Partial oxidation of methane to syngas over Co/MgO catalysts. Is it low temperature?

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Co/MgO catalysts with high Co-loading (>28 wt%) are able to initiate the reaction of methane with oxygen at temperatures around 500°C. High conversions of methane (~ 70%) and very high selectivities for hydrogen and carbon monoxide (~ 90%) are obtained at very high reactant gas space velocities (10^5–10^6 h^{-1}). The temperature of the catalyst at the conditions of partial oxidation of methane to form syngas was found to be extremely high (1200–1300°C); it is about 600–850°C higher than that previously reported by others. At these temperatures, high temperature homogeneous reactions may prevail. It is suggested that combustion of methane to carbon dioxide occurs on the catalyst with major heat release and that methane and water, respectively methane and carbon dioxide are reformed thermally in an endothermic reaction leading to syngas.

Keywords: Partial oxidation of methane; synthesis gas; cobalt; magnesia

1. Introduction

Catalytic partial oxidation of methane to make synthesis gas (a mixture of carbon monoxide and hydrogen) has recently received much attention [1–5]. This process has advantages over the conventional steam reforming of methane to make hydrogen and carbon monoxide [5]. The latter process is highly endothermic; it also produces a mixture of CO and hydrogen having a H_2/CO ratio $\geqslant 3$. The direct partial oxidation of methane, expected to give a mixture of CO and H_2 having H_2/CO ratio of about 2, makes methanol synthesis an ideal follow-up process.

Non-catalytic partial oxidation of methane [6] carried out at high temperatures ($\geqslant$1300°C) and high pressures (150 atm) can produce syngas at high selectivities. To avoid these extreme conditions, Ashcroft et al. used $Ln_2Ru_2O_7$ (Ln = lanthanide), and $Eu_2Ir_2O_7$ [2,7,8], and Lunsford et al. used Ni/Al_2O_3 [9] as catalysts. At temperatures $\geqslant$700°C and atmospheric pressure, these catalysts give high conversion of methane ($\geqslant$90%) and high selectivities to both CO and H_2 ($\geqslant$95%) with gas space velocities of 10^3–10^4 h^{-1}. Selectivity to CO and H_2 decreases significantly with lowering the reaction temperature. In contrast to these findings, Choudhary and co-workers reported that high selectivity to CO and H_2 could be achieved at temperatures as low as 350°C on a variety of catalysts: Co/RE_xO_y (where RE are rare-earth metals) [10], Co/MgO [11], Ni/Al_2O_3 [12], and Ni/CaO [13] with much greater gas space velocities (GHSV: 10^5–10^6 h^{-1}). The latter investigators stated that the extremely high gas space velocity was essential to obtain high selectivity to carbon monoxide and hydrogen. Lowering gas space velocity resulted in lower selectivity to syngas.

It seems that the low temperature results were reported exclusively by the Choudhary group. It was claimed that the high selectivity to hydrogen and carbon monoxide at low temperature is due to a mechanism differing from the conventional, widely accepted one for high temperature catalytic and non-catalytic methane partial oxidation, where the formation of carbon monoxide and hydrogen is the result of secondary reactions between water, unreacted methane, and carbon dioxide. Carbon dioxide and water are formed during the initial combustion reaction, during which all oxygen may be completely consumed. Due to the fact that Choudhary's experiments were carried out at extremely high reactant space velocities (GHSV $\geqslant 10^5$ h^{-1}) without using a diluent, the amount of heat generated from both total oxidation reactions is much higher than the limited amount of heat dissipated through the reactor wall around the catalyst bed. As a result, dramatic temperature increases in the catalyst are hard to avoid. The aim of this work was to try to repeat the Choudhary group's results and to find out if there is an overheating problem in the catalyst bed.

2. Experimental

2.1. CATALYST PREPARATION

Co/MgO catalysts were prepared following a literature procedure [11]. $Co(NO_3)_2 \cdot 6H_2O$ (AR grade, Alfa Chemicals) and $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$ (AR grade, Sigma) were ground and mixed thoroughly before distilled water was added to make a thick paste. The paste was treated in a muffle furnace: 10°C/min to 600°C for 2 h, then it was ground to a fine powder. The powder was calcined at 900°C in air for 4 h. The calcined sample was pelletized and crushed to obtain particles of 30–60 mesh. The latter was used for catalytic testing.

