

A Study of the Kinetics of the Oxidative Coupling of Methane over a Li/Sn/MgO catalyst

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ABSTRACT

The rate of reaction of methane with oxygen in the presence of a Li/Sn/MgO catalyst has been studied as a function of the partial pressures of CH₄, O₂ and CO₂ using a well-mixed reaction system which is practically gradientless with respect to gas-phase concentrations. It is concluded that the rate-determining step involves reaction of a molecule of CH₄ adsorbed on the catalyst surface with an adsorbed di-atomic oxygen species. The kinetics are consistent with a Langmuir-Hinshelwood type mechanism involving competitive adsorption of CH₄, O₂ and CO₂ on a single site. A comparison is made with previously published results for the Li/MgO material.

INTRODUCTION

Methane is present in vast proven reserves worldwide; however most of this production is flared, less than half being used as a source of either energy or chemicals. As a result of its high molecular stability, it is very difficult to activate the carbon-hydrogen bonds in methane in a selective manner. Nevertheless, considerable progress has been made in the development of catalysts for the oxidative coupling of methane. The more promising catalysts include certain members of the lanthanide oxide series [1,2] as well as a number of metal oxides promoted with alkali metal ions [3-8].

We have recently presented results which allowed us to postulate a possible model for the nature of the surface sites involved in the methane coupling reaction over a Li/MgO catalyst [4]. This model involves the creation of active sites on the surface of the catalyst in the presence of oxygen by the gradual loss of CO₂ from surface lithium carbonate species. The addition of CO₂ to the gas feed has two effects: to poison reversibly the active sites for the oxidative coupling reaction but also to stabilise them against deactivation.

We have also studied the rate of reaction of methane with oxygen in the presence of a Li/MgO catalyst as a function of the partial pressures of CH₄, O₂ and CO₂ using a well-mixed reaction system which is practically gradientless with respect to gas-phase concentrations [9]. We concluded that the rate determining step involves reaction of CH₄ adsorbed on the catalyst surface with a relatively weakly adsorbed di-atomic oxygen species. We suggested that a Langmuir-Hinshelwood type mechanism involving competitive adsorption of O₂ and CO₂ applies in this situation; the methane may be adsorbed on the same site as the O₂ and CO₂ or on an

adjacent surface site. These ideas are in agreement with the model for the formation of the active site [4].

We have found that it is possible to improve the activity and stability of a Li/MgO catalyst for the oxidative coupling of methane by the addition of small amounts of the oxides of various transition and rare earth metals [10]. A number of these additives, e.g. SnO₂, TiO₂, Dy₂O₃ and Tb₄O₇, gave a considerable lowering of the temperatures required to give optimum yields of C₂ products, there being little or no difference in the selectivity to C₂ products. A comparison of the various systems showed that Li/Sn/MgO is particularly promising, giving optimum yields at some 70°C lower than the optimum temperature for the unpromoted Li/MgO catalyst.

This paper gives the results of detailed kinetic experiments carried out with a sample of Li/Sn/MgO. These were carried out to allow us to compare the results with the previously published measurements for the unpromoted material [9] and to gain a better understanding of the reaction mechanism for the promoted catalyst. The rate of the oxidative coupling reaction was therefore studied as a function of the partial pressures of O₂, CH₄ and CO₂, the partial pressure of H₂O being kept constant in all the experiments.

EXPERIMENTAL

Reaction System

The kinetic experiments were carried out in a continuous reaction system with external gas recirculation (recycle ratio = 30) which has been described in detail elsewhere [9]. The gas feed mixture (CH₄, O₂, CO₂ and He) was added to the system at a rate of 0.156 cm³(STP)s⁻¹, the composition being controlled to give the desired partial pressure of each reactant; water produced in the reaction was condensed out in a trap maintained at 0°C. A sample of 250 mg of catalyst was placed in the reactor tube (quartz, 6mm id) in a furnace at the desired temperature (720°C) and the gas was preheated by passing it through another equivalent tube maintained at 500°C. Gas analysis was carried out with gas chromatography. Analysis before and after the bed showed that the system could be considered to be perfectly mixed under all the reaction conditions studied [11]. A thermocouple in a quartz tube was placed in the catalyst bed to measure the bed temperature.

