# Catalytic Oxidative Coupling of Methane and Surface Potential Measurements over Pure Samarium Oxide: Evidence for a Heterogeneous C<sub>2</sub> Yield Limitation

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The oxidative coupling of methane has been studied over a pure samarium oxide catalyst by classical tests and surface potential measurements. This latter technique provides some interesting information on the nature of the oxygen species adsorbed over the catalytic surface and on the kinetic parameters of the reactions which take place on the solid. In our experimental conditions ( $P_{CH_d}/P_{O_2} = 2$ ) the negatively adsorbed oxygen species involved in the catalytic process is O<sup>-</sup> below 400 °C and O<sup>2-</sup> at higher temperature. The reactivities of the hydrocarbons follow the order  $C_2 \ge$  methane, whatever the temperature. The activation energy obtained from classical tests (95 kJ mol<sup>-1</sup>) is very close to that obtained from surface-potential experiments. The results lead us to propose that an important part of the  $C_2$  yield limitation is due to the heterogeneous process.

Because of the high percentage of methane in the large reserves of natural gas throughout the world,<sup>1</sup> the transformation of CH<sub>4</sub> into higher hydrocarbons is becoming a real technical and economical challenge. Much research is devoted to this end, *i.e.* to obtain acceptable conversions and selectivities for CH<sub>4</sub> transformation, but unfortunately, the  $C_2$  yield has never been found in excess of 25–30%, whatever the catalyst and the experimental conditions used. From a theoretical approach, Labinger and Ott<sup>2</sup> anticipated this experimental limit by forecasting an upper limit of 30%. Recently, McCarty et al.<sup>3</sup> have confirmed that there is a single-pass limit of ca. 25% yield regardless of the catalyst and reaction conditions. Usually, this limitation is attributed either to the homogeneous phase reactions or to heterogeneous processes.<sup>4</sup> Burch and Tsang<sup>5</sup> have proposed that the limitation could be violated by placing an inert substance, SiC, in the dead volume of the reactor. Other authors propound that the  $CO_x$  formation takes place over the catalytic surface.6-9

The aim of this work is to add to this debate by comparing the reactivities of methane, ethane and ethene, directly on the  $Sm_2O_3$  surface by the help of surface-potential measurements. This technique provides information about the nature of the negatively charged oxygen species involved in the oxidation reaction and adsorbed on the catalytic surface and on the kinetic parameters during the transformation of any reactant. The results will be compared with those we obtained from classical tests performed on the same catalyst.

#### Experimental

# **Catalytic Activity**

The tests were carried out in a conventional single-pass flow system. The reactor comprised a fused alumina tube, o.d. 200 mm, i.d. 150 mm and 50 cm length, mounted vertically in a tubular furnace. The catalyst sample  $(1 \text{ g}, 0.5 \text{ cm}^3)$  was

located 40 cm from the top of the reactor. The reactant-gas stream was 13% (v/v) hydrocarbon and 6.5% (v/v) oxygen in helium at a total pressure of 1 atm;† the total flow rate was 25 cm<sup>3</sup> min<sup>-1</sup> (down-flow) and the reaction temperature was in the range 600–750 °C. The products were analysed using a gas-sampling valve connected directly to the reaction flow system and separated with Porapak Q and Carbosieve columns in a gas chromatograph. Samples of samarium oxide were obtained from Fluka (purity > 99.9%).

### **Surface Potential Measurements**

The surface potential of the samples was measured by the vibrating condenser method with graphite as a reference electrode. Details of the measurements have already been given elsewhere.<sup>10</sup> The samples were deposited on the measuring electrode in a cell connected to a gas-flow system which allowed controlled streams of different gases (Brooks flowmeters) and their mixtures to pass through the apparatus. The surface potential values are relative to the graphite electrode potential:  $V = V_{\text{graphite}} - V_{\text{sample}}$  and an increase of the value of the potential difference indicates that the surface becomes more negative.

