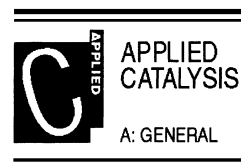




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Letter

Carbon dioxide-induced selective conversion of methane to C₂ hydrocarbons on CeO₂ modified with CaO

Ye Wang^{*}, Yoshimoto Takahashi, Yasuo Ohtsuka

Research Center for Organic Resources and Materials Chemistry, Institute for Chemical Reaction Science, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan

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Abstract

Selectivity and yield of ethane and ethylene in the conversion of methane without O₂ increased remarkably with increasing partial pressure of carbon dioxide over CeO₂ modified with CaO. The chemisorbed carbon dioxide is proposed to be responsible for the selective formation of ethane and ethylene. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Methane; Carbon dioxide; Ethane and ethylene; Chemisorbed species; CaO–CeO₂ catalyst

1. Introduction

The development of new routes for effective utilization of methane and carbon dioxide is of great interest in chemistry. A large amount of research papers have reported on the oxidative coupling of methane with O₂ to produce C₂ hydrocarbons (ethane and ethylene) and a number of catalysts have been found for this reaction [1–4]. The undesirable formation of CO₂, however, seems to be one of the biggest problems from a practical point of view [4]. If CO₂ can be used as an oxidant for the oxidative coupling of CH₄, CO will be the only by-product. Moreover, the utilization of less reactive CO₂ as an alternative to O₂ may increase C₂ selectivity, because gas phase radical reactions which result in the decrease in C₂ selectivity

[5] do not occur in this case. Only a few workers have attempted the oxidative coupling of CH₄ using CO₂. According to Aika and Nishiyama [6], CO₂ showed an enhancing effect on the formation of C₂ hydrocarbons over PbO/MgO in the presence of O₂ but the reaction was not sustained without O₂. Recent results in our laboratory have shown that CH₄ can react more efficiently with CO₂ to give C₂ hydrocarbons over praseodymium and terbium oxides among 30 metal oxides examined [7]. However, C₂ selectivity and yield of 50% and 2%, respectively, are insufficient. Furthermore, although it is suggested that C₂ formation proceeds through a redox-mechanism involving lattice oxygen atoms in these oxides [7], the role of CO₂ is still unclear. In this paper, for the first time, we report high performance of a CaO–CeO₂ catalyst, which shows C₂ yield of more than 5% with C₂ selectivity of 60–70%. A very unique feature of this catalyst is that the presence of CO₂ greatly accelerates the formation of C₂ hydrocarbons, while the reaction

^{*}Corresponding author. Fax: (+81-22)2175652; e-mail: yewang@icrs.tohoku.jp

of CH₄ with lattice oxygen produces CO and H₂ as the main products.

2. Experimental

The precursor of CaO–CeO₂ catalyst was prepared by impregnating CeO₂ with Ca(NO₃)₂ aqueous solution, followed by evaporation in air at 363 K. The atomic ratio of Ca/Ce was 0.5. The granular precursor (2 g) with size of 16–32 mesh was held in a quartz-made reactor and calcined for 1 h at 850°C in air flow. After purging with He for 1 h, CH₄ and CO₂ were introduced to the reactor to start the reaction, the total flow rate of the reactants including He as balance being 100 ml min⁻¹. The products were analyzed with a high speed gas chromatograph with an interval of 5 min.

3. Results and discussion

The lattice oxygen of CaO–CeO₂ was proposed to be responsible for the selective formation of C₂ hydrocarbons in the oxidative coupling of CH₄ by O₂ [8]. However, our result in Fig. 1 shows that CO and H₂ are the main products in the conversion of CH₄ with the lattice oxygen of CaO–CeO₂. CO₂ was formed at the early stage of the reaction and the amount of C₂ hydrocarbons was negligibly small. Similar results have been reported in a gas–solid reaction of CH₄ with CeO₂ alone or CeO₂ modified with several oxides including CaO [9]. Thus, the lattice oxygen of the present catalyst was not effective for C₂ formation.

