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Hetero-homogeneous processes involved in oxidative conversion of methane, ethane and hydrocarbon mixtures over basic oxides

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Abstract

The conversion, selectivities and yields of methane-oxygen and ethane-oxygen mixtures over Li/MgO catalysts have been compared. The differences which are observed are likely to be due to the much shorter life time of ethyl radicals which are rapidly transformed into ethylene, thus preventing subsequent heterogeneous deep oxidation. Data on the oxidative dehydrogenation of ethane over rare earth oxides are also reported. The insensibility of this reaction to the chemical nature of these solids contrasts with what is observed for the oxidative coupling of methane. This is also accounted for by the short life time of ethyl radicals. When mixing methane with another hydrocarbon, cross coupling occurs only if the hydrocarbon C-H bond strength is relatively small (propene, toluene) suggesting that radicals are involved. $^{13}CH_4$ experiments have shown that for the case of toluene, the reaction proceeds via the addition of a C1 block from CH_4. The selectivity of cross coupling compared to homo-coupling is also explained in terms of life time of radicals.

1. INTRODUCTION

Catalysis over the new class of basic catalysts developed for oxidative coupling of methane opens a promising field of investigation for the valorization of heavier hydrocarbons and provides insight into the complex reaction mechanisms. This paper reviews some data available in the literature and presents new results from our laboratory on the oxidative conversion of C_1 and C_2 hydrocarbons taken separately, or mixed with other hydrocarbons to achieve as far as possible cross coupling reactions.

2. EXPERIMENTAL

Most of experiments were carried out over a Li/MgO catalyst which was prepared according to the method described in [1]. The solid was stabilized by running the oxidative coupling reaction at 800°C. After reaction the BET surface area was $0.4 m^2 g^{-1}$ and the Li wt content 4 %. Complementary experiments were carried out over rare earth oxides (REO) provided by Rhône Poulenc Minérale Fine (purity 99.9 %. BET surface areas over the range $2\text{-}6 m^2 g^{-1}$) and Na/ZrO_2

obtained by impregnation of either a flame zirconia (BET surface area, $70 m^2 g^{-1}$, chlorine content 1 wt-%) or of a precipitated zirconia (BET surface area, $60 m^2 g^{-1}$) with a solution of Na_2CO_3.

The catalytic activity experiments were performed in a fixed bed quartz reactor at atmospheric pressure. The catalyst (ca.90 mg unless otherwise specified) was deposited on a quartz wool situated in a quartz tube. The typical reaction conditions are summarized in Table 1.

Table 1
Flow rates in catalytic reactions

Catalysts	Flow rates (ml/mn)					
	O_2	CH_4	C_2H_6	Benzene	Toluene	He
Li/MgO	1.2	2.4	2.4	0.3	0.3	19
REO	1.8	-	4.8	-	-	54

3. RESULTS AND DISCUSSION

3.1. Oxidative conversion of methane and ethane

The oxidative coupling of methane (OCM) and dehydrogenation of ethane (ODE) over Li/MgO catalysts have already been compared in a previous work [2]. We have shown that whatever the temperature the ODE rate is larger than that of CEM. This result has been confirmed by several groups [3-6]. This is in good agreement with the idea that both reactions proceed via radical formation and that this step is rate determining as suggested by kinetic isotopic effects : as a matter of fact, the C-H bond strength is 104 and 98 kcal/mol for CH_4 and C_2H_6, respectively, suggesting strongly that ethyl radical formation is faster. Difference of 6 kcal/mol between transition states would lead to a rate ratio of 19 at 750°C. In this work, the rate ratio is found to be 4.5 at this temperature (Tables 3, 5), in agreement with recent results [5,6].

It should be noted that for these conditions, in the absence of catalyst, ODE proceeds to an appreciable extent in the gas phase. We have thus measured this ratio at 600°C in conditions where gas phase reactions do not occur in the absence of catalyst does not occur in the absence of catalyst. Over 500 mg of Li/MgO, with $P_{HC} = 7.8$ kPa, $P_{O2} = 4.6$ kPa, $P_{HC} = 87{,}6$ kPa and a total flow rate of 60 ml/mn, conversions of ethane and methane are 24 and 5.8 %, respectively : the corresponding rate ratio is found to be 4.1. This figure is quite similar to that obtained at 750°C. The corresponding difference of energy between transition states, 3 kcal/mol is smaller than the difference of bond strengths and we have no explanation for this discrepancy.

