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Oxidative Coupling of Methane over $SrCO_3$ and SrO

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The oxidative coupling of methane has been studied with an $SrCO_3$–SrO mixed catalyst. Two surface states (an SrO-rich surface and an $SrCO_3$-rich surface) were prepared and examined by various methods including XPS. SrO-rich surfaces, prepared by H_2 treatment of $SrCO_3$, had a high C_2 yield, and evolved CO_2 was absorbed by the catalyst at 1023 K. The bulk diffusion of CO_2 was considered to be rapid enough to absorb most of the evolved CO_2 and to keep SrO partly on the surface ($SrCO_3$-rich surface) at 1023 K. $SrCO_3$-rich surfaces gave low C_2 yields, and the surface was composed of both oxides and carbonates. The active sites were considered to be oxides. The SrO surface was more active than MgO in this reaction. However, it was less active under the steady state because of carbonate formation.

The oxidative coupling of methane to give ethane and ethene has interested many researchers as an alternate route to utilize methane.[1,2] Alkaline-earth-metal oxides,[3,4] in addition to lanthanide oxides,[5] have been studied widely as host oxides. Among alkaline-earth-metal oxides, MgO and CaO catalysts are strongly promoted by alkali-metal oxides and have been thoroughly studied.[3,4,6–10] $SrCO_3$ is not strongly promoted by alkali-metal oxides.[11] However, SrO (or $SrCO_3$) has a higher C_2 selectivity, although the activities are lower than those of promoted MgO and CaO.[8,12] The intrinsic high selectivity prompted the study of the catalysis over SrO (or $SrCO_3$). During the catalysis, SrO could be partially converted to $SrCO_3$; $SrCO_3$ could be converted to SrO because of the equilibrium:

$$SrO + CO_2 \rightleftharpoons SrCO_3\text{: } \log P(\text{Torr}) = 10.48 - 11\,500/T$$

The pressure of CO_2 is 0.17 Torr† at 1023 K. Thus, the catalyst should be converted to $SrCO_3$ gradually during the reaction, but what happens to the surface? The purpose of this study was to examine the effect of carbonate on this reaction and to establish a pure SrO surface to compare it with other alkaline-earth-metal oxides such as MgO and CaO. Since the decomposition temperature of $Sr(OH)_2$ is 973 K ($P_{H_2O} = 1$ atm‡), the state of $Sr(OH)_2$ is not considered under the reaction conditions. The reaction profile was also studied over the $SrCO_3$ catalyst.

Experimental

$SrCO_3$ was selected instead of SrO as a starting material because SrO is converted to $SrCO_3$ under the reaction conditions. Another reason is that SrO could react with the quartz glass reactor.

The reaction was performed using a conventional flow reactor (12 mm i.d.) at temperatures from 623 to 1073 K.[7] As a standard condition, CH_4, air and He were charged with flow rates of 1.5 (4.02 mmol h^{-1}), 3.75 and 50 cm^3 min^{-1}, respectively. The $CH_4 : O_2$ ratio was 2.0 ± 0.1 ($2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$). The selectivity and yield were defined as (2 × moles C_2 compounds produced)/(moles CH_4 reacted) and (2 × moles C_2 compounds produced)/(moles CH_4 in the feed), respectively. The pure $SrCO_3$ sample (Kanto Chemical Co., 99.6%) was prepared by soaking with water, drying and pelleting. The sample (2 g) was treated in an He flow at 773 K for 1 h and at 1073 K for 2 h as a standard treatment and used for the reaction. The surface area was measured by the B.E.T. method using N_2 after the heat-treatment. XRD spectra were taken using a Rigaku RAD-B spectrometer. A Shimadzu ESCA 750 spectrometer was used for the XPS measurements. The binding energy was determined by comparing with the peak of Au $4f_{7/2}$ (83.8 ± 0.1 eV). An SEM picture was taken by a Hitachi HFS-2 scanning electron microscope.

