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Transient Studies on the Role of Oxygen Activation in the Oxidative Coupling of Methane over Sm_2O_3, Sm_2O_3/MgO, and MgO Catalytic Surfaces

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The interaction of oxygen with catalytic surfaces of MgO, Sm_2O_3, and Sm_2O_3 (5 mol%)/MgO and the reaction of methane with short-lived surface oxygen species over Sm_2O_3 were studied by transient experiments. The oxygen exchange between gas-phase $^{18}O_2$ and surface oxygen $^{16}O_S$ was investigated in the temperature range from 539 to 1035 K. The oxygen-exchange activity decreased from Sm_2O_3 (E_a = 81 kJ/mol) via Sm_2O_3/MgO (E_a = 96 kJ/mol) to MgO (E_a = 261 kJ/mol). The presence of methane did not influence the exchange rate of $^{18}O_2$ with the surface. This indicates (a) that oxygen activation on the surface is faster than activation of methane and (b) that neither gas-phase oxygen nor nondissociated surface oxygen is involved in the reaction with methane under the reaction conditions applied. It was shown that the surface reaction of methane with oxygen intermediates formed from gas-phase O_2 is faster than the desorption of any diatomic oxygen species. Over Sm_2O_3, the degree of oxidative conversion of methane and the resulting product distribution are determined by the amount of surface-oxygen species formed by dissociation of gaseous O_2 on the catalyst surface. It is suggested that these active oxygen sites consist of highly reactive short-lived species (below 200 ms) and also species having longer lifetimes. © 1994 Academic Press, Inc.

INTRODUCTION

In the oxidative coupling of methane (OCM) it is widely accepted that the catalyst surface acts as a source for producing methyl radicals from methane which then combine to ethane in the gas phase. However, the type of active oxygen sites on the surface responsible for methane activation, i.e., lattice or adsorbed oxygen species, is still a matter of controversial discussion.

Different techniques have been used to study the effect of catalyst properties on oxygen activation and on the role of lattice oxygen mobility in this process (1–11). Temperature programmed isotopic exchange between gas-phase and lattice oxygen as well as step changes in $^{16}O_2$ and $^{18}O_2$ feeds have been applied by Kalenik and Wolf (1, 2) to elucidate the role of oxygen on La_2O_3 and Sr(1%)/La_2O_3 catalysts. Using steady-state isotopic transient kinetic analysis Peil *et al.* (3, 4) studied the exchange of oxygen over MgO and Li/MgO. Results of these studies showed that the increased catalyst activity which was observed after addition of promoters coincided with an increase of lattice-oxygen mobility. For the OCM reaction over $LaCoO_{3-\delta}$ based mixed oxides Hayakawa *et al.* (5) concluded that disordering of oxygen vacancies in the perovskite structure is an important factor for catalyst activity. For different pure and doped rare-earth metal oxides Borchert *et al.* (6) measured the oxygen-ion conductivity which is directly proportional to the concentration of anion vacancies and showed that the C_{2+} selectivity of the catalysts increases with increasing conductivity. To explain this correlation it was assumed that enhancing the amount of surface-anion vacancies leads to a fast transformation of weakly adsorbed oxygen species to lattice oxygen, hereby suppressing nonselective oxidation paths.

Peil *et al.* (3, 4) concluded that under reaction conditions, CH_4 reacts very readily with adsorbed atomic oxygen to carbon oxides and that this process is faster than the surface formation and subsequent desorption of diatomic oxygen. Based on the oxygen exchange and kinetics of methane reaction over alkali/nickel oxides, Sun *et al.* (7) have shown that methane reacts differently with surface-bonded oxygen and lattice oxygen. Choudhary and Rane (8) concluded from pulse-microreactor studies using La_2O_3, Sm_2O_3, Eu_2O_3, and Yb_2O_3 that the presence of gaseous oxygen is essential for a high activity in the OCM reaction while the reactivity of lattice oxygen was very low. Lapszewicz and Jiang (9) showed that no general correlation was possible between the rate of oxygen exchange and the rate of methane conversion for cubic and monoclinic Sm_2O_3 as well as for MgO and Al_2O_3. From results of temperature-programmed reaction of methane

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over Sm_2O_3, Bi/P/K/MgO, and Sr/Bi/Li/MgO catalysts and from results of oxygen exchange Keulks and Liao (10) concluded that surface lattice oxygen is directly responsible for C_2 hydrocarbon formation. The role of adsorbed oxygen species was proposed to replenish the pool of surface lattice oxygen. On the contrary, for Sm_2O_3 it has been shown in our previous work (11) that active surface-oxygen species generated from gas-phase oxygen are responsible for methane activation and C_2 formation.

In the present work, further results are reported on the nature of active oxygen surface sites on Sm_2O_3, Sm_2O_3 (5 mol%)/MgO, and MgO from transient pulse experiments applying the temporal-analysis-of-products (TAP) reactor (11). The catalysts were investigated with respect to oxygen activation using the oxygen-exchange reaction between gas-phase $^{18}O_2$ and catalytic surfaces containing ^{16}O in the absence and presence of methane. The main aim was to obtain quantitative data on the reaction of methane with short-lived oxygen intermediates, *O(s), formed on the Sm_2O_3 surface by its interaction with gaseous oxygen and to determine the dependence of methane conversion and formation of products on the amount of them. Such results should advance the understanding of oxygen pathways in the OCM reaction.