Fig. 2 shows the performance after 1 h of reaction at 850°C over CaO–CeO₂ at different partial pressures of CO₂ (denoted as P(CO₂) hereafter). The presence of CO₂ induced the formation of C₂ hydrocarbons. Not only C₂ selectivity but C₂ yield increased remarkably with increasing P(CO₂), in particular up to 40 kPa. C₂ selectivity and yield reached 70% and 4% at P(CO₂) of 70.7 kPa, respectively. This finding is very unique, because CO₂ usually shows poisoning effect over basic catalysts which are generally used for the oxidative coupling of CH₄.

When time on stream at P(CO₂) of 70.7 kPa and 850°C was prolonged to 10 h, as is seen in Fig. 3, there were no significant changes in CH₄ conversion and C₂

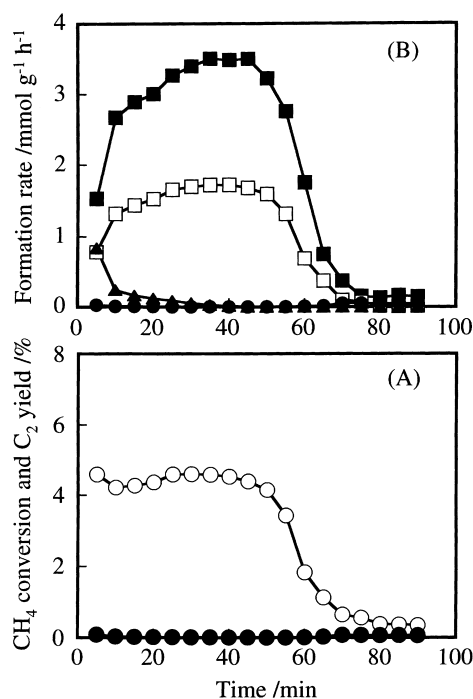


Fig. 1. The reaction of CH₄ in the absence of CO₂ over the CaO–CeO₂ catalyst: (A) CH₄ conversion (○) and C₂ yield (●); (B) formation rate of H₂ (■), CO (□), CO₂ (▲) and C₂ hydrocarbons (●). Conditions: $T=850^{\circ}\text{C}$, $P(\text{CH}_4)=30.3\text{ kPa}$.

selectivity. The runs at different reaction temperatures (Fig. 4) showed that C₂ selectivity exceeded 90% at $\leq 800^{\circ}\text{C}$ and C₂ yield reached $>5\%$ at $\geq 875^{\circ}\text{C}$ with C₂ selectivity of $>60\%$. At 900°C , C₂ yield was maximum of 6.1% with a C₂ selectivity of 61%. Although these values are still insufficient from a practical viewpoint, the observed yield is three times better than the one which was recently reported.

It should be pointed out that, when CeO₂ alone was used as the catalyst under the same conditions as in Fig. 2, the main product was CO and C₂ selectivity was $<5\%$. Lower CH₄ conversion and C₂ selectivity were also observed over CaO alone. Thus, a synergy effect obviously exists between CaO and CeO₂ in increasing C₂ selectivity and yield.

The information about the chemisorption of CO₂ on the CaO–CeO₂ catalyst during reaction can be obtained by CO₂-TPD measurement to clarify the nature of active species for the formation of C₂ hydrocarbons in the presence of CO₂. Fig. 5 shows the CO₂-desorption profiles from the catalyst both in

