Catalysis Letters 56 (1998) 203–206

Remarkable enhancing effect of carbon dioxide on the conversion of methane to C_2 hydrocarbons using praseodymium oxide

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Received 10 August 1998; accepted 28 October 1998

The presence of carbon dioxide remarkably enhanced the conversion of methane to ethane over praseodymium oxide in the absence of gaseous oxygen at 500–650 °C. CO was simultaneously formed from CO_2 accompanying the conversion of methane. The oxygen vacancies in praseodymium oxide were suggested to play key roles in this low-temperature reaction.

Keywords: methane, carbon dioxide, oxygen vacancies, praseodymium oxide

1. Introduction

The activation and utilization of both CH_4 and CO_2 have attracted much attention in recent years. As for direct transformation of CH_4, the oxidative coupling of CH_4 has been studied extensively, and a large variety of catalysts have been reported [1–3]. However, the formation of CO_2, the most undesirable by-product, seems unavoidable using any kind of catalyst. Our approach is to use CO_2 as the oxidant instead of O_2. CO will be the only by-product and high selectivity to C_2 hydrocarbons may be expected. In this case, the activation of CO_2 is required. Thermodynamical calculations for following overall reactions show that the equilibrium conversion of CH_4 to C_2 hydrocarbons can reach 12% (6% for C_2H_6 and 6% for C_2H_4) at 600 °C (reactant mixture of $CH_4/CO_2 = 2$):

$$2CH_4 + CO_2 \rightarrow C_2H_6 + CO + H_2O$$

$$2CH_4 + 2CO_2 \rightarrow C_2H_4 + 2CO + 2H_2O$$

Aika and coworkers [4,5] reported that CO_2 showed a positive role in the formation of C_2 hydrocarbons in the oxidative coupling of CH_4 over a PbO–MgO catalyst, but the reaction could not proceed in the absence of O_2. Previous studies in our laboratory showed that, among 30 metal oxides, praseodymium (Pr) oxide was specific for the conversion of CH_4 into C_2 hydrocarbons by CO_2 in the absence of O_2 at 850 °C [6,7]. Very recently, we have found that C_2 hydrocarbons (mainly C_2H_6) can be obtained with a considerable amount even at 500–650 °C in a temperature-programmed reaction of CH_4 and CO_2 over Pr oxide. The purpose of this work is to investigate the effect of CO_2 on this low-temperature reaction and to clarify the role of oxygen vacancies in Pr oxide.

2. Experimental

Pr oxide was prepared by thermal decomposition of the corresponding nitrate in a He flow (200 ml min^{-1}) at 850 °C. The reaction of CH_4 and CO_2 was carried out using a conventional fixed-bed flow reactor (quartz tube) operated at atmospheric pressure. For a standard pretreatment, the oxide (2.0 g) was first calcined in the reactor in an air flow (100 ml min^{-1}) at 850 °C for 1 h. Then, the remaining air was purged with high-purity He (>99.9999%, 100 ml min^{-1}), and the reactor was cooled to 400 °C in the same atmosphere. The mixture of CH_4 (>99.999%) and CO_2 (>99.99%) was passed over the pretreated oxide at 400–850 °C using a temperature-programmed manner at a rate of 2 K min^{-1}. The products were analyzed by a high-speed gas chromatograph (M-200D, Microsensor Technology, Inc.).

3. Results and discussion

Figure 1 shows the effect of partial pressure of CO_2, denoted as $P(CO_2)$, on the rate of C_2 formation and CH_4 concentration in the effluent. Figure 1(A) reveals that C_2 hydrocarbons are formed at two different temperature ranges, 500–650 °C and >700 °C. The high-temperature C_2 formation at $\geqslant$800 °C has been reported so far [7]. A small amount of C_2 hydrocarbons (C_2H_6 alone) was observed at 500–650 °C in the absence of CO_2. This must be due to the conversion of CH_4 by the lattice oxygen of Pr oxide. The presence of CO_2 greatly increased the rate of C_2 formation. The rates at around 600 °C were comparable to or higher than those at 850 °C, and C_2 yield at 600 °C reached 2.3% (C_2H_6 2.1%, C_2H_4 0.2%) at $P(CO_2)$ of 70.7 kPa. As seen in figure 1(B), the change in CH_4 concentration corresponded well to the profiles of the low temperature C_2 formation.