2.2. CATALYST PRETREATMENT

Catalysts were subject to the following in situ treatments before catalytic reaction was conducted: (1) treated at 900°C in high purity helium (80 cm^3 min^{-1}) for 1 h; (2) reduced at 500°C in 20% hydrogen (H_2: 20 cm^3 min^{-1}, He: 80 cm^3 min^{-1})

for 2 h. The treatments are the same as those used for partial oxidation of methane over Co/MgO catalysts by Choudhary [11].

2.3. CATALYTIC REACTION

Reactions were carried out in a tubular quartz reactor (i.d. 4 mm). 26 mg of catalyst was used for each catalytic run. The reaction temperature was measured by a thermocouple positioned just on top of the catalyst. A thermocouple well (quartz) was used to avoid the catalytic effect of the thermocouple at high temperatures. A pre-mixed methane (125 $cm^3\ min^{-1}$), oxygen (62.5 $cm^3\ min^{-1}$), and nitrogen (10 $cm^3\ min^{-1}$) gas mixture was introduced at 500°C. The present experimental conditions are exactly the same as those used in Choudhary's experiments. The reaction effluent was analyzed by GC with a thermal conductivity detector. A carbon molecular sieve column, Carboxen-1000 (60/80 mesh, 1/8″ × 15 ft), was used to give good separation among hydrogen, oxygen, nitrogen, carbon monoxide, methane, and carbon dioxide. Nitrogen was used as an internal standard for GC quantification. A condenser kept in an ice-bath was placed between the outlet of reactor and the inlet of sampling valve to prevent water formed from entering the GC column.

3. Results

Conversion of methane and oxygen, and selectivities to carbon monoxide and hydrogen were calculated based on the following stoichiometries: each mole of CO_x formed consumes one mole of methane, and each mole of methane converted produces two moles of hydrogen. Thus, selectivity to CO ($S_{CO}\%$), to hydrogen ($S_{H_2}\%$), conversion of methane ($CH_4\%$), and conversion of oxygen ($O_2\%$) can be calculated according to the following:

$$S_{CO}\% = [F_{CO}/(F^{in}_{CH_4} - F^{out}_{CH_4})] \times 100 = [F_{CO}/(F_{CO} + F_{CO_2})] \times 100\,,$$

$$S_{H_2}\% = [0.5F_{H_2}/(F^{in}_{CH_4} - F^{out}_{CH_4})] \times 100 = [F_{H_2}/(F_{H_2} + F_{H_2O})] \times 100\,,$$

$$CH_4\% = [(F^{in}_{CH_4} - F^{out}_{CH_4})/F^{in}_{CH_4}] \times 100\,,$$

$$O_2\% = [(F^{in}_{O_2} - F^{out}_{O_2})/F^{in}_{O_2}] \times 100\,,$$

where F_i is the molar flow rate of species i. Nitrogen was used as an internal standard, and the molar flow rate of other species was estimated from the relation of their gas chromatograms to that of nitrogen.

Ideally, with the methane to oxygen ratio of 2 to 1 used in the present study, complete conversion of methane is expected according to the reaction

$$2CH_4 + O_2 \rightarrow 2CO + 4H_2 . \qquad (1)$$

Tables 1 and 2 present results obtained over Co/MgO(B) (Co/Mg = 0.3/1) and Co/MgO(C) (Co/Mg = 3/1) catalysts, respectively. High selectivities to both carbon monoxide and hydrogen were achieved on both catalysts at temperatures ≥700°C. Conversion of methane and selectivities to carbon monoxide and hydrogen declined as temperature decreased. It seems that Co/MgO(B) and Co/MgO(C) behave similarly.