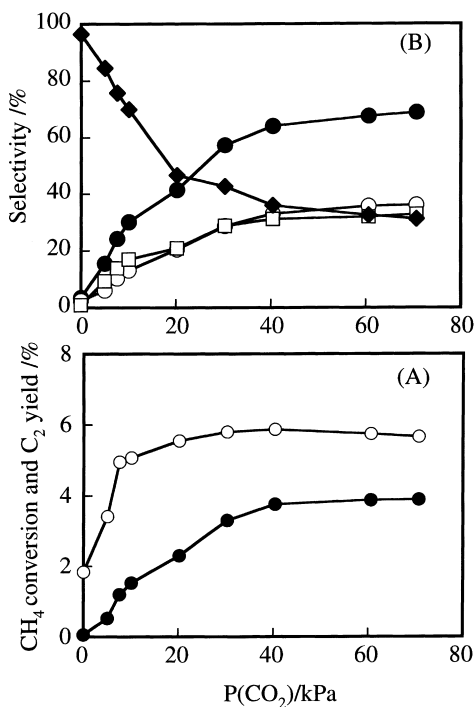


Fig. 2. Effect of partial pressure of CO₂ on the performance of the CaO–CeO₂ catalyst: (A) CH₄ conversion (○) and C₂ yield (●); (B) selectivity of C₂H₆ (○), C₂H₄ (□), C₂ hydrocarbons (●) and CO (◆). Conditions: T=850°C, P(CH₄)=30.3 kPa.

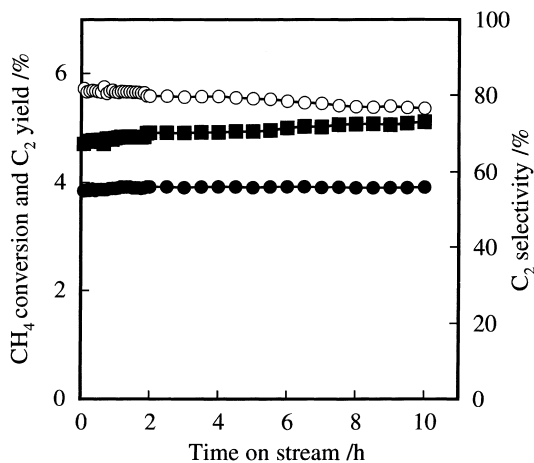


Fig. 3. Change in catalytic performance of CaO–CeO₂ with time on stream. Symbols: (○), CH₄ conversion; (●) C₂ yield; (■) C₂ selectivity. Conditions: T=850°C, P(CH₄)=30.3 kPa, P(CO₂)=70.7 kPa.

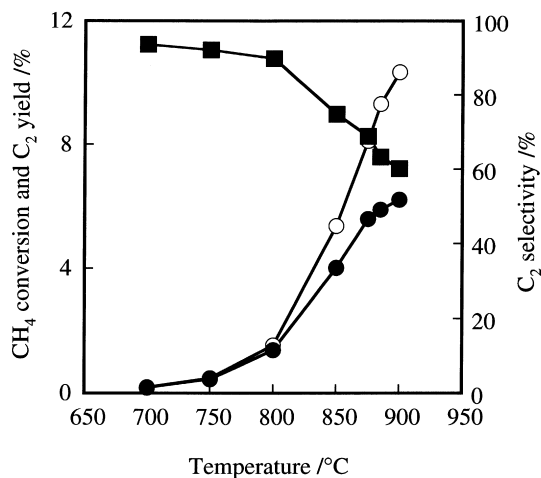


Fig. 4. Effect of reaction temperature on catalytic performance of CaO–CeO₂. Symbols as in Fig. 3. Conditions: P(CH₄)=30.3 kPa, P(CO₂)=70.7 kPa.

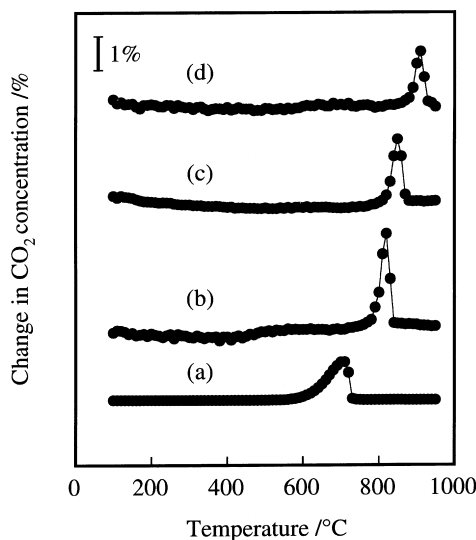


Fig. 5. Profiles of CO₂ desorption from the CaO–CeO₂ catalyst after reaction, followed by TPD measurements at a heating rate of 2.5°C min⁻¹: (a) in He flow, (b), (c) and (d) in CO₂ flow with P(CO₂) of 10.1, 30.3 and 70.7 kPa, respectively.