EXPERIMENTAL

Catalyst Preparation and Characterization

The preparation of MgO (S_{BET} = 9.8 m^2/g) and Sm_2O_3 (S_{BET} = 2.3 m^2/g) by calcination of the respective nitrates has been described elsewhere (11a). Sm_2O_3 (5 mol%)/MgO (S_{BET} = 13.7 m^2/g) was prepared by impregnation of MgO (S_{BET} = 39.3 m^2/g) by the incipient wetness method using an aqueous solution containing the required amount of $Sm(NO_3)_3 \cdot 6H_2O$ (the MgO was prepared by precipitation with NaOH and repeated washing of the precipitate). The impregnated solid was dried overnight at room temperature, followed by calcination at 1123 K for 3 h. The surface concentration of Sm amounted to 11.8 at.% as determined by XPS. After calcination the material was pelletized and after sieving the 255–350 μm fraction was used as catalyst. Similar to Sm_2O_3 (11a) only the cubic form of samaria was found by XRD of Sm_2O_3/MgO.

Gases

High purity CH_4 (99.995%), O_2 (99.996%) and Ne (99.998%) from Messer-Griesheim (Oberhausen, Germany) and $^{18}O_2$ (isotopic purity 97.6 at.% ^{18}O) from MSD Isotopes (Montreal, Canada) were used in the experiments.

TAP Reactor Operation

The set-up of the TAP reactor system has been described in detail elsewhere (11, 12). Therefore, only conditions specific for the present work are mentioned. For each experiment, the catalyst was packed between two layers of quartz of the same particle size. The catalyst was first exposed to oxygen pulses at 1035 K; then the temperature was lowered to the respective temperatures at which O_2 was pulsed until a stable response was observed at the reactor outlet. The reactor was kept at 10^{-4} Pa for 10 min before the pulse experiments started. After 2 or 4 pre-pulses, 6 to 10 pulses were averaged to reduce the signal-to-noise ratio in the response.

Quantitative Data Evaluation

In mass spectroscopic identification of compounds leaving the TAP reactor the following atomic mass units (amu) were used: 44 (CO_2); 36 ($^{18}O_2$); 34 ($^{18}O^{16}O$), 32 ($^{16}O_2$); 30, 29 (C_2H_6); 28 (CO_2, CO, C_2H_6, C_2H_4); 26, 25 (C_2H_6, C_2H_4); 16, 15 (CH_4). The fragmentation patterns of all substances were measured to calculate the contributions of different compounds to a measured amu signal and to deconvolute the experimental data. Relative sensitivities of CH_4, C_2H_6, C_2H_4, CO, CO_2, and O_2 according to their different ionization probabilities were determined to calculate yields and selectivities. The sensitivities of the different isotopic oxygens were assumed to be similar.

Oxygen Exchange

The oxygen exchange between gas-phase O_2 and the catalytic metal-oxide surfaces (MgO, Sm_2O_3 and Sm_2O_3 (5 mol%)/MgO) was studied in the temperature range from 539 to 1035 K using a reactor charge of 690 mg Sm_2O_3, 330 mg MgO, and 280 mg Sm_2O_3 (5 mol%)/MgO resulting in similar volumes of 0.37 ml. The total surface areas for the tested amount of catalyst amounted to 3.3 m^2 for MgO, 3.8 m^2 for Sm_2O_3/MgO, and 1.6 m^2 for Sm_2O_3. To study the oxygen exchange over Sm_2O_3 at high temperatures, experiments with a lower catalyst load of 120 mg were used to achieve conversions of less than 100%.

After oxygen pretreatment (see above), an $^{18}O_2$/Ne = 1 : 2 mixture was pulsed over the catalysts; the pulse size amounted to 2×10^{16} molecules. The influence of methane on the oxygen exchange reaction was studied by simultaneous pulsing of CH_4/Ne (1 : 1) and $^{18}O_2$/Ne (1 : 2) mixtures introduced *via* two beam valves. The ratio of CH_4 to $^{18}O_2$ amounted to 1.1 in these experiments.

The activation energies of the oxygen exchange reaction were estimated from the dependence of oxygen conversion (at constant contact time) on tempeature for $X(O_2) < 50\%$.

Reaction of Methane with Short-Lived Surface Oxygen Species

The influence of surface oxygen species, *O(s), formed by the interaction of gas-phase oxygen with the catalyst

surface, on the activation and reaction of methane was studied by sequential pulses of oxygen (O_2/Ne = 9/1) and methane (CH_4/Ne = 1/1) over Sm_2O_3 (690 mg). First, the oxygen pulse was introduced, then methane was pulsed after a time interval of 50 or 100 ms. For each experiment this procedure was repeated 6 to 10 times with a constant time interval of 1 s between methane and oxygen pulses, then the averaged responses were used. These experiments resulted in the pulse sequence $O_2 \rightarrow CH_4 \rightarrow O_2 \rightarrow CH_4$ ....

The dependence of methane conversion and C_2 hydrocarbon formation on the amount of *O(s) on the surface of Sm_2O_3 was investigated using sequential pulsing of oxygen and methane where the methane pulse intensity was kept stable at 1.9×10^{16} CH_4 molecules/pulse while the intensity of the oxygen pulse was varied between 0.5×10^{15} and 0.4×10^{17} O_2 molecules/pulse. Experiments were performed at 908 K; at this temperature CO_2 that might have been formed was not detectable due to its slow desorption.

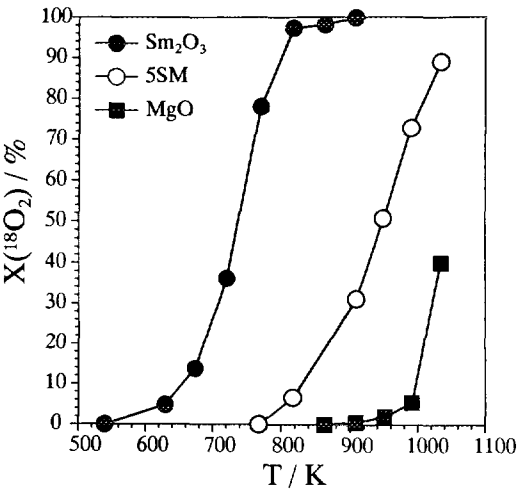

FIG. 1. Dependence of the conversion of gas-phase $^{18}O_2$ (2×10^{16} molecules/pulse) in the isotopic exchange reaction with lattice oxygen on reaction temperature. Sm_2O_3, 690 mg with a total surface area of 1.6 m^2; Sm_2O_3 (5 mol%)/MgO (5SM), 280 mg, 3.8 m^2; MgO, 330 mg, 3.3 m^2.

