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## Surface processes in the catalytic oxidative coupling of methane to ethane <sup>a</sup>

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Abstract. Recent results on surface reaction steps in the oxidative coupling of methane (OCM) obtained from (1) transient experiments and (2) a microkinetic analysis are summarized. The interaction of methane and oxygen with MgO and  $\text{Sm}_2\text{O}_3$  surfaces was investigated by applying H/D- and oxygen-isotope-exchange reactions. The role of short-lived adsorbed oxygen species in methane activation and product formation over MgO and  $\text{Sm}_2\text{O}_3$  catalysts is discussed. Furthermore, elementary reaction steps and their rate constants are derived for the oxidative conversion of methane to  $\text{CO}_x$  and ethane from kinetic data for different  $(\text{CaO})_x(\text{CeO}_2)_{1-x}$  catalysts; the rate constants are related to the solid's properties, *i.e.*, electron and  $\text{O}^{2-}$  conductivity.

## Introduction

In the oxidative coupling of methane (OCM) the interaction of methane and oxygen with catalytic surfaces and hence, the primary function of the catalyst in methane activation, is an important issue which is still not fully understood. It is widely accepted that breaking of a C-H bond is involved in the initial rate-controlling reaction step<sup>1-7</sup>. Some authors<sup>5,8-12</sup> have suggested that the first step of methane interaction with the catalyst surface includes the dissociative adsorption of methane while others assume the direct formation of methyl radicals in the reaction of gas-phase methane with active oxygen surface species by an Eley-Rideal type of mechanism<sup>13-16</sup>. The surface or gas-phase reaction of the methyl radicals with oxygen leads to a total oxidation, *i.e.*,  $CO_x$ , while ethane is formed by methyl-radical coupling in the gas phase. The formation of  $CO_x$  and  $C_2H_6$  is strongly affected by the catalyst's properties, which is reflected by the use of different kinetic models for the primary-reaction steps when different catalysts are applied<sup>17-27</sup>. Surface basicity, lattice-oxygen mobility and *p*-type conductivity have been proposed to be important for high activity and C<sub>2</sub> selectivity in the OCM reaction. The nature of active-surface centers and the role of gas-phase oxygen in their formation have also been considered, and different techniques have been used to study the effect of catalyst properties on oxygen activation and of the role of lattice-oxygen mobility  $2^{8-35}$ .

The main objective of this review is to summarize the recent results of the present authors on the surface reaction steps in the OCM reaction in order to identify the catalyst properties which determine the formation of methyl radicals and their selective or non-selective consecutive reactions to ethane or  $CO_x$ , respectively; the dehydrogenation of ethane to ethylene, an important step

in an eventual industrial OCM process, is not considered. Transient experiments, *i.e.*, pulsing the reactants over the catalyst and analyzing the response at the reactor outlet, were carried out to elucidate the surface processes on MgO and  $Sm_2O_3$  catalysts<sup>36</sup>. The report discusses the results of methane activation by surface-lattice oxygen and adsorbed oxygen species of short lifetime, the differences between MgO and Sm<sub>2</sub>O<sub>3</sub> surfaces with respect to oxygen activation, and the nature of active sites for the OCM reaction. The microkinetic analysis of the OCM reaction on  $(CaO)_x(CeO_2)_{1-x}$  catalysts of different composition<sup>37</sup> was based upon a reaction mechanism obtained by model discrimination and by taking into account the findings of the transient study. The mechanism includes reaction steps on the catalytic surface and in the gas phase. The rate constants of the final model were related to the electron and oxygen-anion conductivity of the  $(CaO)_x(CeO_2)_{(1-x)}$  catalysts forming solid solutions within the range  $0 \le x \le 0.23^{38}$ . An attempt was made to establish the requirements for either total oxidation or selective coupling of methane by analyzing correlations between the estimated rate constants of the surface-catalyzed reaction steps and the solid properties of the catalysts.