The nature of reaction products reveals a fundamental difference of behaviour between OCM and ODE. The former reaction leads mainly to dimerization while the latter to dehydrogenation [2]. The yield of ethylene obtained in ODE is notably larger than the C_2 yield of OCM. For instance, at 680°C a conversion 51 % and a selectivity towards ethylene of 67 % have been reported over Li/MgO [12]. The corresponding yield, 34 %, exceeds the C_2 yield obtained over the same catalyst in OCM by a factor of a least two. Comparable yields of ethylene in ODE over Li/MgO were observed by Morales et al [3], Kolts [4], Kasteren et al [5] and Nelson et al [6].

In the course of this study, we have confirmed and quantified with more accuracy these results : at 750°C, the oxidative conversion of methane yields mainly C_2 hydrocarbons (S_{C2+} = 59 %, Y = 8.6 %, Table 3) ; in contrast the oxidative conversion of ethane in the same conditions gives small amounts of dimers (S_{C3+} = 3 %) and is very selective in ethylene (S = 73 %) : the corresponding yield is 47 % (Table 5). The same tendency is observed at lower temperature : at 600°C over 500 mg Li/MgO, the selectivity towards C_{2+} in OCM is 6.4 % while for ODE, selectivities towards ethylene and C_{3+} are 53 and 3.3 %, respectively.

This situation probably arises from the difference of life time between CH_3 and C_2H_5 radicals [3]. This is strongly suggested by the experiments of radical detection in the gas-phase by matrix isolation EPR [7,8] : in OCM conditions where large amounts of C_2H_6 are formed, CH_3 radicals are easily detected at several cm far from the catalytic bed while much smaller amounts of C_2H_5 are observed.

Ethyl radicals are likely readily transformed into ethylene either before desorbing in the gas phase [5] or just after desorption [2-3] according to the following equations :

C_2H_5 ----> $C_2H_4 + H$ (1)
$C_2H_5 + O_2$ ----> $C_2H_4 + O_2H$ (2)
$C_2H_5 + C_2H_5$ ----> $C_2H_4 + C_2H_6$ (3)

As a consequence, the probability of a C_2H_5 radical colliding with the solid surface is smaller than that of CH_3 radicals. The subsequent heterogeneous deep oxidation of C_2H_5 (or corresponding peroxyradicals) is thus less probable.This should lead to a better selectivity and better yield towards the hydrocarbon reaction products, as is observed.

Rare earth oxides with variable degree of oxidation (3+, 4+) such as Ce, Pr and Tb are non selective towards C_{2+} hydrocarbons in OCM while the others are selective [9-10]. In recent works [11-12] we have shown that when carrying out ODE over Pr_6O_{11}, the selectivity towards ethylene is comparable to that obtained over La_2O_3, Sm_2O_3 and Gd_2O_3 (in Ref. 12 some figures in Table 1 were shifted making data unclear). We have extended this observation to CeO_2, another non selective catalyst in OCM (Table 2).

Table 2
Activity and selectivity data for the oxidative dehydrogenation of ethane over rare earth oxides at 500°C.

Oxides	rate of C_2H_6 consumption (10^{-8}mole/m^2/s)	^{a}Total Conversion (%)	SC_2H_4 (%)	SCO_2 (%)	SCO (%)	SCH_4 (%)
La_2O_3	15	2	8	48	43	6
Sm_2O_3	110	10	9	54	37	0.3
Gd_2O_3	155	17	10	46	44	0.5
CeO_2	26	2	15	83	2	-
Pr_6O_{11}	167	8	6	94	0	0.1

^{a} $P_{C_2H_6}$: 8 kPa, P_{O_2} : 3.1 kPa, P_{He} : 90.2 kPa, flow rate 60 ml/mn.

For these conditions ODE does not occur to an appreciable extent in an empty reactor at T < 630°C.

In this paper, the remarkably low selectivity towards CO of CeO_2 and Pr_6O_{11} will not be discussed ; we will focus on the selectivity towards ethylene which is not very sensitive to the redox properties of rare earth oxides ; we have evidence that this feature is not altered at higher temperatures for the case of Pr_6O_{11} (12).

The difference of behaviour between OCM and ODE towards rare earth compounds lies likely in the difference of life time of ethyl and methyl radicals, as already discussed : ethyl radicals are rapidly transformed into ethylene before colliding with a solid surface, thus explaining why SC_2H_4 in ODE is little sensitive to the nature of the solid surface. In contrast, long-lived methyl radicals can be deeply oxidized by successive surface collisions. Ce and Pr oxides would be more efficient for deep oxidation than the other rare earth oxides. Referring to a proposal by Dubois and Cameron [13] according to which n-type semiconductors (Ce, Pr and Tb oxides) are non selective in OCM, it can inferred that the nature of semiconductivity (p or n type) has not a direct bearing on the rate of formation of radicals from hydrocarbons while n-type semiconductors surfaces would be particularly efficient for the deep oxidation of radicals coming from the gas phase.