Results

Reaction over $SrCO_3$ and SrO Surfaces

$SrCO_3$ (2 g), which had an 8- to 10-mesh size, was used as a catalyst for the oxidative coupling reaction. The sample was handled in several ways: (1) without treatment (*i.e.* treatment at the reaction temperature, 1023 K), (2) with He treatment at a higher temperature than the reaction temperature to eliminate surface carbonates, and (3) with H_2 treatment to eliminate surface carbonates by the shift reaction ($CO_2 + H_2 \rightarrow CO + H_2O$). The catalyst activities were measured at 1023 K using the standard treatment as described in the Experimental section and the results are listed in Table 1. Initial activity (I) under 'measurement time' in Table 1 refers to data taken 0–30 min from the start of the run, and steady activity (S) refers to data taken 1–6 h into the run. In some cases, even the steady activity (S) gives an incomplete carbon balance due to CO_2 absorption (runs 9–13). A sample prepared by a heat treatment of $Sr(OH)_2$ was also used and the results are shown in Table 1. The effects of the treatment temperature under an He atmosphere and the effects of the treatment temperature and time under an H_2 atmosphere are also shown in the table. The B.E.T. surface area of the sample after the treatment is also shown in the table. Time courses of the amount of reactants and products over a heat-treated $SrCO_3$ are shown in Fig. 1. From Table 1 and Fig. 1, the following conclusions can be drawn.

1. Untreated $SrCO_3$ gave a stable activity (7% of C_2 yield) and a good carbon balance. The activity and selectivity were unchanged from the initial sampling within 30 min to the sampling at 6 h during the run.

2. When the sample was treated with He at 1073 K, the initial activity was high (10% of C_2 yield), and the carbon balance was incomplete (6% of unbalanced carbon) (see run 3 in Table 1 and Fig. 1). Evolved CO_2 was adsorbed on the decarbonated surface (SrO surface). Preheating at 1173 K caused slightly higher activity (11% of C_2 yield) and gave more unbalanced carbon (22%) as is seen in run 6 in Table 1.

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† 1 Torr = 133.322 Pa.
‡ 1 atm = 101.325 kPa.

Table 1 Activity[a] of $SrCO_3$ (2 g) treated under various conditions

run	treatment		B.E.T. surface area	measurement	activity at 1023 K (%)				unbalanced	initial	code
no.	atmosphere	T/K	/m^2 g^{-1}	time	O_2 conv.	CH_4 conv.	C_2 yield	CO_x yield	carbon (%)	surface[b]	in Fig. 2
1	untreated	(1023)	2.4	I[c]	90	30	7	23	0	$SrCO_3$	
2	untreated	(1023)	—	S[d]	90	30	7	23	0	$SrCO_3$	
3	He	1073[e]	2.0	I	95	30	10	14	6	SrO	(*b*)
4	He	1073[e]	—	S	88	29	7	20	2	$SrCO_3$	(*c*)
5	He	1123[e]	—	S	80	24	6	21	−3	$SrCO_3$	
6	He	1173[e]	—	I	95	34	11	1	22	SrO	
7	He	1173[e]	—	S	64	23	6	16	1	$SrCO_3$	
8	H_2	1073[f]	1.3	I	95	32	10	1	21	SrO	
9	H_2	1073[f]	—	S	95	32	10	1	21	SrO	
10	H_2	1173[f]	2.2	S	95	34	10	1	23	SrO	
11	H_2	1023[f]	2.2	S	96	31	9	1	21	SrO	(*d*)
12	H_2	1023[g]	1.5	S	95	30	9	1	20	SrO	
13	H_2	1023[h]	—	S	95	33	9	1	23	SrO	
14[i]	He	1427[j]	<0.5	I	70	28	7	7	14	SrO	(*e*)

[a] Activity measured at 1023 K under a flow rate of 1.5 (CH_4), 3.75 (air) and 50 (He) cm^3 min^{-1}. [b] Sample with unbalanced carbon more than 4% identified to be SrO. [c] Initial activity at time course of 0–30 min. [d] Steady-state activity at time course of 1–6 h. [e] Treatment time 2 h after 1 h treatment at 773 K. [f] Treatment time 1 h, followed by He treatment for 30 min. [g] Treatment time 2 h. [h] Treatment time 8 h. [i] Starting compound was $Sr(OH)_2$. [j] Treatment time 30 min after overnight treatment at 673 K.

During the He pretreatment at 1073 K, CO_2 was evolved from the sample.