#### Transient studies on the interaction of methane and oxygen with catalytic surfaces of MgO and $\text{Sm}_2\text{O}_3$ .

To identify the primary steps of the interaction of methane and oxygen with catalyst surfaces, transient experiments allowing the rapid analysis of any short-lived intermediates appeared to be most suitable. The so-called Temporal-Analysis-of-Products (TAP) reactor was applied, which has been described elsewhere in detail<sup>39</sup>. By means of two high-speed beam valves, gas pulses of a half-width of less than 10  $\mu$ s (inlet signal) could be introduced into the micro-catalytic reactor which was located in a high vacuum chamber (approx.  $1 \cdot 10^{-4}$  Pa). The response signal at the reactor outlet recorded by a mass spectrometer is the temporal change of the intensity of the compounds

<sup>&</sup>lt;sup>a</sup> Dedicated to Professor *Wolfgang M.H. Sachtler* on the occasion of his 70th birthday.

leaving the reactor. The response strongly depends on the interaction of the compounds with the catalytic materials (adsorption, desorption, reaction). Since only a small amount of gas  $(10^{15}-10^{17}$  molecules per approx. 1 to 2 m<sup>2</sup> of catalyst-surface area within the reactor) was introduced per pulse, the surface reactions of methane and oxygen could be studied without changing the surface properties significantly, assuming that approx. 10<sup>19</sup> oxygen sites are available per m<sup>2</sup> of catalyst-surface area.

#### (a) Methane interaction

This study was carried out to elucidate whether methane is adsorbed on the surface or whether it reacts according to an Eley-Rideal-type mechanism with the surface-forming gas-phase methyl radicals directly. This work was done before the background work reported in the literature: heterolytic dissociation of an adsorbed methane molecule on the solid surface proposed by *Tanabe* et al.<sup>40</sup> and similarly by *Kembell* et al.<sup>41,42</sup> for the H/D exchange catalyzed by  $Al_2O_3$ , alkaline-earth-metal oxides or  $La_2O_3$ at relatively low temperatures (up to 683K). Using the TAP reactor, the surface reaction of the H/D exchange in methane was investigated in the temperature range corresponding to the OCM reaction in order to elucidate the mechanism of methane activation during H/D exchange and its relation to the OCM reaction<sup>36</sup>. For the situation in which only pure  $CD_4$  was pulsed over  $Sm_2O_3$ in the absence of any gas-phase or adsorbed oxygen, the reactor outlet response to pulsing is shown in Figure 1 as product concentration as a function of response time.

From this it has to be assumed that surface-hydroxyl groups participate in this process as described by Larson and Hall<sup>43</sup> for alumina and silica/alumina surfaces. It is obvious that the surface reaction of isotopic exchange proceeds stepwise. The longer residence times of the exchanged methanes compared to CD4 indicate that a rather strong interaction of methane with the surface takes place. Based on these results it can be safely concluded that methane-surface interaction leading to the dissociative adsorption of methane occurs over the Sm<sub>2</sub>O<sub>3</sub> catalyst and results in H-D exchange between deuterated methane molecules and surface hydroxyl groups. How this type of methane activation is related to the oxidative coupling of methane, in particular, to the formation of ethane via methyl radicals was further studied in the presence of pre-adsorbed oxygen species when oxygen and methane were sequentially pulsed with short time intervals between 0.02 and 20 s. It could be shown that surface-lattice oxygen is responsible for ethane formation on MgO, while adsorbed oxygen species having a very short lifetime (< 0.1 s) on the surface take part in the total oxidation of methane (cf. Figure 2).



Figure 1. Normalized transient responses for isotopic methanes formed when pulsing pure  $CD_4$  over  $Sm_2O_3$  at 1073 K.