Data of methane partial pressure dependence and contact time dependence obtained on Co/MgO (Co/Mg = 0.3/1) catalyst at 700°C are given in figs. 1 and 2. High methane partial pressure is needed to achieve high selectivity to hydrogen. Short contact time is preferred to give high selectivity to hydrogen and carbon monoxide.

To determine the potential contribution from the thermal reactions, blank experiments were carried out in the absence of catalyst under identical conditions. The results are given in table 3. Basically, reactions at temperatures ≤810°C are negligible. However, at high temperatures (≥925°C) there was quite substantial reaction. It is noted that the high temperature thermal reactions give very low selectivity to hydrogen (<35%).

4. Discussion

A dramatic temperature burst was recorded upon introduction of the reaction mixture to both Co/MgO (Co/Mg = 3/1) and Co/MgO (Co/Mg = 0.3/1), and at the same time a significant increase of exit flow (monitored by a mass flow mounted at the down stream side of the water condenser) was also registered. Depending on experimental conditions (catalyst amount, gas flow rate, furnace temperature), the temperature increase varied around 200–350°C. This temperature burst happened within seconds of the introduction of the reaction mixture and

Table 1
Results of reaction of methane with oxygen over Co/MgO(B) [a]

Temp. [b] (°C)	Conversion (mol%)		Selectivity (mol%)			H_2/CO mol.ratio	Carbon balance (%)
	CH_4	O_2	H_2	CO	CO_2		
770	57	99	86	84	16	2.04	101
745	60	99	89	87	13	2.03	100
440	55	99	80	78	22	2.05	100
452 [c]	56	99	80	78	22	2.05	100

[a] Co/MgO(B) (Co/Mg = 0.3/1): 0.026 g; reduced in 20% H_2 (H_2 and He: 100 cm^3 min^{-1}) at 500°C; CH_4: 125 cm^3 min^{-1}; O_2: 62.5 cm^3 min^{-1}; N_2: 10 cm^3 min^{-1}.

[b] Data obtained according to the temperature sequence as listed in the table.

[c] The temperature of the catalyst was 1260°C measured by an IR radiation thermometer.

Table 2
Results of reaction of methane with oxygen over Co/MgO(C) [a]

Temp. [b] (°C)	Conversion (mol%)		Selectivity (mol%)			H_2/CO mol.ratio	Carbon balance (%)
	CH_4	O_2	H_2	CO	CO_2		
821	73	93	96	96	4	2.00	100
720	62	94	88	89	11	1.98	99
614	50	94	80	81	19	1.99	100
540 [c]	46	94	77	75	25	1.99	101

[a] Co/MgO (Co/Mg = 3/1): 0.026 g; reduced in 20% H_2 (H_2 and He: 100 cm^3 min^{-1}) at 500°C; CH_4: 125 cm^3 min^{-1}; O_2: 62.5 cm^3 min^{-1}; N_2: 10 cm^3 min^{-1}.

[b] Data obtained according to the temperature sequence as listed in the table.

[c] The temperature of the catalyst measured by an IR radiation thermometer was 1280°C.

stabilized after a couple of minutes of time on stream. All experimental data were collected after the reaction temperature was stabilized for at least 20 min. The increase in exit flow suggests that the number of product molecules formed is greater than the number of reactant molecules converted, implying that partial oxidation reaction occurs. There were no coupling products observed, suggesting that no oxidative coupling reaction occurs under the present experimental conditions.

For accurate temperature measurement, care must be taken. We used two thermocouples inserted from the front and the rear of the catalyst bed. Depending on experimental conditions, temperatures measured by the rear thermocouple were

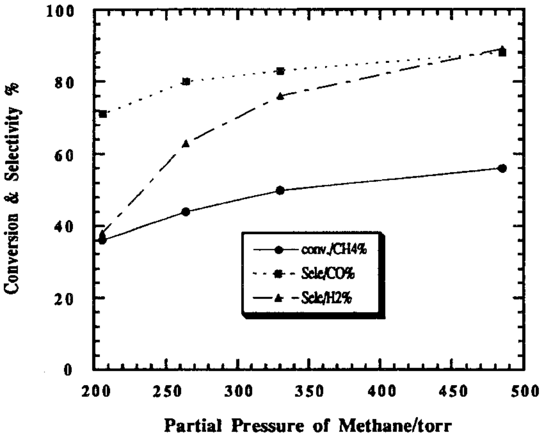

Fig. 1. Effect of partial pressure of methane on the reaction of methane with oxygen over Co/MgO (Co/Mg = 0.3/1) at 700°C (contact time: 1.6 ms; methane/oxygen: 2/1).

