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Competition between gas and surface reactions in the oxidative coupling of methane

2. Isothermal experiments in a catalytic jet-stirred gas phase reactor

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Abstract

The oxidative coupling of methane over a La_2O_3 catalyst was investigated by means of a continuous flow reactor with a perfectly mixed gas phase and a variable number of catalyst pellets. Experiments were carried out isothermally, i.e. at the same temperature for the gas phase and the catalyst, under the following conditions: total pressure equal to 1.05 bar, inlet mixture CH_4:O_2:He = 13.9:2.8:83.3 (mol), temperatures from 650 to 950°C, gas space times ranging from 0.6 to 6 s and pseudo catalytic contact times from 0 to 60 mg s cm^{-3}. Complementary experiments were performed on carbon monoxide oxidation.

Our results are in favour of a reaction mechanism involving, besides gas phase free radical elementary reactions, surface initiation reactions

$CH_4 \rightarrow \cdot CH_3$

$C_2H_6 \rightarrow \cdot C_2H_5$

$C_2H_4 \rightarrow \cdot C_2H_3$

and surface oxidation reactions

$\cdot CH_3 \rightarrow CO_2$

$CO \rightarrow CO_2$

Keywords: Methane coupling; Catalytic jet-stirred reactor; La_2O_3 catalyst; Hetero–homogeneous reaction mechanisms

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1. Introduction

The oxidative coupling of methane has been extensively studied for a number of years, both from an experimental and a theoretical point of view (e.g. [1–22]). For instance, in a recent review paper published by MAITRA, more than 300 papers are quoted [23]. However, several questions still remain open, especially concerning the mechanism of the reaction and in particular, the relative importance of gas phase reactions and surface reactions. In order to address specifically, from an experimental point of view, this last question, we have extrapolated a continuous flow stirred tank reactor, used previously for the study of gas phase reactions [24], for the investigation of catalytic reactions [25]. A description of the reactor and some non-isothermal results (the temperatures of the gas phase and of the catalyst pellets are different) were reported in previous papers [26,27]

In this paper, a comparison of the characteristics of the gas phase and of the catalyzed oxidation of methane and carbon monoxide under isothermal conditions will be presented and discussed.

2. Experimental

The experimental set-up and procedures were previously described [25–27], so that only the characteristics of the reactor will be given here (Fig. 1).

The reactor has a gas phase of constant volume $V = 113$ cm^3. The gaseous volume is perfectly mixed by four jets of gas [28]. Reactants are preheated before entering the reactor, in order to obtain an isothermal gas phase volume [29].

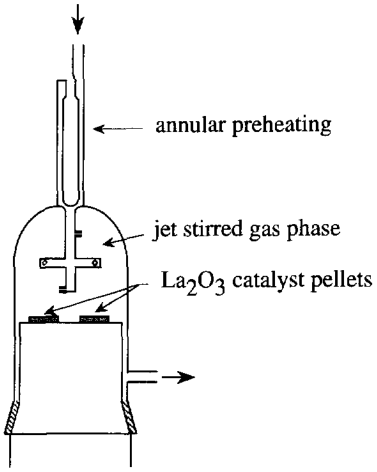

Fig. 1. Catalytic jet stirred reactor.

Catalyst pellets, between 0 and 8, are disposed on a flat surface inside the reactor. A catalyst pellet has a mass $W = 0.45$ g, a diameter equal to 12.6 mm, a thickness equal to 1 mm, a volume equal to 0.125 cm^3, and an external geometric area accessible to gases equal to 1.63 cm^2. The catalyst is La_2O_3 made from lanthanum carbonate, of BET specific area 1.2 m^2 g^{-1}; the particles have a diameter of around 60 μm and are nearly non-porous; the pellet porosity is about 0.55.

The oxidation of methane was carried out in the following conditions: total pressure equal to 1.05 bar, inlet mixture composition CH_4:O_2:He = 13.9:2.8:83.3 (mol), temperatures from 650 to 950°C, gas space times τ_g ranging from 1.4 to 5 s, and pseudo catalytic contact times t_c from 0 to 60 mg s cm^{-3}. τ_g and t_c are defined according to the following relationships:

$$\tau_g = V/F \tag{1}$$

$$t_c = W/F \tag{2}$$

with V gas phase volume, W catalyst mass, F volumetric flow rate at the inlet of the reactor, measured at reaction temperature and pressure.

The oxidation of carbon monoxide was performed at 1.05 bar, 750°C and a gas space time equal to 3.6 s, either in the gas phase or in the presence of 8 catalyst pellets ($t_c = 115$ mg s cm^{-3}).