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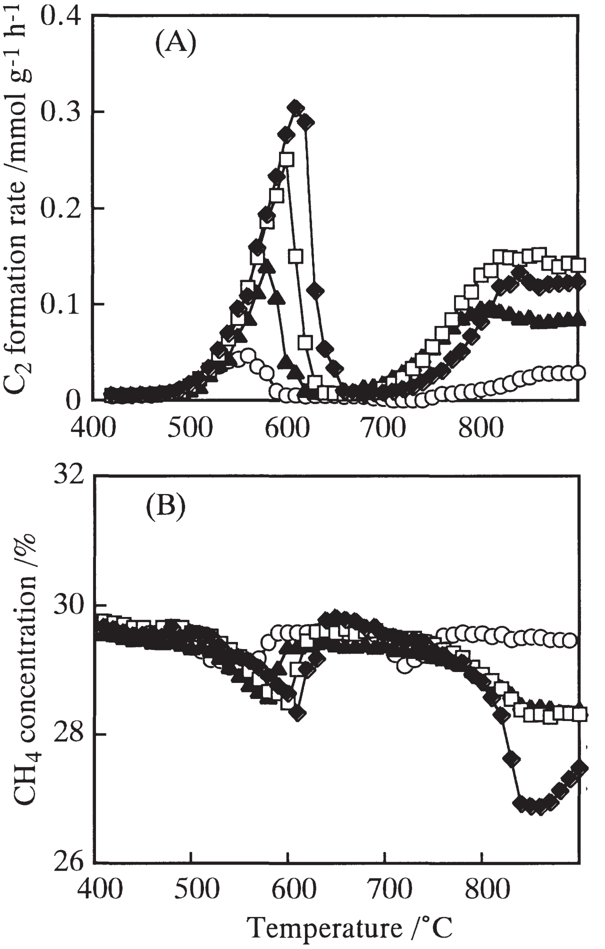

Figure 1. Profiles of formation rate of C_2 hydrocarbons (A) and CH_4 concentration (B) during temperature-programmed reaction of CH_4 and CO_2 on praseodymium oxide: (○) $P(CO_2) = 0$, (▲) $P(CO_2) = 20.2$ kPa, (□) $P(CO_2) = 50.5$ kPa, (◆) $P(CO_2) = 70.7$ kPa. $P(CH_4) = 30.3$ kPa, He balance, total flow rate = 100 ml min^{-1}, catalyst weight = 2.0 g.

