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

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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  $\text{CH}_4 / \text{O}_2$   
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  $\text{La}_2\text{O}_3$  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;  $\text{La}_2\text{O}_3$ .

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  $\text{La}_2\text{O}_3$  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  $\text{H}_2/\text{CO}$  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.

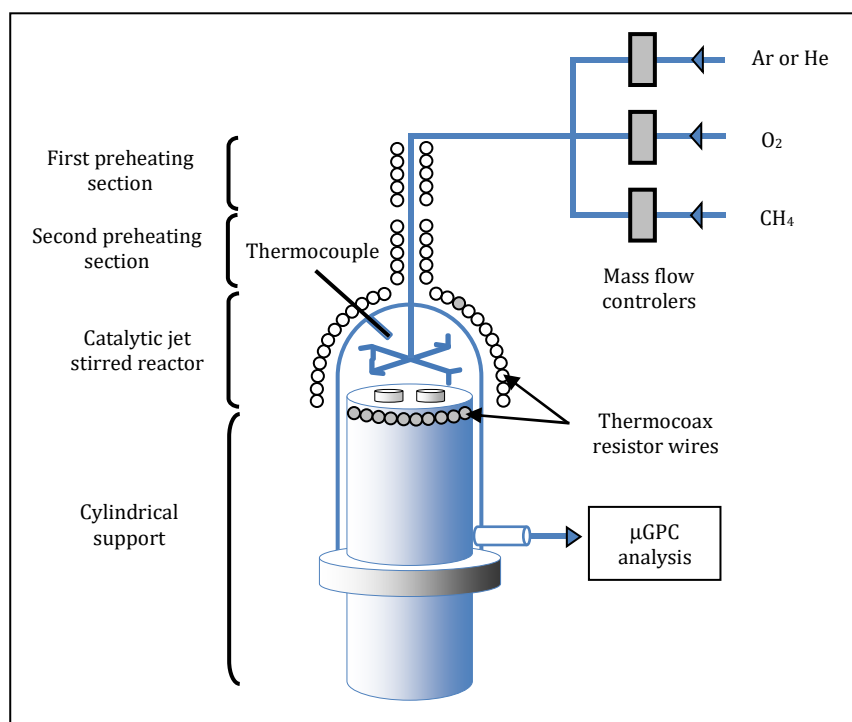
15 The OCM and POM reactions differ only in the ratio  $\text{CH}_4 / \text{O}_2$  used, so their overall  
16 reaction mechanism should be the same. We have therefore tried to represent the results  
17 obtained during the experimental study of OCM and POM over  $\text{La}_2\text{O}_3$  and that of 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

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## 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 cm<sup>3</sup>) 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 La<sub>2</sub>O<sub>3</sub> 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  $\text{La}_2\text{O}_3$   
3 powder was heated for 8 hours at a temperature of  $900^\circ\text{C}$ . 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  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$  and  $\text{CO}_2$  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**

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

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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.

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## 14 3.2. Heterogeneous mechanism

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### 16 3.2.1. Description of the mechanism

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18

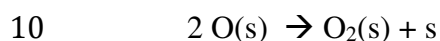
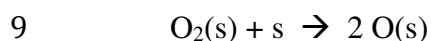
The development of the heterogeneous mechanism takes into account the results from mechanistic studies reported in the literature [28-37]. Despite the many studies carried out on this subject, the exact nature of the active sites on  $La_2O_3$  remains unclear. Yang et al. suggested that  $O^{2-}$  ions 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



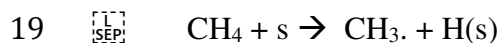
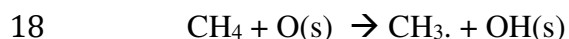
1 surface of lanthanum oxide: a basic site associated with an anionic vacancy which would be  
2 responsible for the dissociation of gaseous oxygen into atomic species and an unsaturated site  
3 on which methyl radical would react to be further oxidized into CO<sub>2</sub>. In summary, there are at  
4 least two types of active sites on the La<sub>2</sub>O<sub>3</sub> 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 O<sub>2</sub> molecule to form two active atomic  
8 oxygen centres according to the following reaction:

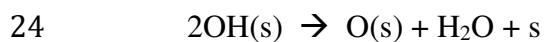
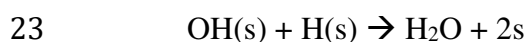
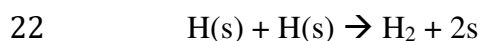


11 In these elementary reactions s represents a surface site and O(s) the atom O adsorbed on the  
12 surface of the La<sub>2</sub>O<sub>3</sub> crystal.

