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Mechanism of the Oxidative Coupling of Methane Using CO_2 as an Oxidant over PbO–MgO

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CO_2 was suggested to be utilized as an oxidant for the oxidative coupling of methane over PbO–MgO and alkaline earth metal-doped CaO catalysts under $P_{CH_4} = 8.3$ kPa, $P_{CO_2} = 8.3$ kPa, and $P_{O_2} = 0.08$ kPa, and at 1073 K. The mechanism of this reaction ($2CH_4 + CO_2 = C_2H_6 + CO + H_2O$ and/or $2CH_4 + 2CO_2 = C_2H_4 + 2CO + 2H_2O$) was studied over a 15 mol% PbO–MgO catalyst by using isotope techniques and kinetics. $^{13}CO_2$ and $^{12}CD_4$ gave exclusively ^{13}CO and $^{12}C_2$ hydrocarbons, and no ^{12}CO was produced under the low *W/F* conditions at 1073 K. One of the oxygen atoms of CO_2 was concluded to be used for the CH_4 coupling reaction through the reverse shift reaction of CO_2. It was also found that C_2 hydrocarbons reacted further with oxygen from CO_2 under conditions of high conversion. © 1990 Academic Press, Inc.

INTRODUCTION

Oxidative coupling of methane is an attractive reaction for the chemical utilization of natural gas and has been studied over various catalysts (*1–10*). Generally, it is believed that the gas-phase oxygen depresses C_2 hydrocarbon selectivity because the methyl radical intermediate is oxidized by the gas-phase oxygen to CO_2, probably by way of CH_3O_2 radicals (*3, 4, 6, 7, 9*) or CH_2O radicals (*11*). However, the surface oxygen must be necessary for the initial step, i.e., hydrogen abstraction from methane. Thus, if we could supply an active surface oxygen without supplying the gas-phase oxygen, we should get a high C_2 selectivity. To that end, oxygen sources other than O_2 need to be developed.

The authors have succeeded in utilizing CO_2 as an oxidant for this reaction over PbO–MgO and alkaline earth metal-doped CaO catalysts (*12, 13*). Over these catalysts, almost 100% C_2 selectivity was obtained from the reaction of CH_4/O_2 (100/1). We obtained even higher C_2 yield by the reaction with $CH_4/CO_2/O_2$ (100/100/1) than that by the reaction with CH_4/O_2 (100/1). Thus, we suggest that one of the two oxygens in CO_2 was used for the abstraction of hydrogen from methane to give C_2 hydrocarbons. Small amounts of O_2 were necessary to stabilize the catalyst used for a long run. In the previous studies (*12, 13*), various catalyst samples have been examined; however, only preliminary work has been done concerning reaction performance and the mechanism. The objective of this study is to understand further the mechanism of this reaction ($2CH_4 + CO_2 = C_2H_6 + CO + H_2O$ and/or $2CH_4 + 2CO_2 = C_2H_4 + 2CO + 2H_2O$) over an effective catalyst (15 mol% PbO–MgO) applying isotope techniques and kinetics.

EXPERIMENTAL

The 15 mol% PbO–MgO catalyst was prepared by impregnation of MgO (Soekawa Chemical Co., 99.9%) with lead nitrate (Kanto Chemical Co., 99.5%) in water. The slurry sample was partly dried, and the paste was extruded using a plastic syringe (*6, 13*). Each sample of 2 g was evacuated at 773 K for 1 h and subsequently at 1073 K for 2 h and used for the reaction. BET surface area of the sample was 120

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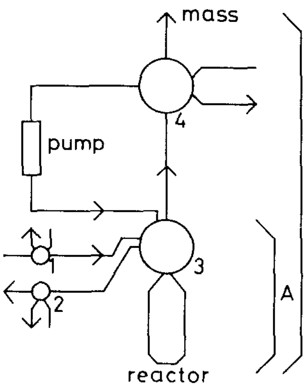

FIG. 1. Schematic diagram of the reaction system. (A) Flow system; (B) circulation system; (1) sampling cock of reactant gas by GC; (2) sampling cock of product gas for GC; (3) 8-way cock for changing the systems; (4) sampling cock for mass spectrometry or GC.

m^2/g after use for 24 h. Reactions were mostly carried out at 1073 K using a conventional flow system (*6, 13*) under atmospheric pressure. The quartz reactor has a size of 6 mm i.d. with about 100 mm length in the furnace.