Figure 2. Effect of the time interval  $(\Delta t)$  between the pulses of  $O_2$  and  $CH_4$  on  $CH_4$  conversion and product formation over MgO at 1073 K. The ordinate shows the ratio between the amounts formed at an offset time  $\Delta t$  to the respective amount for simultaneous pulsing  $(\Delta t = 0)$ .

In contrast to MgO, a significant increase in the formation of ethane over  $\text{Sm}_2\text{O}_3$  was observed in the presence of adsorbed oxygen species. The responses of the primary products of H/D exchange (CD<sub>3</sub>H) and OCM reaction (C<sub>2</sub>D<sub>6</sub>) formed during pulsing of pure CD<sub>4</sub> and during sequential pulsing of O<sub>2</sub> and CD<sub>4</sub> over Sm<sub>2</sub>O<sub>3</sub> are shown in Figures 3a and 3b.

From an analysis of the shape of the response curve, information was derived about the relationship between the OCM reaction and H/D exchange and, in particular, about the difference in the primary steps in methane activation on the catalyst surface for these two reactions. When methane reacts with lattice oxygen only (cf. Figure 3a) the shapes of the ethane and methane curves differ from those obtained in the presence of additional active surface-oxygen species formed by the interaction of gasphase oxygen with the catalyst surface in the sequential pulsing experiments (cf. Figure 3b). In the first case, the ethane response is broader than the methane response, as expected for product formation when time is needed to form methyl radicals (via dissociative adsorption of



Figure 3. Normalized transient responses for the formation of  $CD_3H$ and  $C_2D_6$  over  $Sm_2O_3$  at 1073 K obtained by: (a) pulsing of  $CD_4$  10 min after exposure of the catalyst to oxygen; (b) sequential pulsing of  $O_2$  and  $CD_4$  with a time interval of 0.05 s.

methane on the catalyst surface). In the second case, *i.e.*, in the presence of adsorbed oxygen, the ethane response shifts to shorter times and becomes even more narrow than the methane response. These results suggest that adsorbed oxygen accelerates the formation of ethane, being the primary stable product in the OCM reaction. It might be assumed that the methyl radicals forming ethane are produced rapidly, i.e., by the direct interaction of gas-phase methane with active oxygen species by the Eley-Rideal mechanism, exluding dissociative adsorption of methane. In the H/D exchange reaction the response of the primary product (CD<sub>3</sub>H) was not affected by the presence of adsorbed oxygen. Thus, the methane activation over  $Sm_2O_3$  in the H/D exchange reaction which involves surface hydrogen (in OH groups) via dissociative adsorption of methane, differs from the methane interaction resulting in the formation of methyl radicals.

# (b) The role of oxygen activation in the OCM reaction over MgO and $Sm_2O_3$

As described above, the activity of oxygen species formed during sequential pulsing of oxygen and methane is higher with respect to methane conversion than lattice oxygen. However, an increase in the formation of selective products (ethane and its consecutive product ethylene) in the presence of adsorbed oxygen species was observed only on  $Sm_2O_3$ . For this catalyst, gas-phase oxygen is not only necessary to replenish the lattice oxygen after removal of OH as water formed in the reaction of methane with lattice oxygen, but also to produce active oxygen species which react with methane to form methyl radicals. The process of oxygen activation and the role of adsorbed oxygen species in methane conversion and product formation was further investigated; detailed results are described elsewhere<sup>44</sup>. The capacity of the surfaces of MgO and Sm<sub>2</sub>O<sub>3</sub> for gas-phase oxygen activation was examined applying the oxygen exchange reaction between gas-phase  ${}^{18}O_2$  and surface-lattice  ${}^{16}O_s$ . A mixture of  ${}^{18}O_2/Ne$ (1:2) was pulsed over the catalytic surfaces in the temperature range from 539 to 1035K. Transient responses of  ${}^{18}O_2$ ,  ${}^{16}O{}^{18}O$  and  ${}^{16}O_2$  at the reactor outlet over  $\text{Sm}_2O_3$ 

at 1035K are presented in Figure 4a. It is obvious that the



Figure 4. Normalized responses of oxygen isotopes when pulsing (a)  ${}^{18}O_2$  and (b)  $CH_4 / {}^{18}O_2$  over  $Sm_2O_3$  at 1035 K.