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 <sup>2</sup> , s)	E(cal.mol <sup>-1</sup> )
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<sup>‡</sup> 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<sup>‡</sup> is only due to the vibrational  
 4 component of the activated complex q<sup>‡</sup><sub>v</sub>. 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<sub>t</sub>, an external rotational partition function q<sub>r</sub>, a vibrational partition  
 9 function q<sub>v</sub> and an electronic partition function q<sub>e</sub>. 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<sub>ext</sub> is the external symmetry number, m (kg) the mass of the atom,  
 14 s the spin and ω<sub>i</sub> (cm<sup>-1</sup>) 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.m<sup>2</sup>). In  
 18 this case, the rotational partition function is q<sub>r</sub><sup>2D</sup>. However, there are 3 rotational degrees of  
 19 freedom in a non-linear molecule and the calculation of the partition function q<sub>r</sub><sup>3D</sup> use the  
 20 product of the moments of inertia: D (kg<sup>3</sup>.m<sup>6</sup>). 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 ( $g \cdot mol^{-1}$ ). In the  
 5 second expression, the unit of  $D$  is  $amu^3 \cdot \text{\AA}^6$  and that of  $I$  is  $amu \cdot \text{\AA}^2$ .

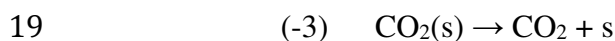
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### 7 **3.2.3. Activation energy**

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)  $CO_2 + s \rightarrow CO_2(s)$



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  $La_2O_3/CaO$  catalyst [50] is about:

23  $-\Delta H_{ads, CO_2} = 44 \pm 7 \text{ kcal} \cdot \text{mol}^{-1} = E_{-3}$ .

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:  $C_2H_6 + s \rightarrow C_2H_5 + H(s)$  may be represented by the following  
 27 homogeneous reaction:  $C_2H_6 + \text{alkyl} \cdot \rightarrow C_2H_5 + \text{alkane}$

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	$A^{\text{fitted}}$ (mol, cm <sup>2</sup> , s)	$E^{\text{fitted}}$ (cal.mol <sup>-1</sup> )
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  
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8

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

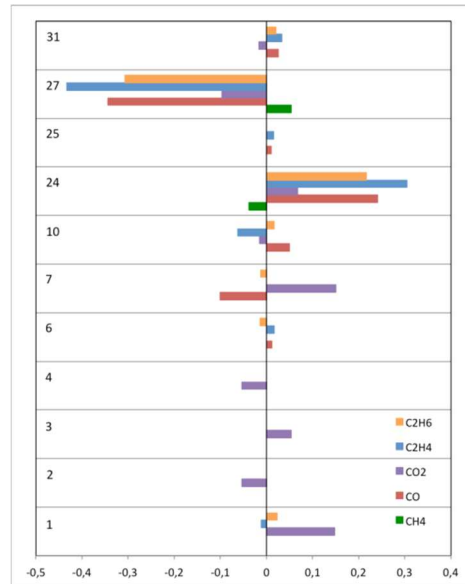
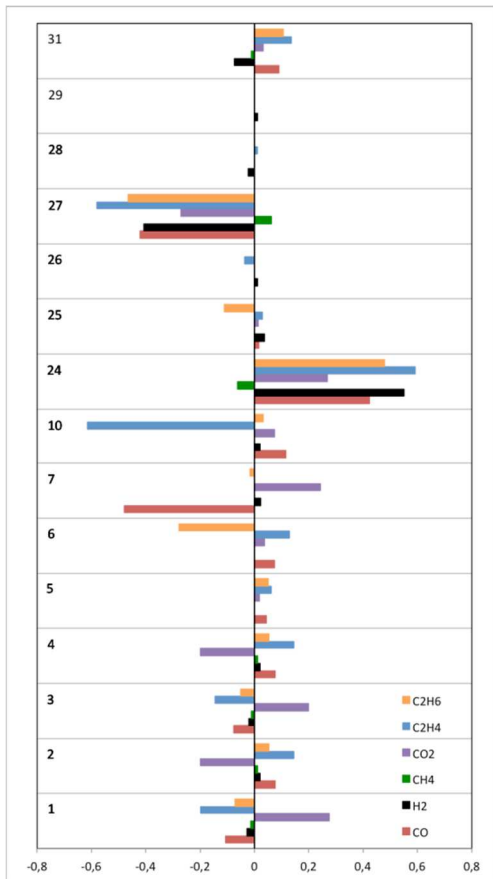