The catalyst was kept for 5h at 720°C under reaction conditions before the kinetic measurements started.

Catalyst Preparation

The Li/MgO material used as precursor for the Li/Sn/MgO material was prepared by wet impregnation of Mg(OH)₂ with an aqueous solution of LiOH; this was done in the presence of a stream of CO₂ [4]. After drying at 140°C, this material was physically mixed with SnO₂. The Li/Sn/MgO mixture was then calcined in air at 850°C for 6h and crushed and sieved to a grain size of 0.1-0.3 mm. Analysis showed that the material contained 5.05 wt% Li (7.27 mmol Li/g),

1.43 wt% Sn (0.120 mmol Sn/g) and 11.1 wt% CO₂ (2.53 mmol CO₂/g).

RESULTS AND DISCUSSION

The Effect of Variation of P_{CH_4} , P_{O_2} and P_{CO_2} at 720°C

Figure 1 shows the rate of reaction of methane as a function of the partial pressure of CH₄, the partial pressures of O₂ and CO₂ being kept constant at 2.2 (± 0.1) kPa and 7.8 (± 0.1) kPa respectively. (The reaction temperature was chosen to be 720°C, as blank reactor tests showed that negligible conversions of methane, ethane or ethylene occurred in the presence of oxygen at this temperature [11]). At lower values of P_{CH_4} , the rate of reaction increases with P_{CH_4} but then begins to level off at higher values of P_{CH_4} (25-40 kPa) (part 1 of the curve). With further increase in P_{CH_4} (> 41 kPa), the rate of reaction increases slightly again, reaching a maximum at about 70 kPa. Finally, above ca. 75 kPa of P_{CH_4} , the reaction rate decreases significantly with increasing partial pressure of methane (part 2 of the curve).

Both the discontinuous increase in the reaction rate at ca. 41 kPa CH₄ and the decrease in the reaction rate above ca. 75 kPa CH₄ were found to be reproducible. The errors given in the partial pressures of CH₄, O₂ and CO₂ are the maximum errors in a series, but the errors were mostly smaller. The curve shown in Figure 1 was found to be completely reversible. The temperature in the catalyst bed remained constant throughout the sequence of experiments.

For purposes of comparison, the calculated reaction rates for Li/MgO [9] under the same reaction conditions are also shown in Figure 1; as will be discussed in more detail elsewhere [10], the Li/Sn/MgO sample is substantially more active than is the Li/MgO material.

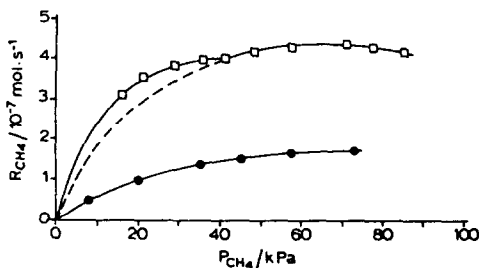


Figure 1 The rate of reaction of CH₄ as function of the partial pressure of CH₄ for Li/Sn/MgO (□) and Li/MgO (•); T = 720°C, P_{O_2} = 2.2 kPa and P_{CO_2} = 7.8 kPa.

The dependence of the reaction rate on the partial pressure of O₂ is shown in Figure 2 for three typical constant partial pressures of methane: 16.0 (± 0.2) kPa, 39.0 (± 0.3) kPa and 52.0 (± 0.5) kPa; these values were chosen to correspond to both parts 1 and 2 of the methane curve

of Figure 1. The partial pressure of CO_2 was again kept constant at $7.8 (\pm 0.1)$ kPa and the temperature at 720°C . The results of Figure 2 show clearly that the rates of reaction of CH_4 are not first order in oxygen but that there is a curvature in the plots of rate vs. P_{O_2} for all three partial pressures of methane.