RESULTS

Oxygen Exchange in the Absence and Presence of Methane

Results are reported for Sm_2O_3, Sm_2O_3 (5 mol%)/MgO, and MgO on (a) oxygen exchange reaction between gas-phase $^{18}O_2$ and surface lattice ^{16}O and (b) the influence of methane on the exchange reaction in order to derive information about the competitive activation of methane and oxygen on the catalyst surface.

(a) Oxygen exchange in the absence of methane. The temperature dependence of the $^{18}O_2$ conversion to isotopic exchange products when pulsing $^{18}O_2$ over the metal oxide (^{16}O) surfaces are summarized for the three catalysts in Fig. 1. The activity for the exchange reaction decreased from Sm_2O_3 via Sm_2O_3/MgO to MgO. Due to the high activity of Sm_2O_3, almost total conversion of $^{18}O_2$ was achieved at 817 K while for the other two materials higher temperatures were needed. All possible oxygen molecules ($^{18}O_2$, $^{16}O^{18}O$, $^{16}O_2$) were detected at the reactor outlet; the oxygen balance in all experiments amounted to 95 ± 5% and hence, the amount of oxygen consumed for any irreversible adsorption that might have occurred was not significant.

The yields of oxygen exchange products obtained when using various catalysts are shown in Figs. 2a–2c. The yield of $^{16}O_2$ over Sm_2O_3 (Fig. 2a) and Sm_2O_3/MgO (Fig. 2b) steadily increased with increasing temperature and it became the main product at $T > 900$ K, while the yield of $^{16}O^{18}O$ passed through a maximum and did not exceed 8% over Sm_2O_3 and 14% over Sm_2O_3 (5 mol%)/MgO. On the contrary, for MgO (Fig. 2c) the formation of $^{16}O^{18}O$ was higher compared to $^{16}O_2$ at all temperatures.

The analysis of the response shapes of the different oxygen isotopes supplied additional information about the mechanism of the reaction. The transient responses of $^{18}O_2$, $^{16}O^{18}O$, and $^{16}O_2$ at the reactor outlet to $^{18}O_2$ pulses over the different catalytic surfaces are presented in Figs. 3a–3c. It is evident that the oxygen exchange proceeds stepwise for all catalysts. One may assume that there is first the formation of $^{18}O^{16}O$ which can desorb from the surface and adsorb again with further exchange to form $^{16}O_2$.

Over Sm_2O_3 (5 mol%)/MgO a marked tailing of the $^{16}O_2$ response was observed indicating a stronger oxygen interaction with surface sites compared to Sm_2O_3 and MgO.

(b) Oxygen exchange in the presence of methane. The influence of methane on the oxygen exchange reaction was investigated using simultaneous pulsing of CH_4/Ne and $^{18}O_2$/Ne mixtures. Reaction of methane yielded CO, CO_2, and C_2 hydrocarbons as products. The presence of methane did not affect to any significant degree the shape and intensity of the $^{18}O_2$ response (see Fig. 4) which corresponds to the part of the oxygen inlet pulse that passed through the reactor without dissociative adsorption on the catalyst surface. However, methane affected the yield of exchange products as demonstrated for Sm_2O_3 (Fig. 5a) and for Sm_2O_3 (5 mol%)/MgO (Fig. 5b); the detected amounts of $^{16}O_2$ and also of $^{16}O^{18}O$ decreased sharply in the presence of methane. Transients of exchanged oxygen molecules ($^{18}O^{16}O$ and $^{16}O_2$) when pulsing a CH_4–$^{18}O_2$

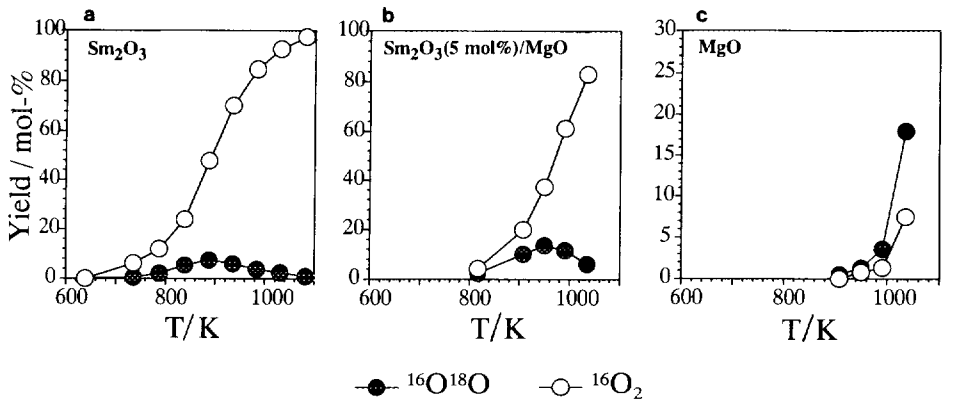

FIG. 2. Dependence of yields of oxygen exchange products $^{16}O_2$ and $^{16}O^{18}O$ on reaction temperature when pulsing $^{18}O_2$ (2×10^{16} molecules/pulse) over different catalyst surfaces: (a) Sm_2O_3, 120 mg with a total surface area of 0.3 m^2; (b) Sm_2O_3 (5 mol%)/MgO (5SM), 280 mg, 3.8 m^2; (c) MgO, 330 mg, 3.3 m^2.

mixture and solely $^{18}O_2$ over Sm_2O_3 are presented in Fig. 6; the responses became more narrow in the presence of methane.

