes of the mechanisms, and also whether the mechanism contains NO_x chemistry and therefore can be used for simulation of NO_x sensitized experiments.

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Short identifier	Reference	Experiment Type	Observed products
Keramiotis 2012	[1]	OCM	H_2, CO,CO_2, C_2H_6, C_2H_4, C_2H_2, C_3H_6, C_3H_4, C_6H_6
Zhang 2011	[2]	OCM	H_2, CO, CO_2, C_2H_4, C_2H_6, HCHO
Rasmussen 2008	[3]	POX	CH_4, O_2, CH_3OH, CO, CO_2, C_2H_6, C_2H_5OH
Rasmussen 2008	[4]	POX	CH_4, O_2, CO, CO_2, C_2H_4, C_2H_6, CH_3OH, C_2H_5OH
Rasmussen 2008	[5]	NO_x sensitized oxidation	CH_4, O_2, CO, CO_2, CH_3OH, NO, NO_2, CH_3NO_2
Cho 2008	[6]	OCM	CO, H_2, C_2H_6, C_2H_4
Bendtsen 2000	[7]	NO_x sensitized oxidation	CH_4, O_2, CO, CO_2, NO, NO_2, CH_2O, C_2H_4, C_2H_6
Amano 1998	[8]	NO_x sensitized oxidation	CH_4, O_2, CO, CO_2, H_2O, C_2H_6, C_2H_4, CH_2O
Chellappa 1997	[9]	POX	CO, CO_2, CH_3OH, HCHO, H_2
Lodeng 1995	[10]	POX	CH_3OH, HCHO, CO, CO_2, C_2H_6, H_2, H_2O
Omata 1994	[11]	POX	CH_3OH, CO, CO_2
Thomas 1992	[12]	POX	CO_2, CO, HCHO, CH_3OH
Rytz 1991	[13]	POX	CO, CO_2, CH_3OH, C_2H_4

Table 1. Summary of the investigated experimental papers.

Mechanism	Ref.	Species	Reactions	NO_X	Line styles used in figures		
Aramco 2013	[14]	124	766	No	black	solid	———
Zaragosa 2011	[15]	79	536	Yes	black	dashed	– – – –
Dooley 2010	[16]	269	1583	No	black	dash dotted	– · – · –
NUIG C5 2010	[17]	293	1593	No	red	solid	———
Konnov v0.6 2009	[18]	129	1231	Yes	red	dashed	– – – –
Lopez 2009	[19]	116	962	Yes	red	dash dotted	– · – · –
Blanquart 2009	[20]	148	928	No	blue	solid	———
Zabetta 2008	[21]	60	371	Yes	blue	dashed	– – – –
Glarborg 2008	[22]	97	779	Yes	blue	dash dotted	– · – · –
Rasmussen 2008	[5]	45	316	No	beige	solid	———
Sun 2008	[23]	25	39	No	beige	dashed	– – – –
Ahmed 2007	[24]	246	1284	No	beige	dash dotted	– · – · –
USC II 2007	[25]	111	784	No	green	solid	———
Konnov v0.5 2005	[26]	127	1213	Yes	green	dashed	– – – –
Hughes 2001	[27]	37	175	No	green	dash dotted	– · – · –
GRI 3.0 1999	[28]	53	325	Yes	orange	solid	———
Zanthoff 1990	[29]	28	164	No	orange	dashed	– – – –

Table 2. The detailed reaction mechanisms investigated. The line styles and colors that are used in the subsequent figures to plot the simulation results with each mechanism are also given here.

We have performed the simulations of all experiments from the referred papers by applying each mechanism to evaluate the performance of these mechanisms at these conditions. It was generally found that smaller mechanisms developed specifically for modeling POX or OCM (e.g Sun 2008, Zanthoff 1990) cannot be applied at a wide range of conditions, and the others had a varying quality of performance for most measurements.

It was also found that some measurements described a relatively slow production of C_2 species or oxygenates while at these conditions none of the experiments could even qualitatively reproduce the experimental results. Therefore the two main possible deviations from the ideal, adiabatic and homogenous conditions, heat-loss and wall reactions, were also investigated.

In the following sections the results and implications are discussed in detail.

Comparison of experimental and simulation results

The simulations of the experiments were performed using the SENKIN program from the CHEMKIN-II package. Both constant pressure adiabatic, and constant temperature simulations were performed. It was found that assuming a constant temperature within the reactor led to a large under prediction of the overall reactivity. Since this behavior was observed for all mechanisms, it could be concluded that the heat produced by the reactions cannot be ignored and therefore adiabatic simulations were performed.