Figure 18. Sensitivity analysis of surface reactions for POM at 1123 K

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

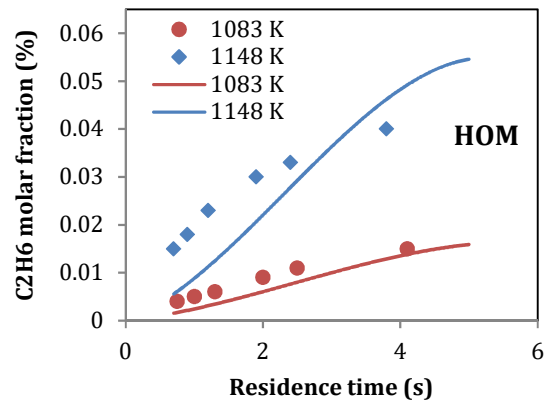
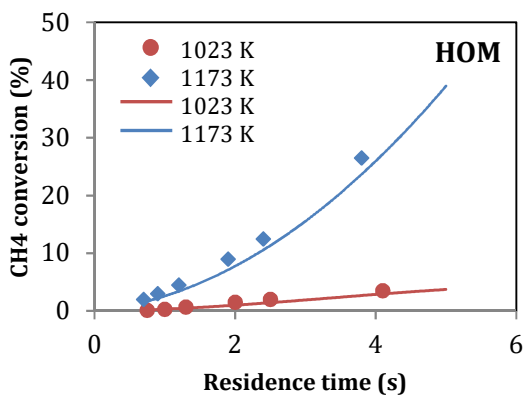
#### 4- RESULTS AND DISCUSSION

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 CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CO, CO<sub>2</sub> and  
7 H<sub>2</sub> versus residence time. The ratio CH<sub>4</sub>/O<sub>2</sub> was fixed to 2. The simulation very well  
8 reproduces the conversion of CH<sub>4</sub> and the production of the most important products.  
9



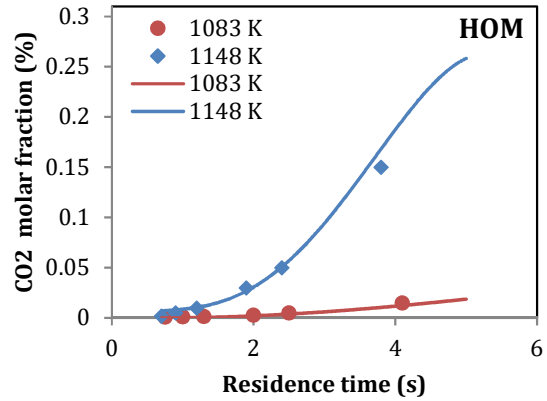
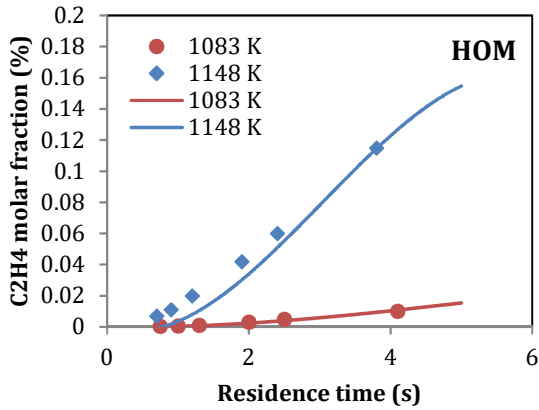
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**Fig.1.** Conversion of CH<sub>4</sub> versus residence time. Comparison between experiment (symbol) and simulation (line).