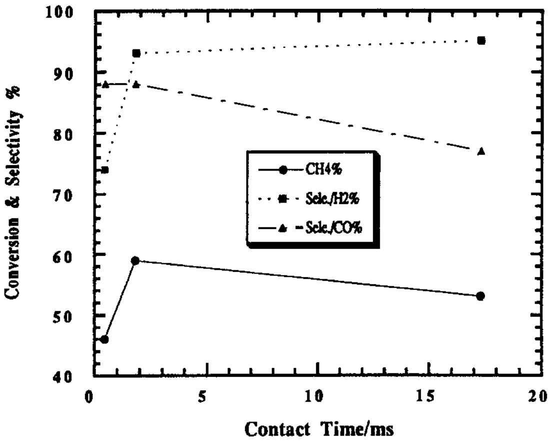

Fig. 2. Effect of contact time on the reaction of methane with oxygen over Co/MgO (Co/Mg = 0.3/1) catalyst at 700°C (methane/oxygen/helium: 50/25/4).

20–100°C lower than those recorded by the former. This is probably due to the use of a layer of quartz wool between the catalyst and the thermocouple positioned at the rear of the catalyst bed. Thus, basically, both thermocouples measured the equilibrated gas temperature. Product gas temperatures were primary data taken in these experiments.

To repeat the Choudhary group's experiment, the reaction temperature was lowered by decreasing the furnace temperature (in their experiment, the lowest temperature studied was 350°C). To our surprise, the measured gas temperature was only slightly affected by the furnace temperature. In fact, the reaction was sustained even when the furnace was removed. Under this circumstance, the lowest temperature we could get without using extra cooling was about 450°C. Despite this low temperature recorded by the thermocouple, the catalyst was glowing. To

Table 3
Results of reaction of methane with oxygen in empty quartz reactor[a]

Temp. (°C)	Conversion CH_4 (mol%)	Selectivity CO (mol%)	Selectivity CO_2 (mol%)	H_2/CO molar ratio
702[b]	0.2	~100	~0	–[d]
810[b]	1.2	90	10	1.6
925[b]	16.1	86	14	0.7
700[c]	0.8	52	48	–[d]
802[c]	4	80	20	1.1
913[c]	34	87	13	0.7

[a] Quartz reactor, thermocouple contained in a quartz jacket.
[b] CH_4: 125 cm^3 min^{-1}; O_2: 62.5 cm^3 min^{-1}; N_2: 10 cm^3 min^{-1}.
[c] CH_4: 62.5 cm^3 min^{-1}; O_2: 31.3 cm^3 min^{-1}; N_2: 5 cm^3 min^{-1}.
[d] Data unavailable.

measure the catalyst temperature, an infrared radiation thermometer (IRCON Series 300) was used after proper calibration. The measured temperature was 1270°C. This is more than 800°C higher than that recorded by the thermocouple. This difference was caused by the inadequacy of using a relatively big thermocouple to measure the temperature of a very small amount of catalyst. To further lower the temperature, nitrogen was blown towards the catalyst zone from the outside. When the gas temperature was down to a threshold of 340°C and the catalyst temperature was down to a threshold of 1150°C the reaction ceased.