Figure 5. Responses of oxygen and methane for determining the reactivity of oxygen species on  $Sm_2O_3$  at 908 K. A: oxygen response when pulsing  $O_2$  (1.4 · 10<sup>16</sup> molecules / pulse); B: oxygen and C: methane responses in sequential pulsing of oxygen (1.4 · 10<sup>16</sup> molecules / pulse) and methane (1.9 · 10<sup>16</sup> molecules / pulse) with a time interval of 100 ms.

oxygen exchange proceeds stepwise with the formation of first <sup>18</sup>O<sup>16</sup>O, followed by <sup>16</sup>O<sub>2</sub>. The surface activity for the exchange of isotopic oxygen decreases markedly from  $\text{Sm}_2\text{O}_3$  to MgO. For MgO, a high activation energy of  $E_A = 297$  kJ/mol was observed; this corresponds to the result described above, that the lattice oxygen of MgO is responsible for methane activation leading to selective products. For  $\text{Sm}_2\text{O}_3$ , the lower activation energy of 78 kJ/mol, resulting in high activity in the oxygen exchange reaction, correlates with the ability to form short-lived oxygen species which are active in the reaction with methane to methyl radicals and hence, the formation of ethane.

The influence of methane on the oxygen exchange reaction on  $\text{Sm}_2\text{O}_3$  was studied using simultaneous pulsing of  $\text{CH}_4/\text{Ne}(1:1)$  and  ${}^{18}\text{O}_2/\text{Ne}(1:2)$  mixtures via two valves. The presence of methane did not affect the shape and intensity of the  ${}^{18}O_2$  response to any significant degree. This leads to the conclusion that (i) oxygen activation on the surface is faster than the activation of methane and (ii) neither gas-phase oxygen nor non-dissociated surface-oxygen species react with methane at temperatures up to 1035K. However, the yield of oxygen exchange products ( ${}^{16}O{}^{18}O$  and  ${}^{16}O_2$ ) decreased and their responses became more narrow (cf. Figure 4b) in the presence of methane. This indicates that the oxygen species, \*O(s), formed on the  $Sm_2O_3$  surface after dissociative adsorption of gas-phase oxygen are consumed more rapidly by methane than they can recombine and desorb as diatomic oxygen, as observed in the absence of methane. The high reactivity of  $^{*}O(s)$  species was confirmed by the experiments with sequential pulsing of oxygen and methane (cf. Figure 5). They are consumed almost instantaneously when methane is introduced; by adjusting the

different surface coverages by these oxygen species. Methane conversion of up to 39% was reached in the presence of an adsorbed oxygen species on a  $\text{Sm}_2\text{O}_3$  surface while reaction with lattice oxygen at the same temperature resulted in methane conversion of only 3% (*cf.* Figure 6). Since in these experiments the amount of \*O(s) was always less than 1% of a monolayer (max.  $1.4 \cdot 10^{16} \text{ atoms/m}^2$ ) it can be concluded that these species provide the main activity for the consumption of methane on the catalyst surface while the reactivity of lattice oxygen is much smaller. For the yield of C<sub>2</sub> hydrocarbons a linear dependence on the amount of active surface-oxygen species was observed, as long as it stayed below  $0.7 \cdot 10^{16}$  oxygen atoms per m<sup>2</sup> (*cf.* Figure 6). No further increase of C<sub>2</sub> formation was observed with higher numbers of

intensity of the oxygen pulse, it was possible to create



Figure 6. Dependence of methane conversion and  $C_2$  yield on the amount of active oxygen species, \*O(s), formed by interaction of gas-phase oxygen with a  $Sm_2O_3$  surface at 908 K.

active oxygen sites. However, compared to lattice oxygen the presence of adsorbed oxygen species greatly enhances the selectivity and yield of ethane and ethylene. An optimum concentration is obviously required to achieve maximum yield or selectivity, because for higher oxygen concentrations on the surface either consecutive total oxidation reactions are favored or other oxygen species acting non-selectively are formed on the surface.