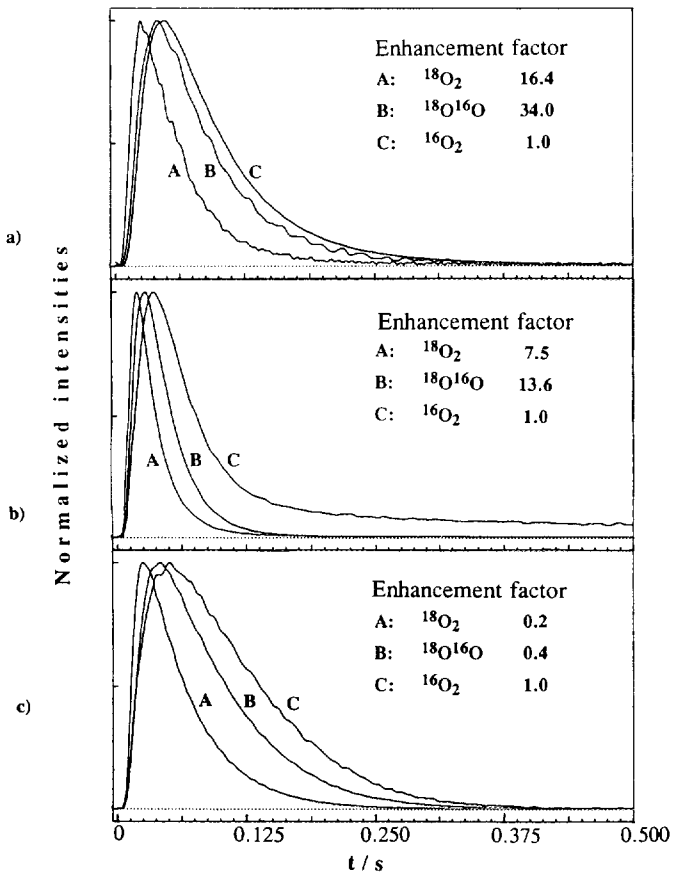

FIG. 3. Normalized responses of oxygen isotopes $^{16}O_2$ and $^{16}O^{18}O$ when pulsing $^{18}O_2$ over (a) Sm_2O_3 at 1083 K (b) Sm_2O_3 (5 mol%)/MgO at 1035 K, and (c) MgO at 1035 K.

Reaction of Methane with Short-Lived Surface Oxygen Species over Sm_2O_3

The pathways of dissociated surface-oxygen species formed by adsorption of O_2 on Sm_2O_3 (see above) and the influence of their amount on methane conversion as well as product formation were investigated by experiments with sequential pulsing of oxygen and methane (see Experimental). Products of the OCM reaction were only observed in response to methane pulses but not to oxygen pulses. This indicates that oxidizable carbon-containing species on the surface (like CH_xO) have only a very short lifetime or they do not stay on the surface at all. The O_2 response to an oxygen pulse without methane (curve A) and to sequential pulsing of oxygen and methane (curve B) are shown in Fig. 7. From this figure it is obvious that a sharp decrease in the oxygen response occurs (see curve B) when methane is introduced to the reactor (curve C) which is due to conversion of oxygen with methane. In accordance with the results on oxygen exchange it can

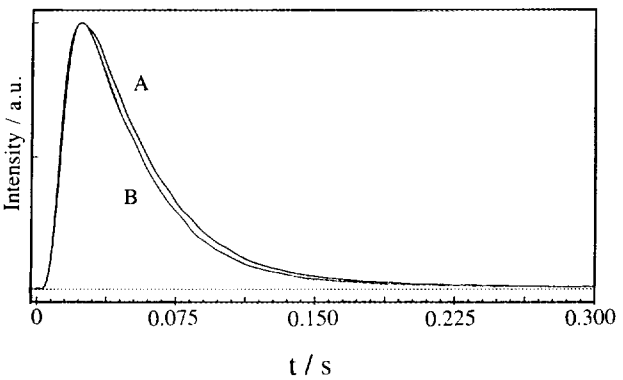

FIG. 4. Transient responses of $^{18}O_2$ over Sm_2O_3 at 1083 K when pulsing (A) $^{18}O_2$ and (B) $CH_4/^{18}O_2$ mixture.

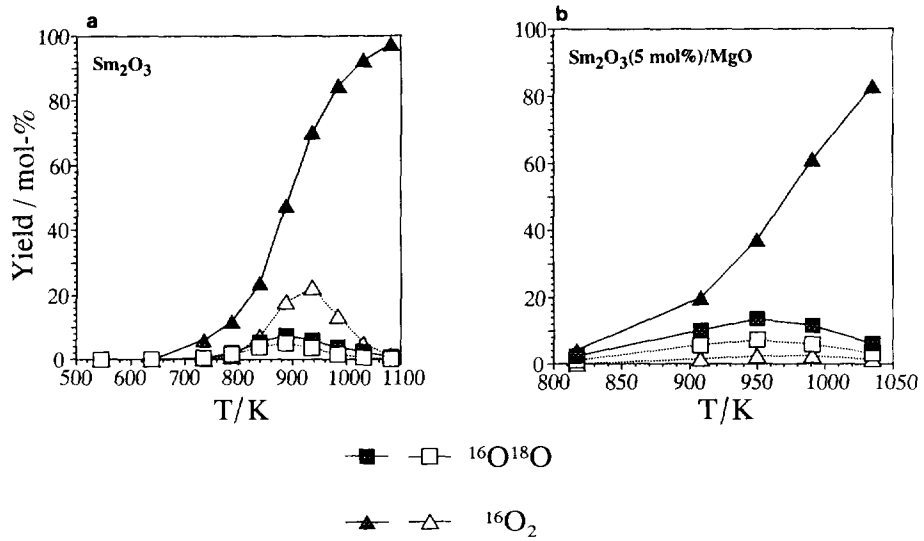

FIG. 5. Dependence of the yields of oxygen exchange products $^{16}O_2$ and $^{16}O^{18}O$ on reaction temperature when pulsing $^{18}O_2$ (filled symbols) and a $CH_4/^{18}O_2$ mixture (open symbols) over (a) Sm_2O_3, and (b) Sm_2O_3 (5 mol%)/MgO.

