Oxidative methane conversion to carbon monoxide and hydrogen at low reactor wall temperatures over ruthenium supported on silica

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Oxidative methane conversion to carbon monoxide and hydrogen is catalyzed over ruthenium supported on silica at reactor wall temperatures as low as 400°C when the flow rate of reactants (methane and oxygen) is significantly high. The conversion of methane and the yields of carbon monoxide and hydrogen increase with increase in the flow rate of the reactants while oxygen is always completely consumed. Addition of carbon dioxide to the reactant flow can increase the yield of carbon monoxide in the reaction, suggesting that carbon dioxide functions as an oxidant and the actual surface temperature of the catalyst is sufficiently high that thermal conversion of methane via carbon dioxide and water can take place.

Keywords: Methane conversion; CO; silica supported ruthenium (Ru/SiO_2)

1. Introduction

The transformation of methane may be accomplished through a number of processes, of varying interest from a practical viewpoint:

$$CO_2 \text{ reforming}: \quad CH_4 + CO_2 \rightarrow 2CO + 2H_2, \tag{1}$$

$$\text{oxidation to syngas}: \quad CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2, \tag{2}$$

$$\text{steam reforming}: \quad CH_4 + H_2O \rightarrow CO + 3H_2, \tag{3}$$

$$\text{total oxidation}: \quad CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \tag{4}$$

as well as partial oxidation and oxidation coupling.

Although there is considerable interest in the direct conversion of methane to more chemically reactive compounds in order to produce liquid fuel from natural gas, the only industrialized process is the steam reforming of methane to carbon monoxide and hydrogen at temperatures of 750–850°C [1]. These gases (synthesis

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gas) are used for synthesis of ammonia and methanol, and can be transformed into higher hydrocarbons, alcohols, and aldehydes by Fischer–Tropsch catalysis [2]. Catalysts containing ruthenium, rhodium, platinum, iridium or nickel have been shown to be effective for conversion of methane to synthesis gas (2), at atmospheric pressure and above 700°C [3–6].

A number of workers [3–5] have suggested that process (2) first produces CO_2 and H_2O which subsequently, through processes (1) and (3) yield CO and H_2, and various data have been advanced in support of this contention. However, processes (1) and (3) only become thermodynamically spontaneous at temperatures in excess of 650°C (table 1).

Recently two research groups have independently developed a new process for the oxidative methane conversion to synthesis gas [7–13]. The process is characterized by very short contact times between the reactants (methane and oxygen) and the catalyst. Schmidt and his co-workers used catalysts containing platinum or rhodium [7,8], and reported that the temperature at the reactor exit was approximately 1000°C [7]. In contrast, Choudhary and his co-workers employed those containing nickel or cobalt and contend that the reaction takes place at a temperature lower than 700°C [9–13]. Both groups have proposed that the reaction is direct methane oxidation to synthesis gas [7–13]. However, the amount of reactants fed was so large, in their reaction conditions, that the reaction heat generated during the exothermic reaction may be sufficiently high to facilitate methane reforming via carbon dioxide (1) and water (3).

In the present work the conversion of methane with oxygen is studied on a ruthenium / silica catalyst at reactor wall temperatures between 400 and 800°C. The reactions of carbon dioxide with methane and with hydrogen are compared with the aforementioned reaction under similar conditions.

2. Experimental

Ruthenium supported on silica (10 wt% Ru/SiO_2) was prepared by impregnation of ruthenium chloride ($RuCl_3 \cdot 3H_2O$, Aldrich) on powdered silica gel

Table 1
Values of ΔG for processes (1) and (3)

T (°C)	ΔG (kJ mol^{-1})	
	process (1)	process (3)
500	41.1	35.0
600	12.8	11.0
700	−15.5	−13.1
800	−43.8	−37.3
1000	−100.4	−86.0

(Davison, grade 407). The solid was heated in air at 700°C for 3 h prior to use in the reaction.

Methane conversion was performed in a conventional fixed-bed continuous flow reactor operated under atmospheric pressure. The catalyst was placed in a quartz tube reactor (4 mm i.d., 6 mm o.d.) and sandwiched with quartz wool plugs whose contribution to the reaction was negligible. The tube reactor was heated with a cylindrical furnace and the temperature of the furnace was detected with a thermocouple located outside of the reactor adjacent to the catalyst bed. The molar ratio of CH_4/O_2 in the feedstream was kept at two. Catalysts (0.002–0.010 g) were preheated in a flow of hydrogen (2 dm^3 STP h^{-1}) for 0.5 h at 400°C immediately prior to their use in the reaction. The reactants and products were analyzed with an on-stream gas chromatograph equipped with a TCD (HP5890). Two columns, one HayeSep Dip (5 m) the other Molecular Sieve 5A (0.5 m) were employed in the analyses. The analyses were carried out after 1 h on-stream. Product yields are defined as molar fractions of methane necessary to generate the products unless otherwise noted, e.g., when 1 mol of each of carbon monoxide and hydrogen are obtained from 10 mol of methane the yields are 10% for carbon monoxide and 5% for hydrogen (two hydrogen molecules can be made from one methane molecule).