3. Preheated $SrCO_3$, once activated initially and used for the reaction for more than 1 h (steady state), gave almost the same activity (6–7% C_2 yield) as that for the untreated $SrCO_3$. Carbon was also balanced, since the surface was saturated with the CO_2 produced (runs 4, 5 and 7 in Table 1 and Fig. 1) ($SrCO_3$ surface). The activity was stable for 66 h.

4. The C_2H_4 fraction in C_2 compounds was 55 ± 3% and the CO_2 fraction in CO_x compounds was 83 ± 3% at 1023 K both on the initial SrO surface and on the final $SrCO_3$ surface.

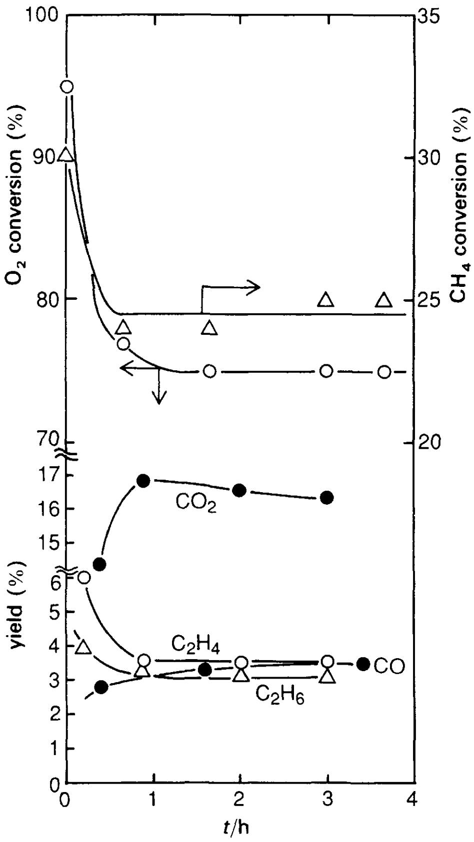


Fig. 1 Time course of the oxidative coupling of CH_4 at 1023 K over 2 g of $SrCO_3$, preheated at 773 K for 1 h and 1073 K for 2 h

5. Treatments at extremely high temperatures caused low activity in CH_4 conversion and O_2 conversion, as in the case of run 7 in Table 1, probably due to the sintering process. The sample treated at 873 K had a surface area of 4.7 m^2 g^{-1}; however, the value decreased to 2.2–2.4 m^2 g^{-1} after 1023 K treatment, 1.3–2.0 m^2 g^{-1} after 1073 K treatment, 2.2 m^2 g^{-1} after 1173 K, and below 0.5 m^2 g^{-1} after 1427 K treatment. Treatment with H_2, leading to an SrO surface, gave a similar surface area to that given by treatment with He or reactant gas.

6. Air treatment at 1073 K gave the same results as He treatment.

7. H_2 treatment led to easier production of an SrO surface. Even H_2 treatment at the same temperature as the reaction temperature gave high activity (9% of C_2 yield) and caused unbalanced carbon (run 11 in Table 1).

8. Since H_2 treatment led to an easier and more extensive production of an SrO surface, this surface, in a state of high activity and unbalanced carbon, continued for at least a 6 h run (steady state) at 1023 K, as shown in Table 1 (runs 9–13). The treatment temperature (1023–1173 K) and time (1–8 h) did not affect the activity as seen in the table (runs 9–13).

9. The above results suggested that the decarbonated state (SrO surface), identified from the unbalanced carbon, was more active than the carbonate state ($SrCO_3$ surface). The high activity continuing for a long time (6 h) suggests that CO_2 diffuses rapidly into the bulk phase and that the carbonated front in the catalyst bed progresses downwards slowly.

10. Pure SrO was prepared from $Sr(OH)_2$ by heating at 1427 K. However, the activity was low (70% of O_2 conversion, see run 14 in Table 1), probably due to the extreme sintering at 1427 K.

