



HAL
open science

A unified mechanism for oxidative coupling and partial oxidation of methane

Yves Simon, Paul-Marie Marquaire

► **To cite this version:**

Yves Simon, Paul-Marie Marquaire. A unified mechanism for oxidative coupling and partial oxidation of methane. *Fuel*, 2021, 297, pp.120683. 10.1016/j.fuel.2021.120683 . hal-03359501

HAL Id: hal-03359501

<https://hal.univ-lorraine.fr/hal-03359501v1>

Submitted on 24 Apr 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

1 **A unified mechanism for oxidative coupling and partial** 2 **oxidation of methane**

3 Yves Simon*, Paul-Marie Marquaire

4 Université de Lorraine, CNRS-Laboratoire Réactions et Génie des Procédés (UMR7274),

5 ENSIC, 1 rue Grandville, BP 20451, F-54001 Nancy Cedex, France

6

7 * Corresponding author. E-mail address: yves.simon@univ-lorraine.fr

8

9 **ABSTRACT**

10 The oxidative coupling (OCM) and the partial catalytic oxidation (POM) of methane
11 as well as the homogeneous oxidation of methane (HOM) differ only in the ratio CH_4 / O_2
12 used and of course in the use of a catalyst. It can therefore be considered that their overall
13 reaction mechanism should be the same with elementary reactions of varying importance
14 depending on the type of oxidation reaction studied. We have therefore tried to represent the
15 results obtained during the experimental study of OCM and POM over La_2O_3 and that of the
16 oxidation of methane in gas phase from a single mechanism. At high temperature, OCM and
17 POM are catalytic reactions but their reaction mechanisms are very complex because the
18 surface reactions are coupled to reactions in gas phase by the intermediary of radicals, so both
19 homogeneous and heterogeneous mechanisms occur at the same time. In this work, the
20 development and the validation of a hetero-homogeneous mechanism is proposed for the three
21 reactions. This mechanism is based on elementary steps at the catalyst surface and elementary
22 steps in gas phase for a large range of temperature (973K – 1173K) and residence time (0.7s –
23 5.5s).

24 **Keywords:** Methane; kinetic mechanism; partial oxidation; oxidative coupling; La_2O_3 .

25

1. INTRODUCTION

Fluctuating prices of fossil fuel and discovery of new natural gas deposits are increasing interest in the upgrading of methane to value-added products. To date, the world reserve of natural gas is estimated about 198.8 trillion cubic meters [1] with steadily increasing in the future. Furthermore, over the past decade, increased production of shale gas has stimulated renewed interest to converting methane into valuable chemicals or liquid fuels.

The oxidative coupling of methane (OCM), first proposed by Keller and Bhasin [2] in 1982, is a direct method of converting methane into higher hydrocarbons especially ethylene. Ethylene is a critical intermediate in the petrochemical industry which is currently produced by steam cracking of hydrocarbon, mainly ethane. It is a highly endothermic reaction that occurs at high-temperature. Unlike steam cracking, the oxidative coupling of methane is exothermic and allows the direct conversion of methane into ethylene at a lower energy cost compared to current indirect industrial processes. During the 1990s, many studies were devoted to the OCM reaction. These studies showed that the yield of the reaction was not really compatible with an industrial application. However, in the last few years, the interest in the OCM reaction has increased because catalysts with higher activity and selectivity have been found. Indeed, with oxides as La_2O_3 acceptable reaction performances have been reached [3].

Another way of methane valorisation is the catalytic partial oxidation (POM). The catalytic partial oxidation of methane is an alternative to steam reforming [4, 5] for synthesis gas ($\text{CO} + \text{H}_2$) production. One advantage of POM is the production of syngas [6-8] with a H_2/CO ratio ideal for a subsequent Fischer–Tropsch synthesis. In contrast to steam reforming, the partial oxidation is an exothermic reaction and therefore requires a smaller amount of heat energy. Furthermore, POM has a good dynamic response time and could therefore be used as an on-board hydrogen generator for fuel cells.

1 OCM and POM are catalytic reactions at high temperatures. Their reaction
2 mechanisms are very complex because the surface reactions are coupled to reactions in gas
3 phase by the intermediary of radicals [9-17], so both homogeneous and heterogeneous
4 mechanisms occur at the same time. Indeed, the general oxidation mechanism includes two
5 sub-mechanisms, one that is related to gas-phase and another that contains the catalytic
6 reactions. Obviously, the homogeneous oxidation of methane (HOM) requires only the gas-
7 phase mechanism. The modelling of the reaction by a detailed mechanism (composed of
8 elementary steps describing the reaction as it occurs at the molecular level) has a lot of
9 advantages. The mechanism and the kinetic analysis results allow a better understanding of
10 the reaction. Indeed, based on this analysis, the reaction pathways, the importance of
11 heterogeneous and homogeneous reactions and the limitative steps can be identified. Since
12 1982, the literature concerning the study of hetero-homogeneous reactions has been abundant
13 [18,19]. However, there are few detailed mechanisms and much less kinetic data of surface
14 reactions that were published.

15 The OCM and POM reactions differ only in the ratio CH_4 / O_2 used, so their overall
16 reaction mechanism should be the same. We have therefore tried to represent the results
17 obtained during the experimental study of OCM and POM over La_2O_3 and that of the
18 oxidation of methane in gas phase [20-23] from a single mechanism. The development and
19 the validation of a hetero-homogeneous mechanism is proposed for the three reactions, based
20 on elementary steps at the catalyst surface and on a homogeneous mechanism in gas phase for
21 a large range of temperature and residence time. The experimental study was carried out in a
22 perfectly stirred reactor in presence of lanthanum oxide. The simulations were done by using
23 the Chemkin® software packages.

24

25

2. EXPERIMENTAL SECTION

The experimental setup was already described in previous articles (21, 23).

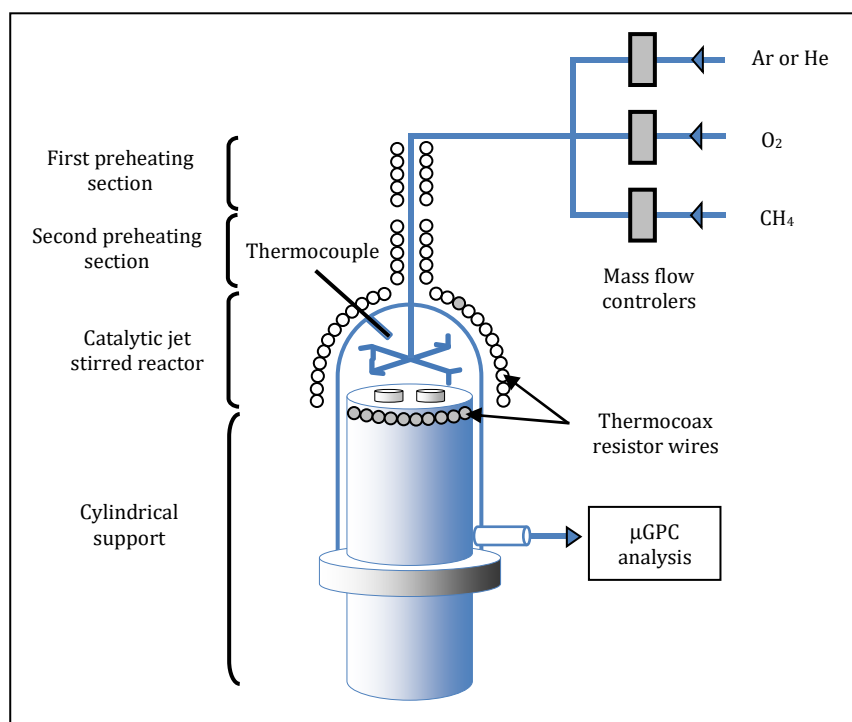


Fig.1. Schematic representation of the catalytic jet-stirred reactor

The reactor developed for the investigation of hetero-homogeneous reactions [24-25] is a continuous stirred tank reactor (CSTR) presented in Fig.1. It consists of two parts: an important well-stirred gas-phase volume (110 cm³) in contact with catalysts pellets laid on a removable cylindrical support. Four Thermocoax resistance wires that are in contact with the wall are used for heating the reactor. Before entering the reactor, the reactant mixture is preheated. The temperature of the first preheating part is 100°C lower than the reactor temperature while the temperature of the second preheating part equals the one of the reactor. The temperature of the gas phase is measured thanks to a thermocouple located inside a quartz finger at the middle of the free volume.

The catalyst used was Lanthanum oxide. The powder of La₂O₃ was pelleted at a pressure of 20 kN into a cylindrical shape thanks to an electromechanical press Instron 5569.

1 The pellets are 12 mm wide (diameter) and 1 mm thick. In order to facilitate the desorption of
2 water and also to decompose the carbonates present on the surface of the pellets, the La_2O_3
3 powder was heated for 8 hours at a temperature of 900°C . The BET surface areas are $1,8$
4 $\text{m}^2\cdot\text{g}^{-1}$ for catalyst pellets used in OCM and $5\text{ m}^2\cdot\text{g}^{-1}$ for pellets used in POM.

5 The outlet gases H_2 , CO , CH_4 , C_2H_4 , C_2H_6 and CO_2 are analysed in line or off line by
6 gas phase chromatography [21 and 23]. Several standard bottles, containing a gas mixture at
7 different concentrations, externally calibrate the chromatograph. All data were collected at a
8 steady state regime and each test was repeated at least three times to verify the stability and
9 repeatability of the measurements.

10 The experimental conditions used for this study are:

11 - Temperatures between 973K and 1173K

12 - Outlet pressure fixed at 1 atm.