be concluded that this proportion of oxygen corresponds to the oxygen intermediates still bonded to the catalyst surface when the methane pulse passed over the catalyst. From these results the conversion of oxygen was determined which corresponds to the amount of oxygen species taking part in methane conversion (shaded part of the oxygen response). By adjusting the intensity of the oxygen pulse it was possible to create different amounts of active oxygen species on the surface. Conversion of CH_4 is shown as a function of the amount of adsorbed oxygen, *O(s), consumed for $T = 908$ K (see Fig. 8); at this temperature the methane reaction with lattice oxygen, i.e., in the absence of adsorbed oxygen, resulted only in a conversion of approx. 3% as can be derived from Fig. 8. The presence of adsorbed oxygen species resulted in an increase in methane conversion from 3 to 39%. The maximum concentration of these species on the surface was 1.4×10^{16} atoms/m^2; this value is less than 1% of a monolayer of lattice oxygen which is approx. 10^{19} atoms/m^2.

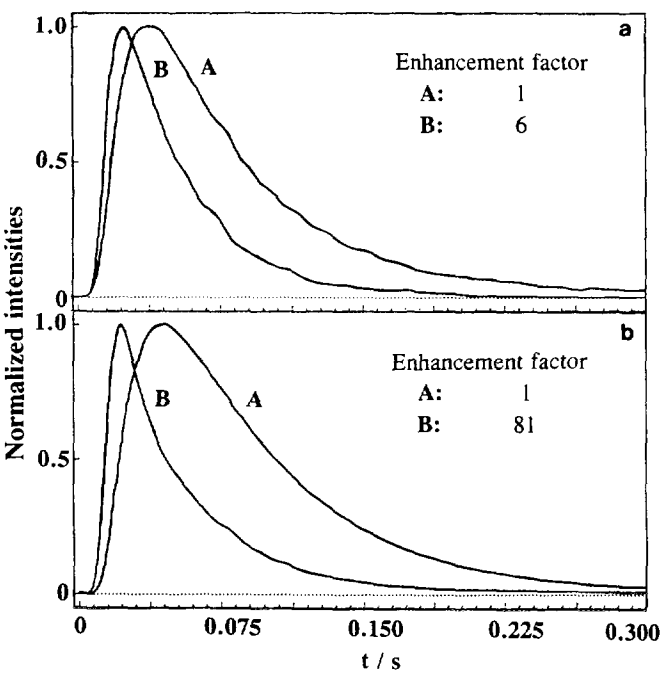

FIG. 6. Normalized responses of the $^{18}O^{16}O$ (a) and $^{16}O_2$ (b) over Sm_2O_3 at 1083 K when pulsing of (A) $^{18}O_2$ or (B) $CH_4/^{18}O_2$.

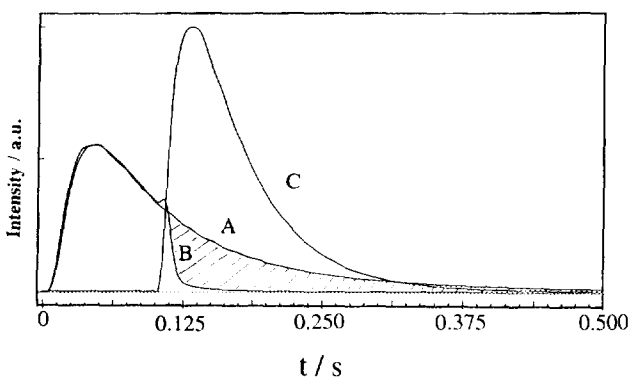

FIG. 7. Reactor outlet responses over Sm_2O_3 at 908 K: (A) oxygen response to O_2 (1.4×10^{16} molecules/pulse); (B) oxygen, and (C) methane responses for sequential pulsing of oxygen (1.4×10^{16} molecules/pulse) and methane (1.9×10^{16} molecules/pulse) with a time interval of 100 ms between pulses.

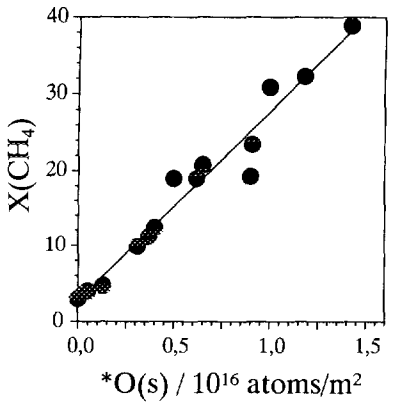

FIG. 8. Dependence of methane conversion on the amount of active oxygen species, *O(s), formed by interaction of gas-phase oxygen on the surface of Sm_2O_3 at 908 K.

The dependences of product selectivities on the amount of *O(s) consumed are shown in Figs. 9a and 9b. Because CO_2 was not detected due to its strong adsorption (11), its amount was estimated from the mass balance. While lattice oxygen of Sm_2O_3 is not selective the presence of small amounts of surface oxygen *O(s) resulted in a sharp increase in C_2 and CO selectivities. A maximum of ca. 24% in C_2 selectivity was obtained at *O(s) = 0.2×10^{16} atoms/m^2 while a further increase of surface concentration of oxygen led to a decrease in selectivity. Ethylene was detected only in the presence of *O(s); the ethylene-to-ethane ratio increased with increasing surface concentration of *O(s). For nonselective product formation an increase in concentration of *O(s) led first to a rise of CO selectivity having a maximum at 0.4×10^{16} oxygen atoms/m^2 which was then followed by further decreasing S(CO) accompanied by an increase in $S(CO_2)$.