**Fig.2.** Molar fraction of C<sub>2</sub>H<sub>6</sub> versus residence time. Comparison between experiment (symbol) and simulation (line).

11

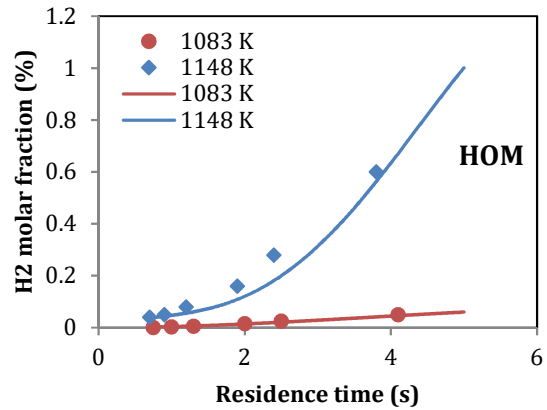
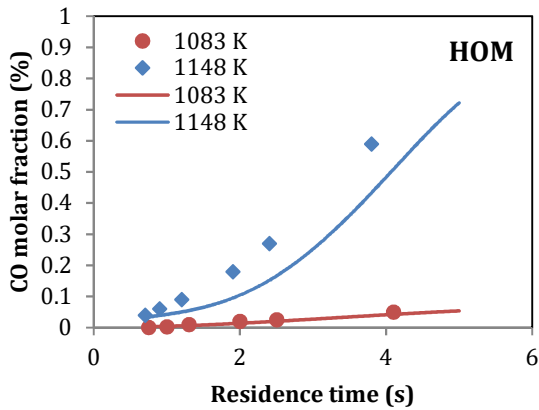
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1

**Fig.3.** Molar fraction of C<sub>2</sub>H<sub>4</sub> versus residence time. Comparison between experiment (symbol) and simulation (line).

**Fig.4.** Molar fraction of CO<sub>2</sub> versus residence time. Comparison between experiment (symbol) and simulation (line).



2

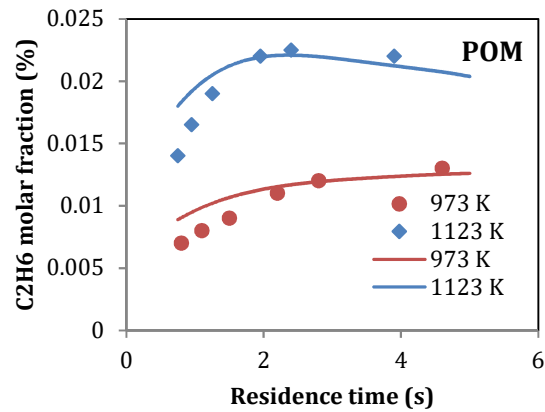
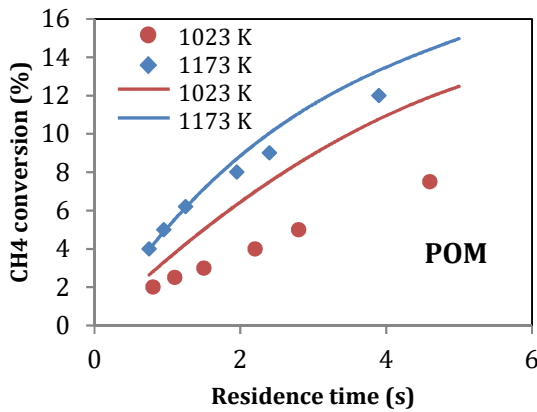
**Fig.5.** Molar fraction of CO versus residence time. Comparison between experiment (symbol) and simulation (line).