## **Results and Discussion**

#### **Catalytic Activity Measurements**

Table 1 summarizes methane conversions and  $C_2$  selectivities obtained on pure  $Sm_2O_3$  at the steady state within the 620–750 °C temperature range. The  $C_2$  yield increases with the temperature to reach *ca*. 10% at 750 °C. This yield is equal to or slightly lower than the values reported in the literature.<sup>5,11</sup>

Thus,  $Sm_2O_3$ , although well known to be one of the best rare-earth-metal oxide catalysts for the oxidative coupling of methane, especially the cubic form,<sup>12</sup> gives a relatively low  $C_2$ 

 $\dagger 1 \text{ atm} = 103 325 \text{ Pa.}$ 

**Table 1** Conversion and selectivity of the oxidative coupling of methane over  $Sm_2O_3^a$ 

T/°C	CH <sub>4</sub> conversion (%)	selectivity (%)							
		СО	CO <sub>2</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub>	$C_2$	$P_{\rm CH_4}/P_{\rm C_2H_6}$	$P_{C_2H_4}/P_{C_2H_6}$
620	10.4	15.5	55	6.8	9.2	13.5	1.66	75.4	1.33
700	26	21	53	6	12.5	7	4.81	68	2
750	43	30	50	9	11		8.6	31.4	1.15

 $^{a}$  CH<sub>4</sub> : O<sub>2</sub> : He = 24 : 12 : 64.

#### Surface Potential Measurements

#### Oxygen Atmosphere

The surface potential values of the Sm<sub>2</sub>O<sub>3</sub> samples under an oxygen-argon mixture ( $P_{O_2} = 0.05$  atm) have been measured in the temperature range 150-450 °C and are reported in Fig. 1. The curve representing V vs. T shows three temperature regions where the potential values are constant or exhibit small evolutions: 150-230 °C; 270-330 °C and > 360 °C. Between these regions, the potential values rise rapidly, the surface becoming more negative when the temperature increases.

Under oxygen, there is an equilibrium between the oxygen species adsorbed in the surface and the gaseous dioxygen [eqn. (1)]:

$$O_2 + n e^- \Leftrightarrow O_{2(ads)}^{n-}$$
 (1)

The mass action law is:

$$K = \frac{[O_2^{n-}]}{P_{O_2} \exp(-neV/k_{\rm B}T)}$$

where  $k_{\rm B}$  is Boltzmann's constant, T is the absolute temperature, e the electron charge and n the number of electrons transferred from the solid to the adsorbed species during the sorption process. From this equation, we can draw a relation between the potential value and the partial pressure of dioxygen [eqn. (2)]:

$$V = \frac{kT}{ne} \ln P_{O_2} + \text{constant}$$
(2)

The value of n depends on the equilibrium between the gaseous molecule and the adsorbed oxygen species. The possibilities are:

$$n = 1$$

$$n = 2$$

$$n = 4$$

$$O_2 + e^- \Leftrightarrow O_{2(ads)}^-$$

$$O_2 + 2 e^- \Leftrightarrow 2O_{(ads)}^-$$

$$O_2 + 4 e^- \Leftrightarrow 2O_{(ads)}^{2-}$$

The slope of the straight lines obtained by plotting V vs. ln  $P_{O_2}$  at constant temperature, gives rise to the *n* values and, consequently, to the nature of the adsorbed oxygen species. On Sm<sub>2</sub>O<sub>3</sub>, in our experimental conditions, the single atomic charged species O<sup>-</sup> is the dominant species within the 250-



Fig. 1 Surface potential variations of pure  $\text{Sm}_2\text{O}_3$  vs. temperature under an oxygen atmosphere:  $P_{\text{Ar}} = 1$  atm ( $\Box$ );  $P_{\text{Ar}} = 0.95$  atm,  $P_{\text{O}_2} = 0.05$  atm ( $\triangle$ )

Table 2 Oxygen species involed on the surface of  $\text{Sm}_2\text{O}_3$  treated under an oxygen-argon atmosphere as determined by surface potential measurements

T/°C	n	oxygen species
180	0.86	$O_2^-$
270	2	0 <sup>-</sup>
>360	3.7	O <sup>2-</sup>

 $350 \,^{\circ}\text{C}$  temperature range, whereas  $O^{2-}$  species appear at higher temperatures (Table 2).

## Interaction between Hydrocarbons and the Oxygen Species

On a surface saturated with adsorbed oxygen, the hydrocarbons react rapidly. As the potential values depend on the negatively adsorbed oxygen species concentration, the method used allows the kinetic parameters of the reaction between any hydrocarbon and these active species to be determined.

