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Oxidative coupling of methane by carbon dioxide: a highly C_2 selective La_2O_3 / ZnO catalyst

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In the oxidative coupling of methane by carbon dioxide, La_2O_3/ZnO catalysts were found to have high C_2 selectivity and good stability. The coupling selectivity on La_2O_3/ZnO is about 90%, which is much higher than that on pure La_2O_3 or ZnO. The consumption ratio of carbon dioxide to methane is approximately one. X-ray diffraction analysis reveals that the structural forms of the oxides are unchanged during the reaction. The reaction mechanism for C_2 formation is discussed.

Keywords: carbon dioxide as the oxidant; oxidative coupling of methane; La_2O_3/ZnO

1. Introduction

The oxidative coupling of methane (OCM) to C_2 hydrocarbons is an attractive process for its potential industrial utilization of the world's abundance of natural gas resource. Extensive studies have been conducted since the work of Keller and Bhasin [1]. The OCM reaction over metal oxides by oxygen is effective, but the selectivity to C_2 hydrocarbons is not high enough because of the non-selective oxidation of methyl radicals with oxygen in the gas phase [2,3], especially when the concentration of oxygen is high [4]. However, active surface oxygen species are necessary for the initial step, i.e., hydrogen abstraction from methane. Thus, in order to avoid non-selective oxidation by oxygen, some novel processes have recently been proposed and are under investigation. One consists of modification of the reaction system, such as the use of a membrane reactor [5]. Another approach is the use of other oxidants which are much less active in the gas phase than O_2, such as CO_2 and/or H_2O [6,7], for the production of active surface oxygen species on metal oxides.

Carbon dioxide is of significance as a less active oxidant. In principle, it is widely reported in heterogeneous catalysis that CO_2 can be dissociatively chemisorbed on several metals and metal oxides surfaces to form CO and O^- adspecies [8]. The role of O^- species in OCM is well recognized [9,10]. Krylov and co-workers [11,12] have shown that carbon dioxide can be used as a selective oxidant for a variety of hydrocarbons on oxide catalysts, mainly based on manganese oxide. Unfortunately in the case of the CH_4–CO_2 reaction, the authors claimed that methane is converted mainly into synthesis gas ($CO + H_2$).

On the other hand, the recent interest in the carbon dioxide reaction is sparked by the necessity to fight against the so-called green-house effect. From the point of view of solving and/or alleviating the green-house effect by chemical means, OCM by carbon dioxide is more important and practible than carbon dioxide hydrogenation. This is due to the fact that no hydrogen is needed and natural gas itself is a source of hydrogen and is abundant.

When carbon dioxide is used as the oxidant, the reactions for the formation of C_2 hydrocarbons from methane can be expressed as follows:

$$2CH_4 + CO_2 \rightarrow C_2H_6 + CO + H_2O \tag{1}$$

$$2CH_4 + 2CO_2 \rightarrow C_2H_4 + 2CO + 2H_2O \tag{2}$$

The equilibrium yield of C_2H_6 at 1073 K is 13% [12]. At the same time, the following side reactions of methane yielding CO are possible:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \tag{3}$$

$$CH_4 + 3CO_2 \rightarrow 4CO + 2H_2O \tag{4}$$

Reactions (3) and (4) are thermodynamically more favorable than reactions (1) and (2). Therefore, the problem of the OCM reaction with carbon dioxide is to find a catalyst which activates the methane molecule suitably to the reactions (1) and (2).

Aika and Nishiyama [9,13–15] have shown that the addition of CO_2 to the CH_4/O_2 reactant mixture can significantly enhance the yield of C_2 hydrocarbons over a broad range of catalysts, in particular PbO/MgO catalysts. It was concluded that the carbon dioxide is involved in the reaction as an oxidant, providing a monatomic oxygen species via degradation to carbon monoxide. However, when the CH_4–CO_2 reaction without O_2 is performed over PbO/MgO, the active life of the catalyst is short and the selectivity of C_2 hydrocar-

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bons is not high due to the formation of stable carbonate species on the catalyst at the reaction temperature [6].