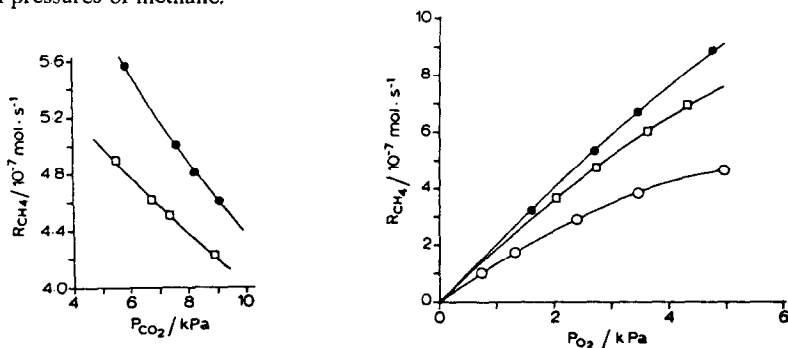


Figure 2 The rate of reaction of CH_4 as function of the partial pressure of O_2 for three partial pressures of methane, P_{CH_4} : 16 kPa (\circ), 39 kPa (\square) and 52 kPa (\bullet), $P_{\text{CO}_2} = 7.8$ kPa, $T = 720^\circ\text{C}$ and Figure 3 The rate of reaction of CH_4 as function of the partial pressure of CO_2 for two partial pressures of methane, P_{CH_4} : 39 kPa (\square) and 52 kPa (\bullet), $P_{\text{O}_2} = 2.2$ kPa, $T = 720^\circ\text{C}$.

Figure 3 shows the effect on the rate of reaction of the partial pressure of CO_2 for a series of experiments with $P_{\text{CH}_4} = 39.0 (\pm 0.5)$ kPa and $P_{\text{CH}_4} = 52.0 (\pm 0.5)$ kPa. The partial pressure of O_2 was kept constant for each experiment at $2.2 (\pm 0.1)$ kPa and the reaction temperature was again 720°C . Figure 3 clearly shows that CO_2 acts as a poison for the reaction; this poisoning probably arises from competitive adsorption of the CO_2 with the methane and/or the oxygen [4,9].

From the results shown in Figure 1 and 2, we suggest that the following sequence of events occurs:



where S_1 and S_2 represent adsorption sites. Reactions 1 and 2 involve equilibrium adsorption of oxygen and methane species respectively. These steps are followed by reaction 3, the rate-limiting reaction step, involving adsorbed methane and oxygen. Reaction step 3 is equivalent to the initiation reaction step found for hydrocarbon oxidation reactions occurring in the gas phase [12,13].

Independent evidence for a rate-limiting step involving the activation of CH_4 (as e.g. in reaction 3) is given by Cant et al. [14]; by comparison of the rate of reaction of CH_4 with that of CD_4 over a Li/MgO catalyst at 750°C , they showed that the C-H bond-breaking reaction is rate-limiting under these conditions. Reaction 3 will be discussed in detail below.

Assuming that the mechanism represented by Equations (1)-(3) holds, the rate of reaction of methane, R_{CH_4} , is determined by step (3) and may be expressed as follows:

$$R_{\text{CH}_4} = k_r \cdot \theta_{\text{O}_2} \cdot \theta_{\text{CH}_4} \quad (\text{a})$$

where θ_{O_2} and θ_{CH_4} are the coverages of O_2 and CH_4 respectively and k_r is the rate constant of the reaction.

Table 1 gives four different situations which may now be considered if we assume that the molecular adsorption of both O_2 and CH_4 given by equations (1) and (2) may be described by Langmuir isotherms and S_1 and S_2 represent different sites on the catalyst surface. (It should be noted that if dissociation of oxygen occurred and reaction of methane with oxygen atoms was rate determining:



the P_{O_2} terms of the equations of Table 1 should be replaced by $(P_{\text{O}_2})^{1/2}$).

In order to attempt to determine which of the various models is applicable, linearised versions of the rate equations shown were plotted to obtain the values of the adsorption constants for each of the models. The adsorption constants for models 1, 2 and 4 were then calculated from the ratios of the slopes to the intercepts of the linearised versions of the equations given in Table 1, in a manner analogous to the procedure used by Otsuka and Jinno [15] and Roos et al. [9].