XPS, SEM and XRD Studies

To confirm the quantity of carbonate on the surface, XPS spectra were measured.[13] Samples were placed in the XPS chamber without contacting the air. The results are shown in Fig. 2. A strong peak at 284.6 eV was thought to be due to the C 1s peak of contaminating hydrocarbon. Peaks at 289.2 and 279.0 eV were assigned to the C 1s peak of carbonate and Sr $3p_{1/2}$. Ratios of peak areas of carbonate carbon to Sr are shown in Fig. 2. The carbonate surface (*a*) was decreased

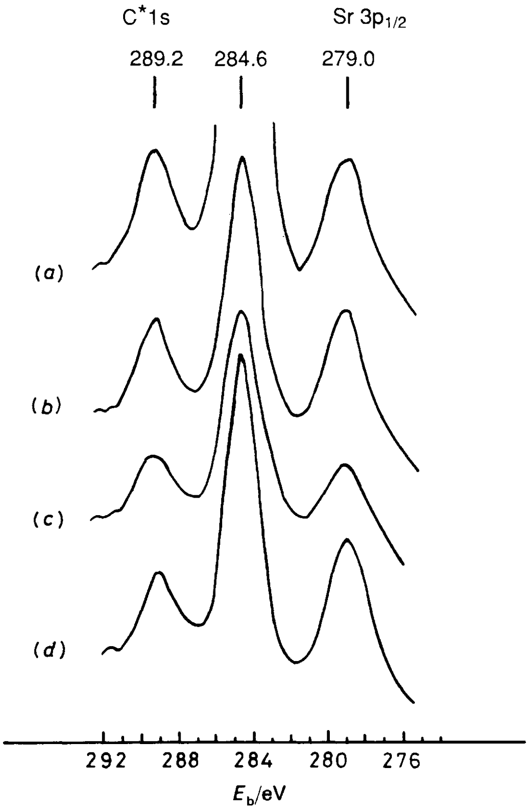


Fig. 2 XP spectra of $SrCO_3$ catalyst at C 1s region. Peaks at E_b = 279.0, 284.6 and 289.2 eV were assigned to Sr $3p_{1/2}$, C $1s_{1/2}$ due to hydrocarbon contamination, and C $1s_{1/2}$ due to carbonate. (*a*) Before pretreatment, (*b*) after 1073 K heat treatment in He, (*c*) after the reaction using the sample (*b*), (*d*) after H_2 treatment at 1023 K. C* 1s/Sr 3p: (*a*) 0.68, (*b*) 0.55, (*c*) 0.53, (*d*) 0.40

by He treatment at 1073 K [Surface (*b*) is the SrO surface]. However, it was not increased after the reaction at 1023 K [surface (*c*), $SrCO_3$ surface], which was contrary to trends of the reaction performance, probably because the method of evaluating peak areas was inaccurate. H_2 treatment clearly decreases the amount of carbonate [surface (*d*), SrO surface]. Strong peaks at 532 ± 0.2 eV were assigned to the O 1s peak of carbonate and were observed for (*a*), (*b*), (*c*) and (*d*). O 1s spectra did not reveal any changes from carbonate to oxide.

An SEM picture of $SrCO_3$ treated in He at 1073 K for 2 h was taken. The average particle size analysed from the picture was 0.78 μm. The particle size calculated from the B.E.T. data (2.0 m^2 g^{-1}) was 0.82 μm whilst the particle size calculated from XRD line broadening was 0.19 μm.[7,14] A single visible particle shown by SEM was thought to be composed of many single crystals.

Reaction on the SrO Surface at Various Temperatures

Decarbonated surfaces (SrO surfaces) were formed by two methods: (1) H_2 treatment of $SrCO_3$ at 1023 K [surface (*d*)] and (2) He treatment of $Sr(OH)_2$ at 1427 K [surface (*e*)]. The reactivity of these surfaces was studied at various temperatures. The results of reactants and products in the initial states is shown in Fig. 3 for surface (*d*). For comparison, the same experiments were performed on MgO which was preheated at 1073 K (Fig. 4). The pretreatments were performed every time before the data were obtained at each temperature. The following conclusions can be drawn.

1. The temperature profiles of surfaces (*d*) and (*e*) in Fig. 4 were similar. CH_4 reacted with O_2 even at 773 K. The CO_2 evolved was adsorbed mostly below 973 K, whereas some CO_2 was observed in the gas phase above 1023 K. The surfaces of (*d*) and (*e*) were mostly SrO, which was in accordance with the results of XPS. C_2 compounds were extensively produced even at 873 K over surfaces (*d*) and (*e*) (SrO).