Based on the simulation results, the experimental data could be divided into two categories. The first category consists of the experiments which could be qualitatively reproduced by some of the detailed kinetic mechanisms. Usually the temperature at which conversion from methane occurs and the product yields are slightly shifted compared to the experiments, but the more recent models capture the overall behavior.

The experiments of Rasmussen *et. al.* [3-5], Amano *et. al.* [8], Bendtsen *et al.* [7] and Keramiotis *et al.* [1] were acceptably reproduced by several mechanisms. Due to the relatively small amount of experimental data that was available it was not possible to clearly state which mechanism captures the experimental results the best. Figures 1-3 show some examples of the experimental data along with the simulated results. It can be seen that the discrepancies between the experimental and simulation results are quite varied, and that while a mechanism might reproduce a set of experimental data well, it is never the case for all experiments. Further experiments are required to cover a wider range of experimental conditions, so that a better global mechanism can be produced. However, it can be seen that most modern mechanisms are able to reproduce the temperatures at which the conversion of methane occurs, and also the approximate amounts of the C_2 species. The partially oxygenated products are generally less well described and also several mechanisms lack alcohol chemistry.
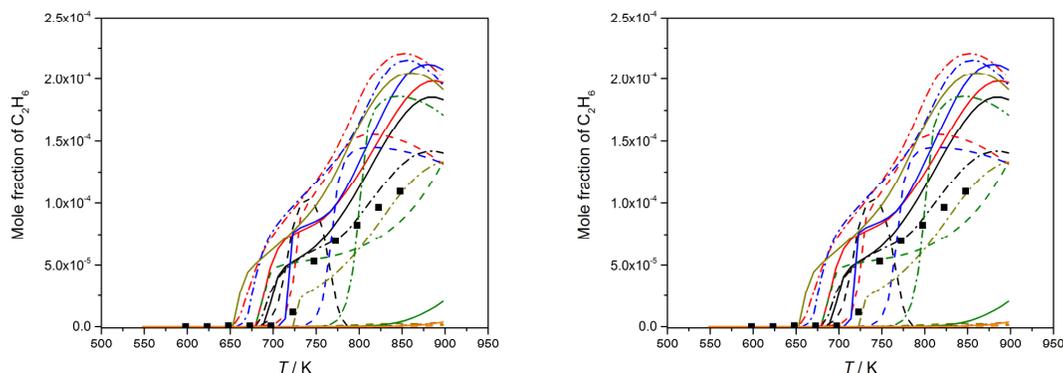
Figure. 1. Experimental data of Rasmussen *et al.* [4] and simulation results obtained with the investigated mechanisms for CH_3OH and C_2H_6 concentration profiles. Conditions are $p = 90$ bar, $\varphi = 25.2$, $x_0(CH_4) = 0.0112$, $x_0(O_2) = 0.000889$, $x_0(N_2) = 0.9878$. See Table 2 for legend.
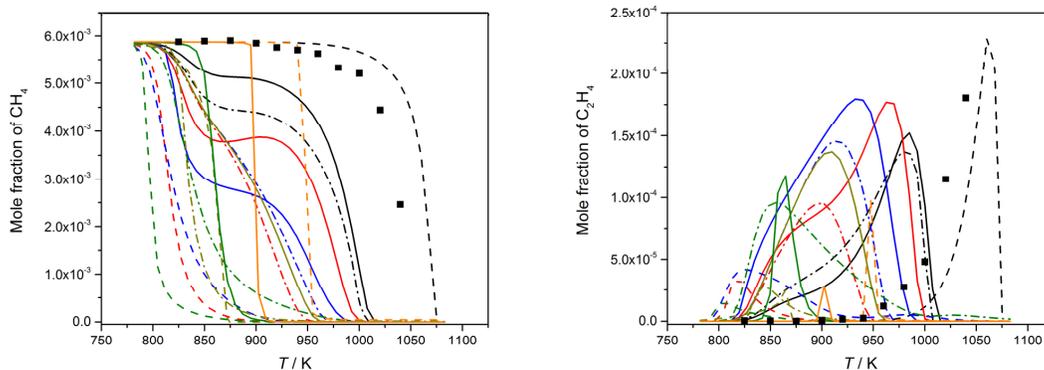
Figure. 2. Experimental data of Amano *et al.* [8] and simulation results obtained with the investigated mechanisms for CH_4 and C_2H_4 concentration profiles. Conditions are $p = 18$ bar, $\varphi = 1.25$, $x_0(CH_4) = 0.00587$ %, $x_0(O_2) = 0.01114$, $x_0(N_2) = 0.9830$. See Table 2 for legend.
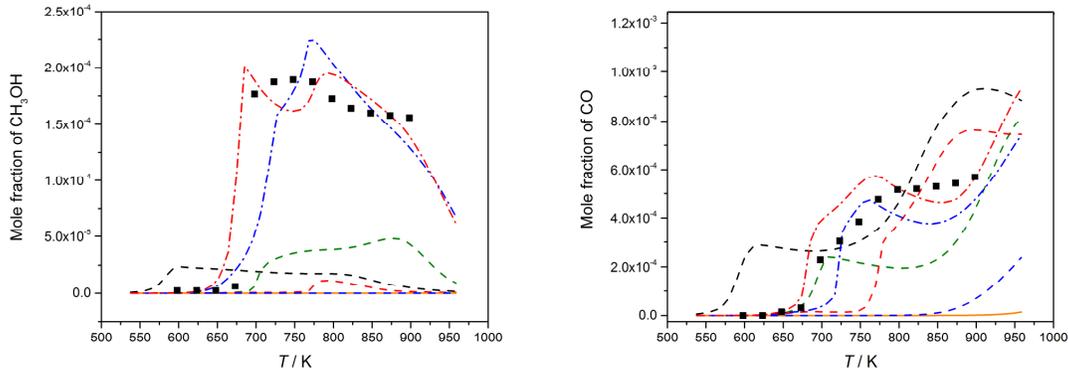
Figure 3. Experimental data of Rasmussen *et al*. [5] and simulation results obtained with the investigated mechanisms for CH₃OH and CO concentration profiles. Simulations were performed only with mechanisms having NO$_x$ submechanisms.
Conditions are p = 100 bar, φ = 116, $x_0(CH_4)$ = 0.0466, $x_0(O_2)$ = 803 ppm, $x_0(NO)$ = 25 ppm, $x_0(NO_2)$ = 168 ppm, $x_0(N_2)$ = 0.9878. See Table 2 for legend.