For the formation of C_2 hydrocarbons a linear dependence of yield on the amount of active oxygen species was observed but only for concentrations less than 0.7×10^{16} oxygen atoms per m^2 (cf. Fig. 10); above this value the loss in C_2 selectivity was no longer compensated by the increase in methane conversion.

DISCUSSION

Oxygen activation over Sm_2O_3, Sm_2O_3 (5 mol%)/MgO, and MgO catalysts

From the temperature dependence of the conversion of $^{18}O_2$ to the various oxygen isotopes activation energies for the exchange reaction were derived (see Table 1). The value of 81 kJ/mol for Sm_2O_3 is in good agreement with the results of Winter (14) who reported an activation energy of 79.5 kJ/mol; the corresponding values increase from Sm_2O_3 via Sm_2O_3/MgO to MgO. The addition of only 5% Sm_2O_3 to MgO results in a considerable decrease of the activation energy for oxygen exchange, i.e., from 261 kJ/mol for pure MgO to 96 kJ/mol for the samaria-doped MgO catalyst. The high activation energy of 261 kJ/mol for MgO indicates that the dissociative adsorption of oxygen is a difficult process on this solid compared to samaria and the Sm_2O_3-containing catalyst. This is partly in agreement with some previous results: Kalenik and Wolf (2) reported that on MgO only 7% of the lattice oxygen are available for exchange compared to 70% on lanthana; Peil *et al.* (4) observed an increase in lattice oxygen mobility when Li was added to MgO with a corresponding decrease in the activation energy of oxygen-anion diffusion from 266 kJ/mol for pure MgO to 61 kJ/mol for Li/MgO. In our previous work (11) we have shown that the

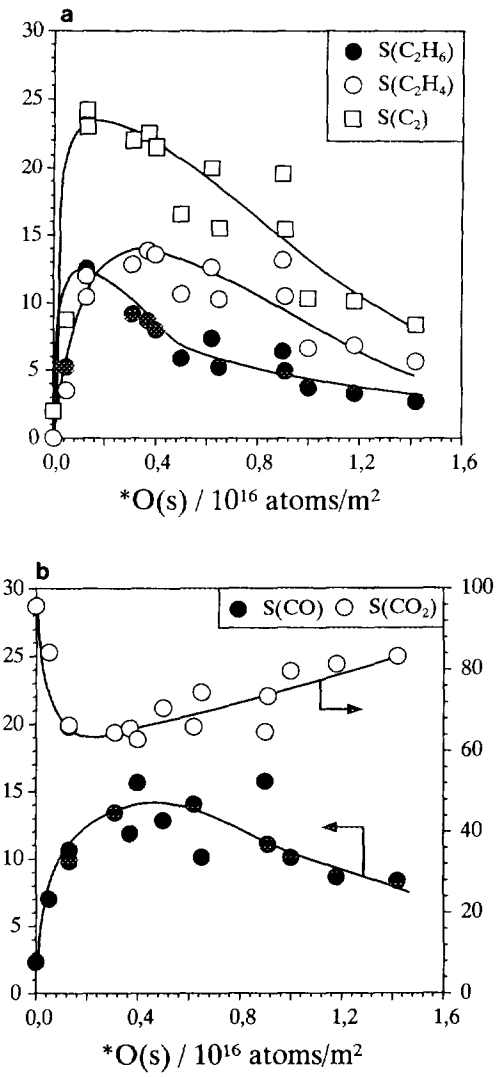

FIG. 9. Dependence of product selectivities on the amount of *O(s) on the surface of Sm_2O_3 at 908 K: (a) ethane, ethylene, and total C_2 selectivities; (b) carbon oxide and carbon dioxide selectivities.

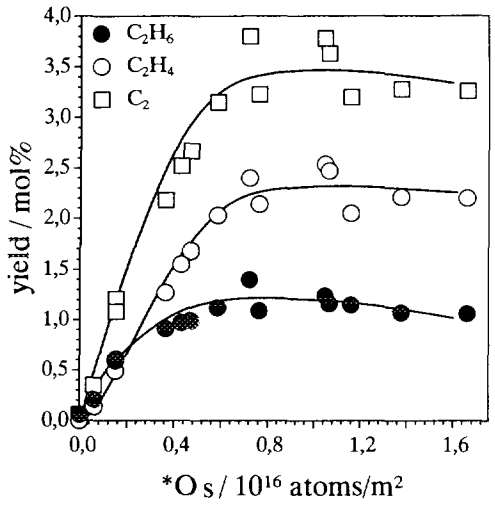

FIG. 10. Dependence of the yield of C_2 hydrocarbons on the concentrations of *O(s) on the surface of Sm_2O_3 at 908 K.

interaction of gas-phase O_2 with MgO is very weak and hence, mainly lattice oxygen species provide the activity for methane conversion and ethane formation via methyl radicals. The activation energy of 261 kJ/mol is, however, much higher than the value of 159 kJ/mol reported for the oxygen exchange on MgO (13) but comparable to the activation energy of 266 kJ/mol for oxygen diffusion (4) which might be the rate-limiting step under the applied conditions.

Because no mixed phases of Sm and Mg oxides are known (6b) the dopant effect of samaria cannot be ascribed to oxygen-anion defect formation resulting in increased oxygen diffusivity as suggested by Kalenik and Wolf (1, 2) for doping of La_2O_3 with 1% SrO and by Peil *et al.* (4) for Li/MgO. It was expected that the presence of Sm_2O_3 on the surface is responsible for the lower activation energy on Sm_2O_3 (5 mol%)/MgO compared to MgO. There is obviously an interaction between the two surface phases which becomes apparent by the long tailing of the $^{16}O_2$ response over Sm_2O_3 (5 mol%)/MgO (Fig. 3b, curve C); this reflects a larger number of strongly bonded oxygen species compared to MgO and Sm_2O_3.

