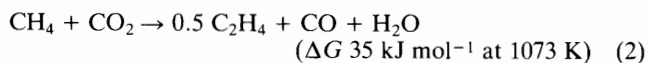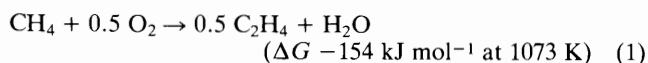# Utilisation of CO_2 in the Oxidative Coupling of Methane over PbO–MgO and PbO–CaO

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Oxidative coupling of CH_4 by O_2 was found to be promoted by combination with the reaction of CO_2 to CO at 1073 K over PbO–MgO, PbO–CaO, PbO–Na_2O–MgO, and Sm_2O_3 catalysts.

Oxidative coupling of methane is an attractive reaction for utilising natural gas as a chemical resource, and many investigations into this reaction have been reported for a variety of catalysts.[1—6] However, the reaction involves an extensive loss of free energy, [reaction (1)]. In order to reduce the heat loss and to utilise the oxygen of CO_2, we decided to combine reaction (1) with reaction (2). When these reactions were combined in a ratio (1)/(2) greater than 0.23/1.0, ΔG of the total reaction was found to become negative, that is, the total reaction was viable. Calculations using C_2H_6 instead of C_2H_4 gave a similar result. The problem was to find a catalyst suitable for both reactions (1) and (2). A survey of the catalysts reported to be active for reaction (1)[1—6] showed that PbO–MgO, PbO–CaO, and several other catalysts were effective for this process.

$$CH_4 + 0.5\,O_2 \rightarrow 0.5\,C_2H_4 + H_2O$$
$$(\Delta G\ -154\ \text{kJ mol}^{-1}\ \text{at 1073 K})\quad (1)$$

$$CH_4 + CO_2 \rightarrow 0.5\,C_2H_4 + CO + H_2O$$
$$(\Delta G\ 35\ \text{kJ mol}^{-1}\ \text{at 1073 K})\quad (2)$$

Catalysts were prepared by the impregnation method.[2,3] Each sample (2 g) was evacuated at 773 K for 1 h and then at 1073 K for 2 h before being used for the reaction in a flow system. Typically, a gas mixture CH_4–CO_2–O_2–He

$(10:10:0.1:40\ \text{ml min}^{-1})$ was charged for 3 h, and then replaced with a mixture of CH_4–O_2–He $(10:0.1:50\ \text{ml min}^{-1})$ and the run continued for another 3 h. The reaction data during 0.5 to 3 h were collected for the runs with or without CO_2 and the average values are listed in Table 1.
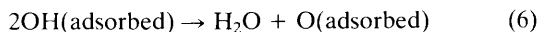
For 15 mol% PbO–MgO (run 4), the CH_4–O_2 (200:1) mixture gave C_2 hydrocarbons (C_2H_4 and C_2H_6) and a small amount of CO_2 at 1073 K. Almost 100% of the O_2 was found to react and the total amount of C_2H_4 and C_2H_6 produced was close to the value (1.5% yield) calculated from the O_2 consumption in reaction (1). The reactant containing CO_2 gave a much higher yield of C_2 hydrocarbons, while a comparable amount of CO was formed from CO_2. The decrease in CO_2 was almost equal to the increase in CO. These results suggested that reaction (2) occurred simultaneously with reaction (1). The amount of C_2 hydrocarbons formed was lower than the theoretical value (6.1% yield) based on both O_2 consumption in reaction (1) and CO_2 decrease in reaction (2). Thus, oxygen balances may not be complete, probably owing to the oxidation of the catalyst; however, the C_2 yield was increased. The ratio of reaction (1)/(2) is close to unity (greater than 0.23) in this case, which means that the total reaction is 'down hill'. One of the two oxygens of CO_2 is considered to be transferred to the lattice or the surface and to be used for hydrogen abstraction from CH_4 reactions (3)—(6). The catalyst activity was stable over 24 h, and results were reproducible. The same result was obtained by changing the

Table 1. $C_2(C_2H_6$ and $C_2H_4)$ yield in the oxidative coupling of methane with and without CO_2,[a] total flow rate of 60 ml min^{-1} over catalysts (2 g) at 1073 K.

