

RESEARCH NOTE

CaO–ZnO Catalyst for Selective Conversion of Methane to C₂ Hydrocarbons Using Carbon Dioxide as the OxidantYe Wang¹ and Yasuo Ohtsuka

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Received October 29, 1999; revised January 5, 2000; accepted January 17, 2000

A binary catalyst of CaO–ZnO is effective for the selective conversion of CH₄ to C₂ hydrocarbons using CO₂ as the oxidant. C₂ selectivity approaches 80% with a C₂ yield of 4.3% over the catalyst with a Ca/Zn ratio of 0.5 at 875°C. The lattice oxygen of the CaO–ZnO converts CH₄ mainly to H₂ and CO. The presence of CO₂ forms a new oxygen species, which is active and selective for the conversion of CH₄ to C₂ hydrocarbons. The CaO component in the catalyst enhances the adsorption of CO₂ and thus suppresses the reaction involving the lattice oxygen. The reduced Zn site is suggested to activate CO₂. © 2000 Academic Press

Key Words: methane; carbon dioxide; ethane and ethylene; CaO–ZnO catalyst.

The use of CO₂ as an oxidant for the partial oxidation of lower alkanes may become an important route for the utilization of natural gas. It is known that the natural gas in many areas contains CO₂ in a large quantity in addition to CH₄ and other lower alkanes. It would be highly desirable to utilize such low-valued natural gas without emission of CO₂ by simultaneous transformation of CH₄ and CO₂ to valuable chemicals or fuels. Many studies on the application of CO₂ in heterogeneous catalysis have been reported (1). However, only a few such studies contributed to the partial oxidation or oxidative dehydrogenation of lower alkanes using CO₂ (2–6). We have focused on the conversion of CH₄ to C₂H₆ and C₂H₄ using CO₂ instead of O₂ (7–9) and recently reported that binary oxide catalysts of CaO–CeO₂ (10, 11) and CaO–CrO_x (12) are effective for this reaction. In the former case, it has been suggested that the redox of Ce⁴⁺/Ce³⁺ relates to the activation of CO₂, i.e., the dissociation to CO and oxygen species which account for CH₄ conversion, and the basic Ca²⁺ in the catalyst greatly enhances the selectivity to C₂ hydrocarbons (11).

As a continuation of this research, we have studied many binary oxides composed of CaO and other transition

metal oxides and found that the CaO–ZnO catalyst exhibits higher C₂ selectivity than the CaO–CeO₂ and CaO–CrO_x catalysts on a similar level of C₂ yield. The present paper attempts to clarify the nature of the reaction occurring on the CaO–ZnO catalyst and to elucidate the role of CO₂ in C₂ formation.

The CaO–ZnO catalyst was prepared by the impregnation method similar to that used for the CaO–CeO₂ catalyst (11). ZnO powder (Wako Pure Chemical Industries, Ltd.; size <5 μm; purity >99.9%) was immersed in an aqueous solution of Ca(NO₃)₂ for 12 h at ambient temperature and then water was evaporated at 90°C. The resultant mixture was finally calcined at 850°C in an air flow (200 ml min⁻¹) for 4 h. The catalyst thus obtained was loaded into a fixed-bed quartz reactor. The reaction was started by introducing a mixture of CH₄ (99.999%) and CO₂ (99.99%) after air calcination of the catalyst and subsequent replacement with He at 850°C took place. The standard reaction conditions were as follows: P(CH₄) = 30 kPa, P(CO₂) = 70 kPa, W = 1.0 g, and F = 100 ml min⁻¹. The products were analyzed by an on-line high-speed gas chromatograph. Data processing was shown in the preceding paper (11). The catalysts before and after reaction were characterized by X-ray diffraction (XRD) analysis. The CO₂-TPD technique was used to examine CO₂ adsorption on the catalyst. The detailed procedure was described elsewhere (11).

Figure 1 shows the effect of the Ca/Zn ratio in the catalyst on the performance at 850°C. As reported previously (11), CH₄ conversion on CaO was lower than 0.5%. Since it is generally accepted that the activation of CO₂ requires electron transfer from the catalyst probably through an anionic CO₂⁻ precursor (13, 14), CO₂ is not activated readily on CaO which cannot donate electrons. On the other hand, ZnO gave a CH₄ conversion of 5.5%. The existence of defect sites such as Zn⁺ or oxygen vacancy centers has been reported on ZnO (15) and may be responsible for CO₂ activation. However, C₂ selectivity was less than 5% and thus C₂ yield was very low over ZnO alone. The binary oxides