Very recently, Asami et al. [16] found that methane reacts with carbon dioxide to form C_2 hydrocarbons over some pure rare earth catalysts which exhibit high C_2 selectivity of about 30% with stable catalytic activity. In our OCM study, Yu [17] found that La_2O_3/ZnO oxides are not sensitive to carbon dioxide addition at the reaction temperature of OCM. This means that at high temperature the surface of La_2O_3/ZnO is not covered with stable carbonate species. Xu et al. [18] demonstrated that different CO_2 adspecies could be formed on promoted rare earth oxides at different temperatures. Asha et al. [19] further showed that on oxygen-deficient LaO_x surfaces, the CO_2 adspecies could be thermally dissociated to yield gas-phase CO and O^- adspecies leading to surface oxidation. All of these made us to think that on some properly supported and/or promoted rare earth oxides, improving the C_2 selectivity may be possible for the CH_4–CO_2 reaction. We found that, when methane and carbon dioxide were co-fed, La_2O_3/ZnO catalysts give a very high selectivity to C_2 hydrocarbons with fairly good catalytic stability. The objective of this communication is to report the results of selective synthesis of C_2 hydrocarbons from methane and carbon dioxide on La_2O_3/ZnO catalysts.

2. Experimental

2.1. Catalyst preparation and characterization

ZnO and La_2O_3 were prepared directly by calcining zinc oxide and lanthanum nitrate, respectively, while La_2O_3/ZnO was prepared by impregnating ZnO with lanthanum nitrate solution (all chemicals were analytical reagents). The powder or paste produced was dried at 383 K and then calcined in air at 1123 K for 5 h. The calcined samples were pressed, crushed and sieved to yield granules of 20–40 mesh. For the sake of simplicity, La_2O_3/ZnO catalysts with different La_2O_3 loading are expressed as *x*LZ, where *x* denotes the nominal content of La_2O_3 in weight percent. The surface area of the individual oxides and their mixtures was measured by N_2 adsorption using the BET method. Phase composition of catalysts was determined by X-ray diffraction (XRD) (Cu Kα line, Rigaku D/max RB) at room temperature. The operating conditions were 40 kV and 100 mA, and a scanning rate of 8 degree/min.

2.2. Catalytic evaluation

The reaction of methane and carbon dioxide was carried out in a fixed-bed flow reactor. The quartz reactor, 250 mm long and 6 mm i.d., was placed vertically in an electric furnace. 0.5 g of the catalyst sample (20–40 mesh) was held in place by a quartz wool plug and a thermocouple was inserted in the catalyst bed. The catalyst was pretreated at 1123 K in He flow for 1.5–2 h (to prevent oxidation of methane by the remaining oxygen). After catalyst pretreatment, reactant gas (with a molar ratio of $CH_4/CO_2 = 2$) was introduced at a total flow rate of 30 ml/min. No dilute was used in all cases. The reaction temperature was 1123 K. The reactant and the reactor effluent were analyzed by an on-line gas chromatograph using a thermal conductivity detector and Porapak Q columns. Gas chromatographic data were processed according to the following assumption: the carbon in carbon dioxide is converted to carbon monoxide and the carbon in methane is converted to ethane, ethylene and carbon monoxide. This assumption is reasonable since the amount of other products such as carbon, acetylene and C_{3+} hydrocarbons is negligible. Then the conversion of methane and carbon dioxide and the C_2 selectivity are calculated as follows:

$$X_{CH_4} = (1 - \text{moles of } CH_4 \text{ out/moles of } CH_4 \text{ in}),$$

$$X_{CO_2} = (1 - \text{moles of } CO_2 \text{ out/moles of } CO_2 \text{ in}),$$

$$C_2 \text{ selectivity} = 2(\text{moles of } C_2H_4 + \text{moles of } C_2H_6)/\text{moles of } CH_4 \text{ reacted},$$

$$C_2 \text{ yield} = \text{methane conversion} \times C_2 \text{ selectivity}.$$

3. Results and discussion

3.1. BET surface area and XRD

Table 1 lists the composition of various La_2O_3/ZnO catalysts and their corresponding BET surface areas. The surface area of pure oxides is higher than that of mixed oxides. As expected, here all of the catalysts have low surface areas; this is beneficial for their stability of running a reaction at a temperature as high as 1123 K.

Fig. 1 shows the XRD patterns of various La_2O_3/ZnO oxides. The XRD results indicate that the crystalline structure of La_2O_3 and ZnO still persists in La_2O_3/ZnO. These initial crystalline forms are retained in every

Table 1
Catalyst compositions and their BET surface areas

Catalyst [a]	Catalyst composition (%)		Surf. area (BET) (m^2/g)
	ZnO	La_2O_3	
ZnO	100	0	4.5
10 LZ	90	10	1.5
20 LZ	80	20	2.3
30 LZ	70	30	2.3
50 LZ	50	50	2.2
La_2O_3	0	100	2.9

[a] ZnO and La_2O_3 were prepared by calcining ZnO and $La(NO_3)_3$, respectively, at 1123 K for 5 h.