The reactor was operated at a steady state temperature which is a function of the heat generated by the exothermic reactions and the heat losses from the reactor. The overall heat generation rate due to the chemical reaction ($\Delta H_{\mathrm{r}}^{\circ}$) is equal to the heat energy (energy/time) carried in the product gases ($\Delta H_{\mathrm{g}}^{\circ}$) and the rate of energy loss from the reactor by conduction, convection, and radiation (ΔH_{ℓ}°):

$$\Delta H_{\mathrm{r}}^{\circ} = \Delta H_{\mathrm{g}}^{\circ} + \Delta H_{\ell}^{\circ} . \tag{2}$$

For a given reaction temperature and catalyst, ΔH_{ℓ}° is fixed, and $\Delta H_{\mathrm{r}}^{\circ}$ increases with total flow; the reactor approaches the limit of adiabatic operation as the total flow of gases increases ($\Delta H_{\mathrm{g}}^{\circ} >> \Delta \mathrm{H}_{\ell}^{\circ}$).

We have estimated the adiabatic temperatures of a number of cases with a reaction mixture comprising CH_4 (125 cm^3 min^{-1}), oxygen (62.5 cm^3 min^{-1}), and nitrogen (10 cm^3 min^{-1}). All the thermodynamic data were taken from literature [14]. In all cases, complete conversion of oxygen was assumed. Thus, with an inlet temperature of 500°C, for selectivities to CO of 0% (methane conversion of 25%), 90% (methane conversion of 77%), and 100% (methane conversion of 100%), the corresponding adiabatic temperatures are 2430, 1480 and 990°C.

It is known that non-catalytic partial oxidation of methane takes place at high temperatures. The commercial non-catalytic hydrocarbon partial oxidation to make carbon monoxide and hydrogen is carried out at 1290–1400°C [6]. The complex of reactions results in a thermal equilibrium at 1300–1400°C. The chemistry of this partial oxidation is believed to be that hydrocarbons react with oxygen according to the highly exothermic combustion reaction. Practically all of the available oxygen is consumed in this phase. The remaining unoxidized hydrocarbons react endothermally with steam and/or carbon dioxide and the combustion products from the primary reaction. The main endothermic reaction is the steam reforming of hydrocarbon. The temperature regime for the reaction of methane with oxygen to form carbon monoxide and hydrogen over Co/MgO is very close to that of non-catalytic partial oxidation. Therefore, although the initiation of the reaction between methane and oxygen at 500°C is due to the presence of Co/MgO catalyst (MgO is unable to facilitate the reaction at temperatures $\leqslant$600°C), once the reaction starts, the non-catalytic partial oxidation may dominate the reaction because of the temperature increase. This implies that if the heat generated from the reaction is not sufficient to reach the temperature required for the non-catalytic partial oxidation then the partial oxidation cannot be sustained. This may explain why the very high flow of methane and oxygen is needed for making hydrogen and carbon monoxide.

The rate of heat loss of the reactor system used in our experiments can be worked out based on the difference between the actual measured temperature and the calculated adiabatic temperature. With the same experimental set-up, a temperature burst of 150°C is estimated for a total flow of 49.4 cm^3 min^{-1} (CH_4: 31.2 cm^3 min^{-1}; O_2: 15.6 cm^3 min^{-1}; N_2: 2.5 cm^3 min^{-1}) and assuming a conversion of methane of 77% and selectivity to carbon monoxide of 90%. With a starting temperature of 500°C, a temperature increase of 150°C is expected. Certainly, the temperature increase with this low flow is not enough to provide the temperature ($\geqslant$1200°C) required for the non-catalytic partial oxidation. Therefore, at this low flow rate, there were no partial oxidation products formed. This explains why we obtained two very different results for two identical experiments. In both experiments, methane to oxygen and to nitrogen (inert internal standard) ratios and methane partial pressure were kept the same. The same residence time was achieved by varying total flow according to the amount of catalyst used. The results are given in tables 4 and 5. Table 4 shows that partial oxidation products are predominant at high temperatures. However, table 5 shows that reaction products are predominantly carbon dioxide even at very high temperatures ($\sim$ 900°C). In terms of heat loss, the two experiments should be very much the same. Their only major difference is the amount of heat generated at the same conversion and product selectivity. The heat generated from the low flow experiment could not maintain the high temperature required for partial oxidation, thus this experiment led predominantly to the formation of carbon dioxide, whereas for the high flow experiment, the partial oxidation reaction was predominant because the heat generated from the partial oxidation reaction can maintain the high temperature required.