13 - Composition of the gas inlet with $\text{CH}_4/\text{O}_2 = 5$ for OCM and $\text{CH}_4/\text{O}_2 = 2$ for POM and HOM.

14 The reactants are highly diluted in argon or helium (94 % in OCM and 84% in POM or HOM)
15 to better control the reaction temperature and to avoid hot spots.

16

17 **3. KINETIC MODELING**

18

19 **3.1. Homogeneous mechanism**

20

21 The mechanism used for simulation includes a heterogeneous part and a homogeneous one.

22 The homogeneous part is described by a set of over 450 elementary reactions. Due to its size,

23 the mechanism cannot be fully presented here; we give only the most significant reactions in

24 Table 1.

25

26

27

	Reactions	A (mol, cm ³ , s)	n	E _a (cal. mol ⁻¹)
1	O ₂ + H = OH + O	1.5 10 ¹⁴	0.0	14810
2	O ₂ + H (+M) = HO ₂ (+M)	4.52 10 ¹³	0.0	0.0
3	O ₂ + CHO = CO + HO ₂	2.6 10 ¹¹	0.0	410
4	O ₂ + CH ₃ = CH ₃ O + O	1.6 10 ¹³	0.0	31300
5	O ₂ + HCHO = CHO + HO ₂	2.0 10 ¹³	0.0	38800
6	O ₂ + CH ₃ = HCHO + OH	3.0 10 ³⁰	-4.69	36600
7	O ₂ + CH ₄ = CH ₃ + HO ₂	4.0 10 ¹³	0.0	56700
8	O ₂ + C ₂ H ₅ = C ₂ H ₄ + HO ₂	8.4 10 ¹¹	0.0	3900
9	O ₂ + C ₂ H ₃ = HCHO + CHO	4.5 10 ¹⁶	-1.39	1000
10	O ₂ + C ₂ H ₃ = C ₂ H ₂ + HO ₂	1.34 10 ⁶	1.61	-400
11	O ₂ + C ₂ H ₂ = 2 CHO	7.0 10 ⁸	1.8	30600
12	O + H ₂ = OH + H	5.1 10 ⁴	2.67	6200
13	O + CH ₃ = HCHO + H	8.4 10 ¹³	0.0	0
14	O + CH ₄ = CH ₃ + OH	7.2 10 ⁸	1.56	8400
15	O + C ₂ H ₆ = C ₂ H ₅ + OH	1.0 10 ⁹	1.5	5800
16	O + C ₂ H ₄ = CH ₃ + CHO	8.1 10 ⁶	1.88	200
17	O + C ₂ H ₄ = HCHO + CH ₂	4.0 10 ⁵	1.88	200
18	O + C ₂ H ₄ = CH ₂ CO + H ₂	6.6 10 ⁵	1.88	200
19	O + C ₂ H ₄ = CH ₂ CHO + H	4.7 10 ⁶	1.88	200
20	O + C ₂ H ₄ = OH + C ₂ H ₃	1.5 10 ⁷	1.91	3700
21	O + HCHO = CHO + OH	4.1 10 ¹¹	0.57	2700
22	OH + H ₂ = H + H ₂ O	1.0 10 ⁸	1.6	3300
23	OH + CH ₃ (+M) = CH ₃ OH (+M)	6.0 10 ¹³	0.0	0
24	OH + CH ₄ = CH ₃ + H ₂ O	1.6 10 ⁷	1.83	2700
25	OH + CO = CO ₂ + H	6.3 10 ⁶	1.5	-500
26	OH + HCHO = CHO + H ₂ O	3.4 10 ⁹	1.18	-400
27	OH + C ₂ H ₄ = C ₂ H ₃ + H ₂ O	2.0 10 ¹³	0.0	5900
28	OH + C ₂ H ₄ = CH ₃ + HCHO	2.0 10 ¹²	0.0	900
29	OH + C ₂ H ₆ = C ₂ H ₅ + H ₂ O	7.2 10 ⁶	2.0	900
30	2 HO ₂ = H ₂ O ₂ + O ₂	4.2 10 ¹⁴	0.0	11980
31	HO ₂ + H = 2 OH	1.7 10 ¹⁴	0.0	900
32	HO ₂ + CH ₃ = CH ₃ O + OH	1.8 10 ¹³	0.0	0
33	HO ₂ + CH ₄ = CH ₃ + H ₂ O ₂	9.0 10 ¹²	0.0	24600
34	HO ₂ + CO = CO ₂ + OH	1.5 10 ¹⁵	0.0	23600
35	HO ₂ + CHO = OH + H + CO ₂	3.0 10 ¹³	0.0	0
36	HO ₂ + HCHO = CHO + H ₂ O ₂	3.0 10 ¹²	0.0	13000
37	HO ₂ + C ₂ H ₆ = C ₂ H ₅ + H ₂ O ₂	1.3 10 ¹³	0.0	20400
38	2 CH ₃ (+M) = C ₂ H ₆ (+M)	3.6 10 ¹³	0.0	0.0
39	2 CH ₃ = C ₂ H ₅ + H	3.0 10 ¹³	0.0	13500
40	2CH ₃ = C ₂ H ₄ + H ₂	2.1 10 ¹⁴	0.0	19300
41	CH ₃ + H (+M) = CH ₄ (+M)	1.7 10 ¹⁴	0.0	0.0
42	CH ₃ + HCHO = CHO + CH ₄	7.7 10 ⁻⁸	6.1	1970
43	CH ₄ + H = CH ₃ + H ₂	1.3 10 ⁴	3.0	8000
44	C ₂ H ₂ + H (+M) = C ₂ H ₃ (+M)	8.4 10 ¹²	0.0	2610
45	C ₂ H ₃ (+M) = C ₂ H ₂ + H	2.0 10 ¹⁴	0.0	39800
46	C ₂ H ₄ (+ M) = C ₂ H ₂ + H ₂ (+ M)	1.0 10 ¹⁷	0.0	71600
47	C ₂ H ₄ + H = C ₂ H ₃ + H ₂	5.1 10 ⁷	1.93	12900
48	C ₂ H ₄ + CH ₃ = CH ₄ + C ₂ H ₃	6.3 10 ¹¹	0.0	1600
49	C ₂ H ₄ + CH ₃ = C ₃ H ₇	2.1 10 ¹⁰	0.0	7350

50	$C_2H_5 (+M) = C_2H_4 + H (+M)$	$8.2 \cdot 10^{13}$	0.0	40000
51	$C_2H_6 (+M) = C_2H_4 + H_2 (+M)$	$2.3 \cdot 10^{17}$	0.0	67400
52	$C_2H_6 + H = C_2H_5 + H_2$	$1.4 \cdot 10^9$	1.5	7400
53	$C_2H_6 + CH_3 = C_2H_5 + CH_4$	$1.5 \cdot 10^{-7}$	6.0	5800
54	$C_2H_6 (+M) = 2CH_3 + (M)$	$1.8 \cdot 10^{21}$	-1.24	90900
55	$CHO (+M) = H + CO (+M)$	$1.6 \cdot 10^{14}$	0.0	15700
56	$CHO + CH_3 = CH_4 + CO$	$1.2 \cdot 10^{14}$	0.0	0.0
58	$HCHO + H = CHO + H_2$	$1.3 \cdot 10^8$	1.62	3100
59	$CH_2CO (+M) = CH_2 + CO + (M)$	$6.57 \cdot 10^{15}$	0.0	57600
60	$CH_2CO + H = CH_3 + CO$	$1.8 \cdot 10^{13}$	0.0	3400
61	$CH_3O_2 = HCHO + OH$	$1.5 \cdot 10^{13}$	0.0	47000
62	$CH_3O_2 + CH_4 = CH_3O_2H + CH_3$	$1.8 \cdot 10^{11}$	0.0	18500
63	$CH_3O_2 + CH_3 = 2 CH_3O$	$5.0 \cdot 10^{12}$	0.0	-1400

1

2
3

Table 1. Adjusted kinetic parameters of most important homogeneous reactions in oxidation of methane.
 $k=A(T)^n \exp(-E/RT)$

4

5

The homogeneous mechanism takes into account all elementary reactions between molecules and radicals including less than three carbon atoms. This gas-phase mechanism is well known and has been confirmed by a vast amount of experimental data for different hydrocarbon reactions for the homogeneous oxidation of methane [20; 23; 26].

9

This mechanism was generated by EXGAS software [27]. In the present work, this mechanism is used in combination with a heterogeneous mechanism for the simulation of the catalytic oxidation of methane reactions.

12

13

14 3.2. Heterogeneous mechanism

15

16 3.2.1. Description of the mechanism

17

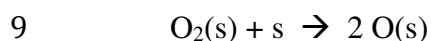
18

The development of the heterogeneous mechanism takes into account the results from mechanistic studies reported in the literature [28-37]. Despite the many studies carried out on this subject, the exact nature of the active sites on La_2O_3 remains unclear. Yang et al. suggested that O^{2-} ions could be the active site for methane activation [38]. On the other hand for Hutchings et al. [39], the formation of CH_3 radicals is due to the O^- ions while O_2^{2-} lead to the formation of CH_2 radicals. Lacombe et al. [40] have identified various active sites on the

23

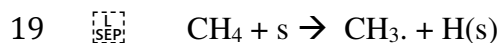
1 surface of lanthanum oxide: a basic site associated with an anionic vacancy which would be
2 responsible for the dissociation of gaseous oxygen into atomic species and an unsaturated site
3 on which methyl radical would react to be further oxidized into CO₂. In summary, there are at
4 least two types of active sites on the La₂O₃ surface [41].