**Fig.6.** Molar fraction of H<sub>2</sub> 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 La<sub>2</sub>O<sub>3</sub>  
 8 catalyst. Like for HOM, the ratio CH<sub>4</sub>/O<sub>2</sub> was 2. The concentration of sites over the surface L

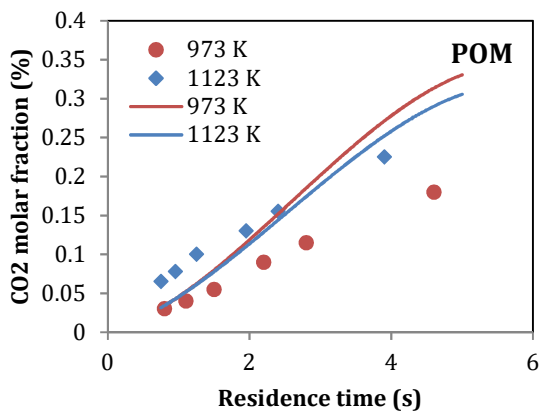
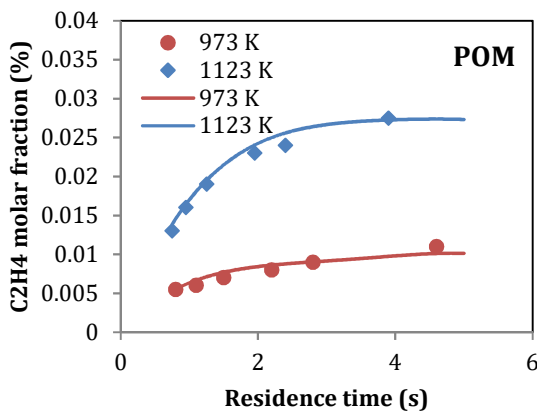
1 was unknown. So we used an average value of  $L = 910^{-11}$  mol.cm<sup>-2</sup> as the starting point. L  
 2 was thus considered as an adjustable parameter and the value used after adjustment was  
 3 finally:  
 4  $L = 2.810^{-11}$  mol.cm<sup>-2</sup>. Figure 7 to 12 show the variation of the molar fraction of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>,  
 5 C<sub>2</sub>H<sub>6</sub>, CO, CO<sub>2</sub> and H<sub>2</sub> 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 CH<sub>4</sub> versus residence time. Comparison between experiment (symbol) and simulation (line).

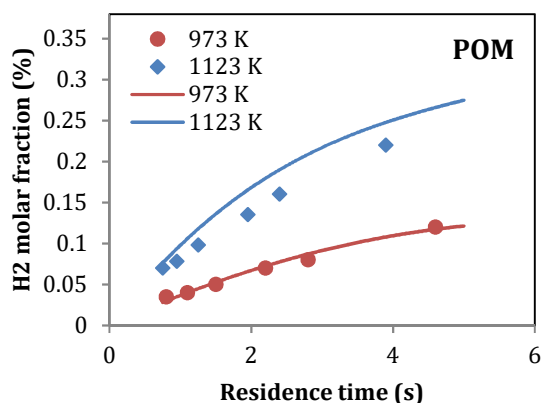
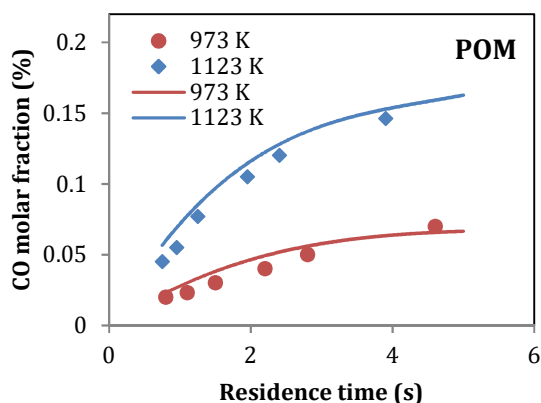
**Fig.8.** Molar fraction of C<sub>2</sub>H<sub>6</sub> versus residence time. Comparison between experiment (symbol) and simulation (line).



8

**Fig.9.** Molar fraction of C<sub>2</sub>H<sub>4</sub> versus residence time. Comparison between experiment (symbol) and simulation (line).

**Fig.10.** Molar fraction of CO<sub>2</sub> versus residence time. Comparison between experiment (symbol) and simulation (line).



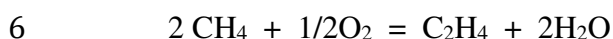
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**Fig.11.** Molar fraction of CO versus residence time. Comparison between experiment (symbol) and simulation (line).

**Fig.12.** Molar fraction of H<sub>2</sub> versus residence time. Comparison between experiment (symbol) and simulation (line).