Figure 4 shows a plot of $(P_{\text{CH}_4}/R_{\text{CH}_4})$ against P_{CH_4} (models 1 or 2) and Figure 5 shows a plot of $(P_{\text{CH}_4}/R_{\text{CH}_4})^{1/2}$ versus P_{CH_4} (model 4) for the data of Figure 1. Both Figures show that the curve in Figure 1 is split in two parts. Figure 4 shows that only part 1 of the curve of Figure 1 gives a linear relationship for $(P_{\text{CH}_4}/R_{\text{CH}_4})$ as a function of P_{CH_4} while Figure 5 shows that both parts of this curve give linear relationships for $(P_{\text{CH}_4}/R_{\text{CH}_4})^{1/2}$ as a function of P_{CH_4} . This means that only model 4 is of significance at $P_{\text{CH}_4} > 41 \text{ kPa}$ (part 2 of the curve). This can also be concluded from Figure 1 since the reaction rate of methane decreases with increasing methane partial pressures at high partial pressures of methane (part 2 of the curve): only model 4 (adsorption on a single site) can give rise to a maximum of this type.

Calculation of the adsorption constants from the various plots showed that all models involving dissociation of oxygen gave negative values of b_{O} ; as negative values have no physical

significance, these models may thus be excluded. We therefore conclude that a di-atomic oxygen species is involved in the rate-limiting reaction with CH₄.

Table 1 Rate equations for different models.

Model	Rate Equation	linear plot
1. S ₁ O ₂ /CO ₂ S ₂ CH ₄	$R = \frac{k_r b_{O_2} P_{O_2} b_{CH_4} P_{CH_4}}{(1 + b_{O_2} P_{O_2} + b_{CO_2} P_{CO_2})(1 + b_{CH_4} P_{CH_4})}$	$\frac{P_r}{R}$ vs. P _r
2. S ₁ O ₂ S ₂ CH ₄ /CO ₂	$R = \frac{k_r b_{O_2} P_{O_2} b_{CH_4} P_{CH_4}}{(1 + b_{CH_4} P_{CH_4} + b_{CO_2} P_{CO_2})(1 + b_{O_2} P_{O_2})}$	$\frac{1}{R}$ vs. P _{CO₂}
3. S ₁ O ₂ /CO ₂ S ₂ CH ₄ /CO ₂	$R = \frac{k_r b_{O_2} P_{O_2} b_{CH_4} P_{CH_4}}{(1 + b_{CH_4} P_{CH_4} + b_{CO_2} P_{CO_2})(1 + b_{O_2} P_{O_2} + b_{CO_2} P_{CO_2})}$	—
4. S ₁ = S ₂ O ₂ /CH ₄ /CO ₂	$R = \frac{k_r b_{O_2} P_{O_2} b_{CH_4} P_{CH_4}}{(1 + b_{CH_4} P_{CH_4} + b_{O_2} P_{O_2} + b_{CO_2} P_{CO_2})^2}$	$\left(\frac{P_r}{R}\right)^{1/2}$ vs. P _r $\left(\frac{1}{R}\right)^{1/2}$ vs. P _{CO₂}

P_r = P_{CH₄} or P_{O₂}

In a similar way, the b_{CH₄} and b_{CO₂} values calculated for model 2 were negative and so this model may also be excluded. Although the rate equation of model 3 could not be linearised, it was shown mathematically that this model also resulted in negative b_{CO₂} values and thus model 3 could also be excluded.

As the adsorption constants for models 1 and 4 were positive and were therefore of significance at P_{CH₄} < 41 kPa, it can be concluded that one of these models is appropriate for part 1 of the curve). At higher methane partial pressures, only model 4 is appropriate. From these results we can distinguish two situations:

- (i) Both parts of the curve correspond with different models and there is a change in adsorption type.
- (ii) The same model is valid for both parts of the curve and there is a change in the adsorption constants as a consequence of e.g. a change in the oxidation state of tin.