He flow and in CO₂ flow. Before TPD measurements, the reaction of CH₄ and CO₂ was carried out for 1 h at 850°C, followed by cooling down to 100°C and then replacing feed gas with He at 100°C. A desorption peak at 710°C was observed with the TPD in He flow. The peak of CO₂ desorption shifted to 810°C, 850°C

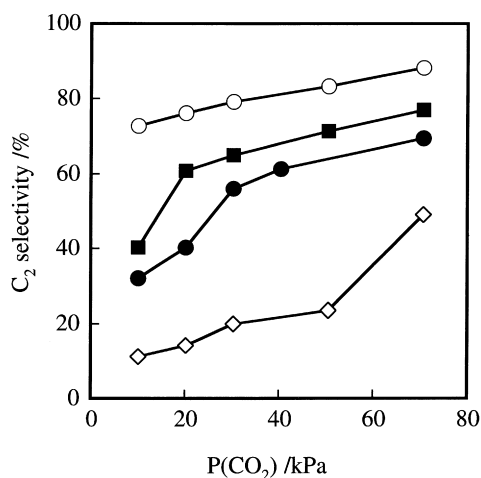


Fig. 6. C_2 selectivity as a function of partial pressure of CO_2 at different reaction temperatures. Symbols: (○) 780°C; (■) 820°C; (●) 850°C; (◆) 900°C. Conditions: $P(CH_4)=30.3$ kPa.

and 910°C in CO_2 flow with $P(CO_2)$ of 10, 30 and 70 kPa, respectively. These results indicate that a pool of chemisorbed CO_2 exists on the catalyst during the reaction when $P(CO_2)$ is higher than 10, 30 and 70 kPa at 810°C, 850°C and 910°C, respectively.

Fig. 6 shows C_2 selectivity after 1 h reaction as a function of $P(CO_2)$ at 750°C, 820°C, 850°C and 900°C. The selectivity increased almost linearly with $P(CO_2)$ at 750°C. However, there were jumps in C_2 selectivity at other reaction temperatures; for example, C_2 selectivity at 850°C increased steeply from 40% to 56% when $P(CO_2)$ was increased from 20 to 30 kPa. The $P(CO_2)$ where the selectivity jump occurred depended on reaction temperature. As summarized in Table 1, the $P(CO_2)$ and temperature where such jumps are observed are in reasonable agreement with those of the desorption peak of CO_2 . The appearance of the chemisorbed CO_2 pool apparently corresponds to a high C_2 selectivity. This strongly suggests that the chemisorption of CO_2 on the surface of CaO–CeO₂ catalyst is one of the key factors for C_2 formation. The details about the chemisorption of CO_2 and subse-

Table 1

Comparison of TPD results and $P(CO_2)$ dependence of C_2 selectivity

Partial pressure of CO_2 and temperature observed for	
Desorption peak of CO_2^a	Jump in C_2 selectivity ^b
10 kPa, 810°C	10–20 kPa, 820°C
30 kPa, 850°C	20–30 kPa, 850°C
70 kPa, 910°C	50–70 kPa, 900°C

^aObserved in Fig. 5.

^bDetermined from Fig. 6.

quent formation of active oxygen species will be the subject of future work.

4. Conclusions

The presence of CO_2 greatly enhanced the conversion of CH_4 to C_2 hydrocarbons over CaO–CeO₂ catalyst. Both C_2 selectivity and C_2 yield increase with increasing partial pressure of CO_2 . The run at 900°C achieves the highest C_2 yield of 6% with a selectivity of 60%, the yield being three times higher than that reported recently. The chemisorbed CO_2 on CaO–CeO₂ may account for this selective conversion.

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