3. Results

3.1. Comparison of the selectivities of gas phase and catalytic reactions at iso-conversion of methane

Experiments were carried out at a gas space time $\tau_g = 2.3$ s for the gas phase reaction, and $\tau_g = 1.4$ s for the catalytic reaction in the presence of 1 catalyst pellet ($t_c = 5.6$ mg s cm^{-3}) in order to obtain the same methane conversion (7%). The results are shown in Table 1.

The selectivities in ethane, ethylene, acetylene, propane, propene and C_{2+} are nearly the same for the gas phase and the catalytic reactions. On the contrary, the selectivity in carbon monoxide is greater for the gas phase reaction than for the catalytic one, whereas the CO_2 selectivity is greater for the catalytic reaction than for the gas phase one. Of course, as it is the case for the C_{2+} selectivities, the CO_x selectivities are roughly equal for the gas phase and the catalytic reactions.

These observations suggest that hydrocarbons, carbon monoxide and carbon dioxide are formed by gas phase reactions, that carbon monoxide can be oxidized catalytically into carbon dioxide, and that carbon dioxide can also directly come from methane or methyl radicals by a catalytic route.

3.2. Comparison of the gas phase and catalytic oxidations of carbon monoxide

In order to confirm the results of the preceding section, experiments were carried out with reacting mixtures containing added carbon monoxide, both in the gas phase and in the presence of 8 catalyst pellets. Results are shown in Table 2.

Table 2
Reactivity of carbon monoxide: $p = 1.05$ bar; $T = 750°C$; $\tau_g = 3.6$ s. Carrier gas: helium

	(a)	(b)	(c)	(d)
Number of La_2O_3 catalyst pellets	0	8	8	8
t_c (mg s cm^{-3})	0	115	115	115
Reactants (mol fractions × 100)				
CH_4	0	0	14	14
O_2	3.6	3.5	3.0	2.9
CO	0.32	0.30	0	0.26
Reaction products (mol fractions × 100)				
CH_4			13	13
O_2	3.6	3.2	1.2	1.2
C_2H_6			0.16	0.16
C_2H_4			0.17	0.16
C_3H_6			6.3×10^{-3}	3.4×10^{-3}
CO	0.098	0.004	0.26	0.45
CO_2	0.22	0.32	0.67	0.77

If we compare the results of columns (a) and (b), we can see that the catalyst promotes the oxidation of CO into CO_2. The comparison of experiments (c) and (d) shows the influence of methane on carbon monoxide formation and oxidation. Again, we can conclude that carbon monoxide is catalytically oxidized into carbon dioxide. But we cannot exclude a catalytic route leading directly from methane to carbon monoxide.

3.3. Comparison of conversions, selectivities and yields for the gas phase and the catalytic oxidations

Three categories of experiments were carried out at the same gas space time $\tau_g = 5$ s:

Table 1
Comparison of selectivities at iso-conversion of methane: $p = 1.05$ bar; $T = 900°C$. CH_4:O_2:He = 13.9:2.8:83.3 (mol). Methane conversion: 7%

	τ_g (s)	t_c (mg s cm^{-3})	C_2H_6	C_2H_4	C_2H_2	C_3H_8	C_3H_6	CO	CO_2	C_{2+}	CO_x
Gas phase reaction	2.3	0	18	26	0.05	0.11	3.3	41	12	48	53
One La_2O_3 catalyst pellet	1.4	5.6	18	27	0.12	0.60	2.8	29	25	48	53

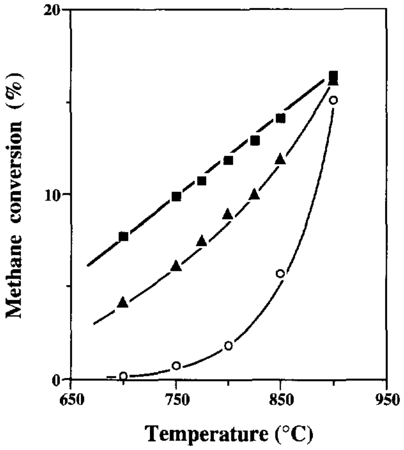

Fig. 2. Methane conversion vs. temperature. CH_4:O_2:He = 13.9:2.8:83.3 (mol). $\tau_g = 5$ s. ○, Gas phase reaction ($t_c = 0$); ▲, 1 La_2O_3 catalyst pellet ($t_c = 20$ mg s cm^{-3}); ■, 3 La_2O_3 catalyst pellets ($t_c = 60$ mg s cm^{-3}).

