

Direct oxidation of methyl radicals in OCM process deduced from correlation of product selectivities

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Abstract

Selectivity of hydrogen in reaction of oxidative coupling of methane (OCM) was evaluated over the M_xO_y -BaCO₃ (M_xO_y : La₂O₃, Sm₂O₃, MgO, CaO) catalysts. Correlation of product selectivities was thus discussed. From the correlation of product selectivities, it is revealed that the carbon oxides (CO and CO₂) were most probably formed from the direct oxidation of methyl radicals under the conditions adopted in the present work. This is also in accordance with the OCM mechanism proposed in literature.

Key words

oxidative coupling; methane; hydrogen; mechanism; radical

1. Introduction

Methane is the major component of natural gas. Oxidative coupling of methane (OCM) is a promising way to convert methane into ethene and ethane (i.e., C₂ hydrocarbons). In the past decades, extensive studies had been done for the OCM reaction since the first report by Keller and Bhasin [1]. Many catalysts such as alkaline earth metal oxides and rare earth metal oxides were found to be effective [2–7]. Regarding the mechanism, it is generally accepted that methane molecule is first activated on catalyst surface to form methyl radicals [8–11], then methyl radicals couple into ethane, mainly in gas phase. Presence of methyl radicals in gas phase was identified experimentally [12]. Ethene is a secondary product, formed from dehydrogenation and oxidative dehydrogenation of ethane [10,13]. The carbon oxides (CO and CO₂) are usually considered to be formed due to oxidation of methane, C₂ hydrocarbon molecules and hydrocarbon radicals.

Formation of hydrogen in OCM was also discussed by several groups [8–10]. It seems most probably that hydrogen is formed from decomposition of the oxygenated intermediates and dehydrogenation of ethane. For example, decomposition of formaldehyde can produce CO and hydrogen. However, data of hydrogen selectivity are scarce in literature. Green et al. reported hydrogen selectivity of 9.7% over a K/BaCO₃ catalyst [14]. Gao et al. measured hydrogen selectivity over the Li/MgO catalysts [15]. As hydrogen gas is

an important energy source, it is worthy to evaluate hydrogen production in OCM reaction besides C₂ selectivity. For this reason, hydrogen selectivity in OCM over M_xO_y -BaCO₃ (M_xO_y : La₂O₃, Sm₂O₃, MgO, CaO) catalysts was measured in this work. Based on this, correlation of product selectivities was revealed.

2. Experimental

The M_xO_y -BaCO₃ catalysts were prepared from aqueous slurry of the two oxide mixture powder, followed by drying at 120 °C for 24 h and calcination at 850 °C for 4 h. All catalysts were verified by X-ray diffraction (XRD) analyses (Shimadzu, XRD-6000, Japan).

OCM reaction was carried out at atmospheric pressure in a quartz tube (8.5 mm in i.d.), in which 400 mg catalyst (40–60 mesh in granular size) was loaded for each run. Methane gas and oxygen gas were kept at 20 ml/min and 5 ml/min, respectively, and nitrogen gas was used as balance gas to make total gas flow rate at 70 ml/min in each run. Reaction products were analyzed by a gas chromatograph (Kechuang, Shanghai), equipped with a thermal conductivity detector and a packed column (3 mm in i.d. and 6 m in length, Shincarbon T 60–80, Japan). This column allows species of H₂, O₂, N₂, CO, CH₄, CO₂, C₂H₄ and C₂H₆ to evolve in order of retention time.

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Product selectivity on C atom basis was calculated for the carbon-containing products, i.e., CO, CO₂, C₂H₄ and C₂H₆. Product selectivity on H atom basis was calculated for the hydrogen-containing products, i.e., H₂, H₂O, C₂H₄ and C₂H₆. Water formed in OCM reaction could not be detected in the gas chromatograph, so selectivity of water was calculated by the difference method as shown below.

Selectivity of *i* on C-basis = 100% × (mole of C atom in product *i*) / mole of C atom in the converted CH₄

Selectivity of *i* on H-basis = 100% × (mole of H atom in product *i*) / mole of H atom in the converted CH₄

Selectivity of H₂O on H-basis = 100% - (selectivity of H₂ + selectivity of C₂H₄ + selectivity of C₂H₆) on H-basis

Besides, C₃₊ hydrocarbons might be formed in a trace amount in some cases. Analyses for these products were omitted in the present work.