2. The activity of surface (*e*) was lower than that of surface (*d*), probably because of the extreme sintering of the surface (1427 K).

3. If Fig. 3 [SrO surface (*d*)] and 4 (MgO) are compared, SrO appears more active than MgO. MgO did not adsorb CO_2 at these reaction temperatures (decomposition temperature of $MgCO_3$ is 813 K at 1 atm).

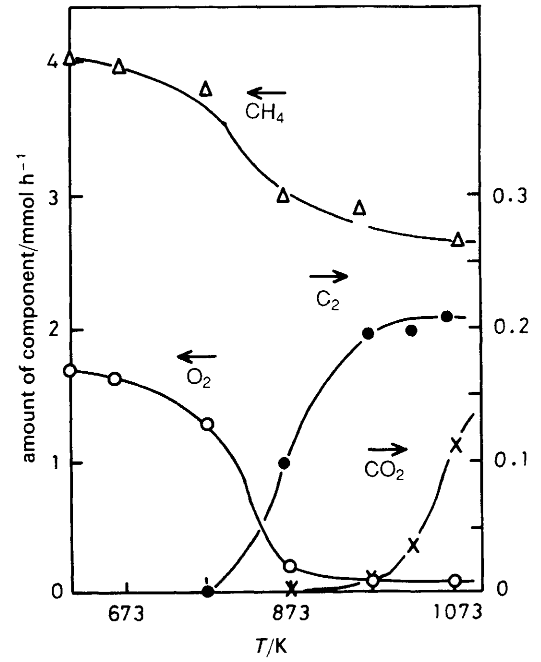


Fig. 3 Reactants and products at the outlet of a reactor with $SrCO_3$ (2 g) catalyst at various reaction temperatures under the standard flow conditions. Data at each temperature were taken within 30 min of pretreatment by H_2 at 1023 K [SrO surface (*d*)]

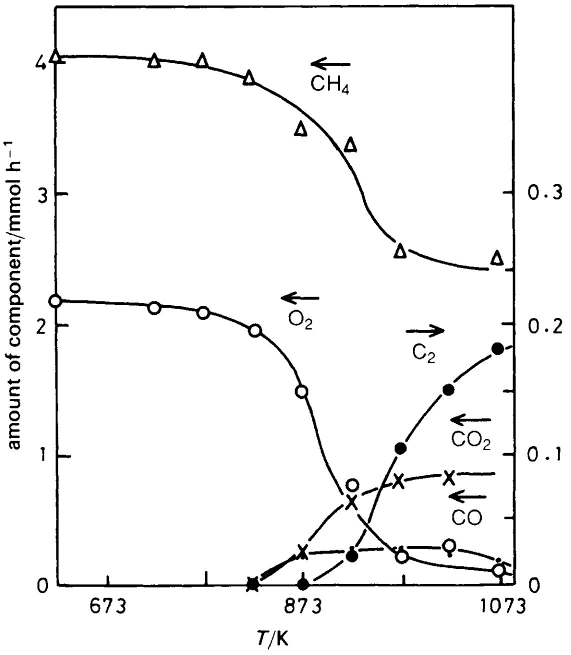


Fig. 4 Reactants and products at the outlet of a reactor with MgO (2 g) catalyst at various reaction temperatures under the standard flow conditions. Data at each temperature were taken within 30 min of the He pretreatment at 1073 K

Effect of *W*/*F* for the Reaction over $SrCO_3$ Surface

The reaction kinetics were studied using He-treated (1073 K) $SrCO_3$. The rate of reaction at 1023 K under steady state [$SrCO_3$ surface (*c*)] was examined as a function of *W*/*F*, which was changed by using catalyst samples with different weights (0.02–4 g). The flow rate was fixed at a standard value so as not to disturb the temperature profile and the contribution of the gas-phase reactions. The results are shown in Fig. 5. CO was not examined because it was too small to be detected by TCD through the MS-5A column. Fig. 5 shows the CO_2 and C_2 yields as a function of *W*/*F*. The contribution of the gas-phase reaction was small but was observed as the product yields were non-zero for *W*/*F* = zero in Fig. 5. Total activity decreased with increasing *W*/*F*, partly because of the inhibition of CO_2 production and partly because of the extensive consumption of CH_4 and O_2 in the high *W*/*F* region. In this region, the contribution of C_2 to CO_2 reaction was appreciable. Addition of CO_2 into the feed decreased the activity of $SrCO_3$ (2 g) at 1023 K.