Since none of the published mechanisms describe well all these "good" experimental data, but the simulation results obtained with one or another mechanism well approximate them, it is possible that a joint, improved detailed mechanism can be created, which describes all these data generally well.

The results show that the GRI 3.0, USC II, Sun 2008 and Zanthoff 1990 mechanisms predict far lower overall reactivity than found in the experiments. The Sun 2008 and Zanthoff 1990 mechanisms were developed specifically for the modelling of POX and OCM conditions, respectively, but both were validated against a small set of experiments, and in the case of Sun 2008 these were all catalytic experiments. While these models could reproduce the experimental data used for their own validation, they cannot describe the other experiments investigated in the present paper. The USC II and GRI 3.0 mechanisms show a similar low reactivity. These mechanisms were developed for high temperature combustion and not validated at ultra-rich conditions.

It is also interesting to note that several experiments cannot be reproduced, even qualitatively, by any of the available kinetic models, such as the experiments of Cho *et al*. [6], Zhang *et al*. [2], Thomas *et al*. [12] and Rytz *et al*. [13]. Figures 4 and 5 present examples of C2 and oxygenated species profiles, and it can be seen that the experiments show a slow buildup of the products in time. Demonstration of the reproducibility of these experiments with new experiments and simulation results is of paramount importance, since these experiments produced conversion and selectivity that are the closest to what is required at an industrial production.
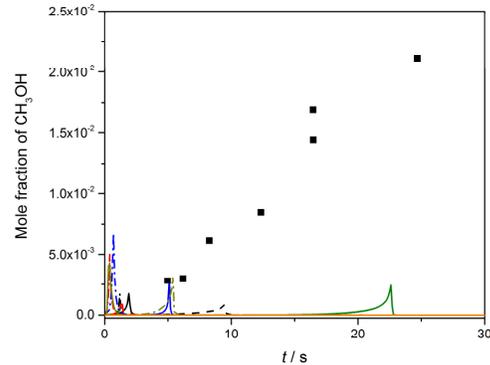
Figure 4. Experimental data of Thomas *et al*. [12] and simulation results obtained with the investigated mechanisms for the CH₃OH concentration profile. Conditions are T = 713 K p = 20 bar, φ = 4.5, $x_0(CH_4)$ = 0.90, $x_0(O_2)$ = 0.10. See Table 2 for legend.
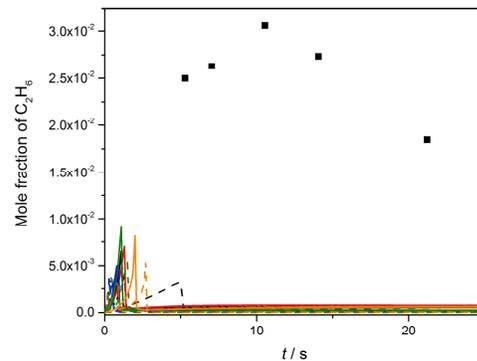
Figure 5. Experimental data of Cho *et al*. [6] and simulation results obtained with the investigated mechanisms for the C₂H₆ concentration profile. Conditions are T = 1023 K, p = 1 bar, φ = 2.5, $x_0(CH_4)$ = 0.833, $x_0(O_2)$ = 0.167. See Table 2 for legend.