## (c) Summary of results from transient studies

For the surface processes in the OCM reaction, it can be concluded that the main reaction step, *i.e.*, the formation of methyl radicals which further recombine in the gas phase to form ethane, strongly depends on the type of catalyst. For MgO, the selective reaction pathway to ethane proceeds with the participation of lattice oxygen only. Catalyst activity is limited by slow dissociative oxygen adsorption, as confirmed by the results of the oxygen exchange reaction. It can be concluded that the ability of the catalyst to adsorb oxygen determines the catalyst's activity in the formation of methyl radicals. The surface concentration of active oxygen species, in turn, determines whether the methyl species desorb into the gas phase for subsequent coupling or react non-selectively to carbon oxides via methoxy or peroxy intermediates. This was clearly demonstrated for  $\text{Sm}_2\text{O}_3$ , being one of the active and selective catalysts for the OCM reaction.

# Microkinetic analysis of the elementary reaction steps over $CeO_2/CaO$ catalysts

To analyze the complex interplay between the various surface and gas-phase reactions on one hand and catalyst properties on the other hand, reaction schemes based on elementary reaction steps of the OCM reaction were derived in which the initial reaction steps leading to ethane and  $CO_x$ , as well as the total oxidation of ethane, were accounted for. No attempt was made to include the consecutive formation of ethylene which was suppressed by keeping the degree of conversion low. The kinetic models examined comprised different heterogeneous reaction pathways for methane activation, surface reoxidation by gas-phase oxygen, and consecutive reaction steps of methyl radicals as well as ethane (see Table I). It was further assumed that  $CH_3O$  and  $CH_3O_2$  radicals yield fast  $CO_x$  formation.

The experimental data against which the various models were tested consisted of gas-phase concentrations of ethane and  $CO_x$  as a function of inlet partial pressure of methane and oxygen at a given contact time; these data were obtained for  $(CaO)_x(CeO_2)_{1-x}$  catalysts of different compositions (x = 0, 0.05, 0.1, 0.2). Kinetic data had been procured in a micro-catalytic fixed-bed reactor. Short contact times in the order of 0.01 g  $\cdot$  s  $\cdot$  ml<sup>-1</sup> and relatively low temperatures (933-1013 K) suppressed primary gas-phase activation of methane and consecutive reactions, particularly of ethane to ethylene. The evaluation of the kinetic data was based on the assumption of pseudo-steady-state concentrations of surface intermediates ( $\theta_i$ ) and of gas-phase intermediates (CH<sub>3</sub>, CH<sub>3</sub>O<sup>-</sup>). Interpar-

Table I Elementary reaction steps in the oxidation coupling of methane (OCM)<sup>a</sup>