An interesting point is that CO_2 and C_2 compounds (the latter consisted mostly of C_2H_6) were formed as parallel reactions. When *W*/*F* = zero, the C_2 and CO_2 selectivities were 46 and 54%, as shown in Fig. 5. Comparable results were obtained for the reaction over Na^+–MgO,[7] and a similar mechanism with a methyl radical intermediate is proposed here. Ethene selectivity in C_2 compounds is also shown in Fig. 5. Note that ethene selectivity was not zero for *W*/*F* = 0. This suggests that ethene is formed from ethane through the gas-phase reaction as described in the next section.

Gas-phase Oxidation of Ethane and Ethene

Oxidation of ethane was examined at 1023 K under a flow rate of 1.5 $cm^3 min^{-1}$ for C_2H_6, 3.75 $cm^3 min^{-1}$ for air, and 50 $cm^3 min^{-1}$ for He with and without the catalyst. Ethane was oxidized mostly to ethene and partly to CO as a gas-phase reaction under these conditions. C_2H_6 conversion (92 ± 2%), CH_4 yield (6–7%), and CO_2 yield (1–2%) were independent of the presence of $SrCO_3$. The presence of $SrCO_3$ increased the C_2H_4 yield slightly (48% for 0 mg, 51% for 20 mg and 55% for 60 mg of $SrCO_3$), while it decreased the CO yield (26% for 0 mg, 18% for 20 mg and 16% for 60 mg of $SrCO_3$).

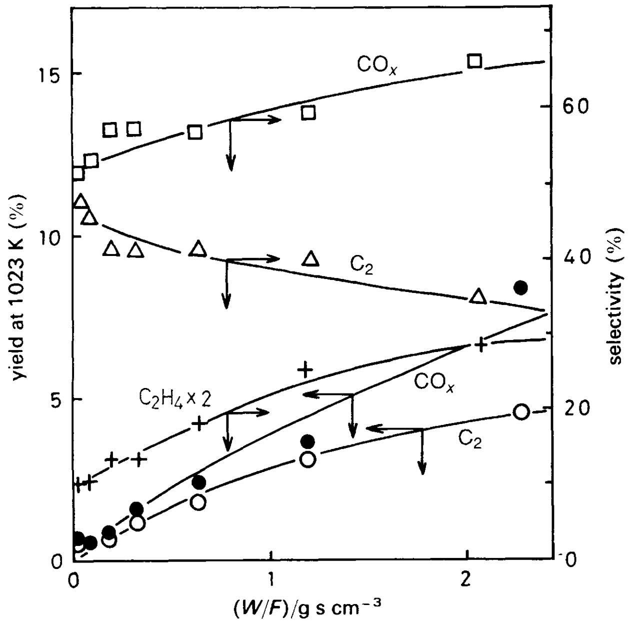


Fig. 5 Total C_2 and CO_x yield and selectivities of total C_2, C_2H_4 and CO_2 at 1023 K over $SrCO_3$ as a function of *W*/*F* (g s cm^{-3}). F is the flow rate of total gases at room temperature ($cm^3 s^{-1}$). Data were recorded at 1.5 h of reaction at 1023 K after He treatment at 1073 K

Oxidation of ethene was also examined under similar conditions to that for ethane, but the flow rate of ethene was 2.25 $cm^3 min^{-1}$. Ethene was converted to CO in a gas-phase reaction, although the carbon balance was poor. C_2H_4 conversion (37 ± 1%), CH_4 yield (3%), CO yield (17 ± 2%) and CO_2 yield (1%) were independent of the existence of $SrCO_3$ (none, 20 mg and 60 mg). Although the partial pressure of C_2 compounds was *ca.* 10 times higher than that under the coupling reaction of CH_4 to give C_2H_6 or C_2H_4, CO was considered to occur mainly in the gas phase.