In order to try to determine which of models 1 and 4 is applicable at P_{CH₄} < 41 kPa, a series of measurements with variation of the oxygen partial pressure at 16 kPa CH₄ and 7.8 kPa CO₂ was carried out (see Figure 2). These measurements show a parabolic relationship for (P_{O₂}/R_{CH₄}) as a function of P_{O₂}; however as shown in Figure 6 (P_{O₂}/R_{CH₄})^{1/2} plotted against

P_{O_2} gives a satisfactory straight line. This means that of the models tested, only model 4, adsorption on a single site, is of significance. Measurements made at a lower temperature were also in agreement with this model [16]. The curves drawn in Figures 1, 2 and 3 are obtained by fitting this model.

The adsorption constants and the k_f values for model 4 are given in Table 2. This Table also shows for purposes of comparison the results for Li/MgO [9] at $T_R = 720^\circ\text{C}$.

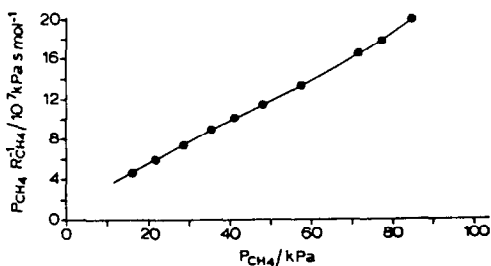


Figure 4 P_{CH_4}/R_{CH_4} as a function of P_{CH_4}

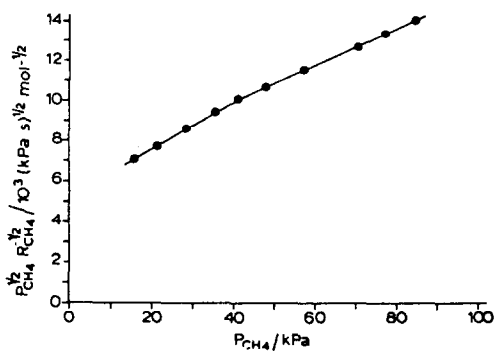


Figure 5 $(P_{CH_4}/R_{CH_4})^{1/2}$ as a function of P_{CH_4} .

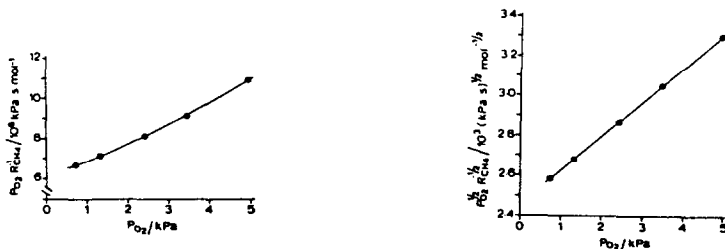


Figure 6 (P_{O_2}/R_{CH_4}) and $(P_{O_2}/R_{CH_4})^{1/2}$ as a function of P_{O_2} for $P_{CH_4} = 16 \text{ kPa}$.

Table 2: Kinetic parameters calculated for model 4. $T_R = 720^\circ\text{C}$.

Li/Sn/MgO					
part	b_{CH_4}	b_{O_2}	b_{CO_2}	k_r	$k_r \cdot b_{\text{O}_2}$
	kPa^{-1}	kPa^{-1}	kPa^{-1}	$10^{-6} \text{ mol.s}^{-1}$	$10^{-7} \text{ mol.(s.kPa)}^{-1}$
1	0.041	0.095	0.072	13.6	
2	0.023	0.041	0.077	32.7	
Li/MgO					
	0.016	-	0.070		4.8

The values of $k_r \cdot b_{\text{O}_2}$ and k_r are calculated from the series of experiments in which P_{CH_4} was varied.

Comparison between Li/Sn/MgO and Li/MgO

For Li/MgO, the reaction rate had a first order dependency on the partial pressure of oxygen ($P_{\text{O}_2} < 11 \text{ kPa}$) and so the independent values of b_{O_2} and k_r could not be calculated for this catalyst [9]. As Table 2 shows however, the values of b_{O_2} for Li/Sn/MgO could be calculated from measurements in which P_{O_2} was varied up to 5 kPa (Figure 2) for both parts of the methane curve (Figure 1). This result indicates that the interaction of oxygen with the Li/MgO catalyst is enhanced by the addition of SnO₂. The adsorption constants of Table 2 also show that the methane is more strongly adsorbed on the Li/Sn/MgO catalyst than on the Li/MgO catalyst; this is so for both parts of the methane curve but particularly in the first part of the curve ($P_{\text{CH}_4} < 41 \text{ kPa}$).