3. Results and discussion

3.1. OCM reactions over the M_xO_y-BaCO₃ catalysts

It was verified that XRD pattern of each component of the catalysts was consistent with that of the reference in the data package provided with the XRD equipment. And no new phase was observed in XRD pattern for the M_xO_y-BaCO₃ catalysts.

Figure 1 shows the results of OCM reaction over the La₂O₃-BaCO₃ catalyst at feed mole ratio CH₄/O₂ = 4 and 800 °C. It is clear that there is a synergistic effect between La₂O₃ and BaCO₃, which promoted CH₄ conversion and C₂ selectivity. As the mass ratio of La₂O₃/(La₂O₃+BaCO₃) increased to 0.25, CH₄ conversion increased to 23.8% and C₂ selectivity increased to 57.7%; whereas H₂ selectivity decreased to 10.1%, lower than the value (ca. 20%) for each of the single component (La₂O₃ and BaCO₃). The synergistic effect could be ascribed to the defect structure formed at the boundary between La₂O₃ and BaCO₃ particles, which was detected by Raman, XPS and ESR analyses [16]. The

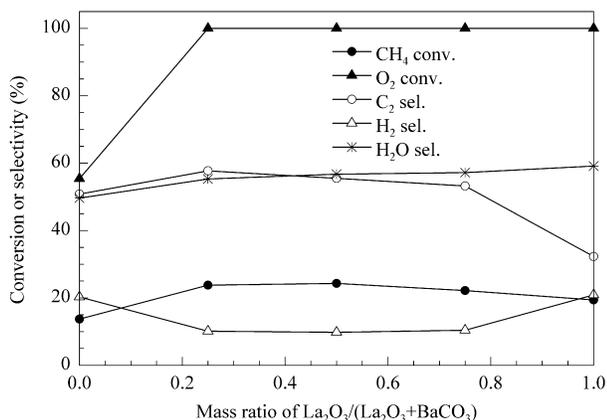


Figure 1. OCM reaction over the La₂O₃-BaCO₃ catalyst at feed mole ratio CH₄/O₂ = 4 and 800 °C

Sm₂O₃-BaCO₃ catalyst had similar results as La₂O₃-BaCO₃ catalyst for the OCM reaction as shown in Figure 2.

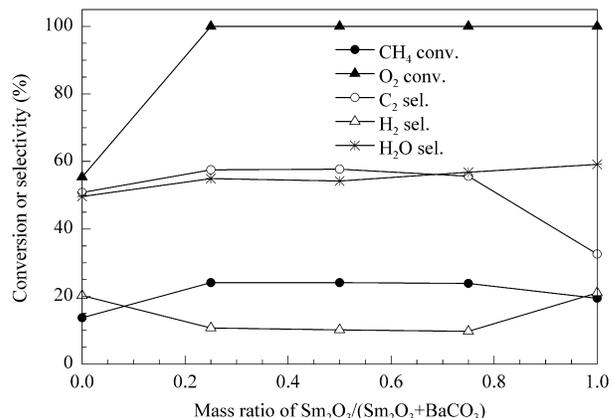


Figure 2. OCM reaction over the Sm₂O₃-BaCO₃ catalyst at feed mole ratio CH₄/O₂ = 4 and 800 °C

Figure 3 shows the results of OCM reaction over the MgO-BaCO₃ catalyst at feed mole ratio CH₄/O₂ = 4 and 800 °C. The MgO-BaCO₃ catalyst exhibited CH₄ conversion of ca. 23%, higher than the value of 20% obtained over the pure MgO catalyst. At the same time, the catalyst inherited high C₂ selectivity from the BaCO₃ component. Compared to the two individual components (MgO and BaCO₃), the binary component catalyst had a lower H₂ selectivity (ca. 15%). For the CaO-BaCO₃ catalyst, as shown in Figure 4, C₂ selectivity is comparable to that of the MgO-BaCO₃ catalyst at the mass ratio of M_xO_y/(M_xO_y+BaCO₃) equal to 0.25.