Run	Sample[b]	CH_4 flow rate[c]	CH_4/O_2	C_2 yield (%) (A) with CO_2	(B) without CO_2	(A)/(B)
1	Blank	10	200	0.02	—	—
2	MgO	10	200	0.25	0.10	2.5
3	PbO	10	100	0.14	0.14	1.0
4	15% PbO–MgO	10	200	3.55[g]	1.49[h]	2.38
5	,,	10	100	4.12	2.98	1.38
6[d]	,,	10	100	4.07	2.94	1.38
7	,,	5	100	3.70	2.74	1.35
8[e,f]	,,	5	—	2.06	—	—
9	50% PbO–MgO	5	100	4.37	3.28	1.33
10	15% PbO–5% Na_2O–MgO	5	100	3.89	2.20	1.77
11	20% PbO–CaO	5	100	2.56	1.53	1.67
12[f]	20% BiO–MgO	5	100	0.76	0.31	2.45
13	15% K_2O–MgO	10	100	2.02	2.25	0.90
14	Sm_2O_3	5	100	1.75	0.67	2.61
15[f]	20% Li_2O–Sm_2O_3	5	100	0.51	2.58	0.20

[a] CO_2, feed rate same as that of CH_4, withdrawn in 3 h. [b] Dopant % based on molar ratio of element against Mg. [c] Unit: ml min^{-1}. [d] CO_2 added to CH_4–O_2 mixture. [e] O_2 absent. [f] C_2 yield (A) decreases during the 3 h run. [g] Accompanied by 4.1% CH_4 decrease, 3.2% CO_2 decrease, and 3.4% CO increase (CH_4 based %). 53% C_2H_4 in C_2. [h] 50% C_2H_4 in C_2.

reaction cycle (without CO_2 to with CO_2) shown in Table 1 (run 5 and 6).

$$CO_2 \rightarrow CO + O(adsorbed) \qquad (3)$$

$$2[O(adsorbed) + CH_4 \rightarrow CH_3{}^{\cdot} + OH(adsorbed)] \qquad (4)$$

$$2CH_3{}^{\cdot} \rightarrow C_2H_6 \qquad (5)$$

$$2OH(adsorbed) \rightarrow H_2O + O(adsorbed) \qquad (6)$$

Preliminary runs of CH_4 and CO_2 [reaction (2)] without O_2 were performed although the active life of the catalyst was short owing to oxygen loss from the catalyst. It was shown that PbO–MgO gave the highest initial C_2 yield by reaction (2) among the catalysts, pure MgO and promoted MgO doped with Li, Na, K, Cs, Rb, Sr, Ba, Ag, Zr, Zn, Pb, Mn, Co, Ni, or Pt ions (e.g. Table 1, run 8). When O_2 was added, the activity increased and become stable (run 7).

The effects of CO_2 on the oxidative coupling of CH_4 were examined over various catalysts and results are shown in Table 1. C_2 yields were improved in the presence of CO_2 over PbO–MgO, PbO–Na$_2$O–MgO, PbO–CaO, BiO–MgO, and Sm$_2$O$_3$. BiO–MgO was deactivated gradually, probably owing to BiO loss. In the case of Sm$_2$O$_3$, the formation of CO as a by-product was approximately 6 times greater than the formation of C_2 hydrocarbons. Although pure MgO (run 2) and PbO (run 3) were not found to be active catalysts, synergetic promotion by both components was observed in the run with CO_2 [(A) in runs 4—9]. The promoter effect of PbO

on MgO has been reported for reaction (1).[5] However, other promoted MgO catalysts for reaction (1)[2] were not effective for the combined process with CO_2. One example is the case of K$_2$O-MgO shown in Table 1 (run 13). It is inferred that PbO acts as an oxygen reservoir from CO_2. Sm$_2$O$_3$ is believed to be a redox system at higher temperature.

The free energy loss by a single process of oxidative coupling of CH_4 by O_2 was reduced by utilising CO_2 as a reactant in addition to O_2.

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