We shall show elsewhere [10] that the poisoning effect of CO₂ is less for the Li/Sn/MgO than with the Li/MgO catalyst. This can also be concluded from the b values given in Table 2 for both parts of the methane curve. The adsorption constants for methane and oxygen are larger in the case of Li/Sn/MgO while b_{CO_2} remains almost the same when compared with Li/MgO. The CO₂ competes less effectively with the more strongly bonded oxygen and methane present on the Li/Sn/MgO catalyst. However, the effect is far less pronounced for the second part of the methane curve as the b_{CH_4} and b_{O_2} values are closer to those for Li/MgO.

The differences between the b values of the second part of the methane curve of Li/Sn/MgO and those for Li/MgO are not very large; the second part of the methane curve for Li/Sn/MgO has a "Li/MgO-like" character. For this reason we suggest that the discontinuous increase in the reaction rate at ca. 41 kPa CH₄ is probably caused by a reversible partial reduction of the SnO₂ of the Li/Sn/MgO catalyst. To attempt to demonstrate this, the dependence of the reaction rate on the partial pressure of O₂ was studied for a number of constant partial pressures of methane

(of which three are shown in Figure 2). Also from these measurements we could conclude that there is a discontinuous increase in R_{CH_4} as a function of P_{CH_4} , the position of which depends on P_{O_2} . For example, for $P_{\text{O}_2} = 1$ kPa, the discontinuous increase in the reaction rate was found at ca. 35 kPa P_{CH_4} compared with at ca. 41 kPa P_{CH_4} for $P_{\text{O}_2} = 2.2$ kPa. These results therefore support the suggestion made above.

We have further confirmed that the catalyst exhibits oxidation/reduction behaviour by carrying out an experiment involving the dosing of methane. For this experiment, 2 g of Li/Sn/MgO was placed in a fused Al_2O_3 reactor and then heated in a flow of oxygen for 48 h at 820°C to remove the CO_2 of the Li_2CO_3 . After the removal of the CO_2 , methane was fed to the catalyst at 800°C in the absence of gas phase oxygen. The main reaction observed under these conditions was the formation of CO and H_2 probably according to the equation:



No CO_2 was detected. (The formation of CO_2 could not be totally excluded since CO_2 could be captured by the Li_2O to form Li_2CO_3). A small amount of C_2H_6 was also formed in the reaction (selectivity: ca. 2%). It is thus possible to use the Li/Sn/MgO catalyst under cyclic operation conditions such as those described by Jones et al. [5]. From these measurements, we therefore conclude that reduction of SnO_2 to SnO (but not to a lower oxidation state) can occur under continuous flow conditions.

Labinger et al. [17] have also found an increase in the reaction rate at a certain methane partial pressure for a Mn/MgO catalyst used in the cyclic reaction mode, analogous to the effect shown in Figure 1, but gave no explanation.

CONCLUSIONS

A kinetic evaluation of the oxidative coupling reaction of CH_4 with O_2 over a Li/Sn/MgO catalyst shows:

1. A di-atomic oxygen species is involved in the rate-determining step.
2. This rate-limiting step is the reaction between adsorbed CH_4 and O_2 molecules, i.e. the breaking of a C-H bond in the CH_4 molecule, in a Langmuir-Hinshelwood mechanism.
3. A Langmuir-Hinshelwood type mechanism, with competitive adsorption of CH_4 , O_2 and CO_2 applies in this situation.
4. Methane and oxygen are more strongly adsorbed on Li/Sn/MgO than on Li/MgO. The poisoning effect of CO_2 is less in the case of Li/Sn/MgO; CO_2 competes less effectively with the more strongly bonded methane and oxygen on this catalyst.
5. The curve giving the reaction rate of methane as a function of the methane partial pressure consists of two parts. The reversible partial reduction of the SnO_2 of the Li/Sn/MgO catalyst appears to be responsible for this effect.

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