Reaction steps	Reaction model nos. for $(CaO)_x(CeO_2)_{1-x}$ catalysts									
	1	2	3	4	5	6	7	8	9	10
$\begin{array}{c} \text{Methane activation} \\ (1) \ CH_4 + [O] \leftrightarrow CH_3 + [OH] \\ (2) \ CH_4 + [O_2] \rightarrow CH_3 O + [OH] \end{array}$	•	•	•	•	•	•	•	•	•	•
Surface oxidation (3) $O_2 + 2[] \leftrightarrow 2[O]$ (4) $O_2 + [] \leftrightarrow [O_2]$ (5) $[O_2] + [] \rightarrow 2[O]$	•	•	•	•	•	•	•	•	•	•
$\begin{array}{c} Dehydration \\ \textbf{(6) 2 [OH]} \rightarrow H_2O + [] + [O] \end{array}$	•	•	•	•	•	•	•	•	•	•
Ethane formation (7) 2 $CH_3 \rightarrow C_2H_6$	•	•	•	•	•	•	•	•	•	•
Consecutive reactions (8) $CH_3 + [O] \rightarrow CH_3O + []$ (9) $CH_3 + [O_2] \rightarrow CH_3O_2 + []$ (10) $CH_3 + O_2 \rightarrow CH_3O_2$ (11) $C_2H_6 + [O_2] \rightarrow 2 CH_3O + []$	•	•	•	•	•	•	•	•	•	•
$\begin{array}{c} CO_2 \ adsorption \\ (12) \ CO_2 + [O] \leftrightarrow [O] - CO_2 \\ (13) \ CO_2 + 2 \ [O] \leftrightarrow [O]_2 = CO_2 \\ (14) \ CO_2 + [] + [O] \leftrightarrow 2[O] = CO \end{array}$						•	•	•		
Average relative error between experimental and predicted data/%	14	30	28	12	8	8	8	8	50	50

<sup>a</sup> The final model 5 is based on the bold-faced reaction steps 1, 4, 5, 6, 7, 8 and 11.

ticle-mass-transfer limitations for oxygen, methyl radicals and ethane have been accounted for. The kinetic parameters of the various models were estimated by a stochastic search algorithm ("genetic algorithm")<sup>45</sup> by which the global minimum of the sum of deviations between predicted and experimental data was found with high probability.

## (a) Model discrimination

The final reaction scheme and hence, the respective kinetic model was selected by discrimination based on the quality of fit between experimental kinetic data and simulated data (see Table I). According to the final model, methane is reversibly activated by monoatomic surface oxygen resulting in methyl radicals and surface OH groups (step 1). Gas-phase oxygen is incorporated into the surface via its molecular adsorption and consecutive dissociation (steps 4 and 5). CH<sub>3</sub> species either react with monoatomic oxygen on the surface (step 8), resulting in total oxidation, or recombine in the gas-phase (step 7). A second source of  $CO_x$  formation, in addition to reaction (8), is the oxidation of ethane by molecular-oxygen species on the surface (step 11). It should be emphasized that, in this reaction step, various possible intermediates are lumped together. However, the further subdivision of this reaction step is irrelevant for the fitting procedure. Thus, this reaction explains the increased C<sub>2</sub>H<sub>6</sub> consumption and the lowering of C2H6 selectivity with increasing partial oxygen pressure as observed experimentally. Therefore, the product distribution is more likely controlled by the ability of the catalysts to dissociate gas-phase oxygen quickly and by the activity of the dissociated oxygen to oxidize CH<sub>3</sub>, compared to its generation and recombination. The addition of different steps of CO<sub>2</sub> adsorption to the model did not improve the fit of the experimental data in the range of low conversion applied.

## (b) Relationship between rate constants and catalyst composition

Rate constants and electrical conductivity data are compared with respect to catalyst composition (see Table II). The uncertainty of the kinetic parameters amounts to 70%. Nevertheless, the constants are considered to be meaningful; this is derived from the fact that the reaction rate constant for homogeneous gas-phase coupling of methyl radicals  $(k_7)$  is in the same order of magnitude as that reported in the literature<sup>46</sup>  $(1.6 \cdot 10^{13} \text{ cm}^3 \cdot \text{mol}^{-1})$ .

Table 11 Electrical conductivity  $\sigma(T = 1023 \text{ K}, n\text{-type: } p(O2) = 3 \cdot 10^{-2} \text{ kPa}, p\text{-type: } p(O2) = 35 \text{ kPa})$  and rate constants (T = 993 K) depending on catalyst composition.