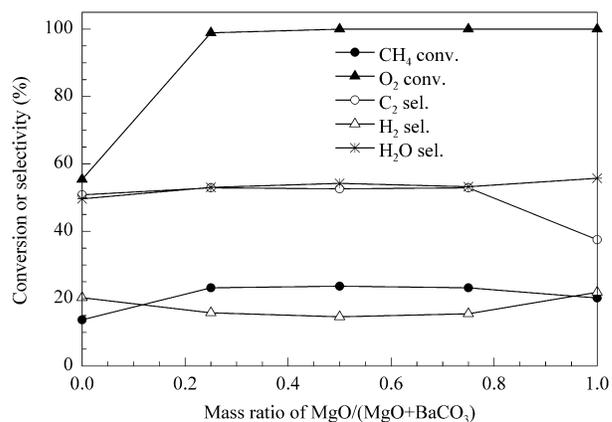


Figure 3. OCM reaction over the MgO-BaCO₃ catalyst at feed mole ratio CH₄/O₂ = 4 and 800 °C

Evidently, every M_xO_y-BaCO₃ catalyst exhibits a synergistic effect, which promoted CH₄ conversion and C₂ selectivity. Barium carbonate, with decomposition temperature at ca. 990 °C, is a stable compound at the usual OCM temperatures, and has characteristic of a higher C₂ selectivity. This is probably due to its less reactive oxygen species on the surface. For this reason, barium carbonate was widely used as a component of catalyst for OCM reaction. Liu et al. evaluated effect of pressure on OCM reaction using 30 mol%

MgO/BaCO₃ catalyst, obtained CH₄ conversion of 22.7% and C₂ selectivity of 67.4% under the conditions of 780 °C, 1 atm and CH₄/O₂ = 4 [17]. Wang and co-workers prepared a series of low-temperature BaCO₃/La₂O₃ OCM catalysts using a urea combustion method [18]. Green et al. using barium carbonate as a support prepared K/BaCO₃ catalyst for OCM reaction [14].

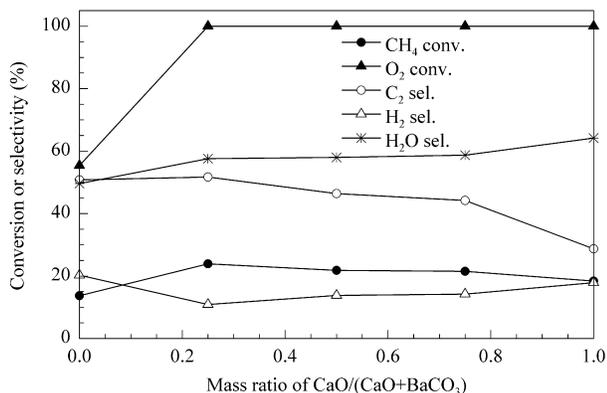
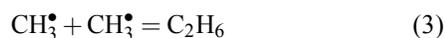
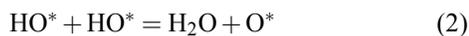


Figure 4. OCM reaction over the CaO-BaCO₃ catalyst at feed mole ratio CH₄/O₂ = 4 and 800 °C

3.2. Correlation of product selectivities in the OCM reaction

As proposed in References [8–11], the OCM reaction would proceed in the following steps.

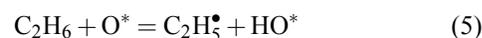


The species of O* in Step (1) is surface active oxygen species, which activates methane molecule into methyl radical. Overall reaction of the three steps above is shown below.

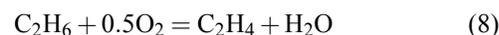
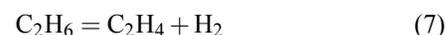


According to Reaction (4), selectivity of H₂O on H-basis in the initial activation step of methane is 25%. This is only the case that oxidative dehydrogenation of ethane into ethene and other deep oxidations to carbon oxides (CO and CO₂) and water would not happen. In fact, Figures 1–4 clearly show that H₂O selectivity on H-basis over the mixture catalysts is higher than 50%. This indicates that water was also formed by other routes.

Like methane molecule, ethane molecule could have a similar elementary step forming ethyl radical on active site of the catalyst surface (Equation 5). And ethyl radical could further turn into ethene molecule via release of a hydrogen atom (Equation 6).

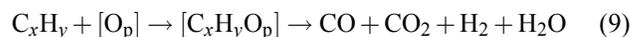


It is reported that ethene is a secondary product, formed from dehydrogenation and most probably oxidative dehydrogenation of ethane [10,13]. In summary, the reactions forming ethene from ethane can be expressed in Equations (7) and (8).



It is obvious that the sum of selectivities of H₂ and H₂O on H-basis in Equations (7) and (8) is equal to the experimental C₂H₄ selectivity on C-basis multiplying 0.25.