## 2 4.3 Oxidative coupling of methane

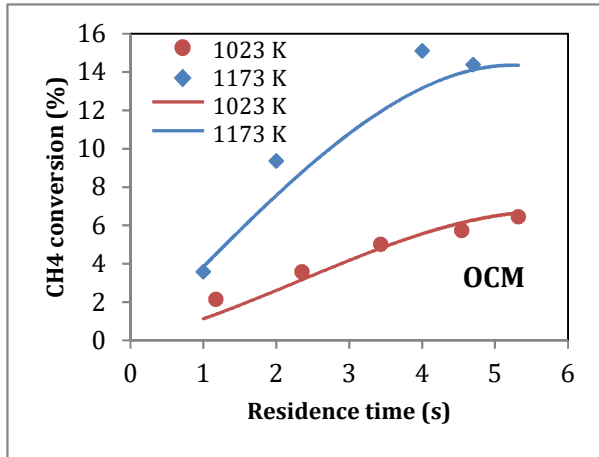
3 The reaction of oxidative coupling of methane has been investigated in a large number  
 4 of laboratories because its development should have led to a direct process to obtain more  
 5 valuable hydrocarbons such as ethylene for the chemical industry:



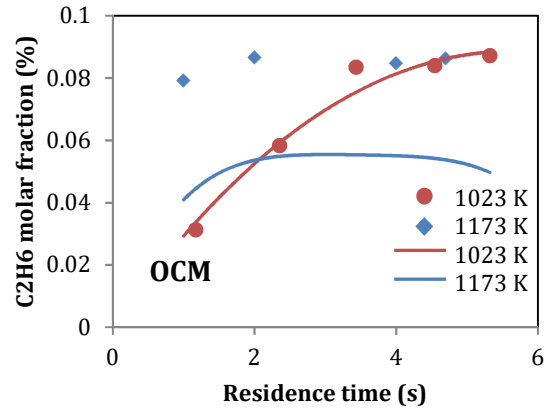
7 This reaction was studied between 1023K and 1173K over La<sub>2</sub>O<sub>3</sub> catalyst with a CH<sub>4</sub>/O<sub>2</sub> ratio  
 8 of 5. Like for POM, the concentration of sites over the surface was  $L = 910^{-11} \text{ mol.cm}^{-2}$  as the  
 9 starting point and the value used after adjustment was  $L = 510^{-11} \text{ mol.cm}^{-2}$ . Figure 13 to 17  
 10 shows the molar fraction of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CO and CO<sub>2</sub> 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

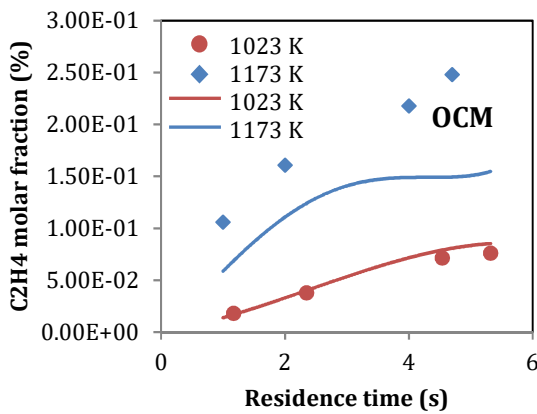


**Fig.13.** Conversion of CH<sub>4</sub> versus residence time. Comparison between experiment (symbol) and simulation (line).

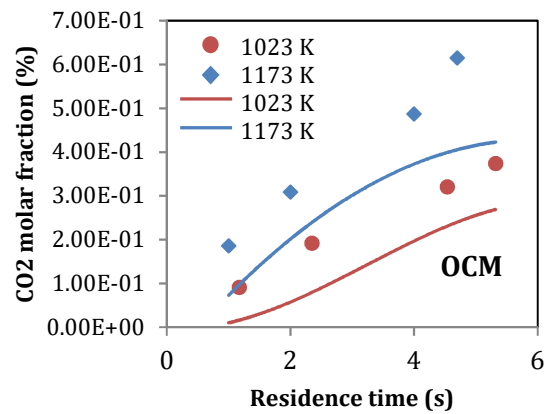


**Fig.14.** Molar fraction of C<sub>2</sub>H<sub>6</sub> versus residence time. Comparison between experiment (symbol) and simulation (line).