5 In our mechanism, the two types of active sites considered are: a reduced site (s) and
6 an oxygenated site O(s). Experimental studies of oxygen chemisorption [42] have shown that
7 this reaction occurs with dissociation of a diatomic O₂ molecule to form two active atomic
8 oxygen centres according to the following reaction:

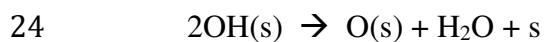
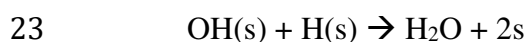
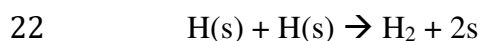


11 In these elementary reactions s represents a surface site and O(s) the atom O adsorbed on the
12 surface of the La₂O₃ crystal.

13 The heterogeneous mechanism was written systematically by considering the possible
14 reactions between these two sites and the major reaction products and free radicals. These
15 reactions were written according to the Eley-Rideal formalism involving the reactions
16 between a gas phase molecule and an active site. For example, methane can react according
17 to:



20 The hydroxylated sites and hydrogenated sites can react according to the Langmuir-
21 Hinshelwood formalism leading to the formation of hydrogen and water via surface steps:



1 Finally, the heterogeneous mechanism is composed of 33 direct elementary steps
 2 involving 9 surface species (Table 2).

3

	Réactions	A (mol, cm ² , s)	E(cal.mol ⁻¹)
1	$O_2 + s \rightarrow O_2(s)$	$1.8 \cdot 10^7$	1500
2	$O_2(s) \rightarrow O_2 + s$	$2,3 \cdot 10^{12}$	45000
3	$O_2(s) + s \rightarrow 2O(s)$	$1.2 \cdot 10^{23}$	25000
4	$2O(s) \rightarrow O_2(s) + s$	$3.3 \cdot 10^{23}$	33000
5	$CH_4 + O(s) \rightarrow CH_3\cdot + OH(s)$	$7.5 \cdot 10^8$	8840
6	$C_2H_6 + O(s) \rightarrow C_2H_5\cdot + OH(s)$	$9.5 \cdot 10^9$	3000
7	$CO + O(s) \rightarrow CO_2 + s$	$4.7 \cdot 10^9$	0
8	$CO_2 + s \rightarrow CO_2(s)$	$6.2 \cdot 10^8$	0
9	$CO_2(s) \rightarrow CO_2 + s$	$2.3 \cdot 10^{13}$	43580
10	$C_2H_4 + O(s) \rightarrow C_2H_3\cdot + OH(s)$	$5.5 \cdot 10^8$	3000
11	$C_2H_5\cdot + O(s) \rightarrow C_2H_4 + OH(s)$	$5.5 \cdot 10^7$	0
12	$C_3H_7 + O(s) \rightarrow C_3H_6 + OH(s)$	$6.1 \cdot 10^7$	0
13	$2OH(s) \rightarrow O(s) + H_2O + s$	$1.3 \cdot 10^{23}$	2400
14	$CH_3\cdot + O(s) \rightarrow CH_2\cdot + OH(s)$	$1.9 \cdot 10^9$	2800
15	$CH_2\cdot + O(s) \rightarrow CH\cdot + OH(s)$	$3.6 \cdot 10^{11}$	11900
16	$CH\cdot + O(s) \rightarrow C + OH(s)$	$8.9 \cdot 10^8$	4700
17	$C + O(s) \rightarrow CO + s$	$1.1 \cdot 10^{11}$	0
18	$CH_3\cdot + O(s) \rightarrow CH_3O(s)$	$9.9 \cdot 10^8$	600
19	$CH_3O(s) + O(s) \rightarrow HCHO + OH(s) + s$	$1.2 \cdot 10^{23}$	0
20	$HCHO + O(s) \rightarrow CHO\cdot + OH(s)$	$3.4 \cdot 10^7$	3000
21	$CHO\cdot + O(s) \rightarrow CO + OH(s)$	$6.9 \cdot 10^7$	410
22	$C_2H_5\cdot + O(s) \rightarrow C_2H_5O(s)$	$1.0 \cdot 10^9$	600
23	$C_2H_5O(s) + O(s) \rightarrow CH_3CHO + OH(s) + s$	$6.6 \cdot 10^{21}$	0
24	$CH_4 + s \rightarrow CH_3\cdot + H(s)$	$8.5 \cdot 10^7$	9850
25	$C_2H_6 + s \rightarrow C_2H_5\cdot + H(s)$	$9.8 \cdot 10^7$	5000
26	$C_2H_4 + s \rightarrow C_2H_3\cdot + H(s)$	$1.9 \cdot 10^7$	5000
27	$H\cdot + s \rightarrow H(s)$	$9.6 \cdot 10^{12}$	0
28	$OH(s) + H(s) \rightarrow H_2O + 2s$	$1.0 \cdot 10^{24}$	0
29	$H(s) + H(s) \rightarrow H_2 + 2s$	$1.3 \cdot 10^{23}$	0
30	$H_2 + 2s \rightarrow 2H(s)$	$6.1 \cdot 10^{16}$	0
31	$H_2 + O(s) \rightarrow OH(s) + H\cdot$	$1.0 \cdot 10^{10}$	0
32	$C + O(s) \rightarrow CO(s)$	$1.1 \cdot 10^{11}$	0
33	$CO(s) + O(s) \rightarrow CO_2(s) + s$	$1.1 \cdot 10^{23}$	0

4

5 **Table 2.** Kinetic parameters of surface reactions in oxidation of methane
 6 (s symbolizes surface site and (s) adsorbed species).

1 To carry out the simulations, it is necessary to calculate the kinetics parameters of this
2 heterogeneous mechanism. There are few models involving a detailed mechanism composed
3 of elementary steps and with estimation of the kinetics parameters. We can quote for example
4 Deutschmann [43], Sinev [44] and Gent University [45, 46]. In our study, pre-exponential
5 factor of elementary steps are calculated by methods derivate from Benson's techniques [47]
6 whereas activation energies are chosen in first approximation by analogy with reactions in gas
7 phase. Simulations were performed using the Chemkin® and Surface Chemkin® software
8 packages in a CSTR reactor [48,49]. The simulations were performed by simultaneously
9 compiling the homogeneous and the heterogeneous sub-mechanisms so that the possible
10 coupling could be taken into account. It should be noted that these methods give only an
11 approximation of the initial numerical value of parameters, usually unknown, which must be
12 adjusted during the optimization from experimental results.

13 14 **3.2.2. Pre-exponential factor**

15 The pre-exponential factor is calculated by using partition functions of gas molecule
16 and activated complex. For the following reaction:



19 where A is a gas molecule, B(s) a surface species and AB^\ddagger the activated complex, the pre-
20 exponential factor is calculated by the following equation:

$$21 \quad A = \frac{k_B T N q^\ddagger}{h q_A q_{B(s)}} \quad (1)$$

22
23 In Eq. (1), k_B is the Boltzmann constant ($1.38 \cdot 10^{-23} \text{ J.K}^{-1}$), N the Avogadro constant
24 ($6.022 \cdot 10^{23} \text{ mol}^{-1}$), T the temperature, h the Planck constant ($6.6262 \cdot 10^{-34} \text{ J.s.}$) and q_A , $q_{B(s)}$, q^\ddagger
25 are the partition functions of A, B(s) and the activated complex. The difference between the
26 degrees of freedom of B(s) and AB^\ddagger is mainly due to the vibrations of the molecule A in the

1 configuration of the activated complex. Indeed, B(s) and AB[‡] are adsorbed species and have
 2 no rotational or translational degrees of freedom. So, to simplify the calculation, we suppose
 3 than the difference between partition function of B(s) and AB[‡] is only due to the vibrational
 4 component of the activated complex q[‡]_v. Then the following expression is obtained:
 5

$$A = \frac{k_B T N q_v^{\ddagger}}{h q_A} \quad (2)$$

6
 7 The partition function of a molecule or a radical is the product of a translational
 8 partition function q_t, an external rotational partition function q_r, a vibrational partition
 9 function q_v and an electronic partition function q_e. These partition functions can be calculated
 10 by the Eq. (3).
 11

$$q_t = \frac{(2\pi m k_B T)^{3/2}}{h^3}$$

$$q_r^{3D} = \frac{\pi^{3/2}}{\sigma_{\text{ext}}} \left(\frac{8\pi^2 k_B T}{h^2} \right)^{3/2} R^{3/2} \quad \text{or} \quad q_r^{2D} = \frac{8\pi^2 I k_B T}{\sigma_{\text{ext}} h^2}$$

$$q_v = \prod_i q_{v,i} \quad \text{and} \quad q_{v,i} = \frac{1}{1 - \exp\left(\frac{-1.44\omega_i}{T}\right)}$$

$$q_e = 2s + 1 \quad (3)$$

12
 13 In these equations, σ_{ext} is the external symmetry number, m (kg) the mass of the atom,
 14 s the spin and ω_i (cm⁻¹) the frequency of the tabulated vibration.

15 The selection of the formula for calculating the rotational partition function depends
 16 on the molecule considered. A linear molecule only possesses two rotational degrees of
 17 freedom. The two moments of inertia about the two axes of rotation are equal to I (kg.m²). In
 18 this case, the rotational partition function is q_r^{2D}. However, there are 3 rotational degrees of
 19 freedom in a non-linear molecule and the calculation of the partition function q_r^{3D} use the
 20 product of the moments of inertia: D (kg³.m⁶). For easier use, these formulas can be rewritten:

$$q_t = 1.88 \cdot 10^{-26} (MT)^{3/2} \quad 1$$

$$q_r^{3D} = 1.48 \cdot 10^{-2} \frac{D^{1/2} T^{3/2}}{\sigma_{ext}} \quad \text{or} \quad q_r^{2D} = 4.12 \cdot 10^{-2} \frac{IT}{\sigma_{ext}} \quad (24)$$

3

4 In the first expression the unit of q_t is m^{-3} and M is the molar mass ($\text{g}\cdot\text{mol}^{-1}$). In the
 5 second expression, the unit of D is $\text{amu}^3\cdot\text{\AA}^6$ and that of I is $\text{amu}\cdot\text{\AA}^2$.