	ь	Catalyst								
		CeO <sub>2</sub>	CaO(5%)/	CaO(10%)/	CaO(20%)/					
		-	CeO <sub>2</sub>	CeO <sub>2</sub>	CeO <sub>2</sub>					
$A_{\rm BET}/m^2 g^{-1}$										
}		2.0	2.3	1.9	2.0					
$\sigma/Ohm^{-1} cm^{-1}$										
$\sigma_{\rm ion}$		0	$0.5 \cdot 10^{-4}$	$2.7 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$					
$\sigma_{\rm e}$ -		$1.6 \cdot 10^{-5}$	$0.1 \cdot 10^{-5}$	0	0					
$\sigma_{\rm h}$		0	0	0	$2.2 \cdot 10^{-5}$					
$k_i / \text{ml} \cdot (\text{g} \cdot \text{s} \cdot \text{Pa}^{\text{b}})^{-1}$										
$k_1$	0	6.104	$5 \cdot 10^{3}$	$8 \cdot 10^{3}$	$5 \cdot 10^4$					
$k_{-1}$	0	9.1015	8.1014	$5 \cdot 10^{13}$	$4 \cdot 10^{15}$					
k <sub>4</sub>	0	1.1012	1.1011	$4 \cdot 10^{11}$	$2 \cdot 10^{13}$					
k_4	-1	$1 \cdot 10^{26}$	$8 \cdot 10^{24}$	$7 \cdot 10^{23}$	$6 \cdot 10^{25}$					
ks	-1	8.10 <sup>15</sup>	8.1014	$5 \cdot 10^{13}$	$7 \cdot 10^{13}$					
$k_6$	-1	5.1011	5.10 <sup>11</sup>	$4 \cdot 10^{11}$	$8 \cdot 10^{13}$					
$k_7$	1	$3 \cdot 10^{3}$	$2 \cdot 10^{3}$	$2 \cdot 10^{3}$	$2 \cdot 10^{3}$					
$k_8$	0	4 · 10 <sup>5</sup>	$2 \cdot 10^{5}$	$1 \cdot 10^{5}$	9·10 <sup>4</sup>					
$k_{11}$	0	3.1011	$8.10^{9}$	$3 \cdot 10^{10}$	$7 \cdot 10^{10}$					

 $s^{-1}$ ; estimated:  $2.6 \cdot 10^{12}$  cm<sup>3</sup> · mol<sup>-1</sup> · s<sup>-1</sup>), and is independent of catalyst composition as opposed to the other constants.

A distinction between the electronic states of the active surface sites, *i.e.*, surface defects  $(V_0, V_0, V_0)$  and surface oxygen species  $(O^-, O^{2^-} \text{ and } O_2, O_2^-, O_2^{2^-})$ , was not incorporated into the modelling procedure. Therefore, the rate constants of the catalytic surface reactions reflect a distribution of various electronic states and of various reactivities of the surface sites. In that manner, n- and *p*-type conductivity affects this distribution by providing electron donors or acceptors for the surface species. Furthermore, the oxygen-anion conductivity is related to the number of surface-oxygen defects on which oxygen-anion mobility depends, assuming that surface and bulk defects are in equilibrium  $^{14,47}$ . The incorporation of CaO into the  $CeO_2$  lattice leads to an increase of oxygen-anion conductivity up to a maximum at about 10 to 15 mole%  $CaO^{48}$ Simultaneously, the proportion of *n*-type conductivity decreases with increasing CaO content while above 15 mole% CaO the catalysts reveal p-type conductivity at high oxygen partial pressure<sup>49</sup>.