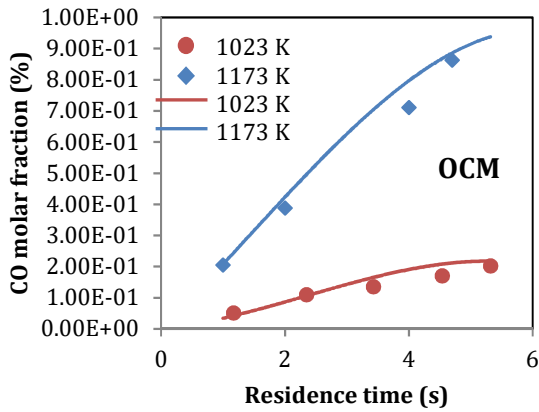
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**Fig.14.** Molar fraction of C<sub>2</sub>H<sub>4</sub> versus residence time. Comparison between experiment (symbol) and simulation (line).



**Fig.16.** Molar fraction of CO<sub>2</sub> 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).

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#### 4.4 Comparison of the three reactions

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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

8

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

10

of HOM, the activation occurs by reaction between  $\text{CH}_4$  and a gas phase radical while in

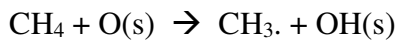
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OCM and POM the initiation takes place mainly on the catalyst by reactions involving surface

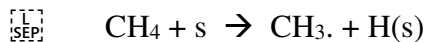
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species.

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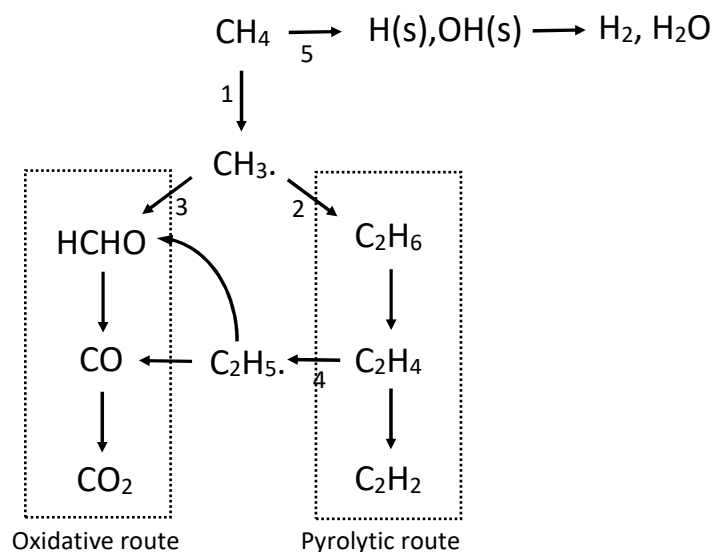


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11 **Fig.20.** Schematic representation of the mechanism

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 CH<sub>3</sub>· 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 C<sub>2</sub>H<sub>4</sub> 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 CH<sub>4</sub> and surface species and therefore

1 accelerates the reaction. In addition, a new source of H<sub>2</sub> formed by heterogeneous reactions  
2 (reaction 5) appears on lanthanum oxide, which increases the yield of H<sub>2</sub> 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<sub>i</sub>: Rate constant for elementary step i

25 A: Arrhenius preexponential factor

26 E: Activation energy (cal.mol<sup>-1</sup>)



- 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 ( $\text{m}^{-3}$ )
- 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 ( $\text{m}^{-3}$ )
- 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 ( $\text{g. mol}^{-1}$ )
- 13 s: spin quantic number
- 14  $\sigma_{\text{ext}}$ : external symmetry number
- 15  $\sigma_{\text{int}}$ : internal symmetry number
- 16 I: moment of inertia ( $\text{amu. \AA}^2$  or  $\text{kg. m}^2$ )
- 17  $I_{\text{red}}$ : reduced moment of inertia ( $\text{amu. \AA}^2$ )
- 18  $\omega$ : frequency of vibration ( $\text{cm}^{-1}$ )
- 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 ( $\text{cal.mol}^{-1}$ )
- 21  $x_n$ : molar fraction for species n
- 22  $S_{i,n}$ : sensibility coefficient of reactions i for species n
- 23
- 24

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