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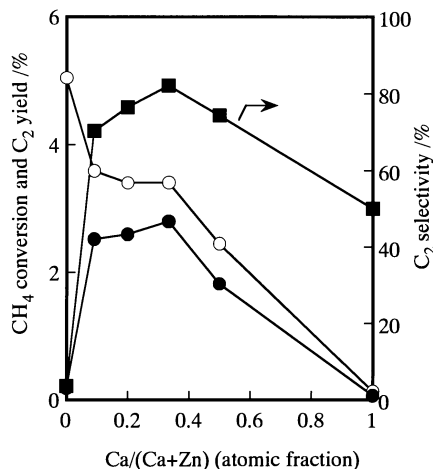


FIG. 1. Effect of catalyst composition on catalytic performances. Symbols: (○) CH₄ conversion; (■) C₂ selectivity; (●) C₂ yield. $T=850^{\circ}\text{C}$, $P(\text{CH}_4)=30\text{ kPa}$, $P(\text{CO}_2)=70\text{ kPa}$, $W=1\text{ g}$, and $F=100\text{ ml min}^{-1}$.

provided remarkably higher C₂ selectivity and yield than either ZnO or CaO, although CH₄ conversion was slightly lower as compared to ZnO alone. Thus, there exist synergistic effects between CaO and ZnO in the composite oxide for C₂ formation. The catalyst with a Ca/Zn ratio of 0.5 ($\text{Ca}/(\text{Ca}+\text{Zn})=0.33$ in Fig. 1) has been investigated in detail since it exhibited the highest C₂ selectivity and yield.

To clarify the role of CO₂, the reactions of CH₄ over the CaO–ZnO in the absence and in the presence of CO₂ are compared in Fig. 2. In the absence of CO₂ (Fig. 2A), H₂ and CO were formed as the main products with a ratio of ca. 2. CH₄ conversion was approximately 2% at the initial stage and decreased abruptly to <0.2% after 4 h. The reaction without CO₂ must arise from lattice oxygen atoms in the catalyst. Thus, the lattice oxygen is not selective for C₂ formation. When CO₂ was co-fed (Fig. 2B), CH₄ conversion increased to 6%, becoming remarkably higher than that without CO₂, even at the initial stage. C₂ hydrocarbons became the main products of CH₄ conversion in the presence of CO₂, the ratio of C₂H₄/C₂H₆ being 1.0. Both CH₄ conversion and C₂ selectivity changed slightly when the time on stream was prolonged to 7.5 h. After 7 h, C₂ selectivity approached 80% with a C₂ yield of 4.3%. This selectivity was higher than those over the CaO–CeO₂ (11) and CaO–CrO_x (12) catalysts under the same reaction conditions and at almost the same level of C₂ yield. In the latter case, C₂ selectivity was 69% and 65% with C₂ yields of 4.4% and 3.9%, respectively. The results described previously indicate that the oxygen species responsible for selective C₂ formation is generated from CO₂ during the reaction.

With the catalyst characterization by XRD, Fig. 3 shows the results after the reaction of CH₄ alone. Only CaO was detected in the catalyst bed (Fig. 3A), whereas metallic Zn was found to deposit downstream on the wall of the reactor

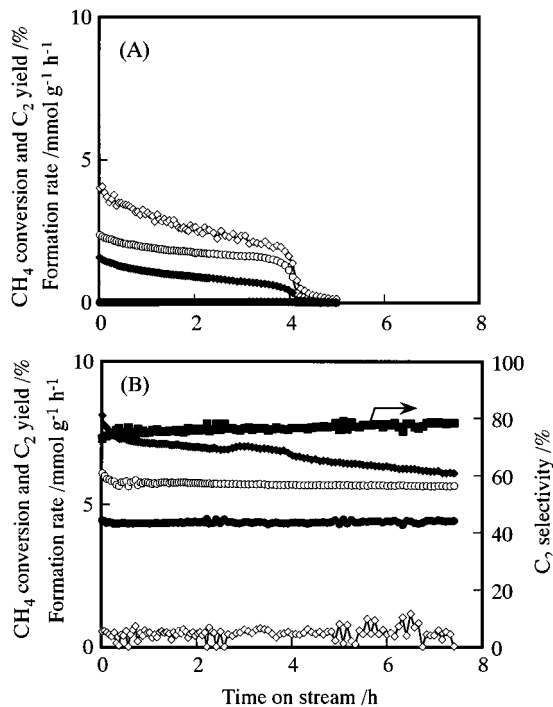


FIG. 2. The reaction of CH₄ in the absence (A) or the presence (B) of CO₂ over the CaO–ZnO catalyst. Symbols: (A), (◇) H₂ formation rate; (◆) CO formation rate; (○) CH₄ conversion; (●) C₂ yield. (B), (◇) H₂ formation rate; (◆) CO formation rate; (○) CH₄ conversion; (■) C₂ selectivity; (●) C₂ yield. $T=875^{\circ}\text{C}$, $P(\text{CH}_4)=30\text{ kPa}$, $P(\text{CO}_2)=70\text{ kPa}$ (in the case of Fig. 2B), $W=1\text{ g}$, and $F=100\text{ ml min}^{-1}$.