For testing the effectiveness of CO_2, a gas mixture containing $CH_4/CO_2/O_2/He$ (5/5/0.05/50 ml/min) (reactant *A*) was fed over 2 g of the catalyst for 3 h and then replaced with $CH_4/O_2/He$ (5/0.05/50 ml/min) (reactant *B*) for another 3 h. The reactants and products were analyzed by gas chromatography every 30 min, and the average values were calculated. The contact time, *W*/*F*, was controlled by changing the catalyst weight under the fixed flow rate.

For an isotopic study, we used a single reactor which was attached to both the circulation system and the flow system. The schematic diagram is shown in Fig. 1. After the reaction was carried out over 0.1 g of the sample for 2 h using the flow system, the isotope experiment was performed using the circulation system containing $^{12}CD_4/^{13}CO_2/O_2$ (8.3/8.3/0.08 kPa) gas. Reactants and products were analyzed by mass spectrometry and gas chromatography at approximately the same time.

Samples used for various reaction times were analyzed by XPS (Shimadzu-ESCA 750) in order to observe changes in the catalyst surface.

RESULTS AND DISCUSSION

Effect of CO_2 and Reaction Temperature

Reactions with reactant *A* (containing CO_2) were compared with those of reactant *B* (CO_2-free) at various temperatures. Figure 2 shows the product yields at reaction temperatures between 923 and 1098 K. The maximum theoretical C_2-compound yield with reactant *B* ($CH_4/O_2 = 100/1$) was 3% if the ethene/ethane ratio was 1/2 ($2CH_4 + 0.5O_2 = C_2H_6 + H_2O$ and $2CH_4 + O_2 = C_2H_4 + 2H_2O$). The C_2 compounds yield (large white circles in Fig. 2) at 1073 K was close to this value (ethane yield of 2% and ethene yield of 1%), indicating quite a high C_2 selectivity. CO was barely observable. When reactant *A* ($CH_4/CO_2/O_2 = 100/100/1$) was employed, C_2 yields (small white circles) at 1023 K were clearly higher than those with reactant *B* (large white circles) and they were even higher than the maximum theo-

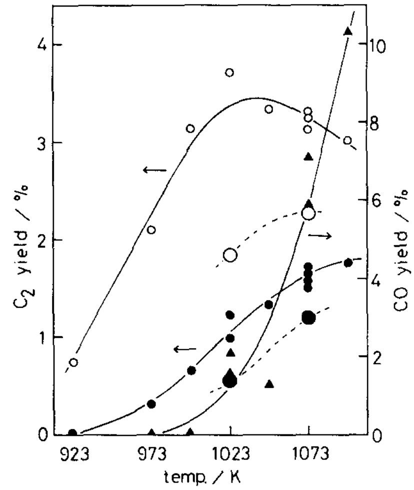

FIG. 2. Effect of reaction temperature on catalytic activity over 15% PbO–MgO. Small symbols with solid lines represent the results for reactant *A* ($CH_4/CO_2/O_2/He$ = 5/5/0.05/50 ml/min). Large symbols with dotted lines represent the results for reactant *B* ($CH_4/O_2/He$ = 5/0.05/50 ml/min). (○) C_2H_6, (●) C_2H_4, (▲) CO.