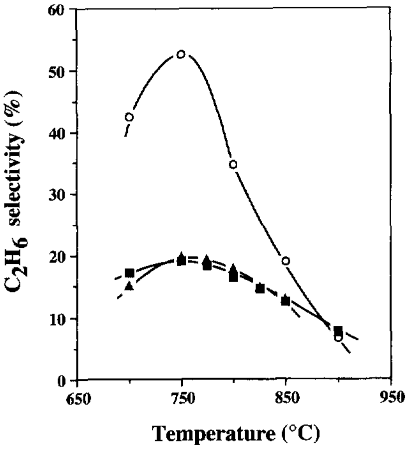

Fig. 3. Ethane selectivity vs. temperature. CH_4:O_2:He = 13.9:2.8:83.3 (mol). $\tau_g = 5$ s. ○, Gas phase reaction ($t_c = 0$); ▲, 1 La_2O_3 catalyst pellet ($t_c = 20$ mg s cm^{-3}); ■, 3 La_2O_3 catalyst pellets ($t_c = 60$ mg s cm^{-3}).

(a) The gas phase reaction without catalyst.

(b) The reaction with one La_2O_3 catalyst pellet.

(c) The reaction with three catalyst pellets.

Figs. 2 to 8 show the variations of (i) methane conversion, (ii) ethane, ethylene, carbon monoxide, carbon dioxide and C_{2+} selectivities and (iii) C_{2+} yield as a function of temperature, for the above a, b and c reaction categories.

Fig. 2 shows that methane conversion increases, at a given temperature, going from the gas phase reaction, to the reaction with one pellet, and to the reaction with three pellets. However, the differences between the conversions decrease when the reaction temperature increases. At 900°C, the three conversions are nearly equal.

Fig. 3 shows that ethane selectivity goes through a maximum in the three cases around 750°C. However, the gas phase reaction selectivity is greater than that of catalytic reaction. Here again, the selectivities are nearly equal at 900°C.

Fig. 4 displays a maximum for ethylene selectivity around 850°C. Below this temperature, the selectivity increases going from the gas phase reaction to the reaction with one pellet, then with three pellets. At 900°C, the three selectivities are nearly equal.

Fig. 5 shows that CO selectivity is always greater for the gas phase than for the catalytic reaction. The two types of reactions exhibit a minimum of CO selectivity between 750 and 800°C.

Fig. 6 shows that CO_2 selectivity is less for the gas phase than for the catalytic reaction,

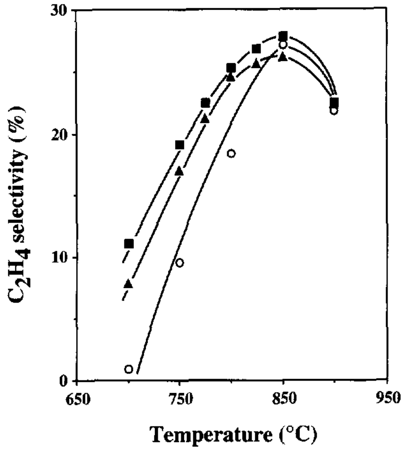

Fig. 4. Ethylene selectivity vs. temperature. CH_4:O_2:He = 13.9:2.8:83.3 (mol). $\tau_g = 5$ s. ○, Gas phase reaction ($t_c = 0$); ▲, 1 La_2O_3 catalyst pellet ($t_c = 20$ mg s cm^{-3}); ■, 3 La_2O_3 catalyst pellets ($t_c = 60$ mg s cm^{-3}).

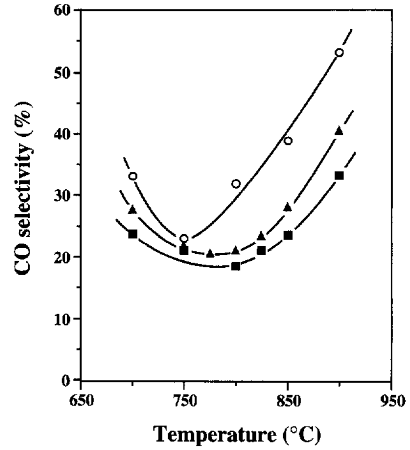

Fig. 5. Carbon monoxide selectivity vs. temperature. $CH_4:O_2:He = 13.9:2.8:83.3$ (mol). $\tau_g = 5$ s. ○, Gas phase reaction ($t_c = 0$); ▲, 1 La_2O_3 catalyst pellet ($t_c = 20$ mg s cm^{-3}); ■, 3 La_2O_3 catalyst pellets ($t_c = 60$ mg s cm^{-3}).

which is the contrary of the CO case. Again, there is a minimum in selectivity, around 850°C for the gas phase reaction, and probably above 950°C for the catalyzed reaction.