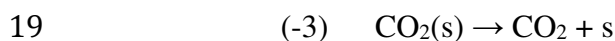
6

7 **3.2.3. Activation energy**

8

9 The activation energy is the most difficult parameter to calculate, especially for
 10 surface reactions, because it depends on the nature of the adsorption site. Since these values
 11 are generally intended to be optimized by simulation of the experimental results, two simple
 12 methods of estimation depending on the type of reaction involved are proposed. For the
 13 adsorption/desorption reactions, the activation energy is calculated from the experimental
 14 value of adsorption enthalpy obtained from the literature. The activation energy of the other
 15 elementary surface reactions can be assumed in first estimate to be the same as the equivalent
 16 gas-phase reaction.

17 For example, the CO_2 adsorption – desorption can be represented by the following
 18 reactions: (3) $\text{CO}_2 + \text{s} \rightarrow \text{CO}_2(\text{s})$



20 The activation energy of the CO_2 adsorption is low; so the activation energy of the step (3) is
 21 supposed to be equal to 0. The adsorption enthalpy of CO_2 on the surface can be found in the
 22 literature; the adsorption enthalpy of CO_2 on $\text{La}_2\text{O}_3/\text{CaO}$ catalyst [50] is about:

23 $-\Delta H_{\text{ads}, \text{CO}_2} = 44 \pm 7 \text{ kcal}\cdot\text{mol}^{-1} = E_{-3}$.

24 For the other types of surface reactions, the activation energy can be chosen, by
 25 analogy with gas phase reactions. The Eley-Rideal reaction of an ethane molecule with the
 26 surface of the catalyst: $\text{C}_2\text{H}_6 + \text{s} \rightarrow \text{C}_2\text{H}_5 + \text{H}(\text{s})$ may be represented by the following
 27 homogeneous reaction: $\text{C}_2\text{H}_6 + \text{alkyl} \cdot \rightarrow \text{C}_2\text{H}_5 + \text{alkane}$

1 We can use, for example, the reaction: $C_2H_6 + CH_3 \cdot \rightarrow C_2H_5 \cdot + CH_4$
2 The activation energy of this gas phase reaction [51] is: $5800 \text{ cal.mol}^{-1}$. At a first
3 approximation, this value for the activation energy of the surface reaction can be used. The
4 activation energy depends on the catalyst surface and these activation energy values can only
5 be considered as a starting point for the simulation. Finally, a hetero-homogeneous
6 mechanism composed of many elementary steps and their kinetic constants (A and E) was
7 obtained.

8

9 **3.3 Sensitivity analysis**

10 For all the reactions studied, a flow consumption analysis or a sensitivity analysis can
11 be realized to better understand the reaction and to find optimal conditions. To determine the
12 most sensitive reactions involved in the mechanism, a sensitivity analysis was performed for
13 each of the three reactions. The analysis was performed for major products. Figures 18 and 19
14 show sensitivity analysis for surface reactions for OCM and POM. The first order sensitivity
15 coefficient for species n and reaction i was defined according to:

$$16 \quad S_{i,n} = \frac{k_i}{dk_i} \frac{dx_n}{x_n} \quad (5)$$

17 where k_i is the kinetic constant of reaction i and x_n is the molar fraction of species n. The
18 higher the $S_{i,n}$ coefficient is, the more sensitive against species n the reaction i is. Moreover, a
19 positive sensitivity coefficient $S_{i,n}$ means that an increase of the kinetic constant k_i leads to an
20 increase of the concentration of species n. Some reactions have sensitivity coefficients lower
21 than $|0.01|$ and can be considered negligible. Table 3 shows the final surface mechanism in
22 which only the most important elementary reactions are present. This simplified mechanism
23 consists of 17 elementary reactions and gives the same result as the complete mechanism with
24 an error of less than 1%.

1

	Réactions	A^{fitted} (mol, cm ² , s)	E^{fitted} (cal.mol ⁻¹)
1	$\text{O}_2 + \text{s} \rightarrow \text{O}_2(\text{s})$	$6.0 \cdot 10^7$	5000
2	$\text{O}_2(\text{s}) \rightarrow \text{O}_2 + \text{s}$	$2,3 \cdot 10^{12}$	38000
3	$\text{O}_2(\text{s}) + \text{s} \rightarrow 2\text{O}(\text{s})$	$2.3 \cdot 10^{23}$	25000
4	$2\text{O}(\text{s}) \rightarrow \text{O}_2(\text{s}) + \text{s}$	$3.3 \cdot 10^{23}$	33000
5	$\text{CH}_4 + \text{O}(\text{s}) \rightarrow \text{CH}_3\cdot + \text{OH}(\text{s})$	$3.0 \cdot 10^8$	8840
6	$\text{C}_2\text{H}_6 + \text{O}(\text{s}) \rightarrow \text{C}_2\text{H}_5\cdot + \text{OH}(\text{s})$	$8.7 \cdot 10^9$	3000
7	$\text{CO} + \text{O}(\text{s}) \rightarrow \text{CO}_2 + \text{s}$	$8.3 \cdot 10^8$	0
10	$\text{C}_2\text{H}_4 + \text{O}(\text{s}) \rightarrow \text{C}_2\text{H}_3\cdot + \text{OH}(\text{s})$	$1.1 \cdot 10^{10}$	3000
13	$2\text{OH}(\text{s}) \rightarrow \text{O}(\text{s}) + \text{H}_2\text{O} + \text{s}$	$3.0 \cdot 10^{23}$	2400
24	$\text{CH}_4 + \text{s} \rightarrow \text{CH}_3\cdot + \text{H}(\text{s})$	$8.5 \cdot 10^7$	9850
25	$\text{C}_2\text{H}_6 + \text{s} \rightarrow \text{C}_2\text{H}_5\cdot + \text{H}(\text{s})$	$9.8 \cdot 10^7$	5000
26	$\text{C}_2\text{H}_4 + \text{s} \rightarrow \text{C}_2\text{H}_3\cdot + \text{H}(\text{s})$	$1.9 \cdot 10^7$	5000
27	$\text{H}\cdot + \text{s} \rightarrow \text{H}(\text{s})$	$9.6 \cdot 10^{12}$	0
28	$\text{OH}(\text{s}) + \text{H}(\text{s}) \rightarrow \text{H}_2\text{O} + 2\text{s}$	$1.0 \cdot 10^{24}$	0
29	$\text{H}(\text{s}) + \text{H}(\text{s}) \rightarrow \text{H}_2 + 2\text{s}$	$4.0 \cdot 10^{23}$	0
30	$\text{H}_2 + 2\text{s} \rightarrow 2\text{H}(\text{s})$	$6.1 \cdot 10^{16}$	0
31	$\text{H}_2 + \text{O}(\text{s}) \rightarrow \text{OH}(\text{s}) + \text{H}\cdot$	$2.0 \cdot 10^8$	0

2
3
4
5
6
7
8

Table 3. Simplified surface mechanism of methane oxidation [s symbolizes surface site and (s) adsorbed species].

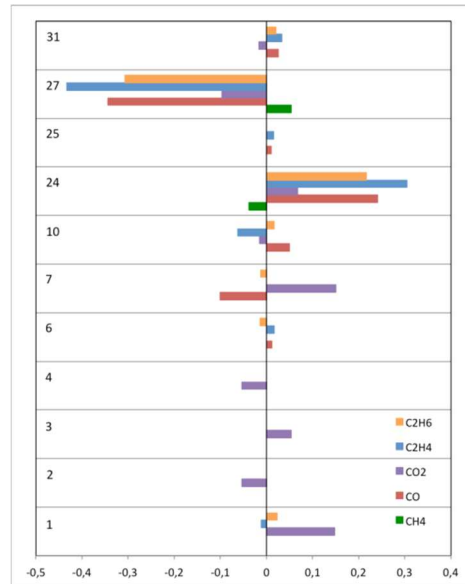
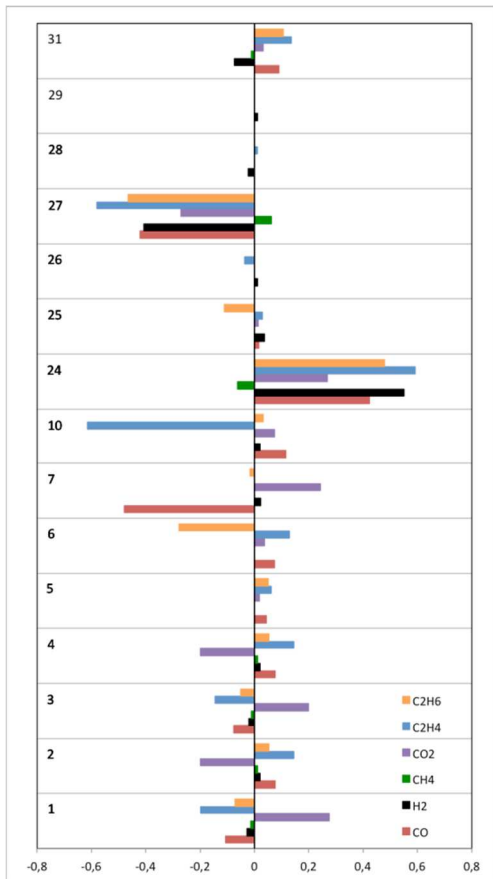