retical yield of reactant *B*. At least the excess C_2 yield should be due to the use of CO_2 and we suggest that CO_2 acts as an oxidant for methane coupling (*12–14*). CO (triangles) was produced at the same time through CO_2. If CH_4 was not present, CO_2 did not react and CO was not produced. The C_2 yield reached a maximum at a temperature of 1023–1048 K and decreased at higher temperature, while ethene yield (small black circles) still increased up to a temperature of 1125 K. The amount of CO increased monotonically with the temperature. It was strange that CO was produced very slightly at 973 K although C_2 yield under reactant *A* was higher than that under reactant *B*. To explain this, two possibilities are considered. First, CO_2 might promote the C_2 production without decomposition. Ross *et al.* have reported that CO_2 promotes the reaction because the surface carbonate stabilizes the alkali promoter (*10*). Secondly, at a rather low temperature (973 K), CO converted from CO_2 might be adsorbed strongly. The second explanation seems plausible, because it was observed that CO and CO_2 which were adsorbed on the catalyst surface during the run under reactant *A* were desorbed during the 3-h run under reactant *B* over the effective catalysts (*13*). Initial run with reactant *B* did not give any CO.

Reaction Products as a Function of Contact Time

Figure 3 represents the rate of product formation as a function of *W*/*F* (weight of catalyst/total flow rate). The experiment was carried out at 1073 K with reactant *A*. At *W*/*F* lower than 0.3 g s/ml, C_2H_6 yield (white circles) increases linearly and then decreases gradually with a maximum at around *W*/*F* of 0.4 g s/ml. On the other hand, C_2H_4 yield (black circles) increases gradually. But CO yield (white triangles) increases monotonically. This indicates clearly that C_2H_6 and CO are the initial products and that C_2H_4 is the secondary product. Black triangles represent the theoretical CO yield assuming that one of the oxygen atoms in CO_2 is used exclusively for the production of C_2 hydrocarbons with the actual ratio of ethene/ethane in this experiment. In the smaller *W*/*F* region, the experimental CO yield (white triangles) is almost the same as the calculated CO yield. Thus, it is suggested that oxygen produced by the reverse shift reaction (Eq. 1) was used selectively for the coupling reaction (Eq. 2).

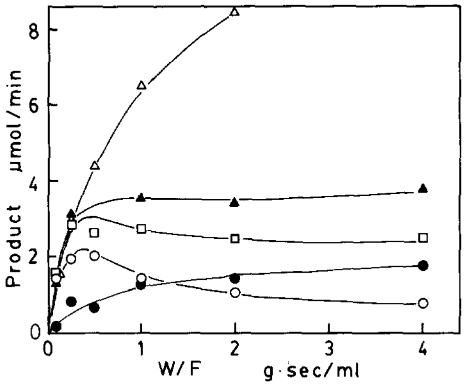

FIG. 3. Effect of contact time (*W*/*F*) on the reaction rate. Reactant *A* ($CH_4/CO_2/O_2/He$ = 5/5/0.05/50 ml/min) was fed at 1073 K over several samples of 15% PbO–MgO with various weights. (○) C_2H_6, (●) C_2H_4, (□) total C_2 hydrocarbons, (△) CO, (▲) theoretical CO yield assuming that one of the oxygen atoms in CO_2 is used for the coupling reaction (Eqs. (1) to (3) in the text).

$$CO_2 \rightarrow CO + O(a) \quad (1)$$

$$2CH_4 + O(a) \rightarrow C_2H_6 + H_2O \quad (2)$$

$$C_2H_6 \rightarrow C_2H_4 + H_2 \quad (3)$$

$$H_2 + O(a) \rightarrow H_2O \quad (4)$$

$$C_2H_6 + O(a) \rightarrow C_2H_4 + H_2O \quad (5)$$

$$C_2H_4 + 4O(a) \rightarrow 2CO + 2H_2O \quad (6)$$

But, in the high *W*/*F* region, Eq. 1 is suggested to occur without increasing the C_2 formation. This is probably because C_2 products further react with the oxygen which was released from CO_2 (Eqs. 3, 4, 5, and 6). CO_2 was not reactive without the presence of methane or C_2 hydrocarbons.