TABLE 1

Activation Energies for the Exchange of Gas-Phase $^{18}O_2$ with Lattice Oxygen (^{16}O) of MgO, Sm_2O_3 (5 mol%)/MgO, and Sm_2O_3

Catalyst	E_a (kJ · mol^{-1})	Temperature range (K)
MgO	261 ± 12	908–1035
Sm_2O_3 (5 mol%)/MgO	96 ± 3	817–1035
Sm_2O_3	81 ± 2	629–1031

The analysis of the responses of the different oxygen isotopes during the exchange of $^{18}O_2$ with the catalyst surfaces reveals information about the mechanism of this reaction (see Figs. 3a–3c). It is obvious that the oxygen exchange proceeds stepwise for all catalysts with the formation of first $^{18}O^{16}O$ followed by $^{16}O_2$. This observation corresponds to the reaction scheme proposed by Winter (13, 14) for the dissociative atomic oxygen exchange:

$$^{18}O_2 + {}^{16}O(s) \rightleftarrows {}^{16}O^{18}O + {}^{18}O(s) \quad [1a]$$

$$^{16}O^{18}O + {}^{16}O(s) \rightleftarrows {}^{16}O_2 + {}^{18}O(s) \quad [1b]$$

(O(s) = surface oxygen without specifying its electronic charge).

Although for all tested solids first $^{18}O^{16}O$ (according to reaction 1a) and then $^{16}O_2$ (according to reaction [1b]) was detected, it cannot be excluded that $^{16}O_2$ is directly formed by reaction [2] if this step is slower than reaction [1a]:

$$^{18}O_2 + 2\ {}^{16}O(s) \rightleftarrows {}^{16}O_2 + 2\ {}^{18}O(s). \quad [2]$$

pathway [2] was called by Winter (13, 14) "molecular reaction" describing the participation of two neighbouring oxygen surface sites in the exchange reaction. The homomolecular exchange via reaction [3].

$$^{16}O_2 + {}^{18}O_2 \rightleftarrows 2\ {}^{16}O^{18}O \quad [3]$$

can be excluded in the present experiments: if this reaction proceeds to any significant extent the response for $^{16}O^{18}O$ should be later than that of $^{16}O_2$ because gas-phase $^{16}O_2$ is required for the formation of $^{16}O^{18}O$. However, for all applied conditions such a sequence has not been observed and therefore the results obtained reflect the oxygen exchange between gas phase and surface only.

Comparison of the Activation of Methane and Oxygen on Sm_2O_3 and Samaria-Doped MgO Surfaces

In experiments with simultaneous pulsing of CH_4 and $^{18}O_2$ neither the shape of the $^{18}O_2$ response (which represents the fraction of unreacted $^{18}O_2$) nor the $^{18}O_2$ consumption and, hence, the activation energies were different from the corresponding results of $^{18}O_2$ pulsing only (cf. Fig. 4). This leads to the conclusion that

(a) oxygen activation on the catalyst surface is faster than activation of methane; (b) gas-phase oxygen does not react with methane under the reaction conditions applied. However, the yield of oxygen exchange products (cf. Fig. 5) and especially their responses (cf. Fig. 6) are drastically changed by the presence of methane; formation of $^{16}O^{18}O$ and $^{16}O_2$ decreased and their responses became more narrow. This indicates that the oxygen species formed on the surface after dissociative adsorption of gas-phase $^{18}O_2$

are consumed faster by methane than they can recombine and desorb as diatomic oxygen as observed in the absence of methane. Also Ekstrom und Lapszewicz (15), Cant *et al.* (16), and Peil *et al.* (4) have reported that under reaction conditions the exchange of gas-phase O_2 with the lattice oxygen of Sm_2O_3 (15) and Li/MgO (4, 16) respectively is greatly reduced.

Based on the above results, it is possible to compare the rates of different elementary reaction steps on Sm_2O_3 and Sm_2O_3 (5 mol%)/MgO in the temperature range between 800 and 1035 K. It can be derived that the initial activation of methane in the OCM reaction which occurs most probably by C–H bond breakage is slower than the initial activation of O_2 through dissociative adsorption:

$$r(O_2 \text{ adsorption}) > r(CH_4 \text{ activation}).$$

No clear conclusion can be drawn concerning the competitive rates of recombination of active surface-oxygen species and their subsequent desorption from the catalyst surface and the rate of methane reaction with these species. The ratio of these rates determines the shape of the oxygen decay curve (curve B in Fig. 7). A preliminary kinetic evaluation indicates, however, that these two reaction rates are most probably of the same order of magnitude; further work on this subject is in progress.

Role of Different Oxygen Species on the Surface of Sm_2O_3 in the Conversion of Methane and the Formation of Products

The results of sequential pulsing of oxygen and methane indicate that active oxygen species, *O(s), formed on the surface by dissociative adsorption of gas-phase O_2 are very reactive for the conversion of methane. They were consumed nearly instantaneously when methane was pulsed over the catalyst (cf. Fig. 7) and they resulted in a much higher conversion of methane compared to its reaction with lattice oxygen (cf. Fig. 8). Since the concentration of *O(s) was always less than 1% of a monolayer 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.