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In the simulations either an ignition event occurred and all C2 and oxygenate products were converted into CO and CO_2 in a very short time, or there was a fast conversion followed by stagnation. This did not match the experimentally observed buildup. The most likely reasons are heat loss, radical loss, recombination or even complex catalytic reactions on the wall of the reactor.

To investigate the effects of the wall, simulations were performed with the Zaragoza 2011 mechanism at the conditions of experiments of Cho *et al.* [6]. Additional simulations were also performed in which a sub-model for radical loss on the reactor wall or methyl radical recombination on the wall were included, or a simulation was performed where a constant rate heat-loss was utilized. These are all very simplistic ways of taking into account non-idealities and the purpose here was not to provide an accurate supplementary model to these experiments, but to investigate if a better qualitative description of the experimental results can be obtained by including these effects. The magnitudes of the effects were selected in such a way, so that the influence on the simulation results can be demonstrated.

Radical loss was taken into account with reactions to the wall for radicals H, O, OH and CH_3 with a rate coefficient expressed with $k_{loss} = 10 \cdot (T/K)^{0.5} \, s^{-1}$. The methyl recombination reaction on the wall was modelled with an added $CH_3 + CH_3 \rightarrow C_2H_6$ reaction with a rate coefficient of $2 \cdot 10^{15} \, cm^3 \, mol^{-1} \, s^{-1}$. For heat loss, a constant value of $340 \, J \, mol^{-1} \, s^{-1}$ was used.

Figure 6 shows the simulation results obtained with the different scenarios. It can be seen that both radical loss and heat loss effects cause the complete conversion of ethane to occur later compared to the ideal homogeneous case, but neither increases the amount of ethane produced or results in a slower depletion after the buildup. By adding an extra methyl recombination pathway on the reactor wall, the amount of ethane formed in the simulations could be increased but even this way an ignition event occurs.

These simple simulations suggest that the influence of the reactor walls is rather complex as none of the simple models could provide results that even qualitatively match with the experiments. This means that further detailed studies on the significance of wall reactions on the POX and OCM processes are needed.
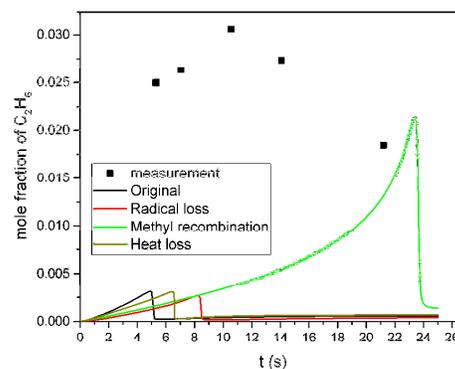
Figure 6. Experimental and simulated C_2H_6 concentration profiles of Cho et al. [6]. Simulations were performed with the Zaragoza mechanism [15], and its extended versions.

Conclusions

A study has been carried out to investigate the possibilities of modeling partial oxidation (POX) and oxidative coupling of methane (OCM) using detailed reaction mechanisms. Up-to-date generic reaction mechanisms usually provided realistic results at many experimental conditions, while mechanisms developed specifically for modeling of POX or OCM did not provide good results at a wide range of conditions. However, no single reaction mechanism could be selected then gave evenly good results at all conditions. Good to acceptable reproduction of a part of the experimental data with homogeneous simulations might indicate that these data could be used as validation targets at the development of an improved detailed mechanism that describes well all these experimental findings.

It was also found that a part of the experimental results could not be reproduced with homogeneous kinetic simulations using any of the mechanisms. A possible explanation is that in these experiments the reactor walls played a very significant role. Attempts were made to take the effects of the wall into account using simple sub-models for radical loss or recombination on the wall, but none of these extended models provided simulation results even qualitatively similar to the experimental data. This suggests that the reactor wall may have a complex effect on the whole reactive system at some conditions.

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