Isotope Experiment

We further studied this reaction under the condition of a small *W/F* region in which C_2 selectivity was almost 100% and C_2 oxidation was negligible. We tried to determine from isotope experiments whether the carbon source of product CO was CO_2 or CD_4. $^{13}CO_2$ and $^{12}CD_4$ were introduced with the presence of small amounts of O_2 over 0.1 g of 15 mol% PbO–MgO catalyst in the circulation system. If ^{12}CO were produced, it should be derived from CH_4. If ^{13}CO were produced, it should be derived from $^{13}CO_2$ by the reverse shift reaction (Eqs. 1 and/or 7).

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad (7)$$

The results shown in Fig. 4 indicate that ^{13}CO is produced only under this reaction condition. An initial high value of ^{12}CO was due to the remaining CO before the system was changed from the flow system to the circulation system. ^{13}CO only increased. Under this condition of low *W/F*, we concluded that CO was not produced from CD_4, but was derived by the reverse shift reaction of CO_2. C_2 selectivity based on the reactant CD_4 was almost 100% under this condition.

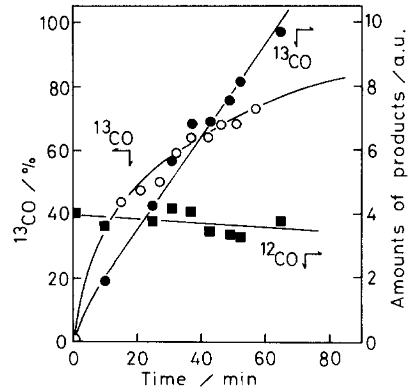

FIG. 4. Results of the isotope tracer experiment. Time course of ^{13}CO (●) and ^{12}CO (■) yield and ^{13}CO percentage (○). Circulation system containing $^{13}CO_2$/CD_4/O_2 (8.3/8.3/0.08 Torr) gas was used at 1073 K over 15% PbO–MgO (0.1 g).

Reaction between C_2 Hydrocarbons and CO_2 in the Gas Phase

Four kinds of reactant gas mixtures—C_2H_6/He (5/55 ml/min), C_2H_4/He (5/55 ml/min), C_2H_6/CO_2/He (5/5/50 ml/min), C_2H_4/CO_2/He (5/5/50 ml/min)—were introduced to the reactor with or without the catalyst (15 mol% PbO–MgO) at 1073 K. The results are summarized in Table 1. Products CO and H_2 could not be measured properly. The main results are summarized as fol-

TABLE 1

Reaction between C_2 Hydrocarbons and CO_2 in the Gas Phase

	No catalyst				15% PbO–MgO	
Reactant	C_2H_6	C_2H_4	C_2H_6 + CO_2	C_2H_4 + CO_2	C_2H_6 + CO_2	C_2H_4 + CO_2
C_2H_6 conv.(%)	80	—	79	—	80	—
C_2H_4 conv.(%)	—	10	—	14	—	19
CO_2 conv.(%)	—	—	7	1	39	21
C_2H_4 yield(%)	68	—	68	—	64	—
C_2H_6 yield(%)	—	1	—	Tr	—	Tr
CH_4 yield(%)	Tr	Tr	2	Tr	6	Tr

Note. Four kinds of reactants—C_2H_6/CO_2/He (5/5/50 ml/min), C_2H_6/He (5/55 ml/min), C_2H_4/CO_2/He (5/5/50 ml/min), C_2H_4/He (5/55 ml/min)—were introduced to the reactor with or without catalyst (2 g, 15 % PbO–MgO) at 1073 K.

lows. (1) Dehydrogenation of C_2H_6 to C_2H_4 occurs in the gas phase (Eq. 3). The extent of this reaction was independent of the presence of the catalyst. (2) Gas-phase decomposition of C_2H_4 is not important. (3) CO_2 was not converted unless hydrocarbons were introduced in the reaction zone with or without catalysts. (4) Reaction of C_2H_6 with CO_2 is observed in the gas phase (Eqs. 3 and 7); however, it is promoted by the catalyst, which suggests the importance of Eqs. 1, 3, and 4 (surface and gas-phase reactions) rather than Eqs. 3 and 7 (gas-phase reaction). (5) Reaction of C_2H_4 with CO_2 (Eqs. 1 and 6) appears to occur over the catalyst surface because the reaction of C_2H_4 with CO_2 is promoted by the catalysts.