Figure 18. Sensitivity analysis of surface reactions for POM at 1123 K

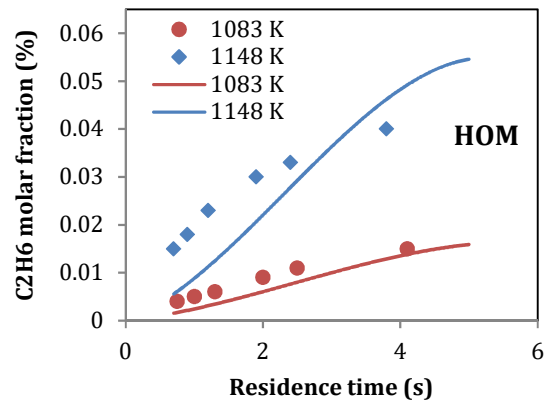
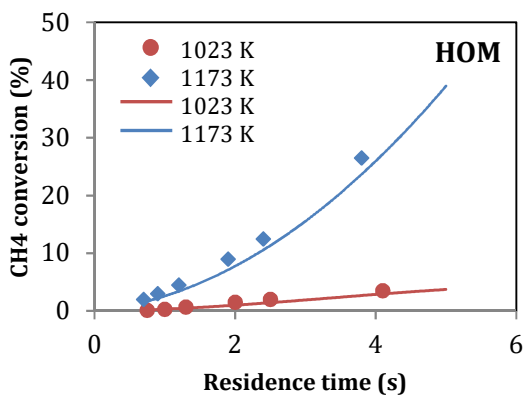
Figure 19. Sensitivity analysis of surface reactions for OCM at 1173 K

4- RESULTS AND DISCUSSION

For the three reactions of OCM, POM and HOM, the experimental curves of reactant consumption and product formation as a function of residence time were simulated. The kinetic parameters of the homogeneous reactions provide from literature [52-60] or are calculated by the Kingas [61] software (Table 1). The kinetic parameters of heterogeneous reactions are estimated using the methodology described here (Table 2) and modified to fit the model to the experimental results (Table 3). This unified hetero-homogeneous mechanism is used for the simulation of the three reactions.

1 4.1 Homogeneous oxidation of methane

2 Homogeneous oxidation of methane doesn't have a real industrial interest because of
3 the stability of the methane molecule. However, the mechanism of this reaction is essential to
4 represent the reactions of OCM and POM. Therefore, we have studied this reaction
5 experimentally over a large temperature range (1083K to 1148 K) in order to determine its
6 reaction mechanism. Figure 1 to 6 show the molar fraction of CH₄, C₂H₄, C₂H₆, CO, CO₂ and
7 H₂ versus residence time. The ratio CH₄/O₂ was fixed to 2. The simulation very well
8 reproduces the conversion of CH₄ and the production of the most important products.
9



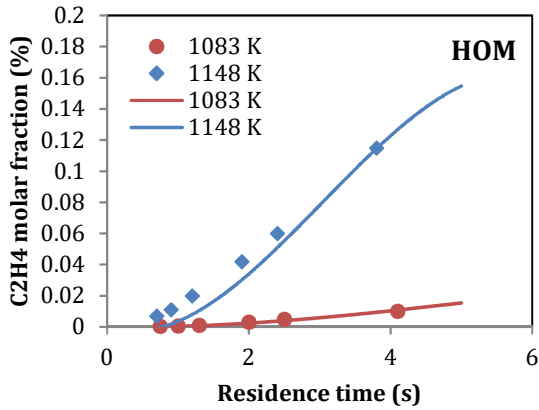
10

Fig.1. Conversion of CH₄ versus residence time. Comparison between experiment (symbol) and simulation (line).

Fig.2. Molar fraction of C₂H₆ versus residence time. Comparison between experiment (symbol) and simulation (line).

11

12



1

Fig.3. Molar fraction of C₂H₄ versus residence time. Comparison between experiment (symbol) and simulation (line).

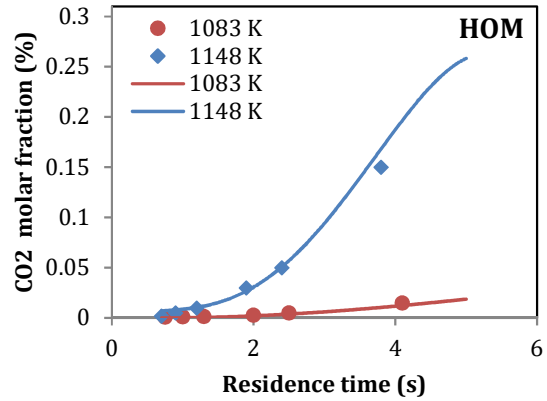
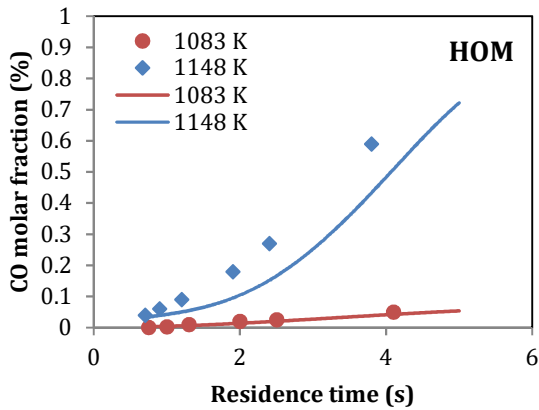


Fig.4. Molar fraction of CO₂ versus residence time. Comparison between experiment (symbol) and simulation (line).



2

Fig.5. Molar fraction of CO versus residence time. Comparison between experiment (symbol) and simulation (line).

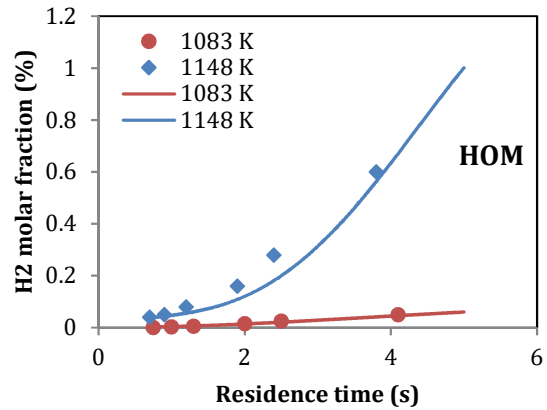
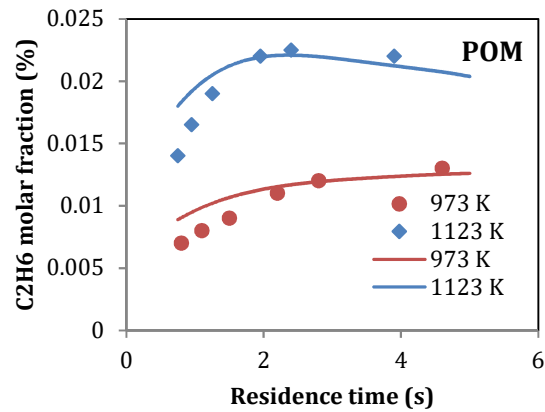
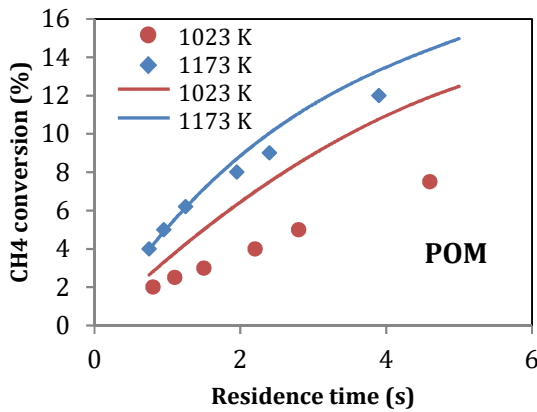


Fig.6. Molar fraction of H₂ versus residence time. Comparison between experiment (symbol) and simulation (line).

3 4.2 Partial oxidation of methane

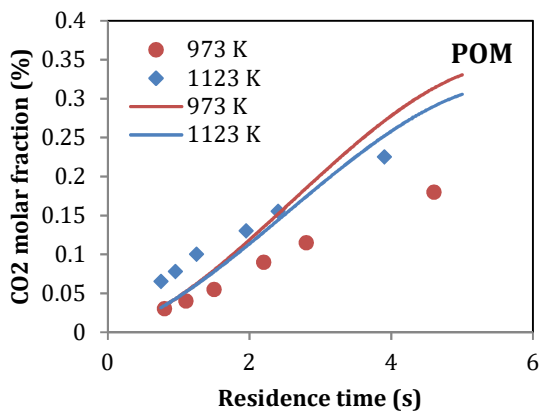
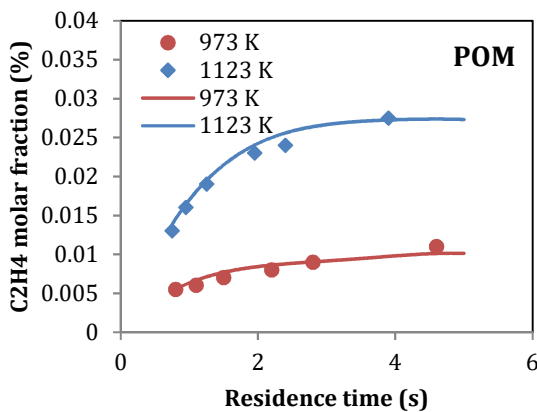
4 Among the proposed methods for the production of hydrogen, the partial oxidation of
 5 methane has many advantages: the reaction is exothermic and it may be carried out in
 6 autothermal conditions. This reaction produces syngas: $\text{CH}_4 + \frac{1}{2} \text{O}_2 = \text{CO} + 2 \text{H}_2$
 7 The reaction was studied at various temperatures between 973K and 1123K over La₂O₃
 8 catalyst. Like for HOM, the ratio CH₄/O₂ was 2. The concentration of sites over the surface L

1 was unknown. So we used an average value of $L = 910^{-11}$ mol.cm⁻² as the starting point. L
 2 was thus considered as an adjustable parameter and the value used after adjustment was
 3 finally:
 4 $L = 2.810^{-11}$ mol.cm⁻². Figure 7 to 12 show the variation of the molar fraction of CH₄, C₂H₄,
 5 C₂H₆, CO, CO₂ and H₂ according to the residence time at two temperatures. A good
 6 agreement between the experimental and theoretical results can be observed.