In a general manner we have [eqn. (3)]:

$$HC + O_{2(ads)}^{n-} \xrightarrow{k_{HC}} ' products'$$
(3)

and the reaction rate is:

$$v = -\frac{d[O_2^{n^-}]}{dt} = k_{\rm HC} P_{\rm HC}[O_2^{n^-}]$$
(4)

Hence,

$$v = -\frac{\mathrm{d}V}{\mathrm{d}t} = k_{\mathrm{HC}} P_{\mathrm{HC}} V \tag{5}$$

By integrating these equations, the following relationship can be obtained:

$$\ln(V_{\infty} - V) = -k_{\rm HC} P_{\rm HC} t \tag{6}$$

where  $V_{\infty}$  is the potential value in the absence of adsorbed oxygen species on the surface.

The  $k_{\rm HC}$  values can be determined from these equations. The reaction rates depend on the temperature, but the C<sub>2</sub> compounds react faster than methane whatever the temperature used (Table 3). Ethane reacts about eight times as fast as methane. The relative reaction rates of ethane and ethene are in favour of ethene at low temperature (Fig. 2); this is not necessarily true at high temperature, but the variation of the surface potential values becomes too fast to determine the  $k_{\rm HC}$  values. However, Burch and Tsang<sup>5</sup> have shown that, on Sm<sub>2</sub>O<sub>3</sub>, the C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub> conversion order is reversed when the temperature increases. Nevertheless, the reactivity observed by surface potential changes, considered as a strictly heterogeneous process, follows the order C<sub>2</sub>  $\gg$  methane.

This order is in agreement with the results of catalytic tests published in the literature over various solids, including  $\text{Sm}_2\text{O}_3$ .<sup>5,13</sup> In their theoretical model, Labinger and Ott<sup>2</sup> and Labinger<sup>14</sup> assume that the relative rates must be ethene : ethane : methane = 1.4 : 1.9 : 1.0; Burch and Tsang<sup>5</sup> have found in their experiments 3.4 : 5.5 : 1.0; that is to say a ratio of ethane to methane of, respectively, 1.9 and 5.5. On

**Table 3** Rate constants and partial pressure ratio of methane to ethane over oxidized  $Sm_2O_3$  samples under a hydrocarbon atmosphere as determined by surface potential measurements

$T/^{\circ}\mathbf{C}$	$k_{C_2H_6}/k_{CH_4}$	$P_{\mathrm{CH_4}}/P_{\mathrm{C_2H_6}}$
540	9.5	19
585	8	16
612	7.5	15



**Fig. 2** Surface potential variations of pure  $\text{Sm}_2\text{O}_3$  vs. time under hydrocarbon atmosphere: ( $\Box$ ) CH<sub>4</sub>, 0.05 atm; ( $\triangle$ ) C<sub>2</sub>H<sub>6</sub>, 0.05 atm; ( $\bigcirc$ ) C<sub>2</sub>H<sub>4</sub>, 0.05 atm.  $T = 270 \text{ }^{\circ}\text{C}$ 

rare-earth-metal oxides,  $k_{\text{ethane}}/k_{\text{methane}}$  is 3.8 at 510 °C.<sup>13</sup> The ratio obtained from surface-potential measurements varies from 7 to 10 depending on the temperature (Table 3).

On the other hand, note that the activation energy value, determined by plotting  $\ln(dV/dt)$  vs. 1/T, is 95 kJ mol<sup>-1</sup> for the overall CH<sub>4</sub> reaction, which is exactly the same value as that obtained by catalytic tests.

## Interaction Sm<sub>2</sub>O<sub>3</sub>-Methane-Oxygen Mixtures

When the catalysts are exposed to reaction mixtures, the surface potential decreases to reach stable value in a few hours. Such steady-state surface potentials depend on the initial ratio  $(P_{O_2}/P_{CH_4})$  and are related to the oxygen species which participate in the oxidation process. The initial decrease of the surface potential is due to a redox mechanism of the superficial sites:<sup>15,16</sup>

$$HC + S_{ox} \rightarrow \text{`products'} + S_{red} + ne^-$$
 (7)

$$O_2 + S_{red} + ne^- \rightarrow S_{ox} \tag{8}$$

where  $S_{ox}$  and  $S_{red}$  are the superficial sites, respectively, oxidized and reduced. At the steady state, the rates of eqn. (7) and eqn. (8) are equal, and the observed variations are in accordance with the following law [eqn. (9)]:

$$V = \frac{k_{\rm B} T}{ne} \ln \frac{P_{\rm O_2}}{P_{\rm CH_4}} + \text{constant}$$
(9)