In statements (1) and (4), C_2H_6 was converted to C_2H_4 through the gas-phase reaction (Eq. 3). However, the catalytic process (Eq. 5) might also be possible. Equilibrium data tell us that about 80% of C_2H_6 could be decomposed to C_2H_4 and H_2 under 1 atm and at 1073 K (Eq. 3) (*1*). From Eqs. 1, 3, and 4 or Eqs. 1 and 5,

$$C_2H_6 + CO_2 \rightarrow C_2H_4 + CO + H_2O \ (\Delta G = 0 \text{ kJ/mol at } 1073 \text{ K}), \quad (8)$$

where about 57% of C_2H_6 is converted to C_2H_4 under 1 atm of the reactant mixture (*13*). The conversion data of C_2H_6 in Table 1 seems quite near to the equilibrium value of Eq. 3 or 8. Thus, the insignificance of the catalyst may be due to the easiness of Eq. 3 or 8, which reaches equilibrium easily without the catalyst. Both processes of Eqs. 3 and 5 can thus be possible.

Analysis of Catalyst Surface

XPS analyses have been performed for samples with different reaction times (such as 3, 6, or 69-h runs, etc.) using reactant *A*. Figure 5 represents the relative surface concentration of elements as a function of reaction time. It is clear that the relative surface Pb concentration (white circles) decreases drastically at the first stage of reaction (0 to 30 min). This phenomenon seems to correspond with the very high C_2 yield at the first stage (black circles). It is assumed that the reactive oxygen of surface PbO is used for the reaction with CH_4 and the reduced lead is evaporated. The relative Pb intensity decreases gradually, while the intensity of oxygen which is bound both with Pb and Mg remains almost constant. C_2 yield seems to be almost constant until 69 h (the end of this run).

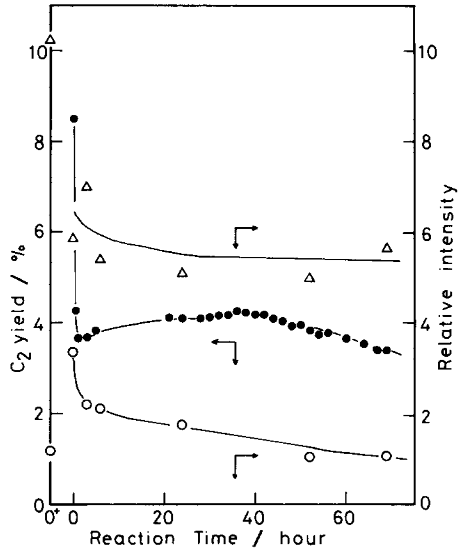

FIG. 5. Results of surface analysis using XPS. The change of the relative surface atom intensity is shown as a function of reaction time. (○) Pb/Mg, (△) O/Mg, (●) C_2 yield percentage. The reaction was performed under the standard condition using reactant *A* (CH_4/CO_2/O_2/He = 5/5/0.05/50 ml/min) at 1073 K. O^+ represents the catalyst state before the pretreatment.

An oxygen balance was calculated. Under reactant *B*, oxygen reacted completely. By the addition of CO_2, C_2 yield increased by about 1.0%. This increase is due to the sacrifice of the oxygen atom in CO_2, the rate of which corresponds to 2.5 mmol(O-atom)/day if the actual C_2H_4/C_2H_6 ratio is a calculational base. On the other hand, 2 g of the starting 15 mol% PbO–MgO catalyst contains 3.72 mmol of PbO, if we consider the weight decrease due to the evolution of NO_x and H_2O (about 10%) during the pretreatment. Probably the actual PbO concentration is even lower than this value because of PbO evaporation during pretreatment. The turnover of oxygen atoms is at least 1.9 times the amount of bulk oxygen in PbO. Thus, PbO is concluded to work as a catalyst, not as a reagent, even though some of it is reduced and evaporated during the catalysis. A nonreducible mixed-oxide catalyst, BaO–CaO, has also been found to be an effective catalyst of this process (*14*), where the adsorbed oxygen could be an intermediate. This fact also suggests that the title reaction can be a catalyzed process.