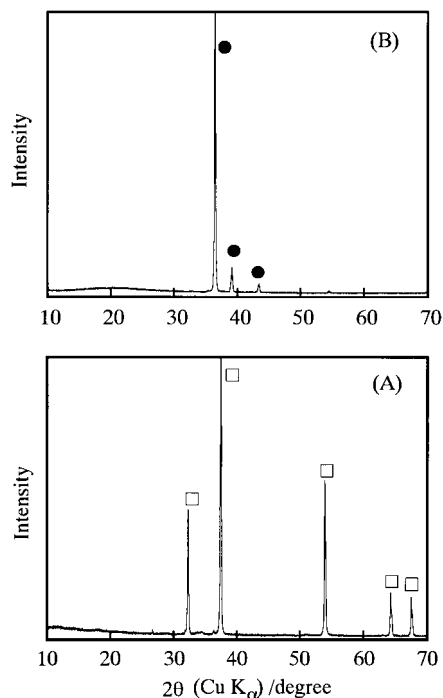


FIG. 3. X-ray diffraction patterns after the reaction of CH₄ in the absence of CO₂: (A) in the catalyst bed and (B) recovered downstream. Symbols: (□) CaO; (●) Zn.

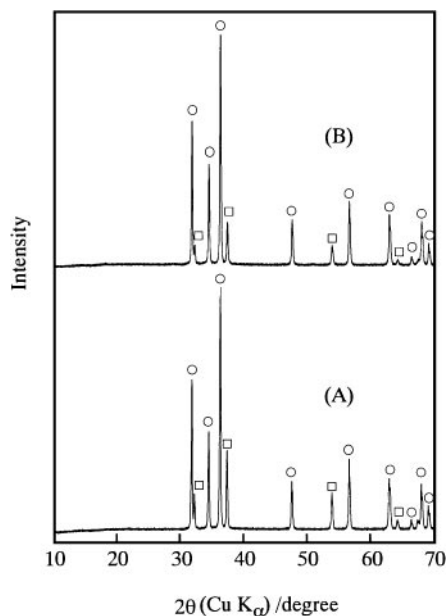


FIG. 4. X-ray diffraction patterns before and after the reaction of CH_4 with CO_2 : (A) before reaction; (B) after reaction. Symbols: (○) ZnO; (□) CaO.

(Fig. 3B). Thus, accompanying the conversion of CH_4 to H_2 and CO in the absence of CO_2 , ZnO in the CaO–ZnO was reduced to Zn, which was removed from the catalyst bed because of its low melting point (420°C). On the other hand, as shown in Fig. 4, the XRD pattern after the reaction of CH_4 with CO_2 was almost the same as that before the reaction, comprising diffraction peaks ascribed to both CaO and ZnO. Moreover, no obvious deposition of Zn metal was observed downstream. These results strongly suggest that the catalyst reduced by CH_4 is instantly reoxidized by CO_2 to form CO and an active oxygen species. In other words, it is likely that the zinc sites at a reduced state (e.g., freshly generated metallic Zn and/or Zn^+) or oxygen vacancies connected to zinc sites account for CO_2 activation. CH_4 would be converted by the active oxygen to a CH_3 radical that is an intermediate for C_2 formation.

The effect of partial pressure of CO_2 (denoted as $P(\text{CO}_2)$) on catalytic performances has been investigated to obtain further information about the reaction. As shown in Fig. 5, CH_4 conversion increased with increasing $P(\text{CO}_2)$ up to 30 kPa, and further increase in $P(\text{CO}_2)$ exerted no significant effect, while C_2 selectivity increased with $P(\text{CO}_2)$ in the whole range investigated.

Figure 6 shows typical TPD profiles obtained in both He and CO_2 flow for the catalyst after reaction. Only one desorption peak was observed in all the cases. The peak temperature in He was 730°C , and it shifted to 840 and 870°C in CO_2 with $P(\text{CO}_2)$ of 10 and 30 kPa, respectively. The amount of CO_2 adsorbed on the catalyst at 850°C under different $P(\text{CO}_2)$ can be calculated from such CO_2 -TPD exper-