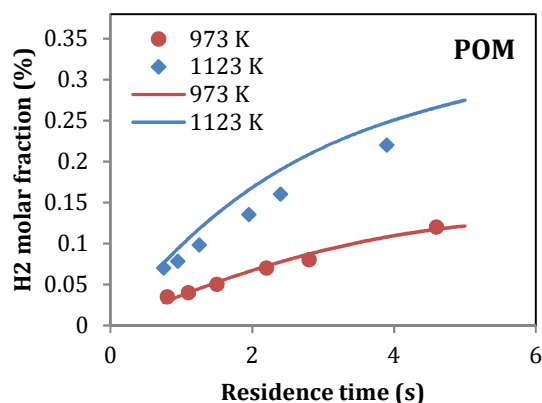
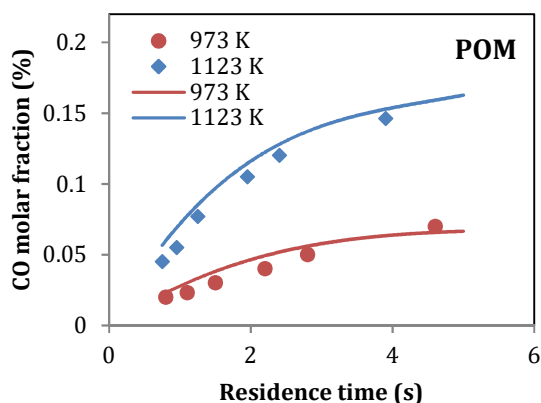
7
Fig.7. Conversion of CH₄ versus residence time. Comparison between experiment (symbol) and simulation (line).

Fig.8. Molar fraction of C₂H₆ versus residence time. Comparison between experiment (symbol) and simulation (line).



8
Fig.9. Molar fraction of C₂H₄ versus residence time. Comparison between experiment (symbol) and simulation (line).

Fig.10. Molar fraction of CO₂ versus residence time. Comparison between experiment (symbol) and simulation (line).



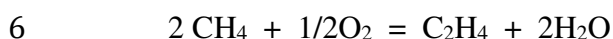
1

Fig.11. Molar fraction of CO versus residence time. Comparison between experiment (symbol) and simulation (line).

Fig.12. Molar fraction of H₂ versus residence time. Comparison between experiment (symbol) and simulation (line).

2 4.3 Oxidative coupling of methane

3 The reaction of oxidative coupling of methane has been investigated in a large number
 4 of laboratories because its development should have led to a direct process to obtain more
 5 valuable hydrocarbons such as ethylene for the chemical industry:



7 This reaction was studied between 1023K and 1173K over La₂O₃ catalyst with a CH₄/O₂ ratio
 8 of 5. Like for POM, the concentration of sites over the surface was $L = 910^{-11} \text{ mol.cm}^{-2}$ as the
 9 starting point and the value used after adjustment was $L = 510^{-11} \text{ mol.cm}^{-2}$. Figure 13 to 17
 10 shows the molar fraction of CH₄, C₂H₄, C₂H₆, CO and CO₂ according to the residence time.
 11 Although the kinetic parameters were only slightly modified the agreement between the
 12 theoretical curves and the experimental points was correct. Therefore the hetero-
 13 homogeneous mechanism was validated in the experimental conditions.

14

1

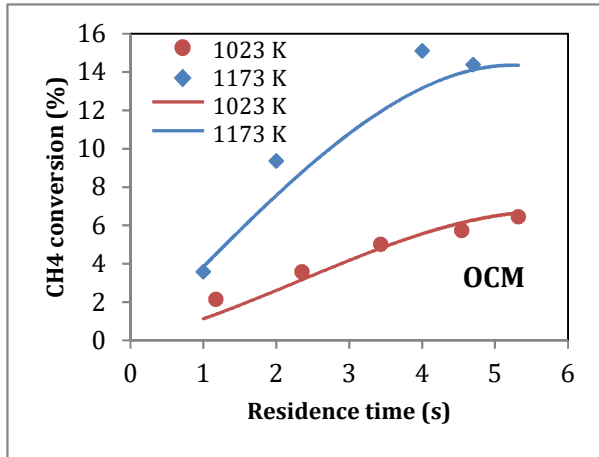


Fig.13. Conversion of CH₄ versus residence time. Comparison between experiment (symbol) and simulation (line).

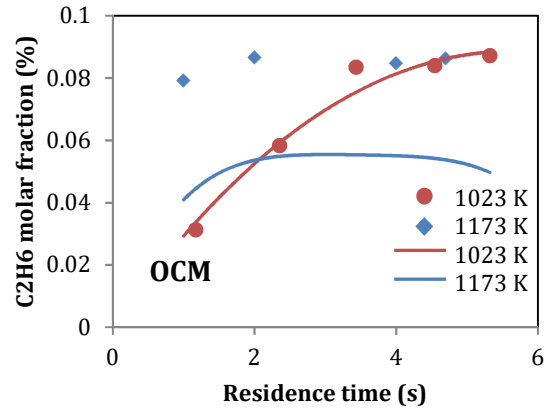


Fig.14. Molar fraction of C₂H₆ versus residence time. Comparison between experiment (symbol) and simulation (line).

2

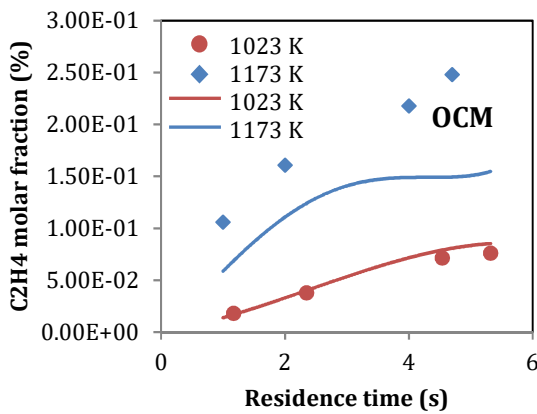


Fig.14. Molar fraction of C₂H₄ versus residence time. Comparison between experiment (symbol) and simulation (line).

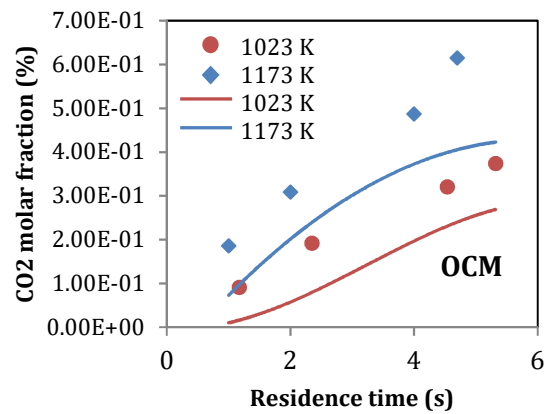
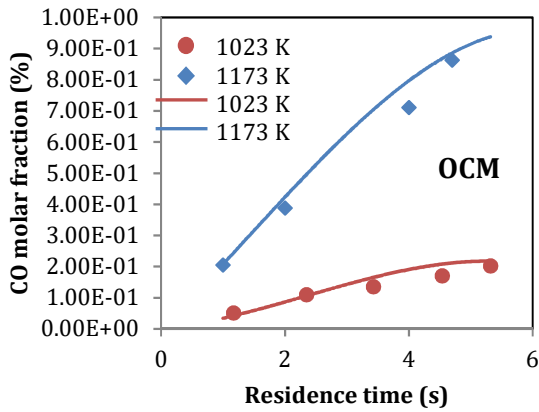


Fig.16. Molar fraction of CO₂ versus residence time. Comparison between experiment (symbol) and simulation (line).



1

Fig.17. Molar fraction of CO versus residence time. Comparison between experiment (symbol) and simulation (line).

2

3

4

4.4 Comparison of the three reactions

5

6

A simplification of the general mechanism can be represented according to figure 20.

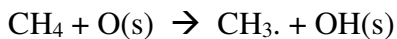
7

The mechanism of oxidation of methane comprises two distinct reaction pathways: an oxidative route and a non-oxidative route.

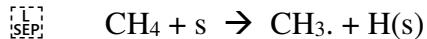
9

The initiation of the oxidation of methane forms $\text{CH}_3\cdot$ radicals (reaction 1). In the case of HOM, the activation occurs by reaction between CH_4 and a gas phase radical while in OCM and POM the initiation takes place mainly on the catalyst by reactions involving surface species.