For the  $CaO/CeO_2$  catalysts the rate constants of methyl. radical formation  $(\tilde{k}_1)$ , its reverse reaction  $(k_{-1})$ , of oxygen desorption and dissociation  $(k_{-4}, k_5)$  as well as of consecutive oxidation of ethane by molecular surface oxygen correlate with electron conductivity ( $\sigma_{h} + \sigma_{e-}$ ). If both n- and p-type conductivity promote these steps, the requirement for the catalyst should be the availabily of electron acceptors and donors. These results imply that reaction steps promoting and impairing ethane formation are coupled via the same properties of the solid. On the other hand, the rate constant of the consecutive methyl radical oxidation  $(k_8)$  decreases with increasing *p*-type and/or decreasing n-type conductivity. Thus, this step is suppressed by avoiding n-type conductivity. The observed correlation between electron conductivity and reducibility of the cations within the catalytic solids on one hand and catalytic performance on the other hand agrees with results of *Lunsford* et al.<sup>13</sup> who found a dependence between the activity of lattice oxygen for the oxidation of CH<sub>3</sub> radicals and the reducibility of different oxide catalysts.

## (c) Summary of results from the microkinetic analysis

The analysis is supported by the TAP results obtained in our laboratory in the following manner. As shown by the transient studies, a high degree of surface coverage by active oxygen species leads to the promotion of non-selective reaction pathways (cf. Figure 6), probably caused by a change of the oxygen state depending on the surface coverage. Corresponding to this findings the microkinetic analysis indicates that the proportion of diatomic surface oxygen sites increases with increasing partial pressure of oxygen and this, in turn, results in a significant decrease in ethane selectivity.

The oxygen exchange experiments mentioned above revealed that dissociatively adsorbed oxygen species are consumed much more rapidly by methane than they can recombine and desorb. Thus, the reverse step of reaction 5 should not be significant under the reaction conditions proposed in the final model.

From the given estimates of  $k_1$  and  $k_{-1}$ , it follows that the equilibrium 1 is strongly to the left-hand side. The reversibility of this step is supported by H–D isotopic exchange in methane which resulted in high exchange selectivity, *e.g.*, up to 70% for Sm<sub>2</sub>O<sub>3</sub> with CD<sub>4</sub> conversion of 90%<sup>36</sup>.

It is also in agreement with earlier findings that methyl species recombine in the gas phase to form ethane<sup>50,36</sup>.

Finally, it could be clearly shown that the rate constants depend on the electrical properties of the catalytic solids.

#### Conclusions

Despite the fact that different catalysts were used in the transient and microkinetic studies the general conclusion can be drawn that certain properties of the solid, in particular the type of conductivity, determine the selective reaction pathway to ethane in the OCM reaction. The transient investigations on oxygen exchange and the reaction of methane with short-lived surface oxygen species, as well as the microkinetic analysis of the elementary reaction steps, showed the importance of dissociative oxygen adsorption for the selective formation of ethane. It was further shown that the high activity of  $Sm_2O_3$  with respect to oxygen exchange, which reflects the capacity of the catalyst for dissociative adsorption of oxygen, correlates with its ability to form the adsorbed oxygen species which are responsible for selective methane activation via an Eley-Redial-type of mechanism. The relationship between the type of conductivity and oxygen adsorption with respect to the OCM reaction was discussed first by Dubois and Cameron<sup>14</sup>. The microkinetic analysis showed that product formation is most likely controlled by the ability of catalysts to dissociate gas-phase oxygen and by the activity of the dissociated oxygen in oxidising CH<sub>3</sub>. If total oxidation is to be avoided the adsorption of diatomic surface oxygen should be slow and its transformation to a monoatomic species should be fast to keep the surface concentration of any diatomic oxygen close to zero. A *p*-type conductor (with high oxygen-anion conductivity) should be chosen as catalyst because, under these circumstances, methane activation is promoted and the oxidation of methyl radicals can simultaneously be avoided. It should be noted that Sm<sub>2</sub>O<sub>3</sub>, being one of the more active and selective catalysts for the OCM reaction, shows both p-type and oxygen-anion conductivity<sup>51</sup>. Using the above findings as a guideline in catalyst design an improvement of ethane yield and presumably also that of ethylene in the OCM reaction is expected; this assumption is supported by recent results which are being published elsewhere<sup>52</sup>.

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