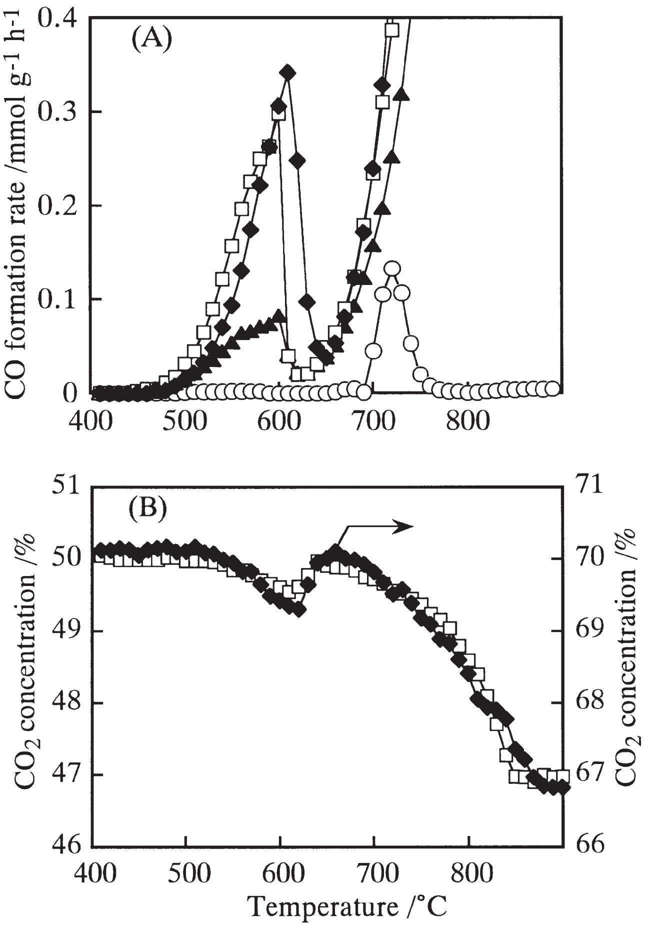

Figure 2. Profiles of formation rate of CO (A) and CO_2 concentration (B) during temperature-programmed reaction of CH_4 and CO_2 on praseodymium oxide: (○) $P(CO_2) = 0$, (▲) $P(CO_2) = 20.2$ kPa, (□) $P(CO_2) = 50.5$ kPa, (◆) $P(CO_2) = 70.7$ kPa. $P(CH_4) = 30.3$ kPa, He balance, total flow rate = 100 ml min^{-1}, catalyst weight = 2.0 g.

For the reaction at the low-temperature range of 500–650 °C, CO was formed only when CO_2 was supplied (figure 2(A)), and the rate of CO formation increased with increasing $P(CO_2)$, with a corresponding decrease in CO_2 concentration, as shown in the results at $P(CO_2)$ of 50.5 and 70.7 kPa (figure 2(B)). The decrease of CO_2 concentration indicates that CO_2 acts as a reactant for the conversion of CH_4 to C_2 hydrocarbons; it is likely that CO_2 is activated on the Pr oxide and the resulting surface species reacts with CH_4 to give C_2 hydrocarbons. CO was formed simultaneously from CO_2. Comparison of figures 1(A) and 2(A) shows that the low-temperature rate of CO formation is comparable to that of C_2 formation, suggesting that the active oxygen generated from CO_2 is selectively used in the conversion of CH_4 to C_2 hydrocarbons. The selectivity to C_2 hydrocarbons exceeded 90% at 500–650 °C under the reaction conditions in figures 1 and 2. On the other hand, the rate of CO formation in the high-temperature region of >700 °C was overwhelmingly higher than that of C_2 formation. In this case, CO was formed not only from CO_2 but also from CH_4, which resulted in much lower C_2 selectivity, the value at 850 °C being about 30%.

Figure 3 shows the change of C_2 yield with contact time (expressed as W/F), which has been varied by changing the gas flow rate (F). The C_2 yield for the low-temperature reaction (at 620 °C) increased almost linearly with contact time and reached ca. 7% at W/F of 0.08 min g ml^{-1} with C_2 selectivity of 90%. On the other hand, C_2 yield for the high-temperature reaction was only 2% at maximum (figure 3). The consecutive oxidation of C_2 hydrocarbons to CO occurred more easily in this temperature region.

The replacement of CO_2 with O_2 caused the formation of CO_2 alone at 500–700 °C over Pr oxide. A small amount of C_2H_6 was observed only at >700 °C.

Other lanthanide oxides (Yb, La, Ce, Nd, Sm, Tb and Eu) were also tested for the conversion of CH_4 in the presence of CO_2. All these oxides except for Tb oxide were inactive at $\leqslant$700 °C. On the other hand, Tb oxide showed almost the same low-temperature conversion of CH_4 to C_2 hydrocarbons as Pr oxide. In a temperature-programmed reaction of CH_4 (30.3 kPa) and CO_2 (70.7 kPa) on Tb oxide, C_2 formation started at 450 °C and showed a peak at