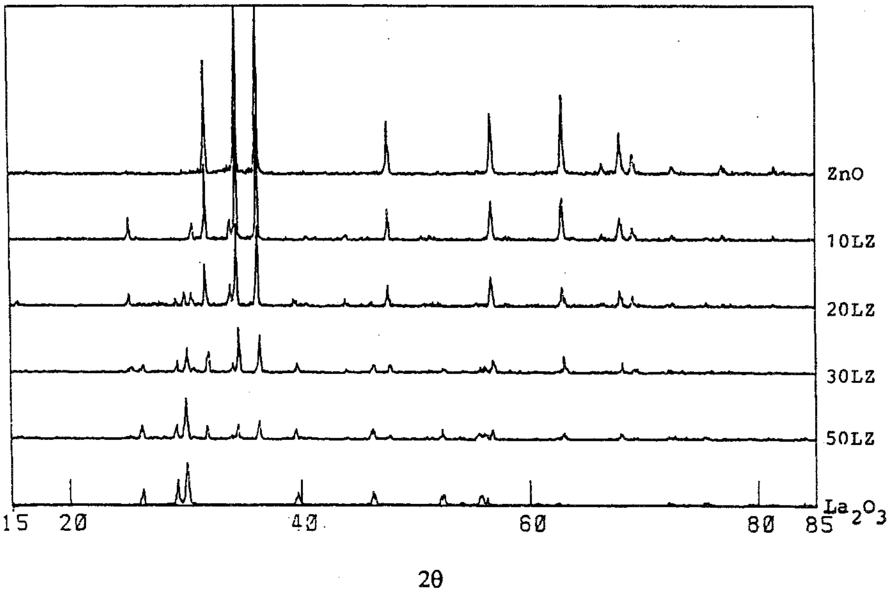

Fig. 1. XRD profile of La_2O_3/ZnO oxides.

case even after 10 h of reaction and no changes can be observed. This may imply that the overall reaction of CH_4–CO_2 does not sacrifice the lattice oxygen of the catalysts. In other words, carbon dioxide may act as an oxidant in the CH_4–CO_2 reaction over various La_2O_3/ZnO catalysts.

3.2. *Catalytic evaluation*

The catalytic activities of the CH_4–CO_2 reaction over various La_2O_3/ZnO catalysts are summarized in table 2. As shown in table 2, although the reaction was carried out at a temperature as high as 1123 K, the roles of various catalysts are obvious, but different. No reaction of methane with carbon dioxide is observed in the absence of catalyst. Pure ZnO gave a C_2 selectivity of 7.6%, while pure La_2O_3 gave a C_2 selectivity of 56.8%. In contrast, all La_2O_3/ZnO catalysts gave a C_2 selectivity of more than 90%. As far as the conversion of methane and carbon dioxide is concerned, ZnO gave the highest conversion of CO_2 while La_2O_3 the lowest conversion of CH_4. LZ catalysts nearly maintain the methane conversion level as the same as for pure ZnO, but heavily suppress the CO_2 conversion level as compared with ZnO. It seems that the interaction between La_2O_3 and ZnO creates a new type of synergetic sites at the La_2O_3–ZnO interfacial area which offer the active and selective performance of the conversion of methane and carbon dioxide into C_2 hydrocarbons over La_2O_3/ZnO catalysts. There is a general tendency that the ethylene yield is lower than the ethane yield over every catalyst. The results of a high C_2 selectivity and a low ethylene-to-ethane ratio are reasonable if we take into account that CO_2 is a much less active oxidant – once active oxygen species are formed, the concentration must be quite low. On the other hand, it must be highly efficient in the abstraction of one hydrogen atom from methane. Meanwhile on ZnO and La_2O_3, carbon dioxide and methane reacted with a molar ratio of about 2.6. On La_2O_3/ZnO catalysts, however, the consumption ratio of carbon dioxide to methane is about 1. A very small amount of hydrogen can be detected in the product so that reaction (3) is negligible. Therefore the total reaction equation will be reaction (1) + reaction (2) + reaction (4) which can be expressed as follows:

$$2CH_4 + CO_2 \rightarrow C_2H_6 + CO + H_2O \quad (1)$$

$$2CH_4 + 2CO_2 \rightarrow C_2H_4 + 2CO + 2H_2O \quad (2)$$

$$CH_4 + 3CO_2 \rightarrow 4CO + 2H_2O \quad (4)$$

$$5CH_4 + 6CO_2 \rightarrow C_2H_6 + C_2H_4 + 7CO + 5H_2O \quad (5)$$

Table 2
Catalytic activities of the CH_4–CO_2 reaction over various La_2O_3/ZnO catalysts[a]