In addition, deep oxidation occurred in the OCM process can be expressed in an overall Equation (9).



The species of C_xH_y in Reaction (9) can be methane molecule, C₂ hydrocarbon molecule or any kind of hydrocarbon radicals, and the [O_p] can be any kind of surface oxygen species and gas phase oxygen species. The [C_xH_yO_p] is an intermediate of the deep oxidation reaction. It is seen that contribution of Reaction (9) to H₂ and H₂O formation can be expressed as follows:

Selectivity of (H₂+H₂O) in Reaction (9) = Experimental H₂ selectivity + experimental H₂O selectivity – 25% – experimental C₂H₄ selectivity on C-basis × 0.25

Table 1 lists product selectivities of the OCM reactions at feed mole ratio of CH₄/O₂ = 4 and 800 °C over the M_xO_y-BaCO₃ catalysts (the mass ratio of M_xO_y/(M_xO_y+BaCO₃) = 0.25), in which selectivities of the carbon-containing products (i. e., CO, CO₂, C₂H₄ and C₂H₆) are based on C atom basis and selectivities of H₂ and H₂O are based on H atom basis. Selectivities of C₂H₄ and C₂H₆ on H-basis can be calculated from their selectivities on C-basis.

Selectivity of C₂H₄ on H-basis = Selectivity of C₂H₄ on C-basis × 0.50

Selectivity of C₂H₆ on H-basis = Selectivity of C₂H₆ on C-basis × 0.75

Table 1. Product selectivities of the OCM reactions over the M_xO_y-BaCO₃ catalysts (the mass ratio of M_xO_y/(M_xO_y+BaCO₃) = 0.25) at feed mole ratio CH₄/O₂ = 4 and 800 °C

Catalysts	CH ₄ conversion (%)	Selectivity (%) ^a					
		CO	CO ₂	C ₂ H ₄	C ₂ H ₆	H ₂	H ₂ O
La ₂ O ₃ -BaCO ₃	23.8	3.4	39.0	34.6	23.1	10.1	55.3
Sm ₂ O ₃ -BaCO ₃	24.1	5.1	37.3	35.3	22.4	10.7	54.9
MgO-BaCO ₃	23.2	8.6	38.4	33.9	19.0	15.8	53.0
CaO-BaCO ₃	23.9	7.1	41.0	29.3	22.5	10.9	57.6

^a Selectivities of the carbon-containing products (i. e., CO, CO₂, C₂H₄ and C₂H₆) are based on C atom basis, selectivities of H₂ and H₂O are based on H atom basis

As an example, calculation detail on the $\text{La}_2\text{O}_3\text{-BaCO}_3$ catalyst is shown as follows. From the data in Table 1, contribution of Reaction (9) to selectivities of H_2 and H_2O is calculated to be 31.75% on H-basis (i.e., $10.1+55.3-25-34.6 \times 0.25 = 31.75$). On the other hand, carbon oxides (CO and CO_2) are expressed to be formed totally in the overall Reaction (9). It is seen from Table 1 that the sum of selectivities of CO and CO_2 on C-basis is 42.4%. It should be noticed that methane is the source of C atom and H atom in OCM process, and the unconverted methane is still more than 70% generally. And one methane molecule has one carbon atom and four hydrogen atoms, so the mole ratio of C atom to H atom consumed in the overall Reaction (9) is estimated to be $42.4\% / (31.75\% \times 4) = 1/3$ for the OCM reaction over the $\text{La}_2\text{O}_3\text{-BaCO}_3$ catalyst shown in Table 1. This ratio is corresponding to the elemental composition of methyl radical. Thus the overall Reaction (9) can be re-written into Reaction (10).



This result, deduced from correlation of product selectivities for the first time, supports the mechanism proposed in Publications [8–11,19,20] and stresses the high possibility of methyl radicals being oxidized into carbon oxides (CO and CO_2) in competition with their coupling into ethane. Product selectivity were also calculated for the other catalysts, and all results support the same conclusion.

Presence of Reaction (10) can be understood from the fact that radicals are much more reactive than neutral molecules, and number of methyl radicals formed in the OCM process is more than the C_2 hydrocarbon molecules. Partial pressure of C_2 hydrocarbons was quite low, only ca. 9% of that of the remaining methane in the reaction systems. As a consequence, methyl radical was the most probable species to be oxidized into carbon oxides in comparison with other hydrocarbon species under the experimental conditions.