In this paper we will not consider the oxidative conversion of ethylene which has been dealt with in another paper [14]. We will just mention that Li/MgO catalysts inhibits the gas phase oxidation of ethylene, likely by trapping chain-carrier radicals (O_2H, OH), and that the reaction products consist mainly in CO_x and small amounts of CH_4, C_2H_6 and C_{3+} hydrocarbons.

3.2. Oxidative conversion of hydrocarbon mixtures

i) Methane + alkenes : As far as we know, the only attempt to react a methane + ethene mixture with oxygen over Li/MgO is reported in [15] : no clear conclusions concerning the possibility of cross coupling can be drawn from this work. It can be speculated, however, that owing to the small quantity of C_3 hydrocarbons which is observed when carrying out OCM, the cross coupling does not occur to an appreciable extent. This is in good keeping with the high vinylic C-H bond strength (100 kcal/mol).

In contrast with what is observed on usual OCM catalysts, it has been claimed that over Na+ doped zirconia the oxidative conversion of methane leads mainly to C_3 hydrocarbons [16] suggesting that the methylation of C_2 hydrocarbons is occurring. To verify this obervation, we have prepared two Na/ZrO_2 samples, but we were unable to reproduce the catalytic results. Obviously further experiments are needed to clarify this situation.

The methylation of propene from the oxidative conversion of propene + methane mixture was found to occur easily over La_2O_3 and Na/La_2O_3 [17]. No methane coupling was observed. This reaction is likely to proceed via allylic radicals C_3H_5 ; as a matter of fact the allylic C-H bond strength is only 89 kcal/mole. Allylic radicals would combine with methyl radicals giving C4 hydrocarbons.

ii) Methane + alkanes : The oxidative conversion of toluene-methane gas mixture to ethylbenzene and styrene has extensively been investigated by Khcheyan et al [18] either in the gas phase or in the presence of oxides (Bi, Mo, Zn, Fe, Co, Ni, Ag, Ti). Furthermore, La_2O_3 promoted with alkali halides was shown to be active and selective for this reaction : yield and selectivity towards C_8 of 11.6 and 31.4 % respectively, were reported [19]. Similar results were obtained on Li/MgO and Li/Y_2O_3-CaO catalysts [20]. An interesting feature of this reaction is that cross-coupling between methane and toluene occurs selectively compared with the homocoupling of methane and toluene, as for the case of the propene + methane mixture [17]. These trends were confirmed by our study over Li/MgO catalysts (Table 3). The C_8 yield thus obtained is 14.5 % and no C_2, C_{14} hydrocarbons are detected. In the absence of catalysts the yield of C_8 hydrocarbons is much smaller, pointing to the efficiency of the catalyst for cross coupling ; methane seems to play an important role in the catalytic formation of C_8 hydrocarbons since the oxidative conversion of toluene alone leads to much smaller, C_8 yields (Table 3). As already suggested by isotope labelling experiments carried out with $C_6H_5CD_3$ and CH_4 [20], we have confirmed that C_8 hydrocarbons results from the addition of a C_1 block originating from CH_4 : $^{13}CH_4$ reacts with unlabelled toluene in the presence of catalyst, giving mainly $^{12}C_7\,^{13}C_1$ hydrocarbons.

Table 3
Oxidative conversion of methane + toluene at 750°C over Li/MgO or in the gas phase.

Reacting mixtures	Conversion (%)			Selectiv. (%)				Yields (%)		
	CH_4	O_2	TL	C_2	BZ	2BZ	ST	C_2	BZ	EBZ+ST
CH_4, TL, O_2										
*empty react	1.5^a	23.0	32.5	-	2.6	2.7	0.5	-	0.8	1.1
* Li/MgO	6.1	54.1	55.2	-	3.1	12.2	14.1	-	1.7	14.5
TL, O_2										
*empty react	32.8	48.3	-	-	5.1	1.0	0.3	-	2.5	0.6
* Li/MgO	-	56.1	60.6	-	4.3	2.2	2.8	-	3.0	1.4
CH_4, O_2										
*empty react	-	-	-	-	-	-	-	-	-	-
* Li/MgO	14.6	-	-	58.6	-	-	-	8.6	-	-

a this figure is negative since extra methane is formed from toluene reaction.