Figs. 7 and 8 are a combination of the preceding figures and simply confirm that the optimum temperature stands around 800°C. Around 900°C, the gas phase and catalyzed reactions proceed at the same rate (Fig. 1), with the same C_{2+} selectivity (Fig. 7) and yield (Fig. 8); the

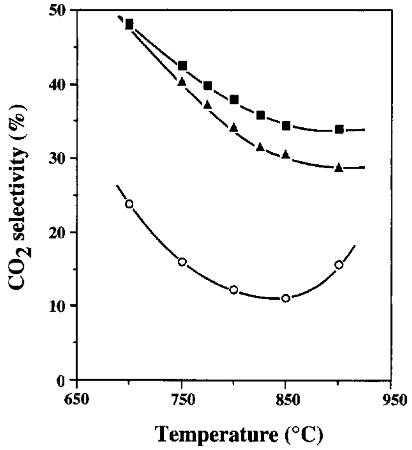

Fig. 6. Carbon dioxide selectivity vs. temperature. $CH_4:O_2:He = 13.9:2.8:83.3$ (mol). $\tau_g = 5$ s. ○, Gas phase reaction ($t_c = 0$); ▲, 1 La_2O_3 catalyst pellet ($t_c = 20$ mg s cm^{-3}); ■, 3 La_2O_3 catalyst pellets ($t_c = 60$ mg s cm^{-3}).

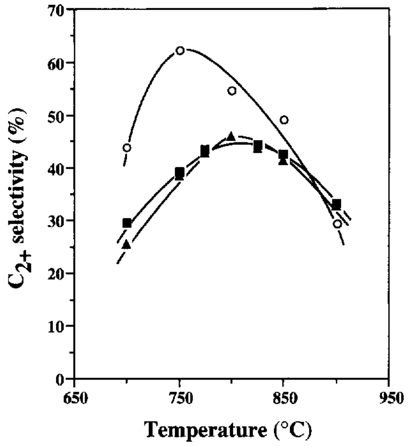

Fig. 7. C_{2+} selectivity vs. temperature. $CH_4:O_2:He = 13.9:2.8:83.3$ (mol). $\tau_g = 5$ s. ○, Gas phase reaction ($t_c = 0$); ▲, 1 La_2O_3 catalyst pellet ($t_c = 20$ mg s cm^{-3}); ■, 3 La_2O_3 catalyst pellets ($t_c = 60$ mg s cm^{-3}).

catalyst makes CO selectivity decrease (Fig. 5) and CO_2 selectivity increase (Fig. 6).

4. Discussion

We shall discuss our experimental results by addressing the following questions: (i) the state of mixing of the gas phase; (ii) the reaction temperature; (iii) the rate limitations due to

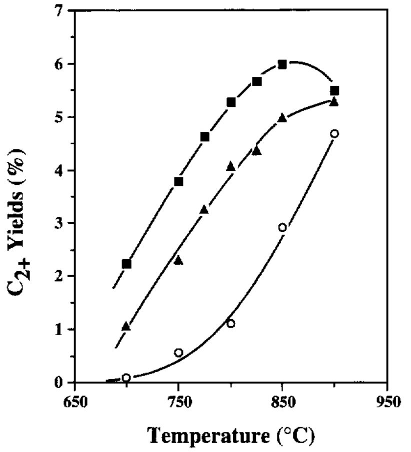

Fig. 8. C_{2+} yield vs. temperature. $CH_4:O_2:He = 13.9:2.8:83.3$ (mol). $\tau_g = 5$ s. ○, Gas phase reaction ($t_c = 0$); ▲, 1 La_2O_3 catalyst pellet ($t_c = 20$ mg s cm^{-3}); ■, 3 La_2O_3 catalyst pellets ($t_c = 60$ mg s cm^{-3}).

external and internal diffusions; (iv) the gas-phase reaction mechanism; (v) the surface reaction mechanism.

4.1. The state of mixing of the gas phase inside the jet-stirred reactor

Our reactor has been designed according to the rules defined by David and Matras [28], and established from residence time distribution experiments. The perfect macromixing was confirmed by kinetic experiments performed on well-known gas phase reactions [24,29].

4.2. Reaction temperature

This point was already discussed in our previous paper [27], where results were reported for a reaction occurring at different temperatures for the gas phase and for the catalyst pellets. In the present work, the temperatures of the gas phase and of the catalyst pellets are roughly equal and defined as the reaction temperature.