The Possibility of Obtaining Higher C_2 Yields

The calculated ethane yield from CH_4/CO_2 (= 1/1) is 13% under equilibrium at 1073 K (*13*). If Eqs. 1 and 2 could be combined properly, a good yield and high selectivity should be obtained. In fact, we were able to obtain a high C_2 selectivity by using CO_2, but the C_2 yield is still lower than the equilibrium value. CH_4 was converted only to C_2 hydrocarbons and CO_2 was converted only to CO by the reverse shift reaction under low *W*/*F* and at the proper temperature (973 to 1073 K). Since the existence of hydrocarbons is necessary for CO_2 decomposition, the two reactions (Eqs. 1 and 2) can be combined, but the condition is restricted. Methane reacts with the active oxygen on the catalysts surface through the reverse shift reaction of CO_2. The redox nature of the catalyst may be important to yield the active oxygen from CO_2 (*1, 5, 7, 13*). We speculate that good C_2 yield can be obtained when each step of Eqs. 1, 2, 3, and 4 can be controlled kinetically without allowing Eq. 6.

CONCLUSION

It was found that $^{13}CO_2$ and $^{12}CD_4$ produced exclusively ^{13}CO and $^{12}C_2$ hydrocarbons and that no ^{12}CO was produced under the low *W*/*F* condition of the title reaction over 15 mol% PbO–MgO at 1073 K. The oxidative coupling of CH_4 is assisted by the reverse shift reaction of CO_2, and one of the oxygen atoms of CO_2 is used for the CH_4 coupling reaction. It was also found that products of C_2 hydrocarbons reacted with oxygen from CO_2 under high conversion or high temperature.

REFERENCES

1. Keller, G. E., and Bhasin, M. M., *J. Catal.* **73,** 9 (1982).
2. Hinsen, W., and Baerns, M., *Chem. Ztg.* **107,** 223 (1983).
3. Sinev, M. Y., Vorobeva, G. A., and Korchak, V. N., *Kinet. Katal.* **27,** 1164 (1986).
4. Ito, T., Wang, J.-X., Lin, C.-H., and Lunsford, J. H., *J. Amer. Chem. Soc.* **107,** 5062 (1985).
5. Asami, K., Shikada, T., Fujimoto, T., and Tominaga, H., *in* "Preprint of 52nd Annual Meeting of Chem. Soc. Japan," Vol. 1, p. 110 (2c 41), 1986.
6. Moriyama, T., Takasaki, N., Iwamatsu, E., and Aika, K., *Chem. Lett.*, 1165 (1986); Iwamatsu, E., Moriyama, T., Takasaki, N., and Aika, K., *J. Catal.* **113,** 25 (1988).
7. Iwamatsu, E., and Aika, K., *J. Catal.* **117,** 416 (1989).
8. Labinger, J. A., and Ott, K. C., *J. Phys. Chem.* **91,** 2682 (1987).
9. Sofranko, J. A., Lenoard, J. J., and Jones, C. A., *J. Catal.* **103,** 302 (1987).
10. Korf, S. J., Roos, J. A., De Bruijn, N. A., Van Ommen, J. G., and Ross, J. B. H., *J. Chem. Soc. Chem. Commun.*, 1433 (1987).
11. Geerts, J. W. M. H., Van Kasteren, J. M. N., and Van der Wiele. K., *Catal. Today* **4,** 453 (1989).
12. Aika, K., and Nishiyama, T., *J. Chem. Soc. Chem. Commun.*, 70 (1988).
13. Aika, K., and Nishiyama, T., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 2, p. 907. Chem. Institute of Canada, Ottawa, 1988.
14. Aika, K., and Nishiyama, T., *Catal. Today* **4,** 271 (1989).