The very same experiment carried out in an empty reactor leads mainly to $^{12}C_8$ hydrocarbons, suggesting than the non-catalytic formation proceeds via another route ; it likely involves phenyl radical formation, coupling to C_{14} hydrocarbons and subsequent cracking of the dimer into C_6 and C_8 hydrocarbons. This is confirmed by the fact that the yield of benzene which is observed is nearly equal to that of C_8 hydrocarbons when reaction proceeds in the gas phase.

iii) Methane or ethane + benzene : When replacing toluene which gives easily benzyl radicals (the C-H bond strength of the methyl group is 85 kcal/mol) by a much more stable molecule such as benzene (C-H bond strength, 110 kcal/mol), the cross coupling reaction occurs only to a minor extent (Table 4), while oxidative coupling of methane takes place as a first approximation, without being modified by the presence of benzene. The latter molecule can be considered as inert towards OCM. Similar conclusions can be drawn from experiments carried out with benzene + ethane mixtures, as can be seen in Table 5.

From these results, it can be inferred that cross coupling requires radical formation from both hydrocarbons, followed by radical recombination. For the case of methane + toluene, the recombination reaction can be written in the following way :

$$C_6H_5 - CH_2 + CH_3 \rightarrow C_6H_5 - C_2H_5 \qquad (4)$$

compared with the analogous homocoupling reaction :

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad (5)$$

it has been observed that reaction (4) occurs selectivity. This can be explained assuming that in contrast with reaction (5), reaction (4) does not require a third body to accommodate the reaction energy release, owing to the large number of vibrators in ethylbenzene. In other words life time of benzyl and methyl radicals is likely very short in cross coupling reactions. This situation is favourable to avoid heterogeneous deep oxidation of radicals and to obtain good selectivities in C_8 hydrocarbons. The homocoupling of benzyl radicals would not occur owing to their much smaller concentration compared to that of methyl radicals.

The reaction between toluene and ethane in lieu of methane gives propylbenzene as main product [19]. This result indicates that the life time of ethyl and benzyl radicals in cross coupling reaction is smaller than that of ethyl radicals in ODE. As a matter of fact, the reverse situation would lead to the formation of large amounts of ethylene, in contrast with what is observed.

Table 4
Oxidative conversion of benzene + methane at 750°C over Li/MgO.

Reacting mixtures[a]	Conversion (%)			Selectivity/CH_4 (%)		Selectivity/BZ (%)	
	CH_4	O_2	BZ	C_{2+}	CO_x	TL	ST + EBZ
$CH_4 + O_2$	11	17	-	76	24	-	-
$CH_4 + BZ + O_2$	16	58	9	78	22	3.1	0.6

[a] carbon mass balance, 0.4 and 3.5 %, respectively.

Table 5
Oxidative conversion of benzene + ethane at 750°C over Li/MgO.

Reacting mixtures[a]	Conversion (%)			Selectivity/C_2H_6 (%)				Selectivity/BZ (%)		
	C_2H_6	O_2	BZ	C_1	C_2H_4	C_3	CO_x	TL	ST	EBZ
$C_2H_6 + O_2$	65	76	-	4	73	3	21	-	-	-
$C_2H_6 + BZ + O_2$	59	93	8	5	81	2	17	1.9	6.3	0.3

[a] carbon mass balance, 0.8 and 3.0 %, respectively.

4. CONCLUSIONS

From literature inspection and data reported in this work, the following conclusions can be drawn :

i) the fundamental difference of behavior between oxidative conversion of methane and of ethane which both proceed via radical formation can be attributed to the difference of life-time and fate of the corresponding radicals : long-lived methyl radicals can either dimerize in the gas phase or deeply oxidize on solid surface while ethyl radicals are readily transformed into ethylene.

ii) this hypothesis is also in good keeping with data obtained by carrying out oxidative dehydrogenation of ethane over rare earth compounds : the selectivity towards ethylene is found to be insensitive to the redox properties of these solids, in contrast with the selectivity towards C_{2+} in oxidative coupling of methane.

iii) surface-assisted cross coupling reaction between methane and another hydrocarbon occurs only when the C-H bond strength of the latter is low (this is the case of propene and toluene, in contrast to benzene). The reaction takes place via the addition of a methyl group originating from methane and of the other hydrocarbon radical. This step is very rapid compared to homocoupling of methyl radicals, due to the large size of allyl and phenyl radicals.

iv) catalysis over the new class of basic catalysts developed in the last decennium appears to be promising for processing various hydrocarbons, either separate, or mixed together. Moreover, it helps to better understand mechanisms of hetero-homogeneous.

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