In fact, ethyl radical would also be possible to be oxidized into carbon oxides in competition with Reaction (6) when combined with oxygen species. However, because ethyl radical is a C_2 species, deep oxidation of ethyl radical into carbon oxides needs more oxygen species to participate. In other words, deep oxidation of ethyl radical contains more elementary steps than deep oxidation of methyl radical. This implies that the former oxidation is relatively slower in kinetics than the latter oxidation. Especially, as OCM reaction proceeded, oxygen became very dilute in gas phase. As shown in Figure 5, for the OCM reaction over the $\text{La}_2\text{O}_3/\text{BaCO}_3$ catalyst (the mass ratio of $\text{La}_2\text{O}_3/(\text{La}_2\text{O}_3+\text{BaCO}_3) = 0.25$) at feed mole ratio $\text{CH}_4/\text{O}_2 = 4$ and 650°C , CH_4 conversion was 14.3%, but O_2 conversion had reached 69.5%. Mole ratio of CH_4/O_2 in the outlet gas mixture became 11.2 in this case. On the other hand, concentration of ethyl radical was much lower than that of methyl radical in gas phase. It can thus be concluded that direct oxidation of methyl radicals is the main source of formation of carbon oxides. Olsbye et al. also draw a similar conclusion for OCM reaction over

$\text{BaCO}_3/\text{La}_2\text{O}_n(\text{CO}_3)_{3-n}$ catalyst from a kinetic study [21].

C_{3+} products might be formed in the OCM process. However, selectivity of C_{3+} hydrocarbons is known to be below 5% [22]. Wang et al. have reported a carbon balance of $100 \pm 1\%$ in the OCM reactions over the $\text{BaCO}_3/\text{La}_2\text{O}_3$ catalysts without consideration of C_{3+} hydrocarbons [18]. This means that C_{3+} hydrocarbons were in trace amount, if formed. In the present experiments, carbon balance in $\text{C}_1\text{-C}_2$ carbon-containing species was within the range of experimental error. So the total selectivity of C_2 and carbon oxides on C-basis was normalized to 100%. It can be believed that presence of even a trace amount of C_{3+} products does not influence the conclusion deduced above from the correlation of product selectivity.

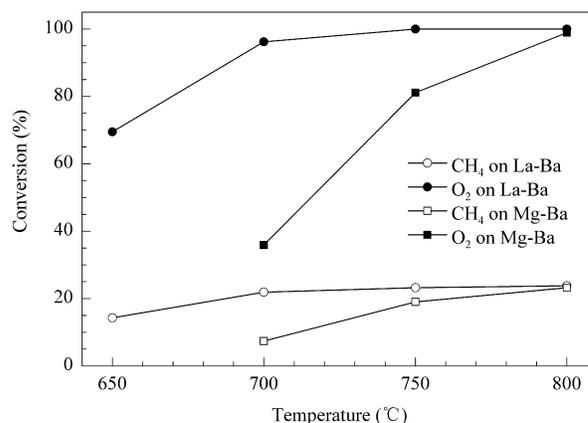


Figure 5. Conversions of CH_4 and O_2 as functions of temperature over the catalysts $\text{La}_2\text{O}_3\text{-BaCO}_3$ and MgO-BaCO_3 (the mass ratio of $\text{M}_x\text{O}_y/(\text{M}_x\text{O}_y+\text{BaCO}_3) = 0.25$) at feed mole ratio $\text{CH}_4/\text{O}_2 = 4$

4. Conclusions

Selectivity correlation between different products in OCM reaction over the $\text{M}_x\text{O}_y\text{-BaCO}_3$ catalysts was discussed. Calculation results clearly present that the overall deep oxidation Reaction (9) consumed C atom and H atom at mole ratio of 1 to 3 on the mechanism of Reactions (1)–(9). This value shows that methyl radical, among all the hydrocarbon species, is in most probability to be oxidized into carbon oxides by oxygen species $[\text{O}_p]$. The oxygen species $[\text{O}_p]$ may be on catalyst surface or in gas phase. It is anticipated that type of the oxygen species $[\text{O}_p]$ attacking methyl radicals will affect product distribution (i.e., mole ratios of CO/CO_2 and $\text{H}_2/\text{H}_2\text{O}$) of the deep oxidation Reaction (10).

Ethyl radical may be oxidized by multiple oxygen species into carbon oxides, but its probability would be very low in comparison with that of methyl radical oxidation.

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