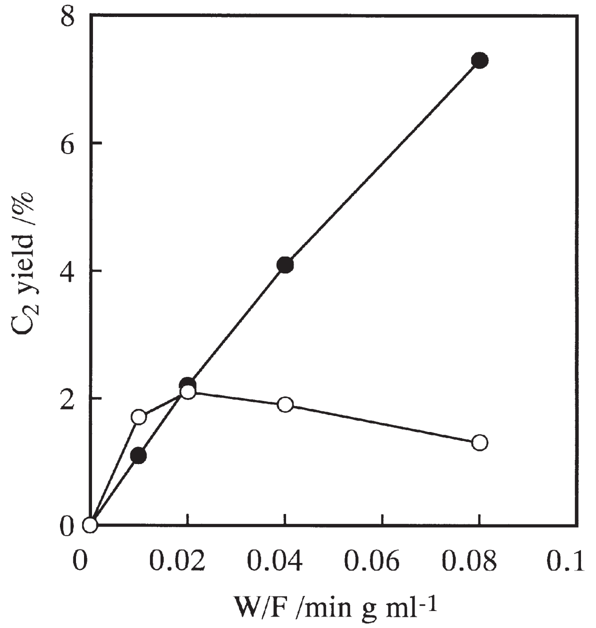

Figure 3. Effect of contact time (W/F) on C_2 yields for low-temperature (620 °C) (●) and high-temperature (850 °C) (○) reactions on praseodymium oxide. $P(CH_4) = P(CO_2) = 30.3$ kPa, He balance, total flow rate = 100 ml min^{-1}, catalyst weight = 2.0 g.

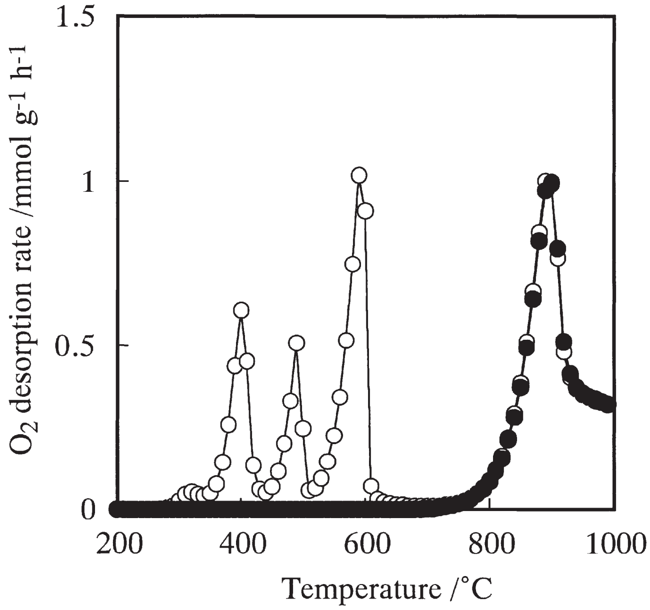

Figure 4. Profiles for O_2 desorption from praseodymium oxides after standard (●) and optional (○) pretreatment. The TPD experiments were carried out in He (100 ml min^{-1}) from 200 to 1000 °C at a rate of 4 K min^{-1}.

Table 1
Mode of pretreatment of Pr oxide before TPD measurements.

Mode	Atmosphere and temperature		
	After air calcination[a]	During cooling	Just before TPD
Standard	He, 850 °C	He, 850 → 200 °C	He, 200 °C
Optional	Air, 850 °C	Air, 850 → 200 °C	He, 200 °C

[a] 850 °C.

530 °C, which was lower by 70 °C than that for Pr oxide. Since oxygen vacancies can be generated much more easily in Pr and Tb oxides than in other lanthanide oxides due to the high lability of lattice oxygen atoms in these two oxides, it is likely that the oxygen vacancies of Pr and Tb oxides are important for the activation of CO_2 and thus for the low-temperature conversion of CH_4.

In order to investigate the effect of oxygen vacancies on the reaction performance, temperature-programmed desorption (TPD) measurements of O_2 were carried out for Pr oxide pretreated at different modes (table 1). As shown in figure 4, the standard pretreatment provided one O_2 desorption peak at 900 °C. On the other hand, the optional pretreatment, that is, the replacement of He with air after air calcination and subsequent cooling, resulted in the appearance of four O_2 desorption peaks at 400, 490, 590, and 900 °C. This indicates a higher concentration of oxygen vacancies in the oxide with the standard pretreatment. The compositions of Pr oxides after the standard and optional pretreatments were estimated to be $PrO_{1.73}$ and $PrO_{1.83}$, respectively.