Catalyst	Conv. (%)		C_2 (%)		C_2H_4/C_2H_6	Reacted CO_2/CH_4 (mole/mole)
	CO_2	CH_4	sel.	yield		
blank	0	0	–	–	–	–
ZnO	16.4	3.0	7.6	0.2	0.5	2.7
10LZ	3.7	2.1	97.0	2.0	0.5	0.9
20LZ	6.8	3.1	90.6	2.8	0.7	1.0
30LZ	5.5	2.9	91.2	2.6	0.7	1.0
50LZ	5.3	2.5	90.7	2.3	0.6	1.0
La_2O_3	6.0	1.3	56.8	0.8	0.4	2.6

[a] Reaction conditions: atmospheric pressure, temperature: 1123 K, flow rate: 30 ml/min, $CH_4/CO_2 = 2$ (mole ratio), catalyst charge: 0.5 g, pretreated in pure He at 1123 K for 1.5 to 2 h. The results presented were obtained after 4 h of reaction.

It is clear from the above reactions that the higher the ratio of reacted CO_2 and reacted CH_4 on a catalyst, the lower the C_2 selectivity is. Our results indicate that the reaction of methane and carbon dioxide over La_2O_3/ZnO catalysts mainly proceeds via reaction steps (1) and (2), which correspond to the product selectivity to ethane and ethene, respectively, on the basis of the carbon in methane.

The changes in C_2 yield with time-on-stream over various La_2O_3/ZnO catalysts are shown in fig. 2. When the ratio of the Y_{C_2} values after 2 and 10 h may be used as an index for expressing the change with time, the values of Y_{C_2} (10 h)/ Y_{C_2} (2 h) on various catalysts are summarized in table 3. When the ratio is equal to 1, C_2 yield is unchanged with time. It is interesting to notice that on ZnO, C_2 yield increased gradually. On La_2O_3 and La_2O_3/ZnO catalysts, C_2 yield decreased very slightly with the progress of the reaction. This might be caused by the deposition of a very small amount of carbon on the catalysts.

3.3. *The role of CO_2 in the reaction*

In order to study the role of the lattice oxygen in the oxides, methane alone was passed over the 20LZ catalyst which was pretreated with pure He at 1123 K for 1.5 h. At the initial stages, a methane conversion of about 1.2% was observed with a C_2 selectivity of about 82%. Gradually, the catalytic activity decayed with time-on-stream owing to oxygen loss from the catalyst and its color became dark gray. This color disappeared after the catalyst was calcined at 973 K in air and the catalytic activity was almost restored. Under CH_4–CO_2, the catalytic activity was only very slightly changed after 10 h reaction and the color of the catalyst remained white. Combining these results it seems that the oxygen species stored in the lattice of the La_2O_3/ZnO oxide is probably responsible for methane activation and for the selective formation of C_2 hydrocarbons. Moreover, such kind of oxygen species can be reproduced via dissociative chemisorption of CO_2 on the oxide surface. The reactive oxygen species responsible for the selective formation of C_2 hydrocarbons are tentatively ascribed to be O^- from the initial dissociation of CO_2.

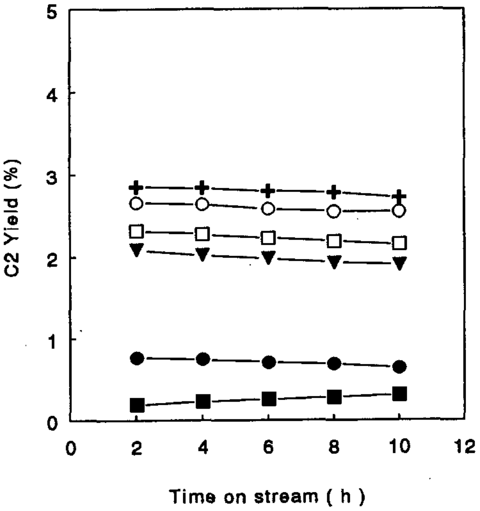

Fig. 2. Variation of C_2 yield with time-on-stream. (■) ZnO; (▼) 10LZ; (+) 20LZ; (○) 30LZ; (□) 50LZ; (●) La_2O_3.