Besides *O(s) also a small number of molecularly adsorbed O_2 species exists on the surface. This was derived from sequential pulsing of isotopic oxygen, $^{18}O_2$, and of CH_4. The response of $^{18}O_2$ (cf. Fig. 11) reflects that part of the oxygen pulse which was neither exchanged nor converted. The introduction of methane resulted in a second maximum of the $^{18}O_2$ response possibly corresponding to weakly bonded $^{18}O_2$ surface species that are displaced from the surface by the incoming methane pulse; however, no reaction occurred as derived from the constant area of the $^{18}O_2$ response in the absence and presence of methane. Thus, it can be concluded that neither gas-phase O_2 nor oxygen that interacts with the surface without dissociative adsorption is involved in the reaction with methane.

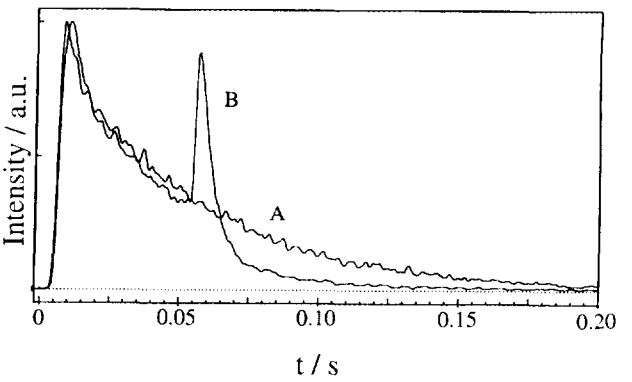

FIG. 11. Transient responses of $^{18}O_2$ over Sm_2O_3 at 908 K when pulsing of $^{18}O_2$ (A) and for sequential pulsing of $^{18}O_2$ and CH_4 with time interval of 50 ms (B).

The influence of the concentration of the active species, *O(s), on the product formation is depicted in Figs. 9 and 10. An increase of the C_2 and CO yields (Fig. 10) occurs only up to concentrations of less than 0.7×10^{16} oxygen atoms/m^2 while the yield of CO_2 continues to increase. There are two possible explanations for this behaviour:

(1) The product distribution is determined by the concentration of the active oxygen sites on the surface. At concentrations of less than 0.7×10^{16} atoms/m^2 the conversion of methane leads preferentially to both C_2 hydrocarbons and CO; only a small methane proportion is converted to CO_2. At higher concentrations, the higher "density" of active surface-oxygen sites results in a higher probability that a reacting methane molecule is in the neighbourhood of two (or more) active oxygen sites leading to its total oxidation or to a consecutive oxidation of ethane. Table 2 summarizes methane conversions (X) and product selectivities (S) obtained by sequential pulsing of O_2 and CH_4 with applying different time intervals between the pulses and different oxygen pulse sizes but similar amounts of converted surface oxygen species. There is no influence of the time interval on $X(CH_4)$ and the selectivities indicating that both values are mainly determined by the concentration of *O(s). However, this conclusion is only valid in the relatively short time interval of 50 to 100 ms.

(2) On the other hand, it might be assumed that not only one type of *O(s) is formed by the interaction of gas-

TABLE 2

Results of Sequential Pulsing of Oxygen and of Methane over Sm_2O_3 for Different Time Intervals Δ between Pulses of O_2 and of CH_4(1.9×10^{16} Molecules/Pulse) at 908 K

Δt (ms)	O_2 pulse size (10^{15} molecules)	*O(s), (10^{15} atoms · m^{-2})	$X(CH_4)$ (%)	$S(C_2H_6)$ (%)	$S(C_2H_4)$ (%)	$S(CO)$ (%)
50	3.4	3.5	11.2	8.6	13.8	11.7
100	7.3	4.0	12.4	8.0	13.5	15.6
50	12.8	9.3	20.9	5.7	12.1	12.6
100	26.5	9.0	19.3	6.4	13.2	15.8

phase O_2 with the surface of Sm_2O_3 but that different kinds of species exist. According to this interpretation there are approx. 0.7×10^{16} sites/m^2 which enhance both C_2 and CO formation. These sites to which oxygen is strongly bonded are preferably occupied when small oxygen pulses are introduced. Oxygen pulses resulting in a coverage of more than 0.7×10^{16} atoms/m^2 will lead to the formation of another type of active oxygen species which are more weakly bonded to the surface and which favour the nonselective oxidation of methane to carbon dioxide. The existence of different sites for oxygen adsorption is in agreement with the results of Keulks and Liao (10) who observed three oxygen desorption peaks in the temperature range between 523 and 1073 K during O_2-TPD over Sm_2O_3. These results lead to the tentative conclusion that during the pretreatment of the catalyst applied in the present TAP experiments (heating in vacuum to 1073 K, treatment with oxygen pulses, keeping in vacuum for 10 min) different kinds of oxygen vacancies are created on the surface which act as active sites for oxygen adsorption.

Based on the results of the present work it is not possible to distinguish between the two hypotheses put forward above. It is, however, evident that the presence of adsorbed oxygen species greatly enhances the C_2 selectivity and yield compared to lattice oxygen. An optimum concentration is necessary to achieve maximum yield or selectivity, respectively, because at higher concentrations total oxidation reactions are favoured.

CONCLUSIONS

Dissociative adsorption of oxygen was found to be an important reaction step determining high activity and C_2 selectivity of catalysts in the OCM reaction. Several kinds of oxygen species are involved in the OCM reaction on the surface of Sm_2O_3. There is a large number of lattice oxygen species (approx. 10^{19} sites/m^2) which provide only a limited activity for the methane conversion to CO_2 mainly. The interaction of gas-phase oxygen with the catalyst surface results in the formation of "adsorbed" oxygen species, *O(s), via dissociative adsorption. These species are highly reactive towards methane conversion and enhance C_2 formation; however, an optimum surface coverage is necessary to obtain maximum C_2 yield and/or selectivity while exceeding this optimum CO_2 is preferentially formed. Gas-phase oxygen adsorbs also molecularly on the surface resulting in the formation of weakly bonded species which are not involved in the methane conversion.

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