XRD measurements of Co/MgO(C) catalyst before and after use showed a dramatic loss of Co (almost exclusively Co_3O_4 phase) after the reaction. The loss of

Table 4
Results of reaction of methane with oxygen over Co/MgO(B) [a]

Temp. [b] (°C)	Conversion (mol%)		Selectivity (mol%)			H_2/CO mol. ratio	Carbon balance (%)
	CH_4	O_2	H_2	CO	CO_2		
709	60	100	92	89	11	2.10	101
652	45	99	83	74	26	2.24	100
573	42	99	80	70	30	2.30	101
545	39	99	78	66	34	2.35	101
453	35	99	70	59	41	2.36	101
404	32	99	65	54	46	2.43	101

[a] Co/MgO(B) (Co/Mg = 0.3/1): 0.10 g; reduced in 20% H_2 (100 cm^3 min^{-1}) at 500°C; CH_4: 125 cm^3 min^{-1}; O_2: 62.5 cm^3 min^{-1}; N_2: 10 cm^3 min^{-1}.

[b] Data obtained according to the temperature sequence as listed in the table.

Table 5
Results of reaction of methane with oxygen over Co/MgO(B) [a]

Temp. [b] (°C)	Conversion (mol%)		Selectivity (mol%)			H_2/CO mol. ratio	Carbon balance (%)
	CH_4	O_2	H_2	CO	CO_2		
672	26	100	5	1	99	7.32	102
750	26	100	6	2	98	5.32	100
835	27	100	11	8	92	2.67	101
893	30	100	32	32	68	1.95	101

[a] Co/MgO(B) (Co/Mg = 0.3/1): 0.026 g; reduced in 20% H_2 (100 cm^3 min^{-1}) at 500°C; CH_4: 31.2 cm^3 min^{-1}; O_2: 15.6 cm^3 min^{-1}; N_2: 2.5 cm^3 min^{-1}.

[b] Data obtained according to the temperature sequence as listed in the table.

cobalt of Co/MgO(B) catalyst was less significant. The significant loss of cobalt from the high Co-loading catalyst seems to suggest that the catalyst must have gone through extremely high temperatures. This also indicates that the reactions occurred at very high temperatures.

The methane partial pressure dependence study (fig. 1) shows that higher partial pressure of methane is needed to obtain higher selectivity to hydrogen and carbon monoxide, and higher conversion of methane. In other words, introduction of diluents is not desired because it results in lower conversion and lower selectivity to carbon monoxide and hydrogen.

Fig. 2 suggests that a contact time of ~ 2 ms seems to be optimal because although longer contact time leads to somewhat higher selectivity to hydrogen it is accompanied by a decrease in selectivity to carbon monoxide, and shorter contact time results in lower selectivity to hydrogen. This is in disagreement with previous observation [2,9] where it was found that longer contact time (lower gas space velocity) results in higher conversion of methane and high selectivity to carbon monoxide and hydrogen. The latter investigations used much lower gas space velocity, implying non-adiabatic operation.

5. Conclusions

Co/MgO catalysts with high Co-loading (>28 wt%) are able to initiate the partial oxidation of methane to make syngas at temperatures around 400°C. Thermal reactions are not important at temperature below ~ 900°C.

Due to the high exothermicity of both total oxidation and partial oxidation, and the high reactant flow rate used (in the absence of a diluent), our experiments (which are designed to repeat literature results [10–13]) are carried out under conditions very close to adiabatic operation. By so doing, the high temperature homogeneous reactions prevail, that is, methane reacts wit oxygen according to the highly exothermic combustion reaction, leading to extremely high temperatures, as the result of this, the remaining methane reacts with steam (steam reforming) and with carbon dioxide to produce carbon monoxide and hydrogen. This makes the catalyst an initiator for the reaction. The low temperature results of partial oxidation of methane to syngas over Co/MgO catalysts and other supported Co and Ni catalysts previously reported [10–13] are most probably the result of inadequate temperature measurement. The actual reaction temperatures are much higher than those reported.

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