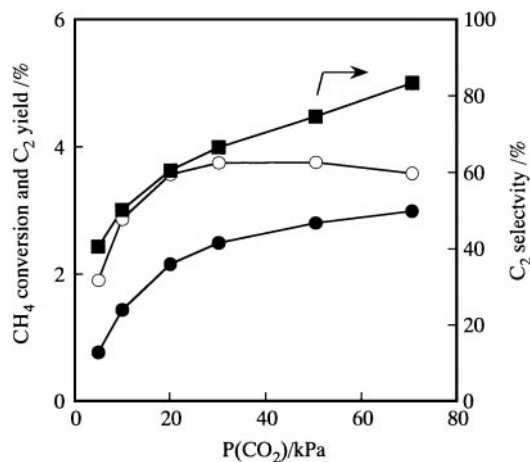


FIG. 5. Dependence of catalytic activity of the CaO–ZnO on partial pressure of CO_2 . Symbols: (○) CH_4 conversion; (■) C_2 selectivity; (●) C_2 yield. $T = 850^\circ\text{C}$, $P(\text{CH}_4) = 30$ kPa, $W = 1$ g, and $F = 100$ ml min^{-1} .

iments and the results are summarized in Fig. 7. The amount increased with increasing $P(\text{CO}_2)$. Since almost no CO_2 was adsorbed on ZnO alone at 850°C , it is evident that the CaO component in the composite catalyst plays an important role in CO_2 chemisorption. Such CO_2 adsorbed would lead to the selective formation of C_2 hydrocarbons because both CO_2 chemisorption and C_2 formation are greatly enhanced not only by the existence of CaO in the catalyst but also by the raising of $P(\text{CO}_2)$.

It is noteworthy that such a remarkable increase in C_2 selectivity with $P(\text{CO}_2)$ likewise occurred over the CaO– CeO_2 (11) and CaO– CrO_x (12) catalysts reported previously. For all these catalysts, lattice oxygen atoms converted CH_4 to H_2 and CO , and the profiles for CO_2 adsorption versus $P(\text{CO}_2)$ were very similar. Therefore, the following reaction mechanism could be proposed. At low $P(\text{CO}_2)$,

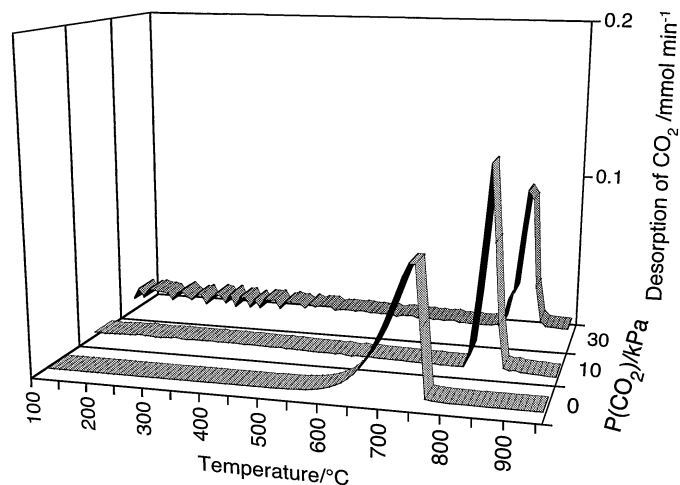


FIG. 6. Profiles of CO_2 desorption from the CaO–ZnO catalyst in He and CO_2 flow with different $P(\text{CO}_2)$ after reaction. The rate for the raising of the temperature is $3^\circ\text{C}/\text{min}$.

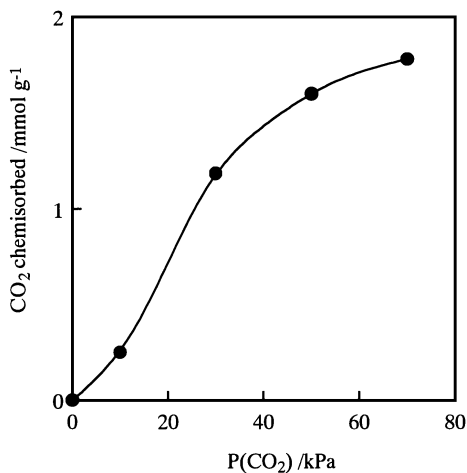


FIG. 7. Amount of CO₂ chemisorbed versus $P(\text{CO}_2)$ on the CaO-ZnO catalyst at 850°C.

because the amount of the CO₂ chemisorbed is small, some lattice oxygen would partially take part in the reaction and convert CH₄ mainly to H₂ and CO, leading to low C₂ selectivity. As $P(\text{CO}_2)$ increases, the CO₂ adsorbed becomes plentiful on the catalyst. As a result, the reaction involving the lattice oxygen would be suppressed, and the selective conversion of CH₄ to C₂ hydrocarbons by active oxygen species generated from CO₂ would be predominant. Higher selectivity observed over the CaO-ZnO than over the CaO-CeO₂ and CaO-CrO_x is probably caused by the

lower reactivity of lattice oxygen of the CaO-ZnO catalyst.

ACKNOWLEDGMENT

This work was supported in part by a Grant-in-Aid for Scientific Research (B) from the Ministry of Education, Science, Sports and Culture, Japan (No. 10555275).

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