4.3. External and internal diffusion

A work in progress in our laboratory [30,31] has established from experiments and chemical reaction engineering correlations that the reaction rate is only limited to a small extent by the external transport from the bulk of the gas phase to the catalyst surface, but is in a strong internal diffusion regime, which means that the catalyst surface available to reactants is only the apparent geometric surface. In view of these conclusions our reactor appears as a very convenient tool for studying hetero–homogeneous reaction kinetics.

4.4. Gas phase reaction mechanism

A comprehensive reaction mechanism, involving 57 species and 835 elementary reactions has been built up and validated in our laboratory [32]. These reactions do occur in the temperature range of the present work. Simple conclusions derived from a model of this complexity are not easy to reach without the help of numerical simulations. Such simulations show that in our conditions, ethane and carbon monoxide come mainly from methyl radicals, that ethylene comes from ethane and is a rather stable product, and that carbon dioxide is produced in lesser amounts than carbon monoxide, and comes mainly from CO oxidation [25].

4.5. Surface reaction mechanism.

Our results can be interpreted qualitatively on the basis of the following reactions

Surface initiation processes

$$CH_4(g) \rightarrow \cdot CH_3(g) \tag{3}$$

$$C_2H_6(g) \rightarrow \cdot C_2H_5(g) \tag{4}$$

$$C_2H_4(g) \rightarrow \cdot C_2H_3(g) \tag{5}$$

Surface oxidation processes

$$\cdot CH_3(g) \rightarrow CO_2(g) \tag{6}$$

$$CO(g) \rightarrow CO_2(g) \tag{7}$$

Reaction (3) explains the primary acceleration of the global reaction due to the catalyst, and observed in Fig. 2 below 900°C.

If we assume that gas phase initiation reactions have higher activation energies than surface initiation reactions, then we can understand why the methane conversion of gas phase and catalytic reactions become closer and closer when the temperature increases (Fig. 2). Also we cannot completely rule out a limitation by the external diffusion at the highest temperatures.

Reaction (4) accounts for a smaller ethane selectivity in the catalytic than in the gas phase reaction, as shown in Fig. 3.

Symmetrically, the ethylene selectivity must be higher for the catalytic than for the gas phase reaction, due to the easy gas phase decomposition of ethyl radical

$$\cdot C_2H_5 \rightarrow C_2H_4 + \cdot H \tag{8}$$

as observed in Fig. 4.

Let us notice that the $\cdot H$ free radicals generated by reaction (8) could enter in an homogeneous branching process

$$\cdot H + O_2 \rightarrow \cdot OH + \cdot O \cdot \qquad (9)$$

This branching reaction (9) could have a large accelerating effect on the global reaction.

Reaction (5) explains the formation of acetylene due to the subsequent decomposition of the vinyl radicals

$$\cdot C_2H_3 \rightarrow C_2H_2 + \cdot H \qquad (10)$$

This increase in acetylene selectivity due to the catalyst is shown in Table 1.

The open sequence of surface reactions (6) and (7) can explain the higher CO selectivity and the lower CO_2 selectivity observed in Table 1, Figs. 5 and 6 for the gas phase reaction with respect to the catalytic one.

Surface reaction (7) accounts for the results of Table 2; in this reaction the catalyst transforms CO into CO_2.

Finally, the results of Table 1 seem to show that C_2H_5 free radicals and C_2H_4 molecules are not readily oxidized on the catalyst, since the C_2 selectivities are roughly equal for the gas phase and the catalytic reactions.

As a conclusion, methyl free radicals appear to be the main source of C_2 species and CO_x, both by gas phase reactions and by surface reactions (3) to (7). However, we do not claim that the above surface mechanism is comprehensive; it is rather a minimal set of reactions, able to explain our experimental results.

5. Conclusions

By using a continuous flow stirred tank reactor operated with a constant gas phase volume and a variable number of catalyst pellets, it has been possible to study in the same conditions both the gas phase and the catalyzed oxidation of methane and carbon monoxide.

The comparison of the characteristics of the reaction, mainly methane conversion and selectivities, have enabled us to suggest a reaction mechanism, involving both a detailed gas phase reaction mechanism, and a small set of surface reactions. These surface reactions include initiation reactions, accounting for the acceleration of the reaction due to the catalyst, and oxidation reactions of methyl radicals and carbon monoxide, accounting for the changes in selectivities.

In this mechanism, methyl free radicals appear to be the crossroad leading both to C_2 and CO_x species.

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