Table 3
Variation of the values of Y_{C_2} (10 h)/ Y_{C_2} (2 h) of the CH_4–CO_2 reaction over various La_2O_3/ZnO catalysts [a]

Catalyst	Y_{C_2} (10 h)/ Y_{C_2} (2 h)
ZnO	1.5
10LZ	0.9
20LZ	1.0
30LZ	1.0
50LZ	0.9
La_2O_3	0.8

[a] Reaction conditions: as shown in table 2.

Under the reaction conditions, La_2O_3 and ZnO may easily become non-stoichiometric oxides (e.g. LaO_x, ZnO_x), which may act as a transitional state. Au et al. [20] have demonstrated that on the defects (oxygen vacancies) of ZnO, the adsorption of CO_2 is remarkably enhanced. Recently, Asha et al. [19] have shown that on the oxygen-deficient (partially reduced) LaO_x surface there is a greater probability for irreversible adsorption of CO_2, which then thermally dissociated leading to surface oxidation with the evolution of CO.

All these findings suggest the possibility of a consumption–regeneration cycle of reactive surface oxygen species on La_2O_3/ZnO catalysts with co-fed methane and carbon dioxide as shown below:

$$\mathrm{O(surface)} + 2CH_4 \rightarrow 2CH_3\cdot + H_2O + \square$$

$$2CH_3\cdot \rightarrow C_2H_6$$

$$\square + CO_2 \rightarrow \mathrm{O(surface)} + CO$$

where □ represents a surface oxygen-deficient site.

The surface reactive oxygen species on La_2O_3/ZnO abstract hydrogen from methane to give methyl radicals, which in turn are converted to hydrocarbons. Carbon dioxide is then adsorbed on the oxygen-deficient surface. The adsorbed carbon dioxide is thermally dissociated to yield gas-phase CO and also leading to surface reoxidation.

On the basis of the above discussion, the reasons why La_2O_3/ZnO is effective for the CH_4–CO_2 reaction can be attributed to both the mobility of oxygen and the non-stoichiometry would be changed by combining La_2O_3 and ZnO on one hand and the concentration of the reactive surface oxygen species due to lattice distortion or defects is increased by the combination on the other hand.

Asami et al. [16] found that pure rare earth oxides such as yttrium oxide, lanthanum oxide and samarium

Table 4
Catalytic activities of the CH_4–CO_2 reaction over some ZnO-supported rare earth oxides [a]

Catalyst	Conv. (%)		C_2 (%)		Reacted CO_2/CH_4 (mole/mole)
	CO_2	CH_4	sel.	yield	
20% La_2O_3/ZnO	6.8	3.1	90.6	2.8	1.02
20% Y_2O_3/ZnO	26.8	5.6	2.9	0.2	2.40
20% Sm_2O_3/ZnO	26.0	5.3	3.6	0.2	2.40

[a] Reaction conditions: as shown in table 2.

oxide showed high C_2 selectivity of about 30% with stable catalytic activity in the CH_4–CO_2 reaction. However, the corresponding ZnO-supported rare earth oxide catalysts have extremely different C_2 selectivity. For comparison, several typical results are shown in table 4. On Y_2O_3/ZnO and Sm_2O_3/ZnO, the main product is CO with a trace amount of C_2 hydrocarbons. This is quite different from that of La_2O_3/ZnO. The different results obtained may be due to the different type of interaction between the rare earth oxides and ZnO. Further study is necessary to reveal the reason.

Methane reacts with the reactive oxygen species on the catalyst surface through the reverse shift reaction of CO_2. The redox nature of the catalyst may be important to yield the reactive oxygen species from CO_2. Further investigation is now underway to explore the factors affecting the production of active oxygen species which favor C_2 hydrocarbons formation on oxide surface via CO_2 dissociation.

4. Conclusion

La_2O_3/ZnO catalysts exhibit high coupling selectivity for the oxidative coupling of methane with carbon dioxide as the oxidant. About 90% of the carbon in methane was converted to C_2 hydrocarbons, the rest to carbon monoxide. The ratio of reacted carbon dioxide to methane is approximately one. The chemical forms of the oxides are unchanged during the reaction.

In the oxidative coupling of methane by carbon dioxide, the consumption–regeneration cycle of surface reactive oxygen species may be as follows: (1) the surface oxygen species of La_2O_3/ZnO abstract hydrogen from methane to give methyl radicals which in turn are converted to hydrocarbons; (2) carbon dioxide oxidizes oxygen-deficient (partially reduced) catalysts.

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