13



14

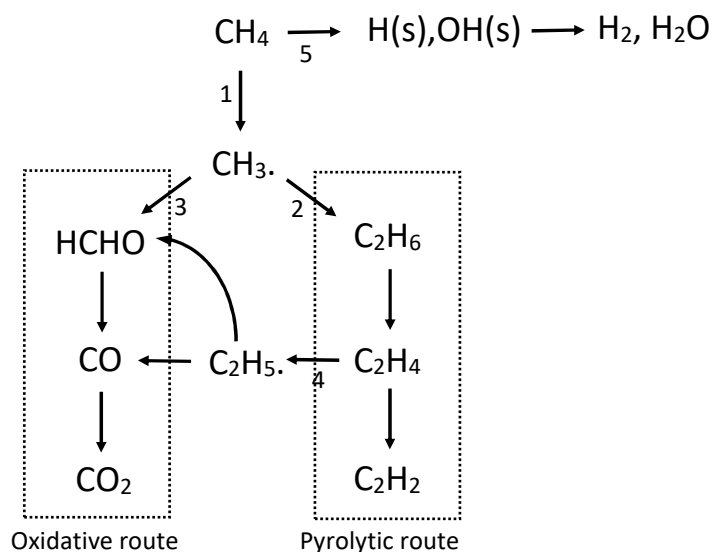


15

16

17

18



11 **Fig.20.** Schematic representation of the mechanism

12
13
14 Heterogeneous initiations represent 80% of the methane activation in the case of POM
15 and 100% in the case of OCM. The main effect of the catalyst is the generation of free
16 radicals.

17 Then, the CH₃· radicals can react according to the pyrolytic route (reaction 2) to form
18 hydrocarbons or the oxidative route (reaction 3) to form oxygenated compounds. The
19 pyrolytic route and therefore the formation of hydrocarbons is favored when the concentration
20 of oxygen is low, which is the case for OCM. When the conversion is high, an oxidative step
21 appears (reaction 4). This step decreases the concentration of C₂H₄ and may explain why the
22 yield of hydrocarbons in OCM does not exceed 22% to 27% for all catalysts tested, like
23 reported by numerous authors.

24 In POM and HOM, the oxygen concentration favors the oxidative pathway. However,
25 lanthanum oxide is an excellent generator of free radical. Thus, in POM, the catalyst more
26 easily generates radicals by reactions between CH₄ and surface species and therefore

1 accelerates the reaction. In addition, a new source of H₂ formed by heterogeneous reactions
2 (reaction 5) appears on lanthanum oxide, which increases the yield of H₂ in POM.

3

4

5

6 **5. CONCLUSION**

7 The study of catalytic oxidations of methane has met with renewed interest in the past
8 10 years due to the discovery of new natural gas fields and the rising price of oil. These
9 catalytic reactions are carried out at high temperature and thus comport a homogeneous and
10 heterogeneous part, which make their mechanism more complex. This reaction mechanism is
11 essential for the development of industrial processes. We have therefore developed a reaction
12 mechanism that allows representing, at the same time, three methane oxidation reactions:
13 homogeneous oxidation, partial oxidation and oxidative coupling. The homogeneous
14 mechanism may be found in the literature or determined from an automatic generator of
15 mechanism. The heterogeneous mechanism was written following the Eley-Rideal and
16 Langmuir-Hinshelwood formalisms. The pre-exponential factor was determined by methods
17 derived from Benson's technics whereas the activation energy was chosen, in a first time, by
18 analogy with gas phase reactions. Finally, the mechanism used for the simulation give good
19 results although the values of the rate constants were only slightly modified. Thanks to the
20 sensitivity analysis, the heterogeneous mechanism has been simplified and contains only 17
21 elementary reactions.

22

23 **NOMENCLATURE**

24 k_i: Rate constant for elementary step i

25 A: Arrhenius preexponential factor

26 E: Activation energy (cal.mol⁻¹)

- 1 T: temperature (K)
- 2 k_B : Boltzmann constant: $1.381 \cdot 10^{-23} \text{ J.K}^{-1}$
- 3 h: Planck constant : $6.6262 \cdot 10^{-34} \text{ J.s.}$
- 4 N: Avogadro number: $6,022 \cdot 10^{23}$
- 5 q_i : total partition function for species i (m^{-3})
- 6 q_{iv} : vibrational partition function for species i
- 7 q_{ir} : rotational partition function for species i
- 8 q_{it} : translational partition function for species i (m^{-3})
- 9 q_{ie} : electronic partition function for species i
- 10 \neq : in relation with the activated complex
- 11 m: molecule mass (kg)
- 12 M: molar mass (g. mol^{-1})
- 13 s: spin quantic number
- 14 σ_{ext} : external symmetry number
- 15 σ_{int} : internal symmetry number
- 16 I: moment of inertia (amu. \AA^2 or kg. m^2)
- 17 I_{red} : reduced moment of inertia (amu. \AA^2)
- 18 ω : frequency of vibration (cm^{-1})
- 19 D: product of the moments of inertia ($\text{amu}^3 \cdot \text{\AA}^6$ or $\text{kg}^3 \cdot \text{m}^6$)
- 20 $\Delta H_{\text{ads},i}$: heat of adsorption for species i (cal.mol^{-1})
- 21 x_n : molar fraction for species n
- 22 $S_{i,n}$: sensibility coefficient of reactions i for species n
- 23
- 24

1 BIBLIOGRAPHY

- 2 [1] BP statistical review of world energy **2020**.
3
- 4 [2] Keller GE, Bhasin MM. Synthesis of Ethylene via Oxidative Coupling of Methane I.
5 Determination of Active Catalysts, *J. Catal.* **1982**, 73, 9-19.
6
- 7 [3] Choudhary VR, Mulla SAR, Uphade BS. Oxidative coupling of methane over alkaline
8 earth oxides deposited on commercial support precoated with rare earth oxides, *Fuel* **1999**, 78,
9 427-437.
10
- 11 [4] Rostrup-Nielsen JR, Christiansen LJ, Bak Hansen JH. Activity of steam reforming
12 catalysts: role and assessment, *Appl. Catal.* **1988**, 43(2), 287.
13
- 14 [5] Rostrup-Nielsen JR, Sehested J, Nørskov JK. Hydrogen and Synthesis Gas by Steam and
15 CO₂ Reforming, *Adv. Catal.* **2002**, 47, 65.
16
- 17 [6] Corbo P, Migliardini F. Hydrogen production by catalytic partial oxidation of methane
18 and propane on Ni and Pt catalysts, *Int. J. Hydrogen Energy* **2006**, 32, 55-66.
19
- 20 [7] Requies J, Barrio VL, Cambra JF, Güemez MB, Arias PL, La Parola V, Pena MA, Fierro
21 JLG. Effect of redox additives over Ni/Al₂O₃ catalysts on syngas production via methane
22 catalytic partial oxidation, *Fuel* **2008**, 87, 3223-3231.
23
- 24 [8] Subramanian R, Panuccio GJ, Krummenacher JJ, Lee IC, Schmidt LD. Catalytic partial
25 oxidation of higher hydrocarbons: reactivities and selectivities of mixtures, *Chem. Eng. Sci.*
26 **2004**, 59, 5501.
27
- 28 [9] Bistolfi M, Fornasari G, Molinari M, Palmery S, Dente M, Ranzi E. Kinetic Model for
29 methane oxidative coupling reactors, *Chem. Eng. Sci.* **1992**, 47, 2647.
30
- 31 [10] Driscoll DJ, Lunsford JH. Gas-Phase Radical Formation during the Reaction of Methane,
32 Ethane, Ethylene and Propylene over selected Oxide Catalysts, *J. Phys. Chem.* **1985**, 89,
33 4415.
34
- 35 [11] Driscoll DJ, Martir W, Wang J, Lunsford, JH. Formation of Gas Phase Methyl Radicals
36 over MgO, *J. Am. Soc.* **1985**, 107, 58.
37
- 38 [12] Sinev MY. Kinetic modeling of heterogeneous-homogeneous radical processes of the
39 partial oxidation of low paraffins, *Catal. Today* **1995**, 24, 389.
40
- 41 [13] Baerns M, Buyevskaya OV, Mleczko L, Wolf D. Catalytic partial oxidation of methane
42 to synthesis gas - catalysis and reaction engineering, *Stud. Surf. Sci. Catal.* **1997**, 107.
43
- 44 [14] Deutschmann O, Schmidt LD. Modeling the partial oxidation of methane in a short-
45 contact-time reactor, *AIChE J.* **1998**, 44, 2465.<sup>[L]
[SEP]</sup>
46
- 47 [15] Goralski CT, O'Connor RP, Schmidt LD. Modeling homogeneous and heterogeneous
48 chemistry in the production of syngas from methane, *Chem. Eng. Sci.* **2000**, 55, 1357.
49