Discussion

Active Site of $SrCO_3$ Catalyst

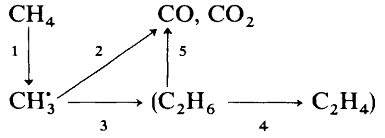
The activities of various $SrCO_3$-originated catalysts were classified into two states. The decarbonated surface had a C_2 yield of 9–11% and the CO_2 produced was adsorbed during the reaction, whereas the carbonated surface had a C_2 yield of 6–7% and the CO_2 produced was recovered in the gas phase under the standard reaction conditions (see Table 1). Thus, the active phase is assumed to be the SrO surface. H_2-treated $SrCO_3$ retained its high activity for at least 6 h (Table 1). Since the rate of CO_2 production is 0.97 mmol h^{-1} (23% yield) and highest at 1023 K, CO_3^{2-} fixed during 6 h is estimated to be 43% of 2 g of $SrCO_3$. This suggests that the H_2 treatment for 1 h at 1023 K removes at least 43% of CO_2 from $SrCO_3$, in accordance with the XPS results (Fig. 2). The CO_2 diffusion into the bulk is also considered to be rapid enough to produce SrO on the surface. Once CO_3^{2-} is saturated to give an $SrCO_3$ bulk phase, the 'surface' state should be composed of oxides and carbonates which are governed by CO_2 pressure. Since CO_2 is a poison in the reaction, SrO should be an active site for this reaction. Under the constant CO_2 pressure (steady state), $SrCO_3$–SrO surface gives a constant activity, as shown in Table 1. The initial surface of $SrCO_3$ in Table 1 should be an $SrCO_3$–SrO mixed surface. Addition of CO_2 into the steady-state reaction on the $SrCO_3$–SrO surface caused a decrease in activity.

Comparison of the Activities of SrO and MgO

The activity of SrO is compared with MgO in Fig. 3 and 4. SrO is apparently more active than MgO. Several factors are used to determine the activity for this reaction. The main factors are surface-active centres and the morphology.[7] The surface area of SrO was *ca.* 2 $m^2 g^{-1}$ (Table 1). MgO has a B.E.T. surface area of 70 $m^2 g^{-1}$. A previous study suggested that a suitable (rather small) surface area gives maximum selectivity at the same conversion.[15] Thus, one of the reasons for the high C_2 yield on SrO might be the morphology. However, if the activity is compared at the low conversion state at lower temperatures (773 or 873 K), SrO is apparently more active. It is suggested that the adsorbed oxygen on SrO is more active for CH_4 than that adsorbed on MgO.

Reaction Profile over $SrCO_3$ Catalyst

The kinetic study over an $SrCO_3$ catalyst suggests the following reaction mechanism:



This mechanism is at least as good as that proposed for Na^+–MgO.[7,15] Since CO_2 and C_2 compounds are produced for $W/F = 0$ (Fig. 5), the two reactions are considered to occur in parallel with a common intermediate, probably $^{\bullet}CH_3$. The secondary reactions (paths 4 and 5) are considered to occur in the gas phase. This mechanism is similar to that proposed for Na^+–MgO.[15] However, CO_2 is a poison on SrO, whereas it is not a poison on Na^+–MgO under these conditions.

Although CO_2 poisons the CH_4–O_2 reaction over SrO, CO_2 is proven to have some activity towards CH_4. Although the activity is not very high, CO_2 and CH_4 react to give C_2 compounds over PbO–CaO[16,17] and BaO–CaO[18] catalysts. Surface carbonates have sometimes positive effects on other systems.[19,20]

Conclusions

The strongly basic SrO surface proved to be more active than the MgO surface. However, SrO bulk phase is turned to $SrCO_3$ bulk phase by the CO_2 produced during the oxidative coupling of methane. The diffusion of CO_2 into the bulk is considered to be rapid enough to regenerate SrO partly on the surface on which activity is reduced. Even $SrCO_3$ bulk phase has some active sites of SrO on the surface under steady-state conditions depending on the CO_2 pressure. The reason for $SrCO_3$ being selective, but less active under the usual reaction conditions, was clarified.

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