Figure 5 shows the formation rates of C_2 hydrocarbons and CO during the reaction of CH_4 and CO_2 on Pr oxides

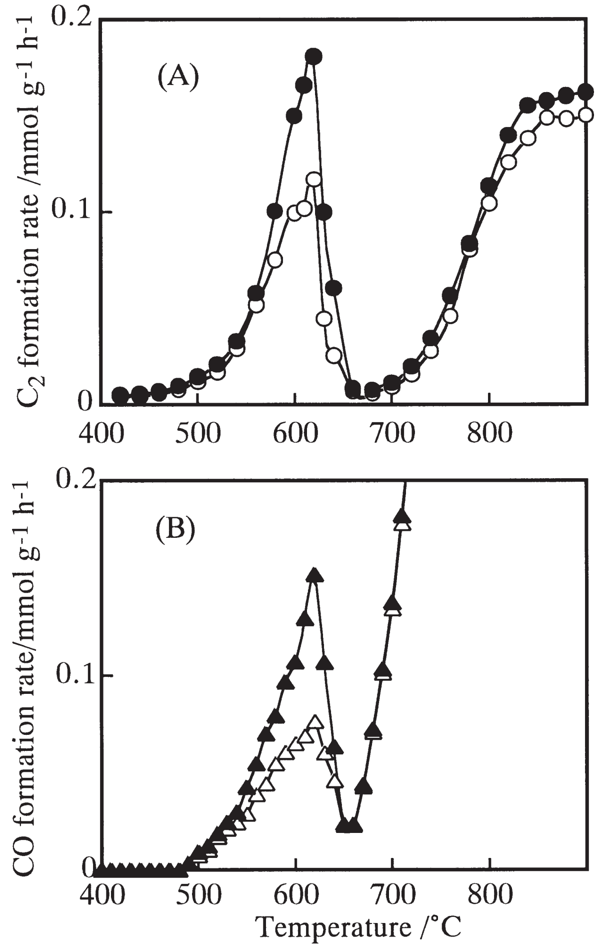

Figure 5. Profiles of formation rate of C_2 hydrocarbons (A) and of CO (B) on praseodymium oxides after standard (●, ▲) and optional (○, △) pretreatment. $P(CH_4) = P(CO_2) = 30.3$ kPa, He balance, total flow rate = 100 ml min^{-1}, catalyst weight = 2.0 g.

pretreated above. Both rates at 500–650 °C were higher on the oxide after the standard pretreatment, i.e., on that with a higher concentration of oxygen vacancies. On the other hand, these rates at $>700\,^{\circ}C$ were not dependent on the mode of pretreatment.

We have attempted to clarify why the increase of temperature above ca. 600 °C decreased the formation rates of both C_2H_6 and CO, as shown in figures 1 and 2. The reaction under the conditions shown in figure 1 ($P(CO_2) = 70.7$ kPa) was stopped at 650 °C, and the Pr oxide was then characterized. No desorption of O_2 was observed from the oxide at the temperature range of 100–1000 °C in the O_2-TPD measurement and the composition was calculated to be $PrO_{1.5}$ (Pr_2O_3). The Pr_2O_3 showed a structure similar to La_2O_3, notably different from that of $PrO_{1.73}$ or $PrO_{1.83}$ which possess the structure of defective fluorite. This indicates the reduction of Pr oxide, in other words, the change of the structure from the defective fluorite to a non-defective one. We think that this is the main reason for the decreased activity as reaction temperature was increased above ca. 600 °C. For the same reason, the reaction was also not sustained for a long time at 600 °C. Further modification of Pr oxide is needed to make the reaction proceed catalytically.

All the observations obtained above strongly suggest that the oxygen vacancies in Pr oxide play crucial roles in the low-temperature conversion of CH_4 to C_2 hydrocarbons by CO_2. It is plausible that CO_2 adsorbs on the oxygen vacancy to form surface oxygen species, which then activate CH_4. Further investigations on the adsorption and activation mechanisms of CO_2 over vacant sites of Pr oxide are underway.

Acknowledgement

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

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