Under a given catalytic mixture, the effective oxygen species implied in the mechanism can be deduced from the slope of the curve V vs.  $\ln P_{\text{reactants}}$ . We can see (Table 4) that the oxygen species implicated on pure  $\mathrm{Sm}_2\mathrm{O}_3$  is  $\mathrm{O}^-$  at temperatures below 360 °C and  $\mathrm{O}^{2-}$  at higher temperatures. This latter  $\mathrm{O}^{2-}$  species, has already been involved in methane oxidation<sup>17,18</sup> but generally, it is assumed that this species is responsible for the total oxidation. Nevertheless, different surface oxygen species can be responsible for the oxidative coupling activity as far as different catalytic systems are concerned. Besides, one can recall that Bielanski and Haber<sup>19</sup>

**Table 4** Oxygen species involved on the surface of pure  $Sm_2O_3$  treated under a hydrocarbon—oxygen atmosphere as determined by surface potential measurements

$T/^{\circ}\mathrm{C}$	n	oxygen species	
180	1.95	0-	
270	1.96	O <sup>-</sup>	
360	1.91	O <sup>-</sup>	
450	3.3	O <sup>2 –</sup>	
540	3.84	<b>O</b> <sup>2</sup> <sup>-</sup>	

postulated that  $O^{2-}$  should preferentially lead to partial oxidation, and this was confirmed on  $V_2O_5/TiO_2^{20}$  and on  $Bi_2Mo_3O_{12}^{10}$  systems. Owing to the high reactivity of the  $C_2$  compounds with the oxygen species, we should observe a  $C_2$  yield limitation with increase of  $CH_4$  conversion.

Indeed, in the case of a heterogeneous limitation, any hydrocarbon, including  $CH_4$  and the  $C_2$  products, must compete for the active site, as recently proposed by Statman *et al.*,<sup>21</sup> and react with the oxygen species:

$$CH_4 + O_2^{n-} \xrightarrow{k_{C_{2}H_6}} \text{`products'}$$

$$C_2H_6 + O_2^{n-} \xrightarrow{k_{C_{2}H_6}} \text{`products'}$$

$$C_2H_4 + O_2^{n-} \xrightarrow{k_{C_{2}H_4}} \text{`products'}$$

Hence

$$v_{CH_4} = k_{CH_4} P_{CH_4} [O_2^{n-}]$$
$$v_{C_{2H_6}} = k_{C_{2H_6}} P_{C_{2H_6}} [O_2^{n-}]$$
$$v_{C_{2H_4}} = k_{C_{2H_4}} P_{C_{2H_4}} [O_2^{n-}]$$

the higher reactivity of the  $C_2$  compounds leads to a limit of their amount and to a steady state where:

$$P_{C_2H_6}/P_{C_2H_4} = f(k_{C_2H_4}/k_{C_2H_6})$$

$$P_{\rm CH_4}/P_{\rm C_2H_6} = f(k_{\rm C_2H_6}/k_{\rm CH_4})$$

Fig. 3 and 4 summarize typical catalytic results found in literature and our own data. We observe that the  $P_{C_2H_6}/P_{C_2H_4}$ ratio is effectively constant whatever the CH<sub>4</sub> conversion (Fig. 3). Moreover, the  $(P_{C_4H_4}/P_{C_2H_6})$  ratio also tends towards a limit value, whatever the catalyst used (Fig. 4). This latter limit (*ca.* 10) is very close to that determined by surface potential measurements (Table 3), confirming that the C<sub>2</sub> yield limitation is due, at least in part, to a heterogeneous process.



**Fig. 3**  $P_{C_2H_4}/P_{C_2H_4}$  ratio vs. CH<sub>4</sub> conversion (%) over various catalysts: ( $\Box$ ) this work, ( $\bigcirc$ ) ref. 17, (\*) ref. 11, ( $\blacksquare$ ) ref. 22



**Fig. 4**  $P_{CH_4}/P_{C_2H_6}$  ratio vs.  $CH_4$  conversion (%) over various catalysts: ( $\Box$ ) ref. 22, ( $\triangle$ ) ref. 17, ( $\bigcirc$ ) ref. 11, (\*) ref. 23, ( $\blacksquare$ ) this work

## Conclusion

The surface potential measurements of  $\text{Sm}_2\text{O}_3$  samples treated under hydrocarbon-oxygen mixtures show that ethene and ethane react faster than methane whatever the experimental conditions. Comparison of these results obtained by this technique, which can be considered as a probe for investigating gas-solid interactions with those of classical catalytic tests suggests that an important part of the C<sub>2</sub> yield limitation observed in OCM is due to a heterogeneous competition between the initial reactant and the products.

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