- 1 [16] Fleys M, Simon Y, Marquaire PM. Discussion on the oxidative and the pyrolysis routes
2 of the CH₃ radicals in the partial oxidation of methane over La₂O₃, J. Anal. Appl. Pyrol.
3 **2007c**, 79, 259.^[SEP]
4
- 5 [17] Thybaut JW, Sun J, Olivier L, Van Veen AC, Mirodatos C, Marin GB. Catalyst design
6 based on microkinetic models: oxidative coupling of methane, Catal. Today **2011**, 159, 29.
- 7 [18] Hickman DA, Schmidt LD. Production of syngas by direct catalytic oxidation of
8 methane, Science **1993**, 259, 343.
- 9 [19] Vlachos DG. Homogeneous-heterogeneous oxidation reactions over platinum and inert
10 surfaces, Chem. Eng. Sci. **1996**, 51, 2429.
11
- 12 [20] Fleys M, Simon Y, Marquaire PM. Detailed kinetic study of the partial oxidation of
13 methane over La₂O₃ catalyst. Part 2: mechanism, Ind. Eng. Chem. Res. **2007a**, 46, 1069 -
14 1078.
15
- 16 [21] Fleys M, Shan W, Simon Y, Marquaire PM. Detailed kinetic study of the partial
17 oxidation of methane over La₂O₃ catalyst. Part 1: Experimental results, Ind. Eng. Chem. Res.
18 **2007b**, 46, 1063.^[SEP]
19
- 20 [22] Fleys M, Simon Y, Swierczynski D, Kiennemann A, Marquaire PM. Investigation of the
21 reaction of partial oxidation of methane over Ni/La₂O₃ catalyst, Energy & Fuels **2006**, 20,
22 2321.^[SEP]
23
- 24 [23] Simon Y, Baronnet F, Marquaire PM. Kinetic modeling of the oxidative coupling of
25 methane, Ind. Eng. Chem. Res. **2007**, 46, 1914–1922.
26
- 27 [24] Barbé P, Li YD, Marquaire PM, Côme GM, Baronnet F. Competition between the gas
28 and surface reactions for the oxidative coupling of methane. 1. “Non-isothermal” results in
29 catalytic jet-stirred reactor, Catal. Today **1994**, 21, 409.
30
- 31 [25] Barbé P, Li YD, Marquaire PM, Côme GM, Baronnet F. A new “catalytic jet-stirred
32 reactor” Application to the study of the oxidative coupling of methane, Oxid. Commun **1996**,
33 19, 173.
34
- 35 [26] Hognon C, Simon Y, Marquaire PM, Courson C and Kienneman A. Hydrogen
36 production by catalytic partial oxidation of propane over CeO₂, Chem. Eng. Sc. **2018**, 181,
37 46-57.
38
- 39 [27] Warth V, Battin-Leclerc F, Fournet R, Glaude PA, Côme GM, Scacchi G. Computer
40 based generation of reaction mechanisms for gas-phase oxidation, Comput. Chem. **2000**, 24,
41 541.
42
- 43 [28] McCarty JG. Methane Conversion by Oxidative Processes, Wolf EE, Ed. Van Nostrand
44 Reinhold, **1992** New York.
45
- 46 [29] Martin GA, Mirodatos C. Surface chemistry in the oxidative coupling of methane. Fuel
47 Process. Technol. **1995**, 42, 179.
48

- 1 [30] Lacombe S, Durjanova Z, Mleczko L, Mirodatos C. Kinetic modelling of the oxidative
2 coupling of methane over lanthanum oxide in connection with mechanistic studies, Chem.
3 Eng. Technol. **1995**, 42, 216.
4
- 5 [31] Couwenberg PM, Chen Q, Marin GB. Kinetics of a gas- phase chain reaction catalysed
6 by a solid: The oxidative coupling of methane over Li/MgO-based catalysts, Ind. Eng. Chem.
7 Res. **1996**, 35, 3999.
8
- 9 [32] Wolf D, Slinko M, Baerns M, Kurkina E. Kinetic simulations of surface processes of the
10 oxidative coupling of methane over a basic oxide catalyst, Appl. Catal. A **1998**, 166, 47.
11
- 12 [33] Coulter K, Goodman DW. The role of carbon dioxide in the oxidative dimerization of
13 methane over Li/MgO, Catal. Lett. **1993**, 20, 169.
14
- 15 [34] Shi C, Xu M, Rosynek MP, Lunsford JH. Origin of kinetic isotope effects during the
16 oxidative coupling of methane over a lithium (1+)/magnesia catalyst, J. Phys. Chem. **1993**,
17 97, 216.^[SEP]
18
- 19 [35] Sinev MYu, Fattakhova ZT, Lomonosov VI, Gordienko AYu. Kinetics of oxidative
20 coupling of methane: Bridging the gap between comprehension an description, J. Nat. Gas
21 Chem. 18, **2009**, 273-287.
22
- 23 [36] Karakaya C, Zhu H, Loebick C, Weissman JG, Kee RJ. A detailed reaction mechanism
24 for oxidative coupling of methane over Mn/Na₂WO₄/SiO₂ catalyst for non-isothermal
25 conditions, Catal. Today. **2018**, 312, 10.
26
- 27 [37] Beck B, Fleischer V, Arndt S, Hevia MG, Urakawa A, Hugo P, Schomäcker R, Catal.
28 Today. **2014**, 228, 212.
29
- 30 [38] Yang T, Feng L, Shen S. Oxygen species on the surface of La₂O₃/CaO and its role in the
31 oxidative coupling of methane, J. Catal. **1994**, 145, 384.
32
- 33 [39] Hutchings GJ, Woodhouse JR, Scurrrell MS. Partial oxidation of methane over oxide
34 catalysts. Comments on the reaction mechanism, J. Chem. Soc. Faraday Trans. **1989**, 85,
35 2507.
36
- 37 [40] Lacombe S, Geantet C, Mirodatos C. Oxidative coupling of methane over lanthana
38 catalysts. I. Identification and role of specific active sites, J. Catal. **1994**, 151, 439.
39
- 40 [41] Huang S-J, Walters AB, Vannice MA. Adsorption and decomposition of NO on
41 lanthanum oxide, J. Catal. **2000**, 192, 29.
42
- 43 [42] Gambo Y, Jalil AA, Triwahyono S, Abdulrasheed AA. Recent advances and future
44 prospect in catalysts for oxidative coupling of methane to ethylene : A review, J. Ind. Eng.
45 Chem. **2018**, 59, 218-229.
46
- 47 [43] Zerkle DK, Allendorf MD, Wolf M, Deutschmann O. Understanding homogeneous and
48 heterogeneous contributions to the platinum-catalyzed partial oxidation of ethane in a short-
49 contact-time reactor, J. Catal. **2000**, 196, 18-39.

- 1 [44] Sinev MY. Free radicals in catalytic oxidation of light alkanes: kinetic and
2 thermochemical aspects, *J. Catal.* **2003**, 216, 468-476.
3
- 4 [45] Sun J, Thybaut JW, Marin GB. Microkinetics of methane oxidative coupling, *Catal.*
5 *Today* **2008**, 137, 90-102.
6
- 7 [46] Thybaut JW, Sun J, Olivier L, Van Veen AC, Mirodatos C, Marin GB. Catalyst design
8 based on microkinetic models: oxidative coupling of methane, *Catal. Today* **2011**, 159, 29.
9
- 10 [47] Benson SW. Thermochemical kinetics : methods for the estimation of thermochemical
11 data and rate parameters, J. Wiley & sons, New York **1976**.
12
- 13 [48] Glarborg P, Kee RJ, Grcar JF, Miller JA. PSR: a Fortran program for modeling $\frac{[1]}{[SEP]}$
14 well-stirred reactors, Sandia Report, SAND86-8209 UC-4, **1990**.
15
- 16 [49] Coltrin ME, Kee RJ, Rupley FM, Surface Chemkin (v 4.0): a Fortran package for 16
17 analyzing heterogeneous chemical kinetics at a solid surface - gas phase interface, Sandia
18 Report, SAND90-8003C – UC-706, **1991**.
19
- 20 [50] Toops TJ, Walters AB, Vannice MA. The effect of CO₂ and H₂O on the kinetics of NO
21 reduction by CH₄ over La₂O₃/γ-Al₂O₃ catalyst, *J. Catal.* **2003**, 214, 292-307.
22
- 23 [51] Baulch DL, Cobos CJ, Cox RA, Esser C, Frank P, Just T, Kerr JA, Pilling MJ, Troe J,
24 Walker RW, Warnatz J. Evaluated kinetic data for combustion modelling, *J. Phys. Chem. Ref.*
25 *Data* **1992**, 21, 411-429.
26
- 27 [52] Tsang W, Hampson RF. Chemical kinetic data base for combustion chemistry. Part I.
28 methane and related compounds, *J. Phys. Chem. Ref. Data* **1986**, 15(3), 1087.
29
- 30 [53] Ranzi E, Sogaro A, Gaffuri P, Pennati G, Faravelli T. A wide range modelling study of
31 methane oxidation, *Comb. Sci. and Technol.* **1994**, 96, 279.
32
- 33 [54] Cavanagh J, Cox RA, Olson G. Computer modeling of cool flames and ignition of
34 acetaldehyde, *Comb. Flame* **1990**, 82, 15.
35
- 36 [55] Schulz G, Klotz H-D, Spangenberg H-J. Reaktionsmodell zur bruttokinetik der pyrolyse
37 von methan im stosswellenrohr bei temperaturen von 1800 K bis 2500 K, *Z. Chem.* **1985**, 25,
38 88.
39
- 40 [56] Knyazev VD, Bencsura A, Stoliarov SI, Slagle IR. Kinetics of the C₂H₃ + H₂ = H + C₂H₄
41 and CH₃ + H₂ = H + CH₄ reactions, *J. Phys. Chem.* **1996**, 100, 11346.
42
- 43 [57] Zhang HX, Ahonkhai SI, Back MH. Rate constants for abstraction of hydrogen from
44 benzene, toluene, and cyclopentane by methyl and ethyl radicals over the temperature range
45 650-770 K, *Can. J. Chem.* **1989**, 67, 1541.
46
- 47 [58] Benson SW. Oxygen Initiated Combustion: Thermochemistry and Kinetics of
48 Unsaturated Hydrocarbons, *Int. J. Chem. Kin.* **1996**, 28, 665.
49

- 1 [59] Mahmud K, Marshall P, Fontijn A. A High-Temperature Photochemistry Kinetics Study
2 of the Reactions of O Atoms With Acetylene From 290 to 1510 K, J. Phys. Chem. **1987**, 91,
3 1568.
4
- 5 [60] Glarborg P, Miller JA, Kee RJ. Kinetic modeling and sensitivity analysis of nitrogen
6 oxide formation in well-stirred reactors, Comb. Flame **1986**, 65, 177.
7
- 8 [61] Warth V, Stef N, Glaude PA, Battin-Leclerc F, Scacchi G, Côme G-M. Computed aided
9 design of gas-phase oxidation mechanisms: Application to the modelling of normal-butane
10 oxidation, Comb. Flame **1998**, 114, 81-102.
11
12
13
14