3. Results and discussion

Methane conversion to carbon monoxide and hydrogen proceeded over a 10 wt% Ru/SiO_2 catalyst at a reactor wall temperature of 400°C while carbon dioxide and water were also produced (fig. 1 and table 2). Oxygen in the feedstream was completely consumed during the reaction. The mass balance between reactants

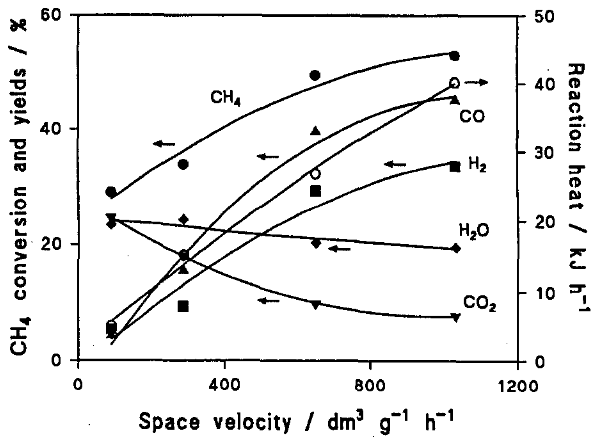

Fig. 1. Oxidative methane reforming over 10 wt% Ru/SiO_2. Catalyst, 0.010 g; reactor wall temperature, 400°C; CH_4/O_2 = 2.0; O_2 conversion, 100%.

Table 2
Oxidative methane reforming over 10 wt% Ru/SiO_2. Flow rate, 10.3 $dm^3 h^{-1}$ ($CH_4/O_2 = 2.0$); O_2 conversion, 100% except for run 5

Run	Amount of catalyst (g)	Reactor wall temperature (°C)	CH_4 conversion (%)	Yield (%)			
				CO	CO_2	H_2	H_2O
1	0.002	400	47	32	15	28	19
2	0.005	400	49	42	7	27	22
3	0.010	400	53	45	8	33	20
4	0.010	600	60	51	9	44	16
5	0.010	300	0	no reaction			

and products was $100 \pm 2\%$. As shown in fig. 1 the conversion of methane and yields of carbon monoxide and hydrogen increased with increase in the flow rate of the reactants ($CH_4/O_2 = 2.0$). At the beginning of the reaction a sudden increase in the temperature of the reactor was detected although the reactor was well regulated with a temperature controller. This suggests that a substantial quantity of heat was generated during the reaction. An estimate of the heat was obtained from the product distribution and the enthalpies at 400°C (see fig. 1). Assuming that the heat capacity of the catalyst is the same as that of quartz glass (0.8 J deg^{-1} g^{-1}) and the reactor system operates adiabatically, the rate of increase in the temperature of the catalyst is calculated as 200–1400 deg s^{-1}. Although in the actual process diffusion of the reaction heat takes place, the heat generated is not negligible.

Although the conversion of CH_4 and the yields of CO and H_2 increase with increase in the flow rate of the reactants the yields of CO_2 and H_2O decrease (fig. 1). At relatively low space velocities the yields of CO_2 and H_2O are factors of 4–5 higher than those observed for CO and H_2 while at the highest flow rates the latter are approximately twice as large as the former. The estimated reaction heat increases with space velocity approximately proportional to the increase in the yields of CO and H_2. These observations suggest that at the lower space velocities where the heat generated in the reaction is low, methane is primarily undergoing deep oxidation to form CO_2 and H_2O as in (4). As the space velocity is increased, the heat produced increases with consequent increase in the catalyst temperature so that the reactions of CO_2 and H_2O with CH_4 (eqs. (1) and (3)) become thermodynamically allowed, thereby producing enhanced yields of CO and H_2. The equilibrium yields of carbon monoxide or hydrogen produced from the interaction of carbon dioxide and water with methane are calculated as 4% at 400°C, 36% at 600°C, and 86% at 800°C under the reaction conditions. Ashcroft et al. carried out the methane reforming over ruthenium compounds at 777°C (space velocity, 25 dm^3 g^{-1} h^{-1}) and obtained the yields of carbon monoxide and hydrogen very close to those expected at equilibrium [3].

In order to change the contact time of the reactants, a nitrogen flow was added to the feedstream in which the flow rate of methane and oxygen was kept at 2.9 dm^3 h^{-1} (fig. 2). Although dilution of the reactant flow with nitrogen resulted

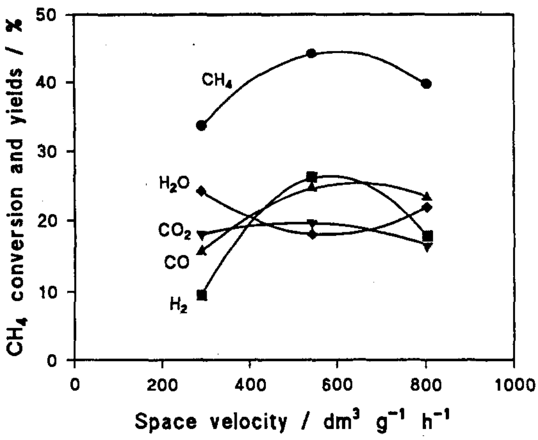

Fig. 2. Addition of nitrogen flow to the reactant flow (2.9 dm^3 h^{-1}, $CH_4/O_2 = 2.0$). Catalyst, 0.010 g; reactor wall temperature, 400°C; O_2 conversion, 100%.

in increases in methane conversion and in yields of carbon monoxide and hydrogen, the increase did not relate to the flow rate. In the case of a higher flow rate ($CH_4 + O_2$, 6.5 dm^3 h^{-1}; N_2, 4.3 dm^3 h^{-1} if present), the methane conversion did not increase with addition of nitrogen to the feedstream (cf. fig. 1 and run 7 in table 3). Thus, it appears that the formation of carbon monoxide and hydrogen is not due to the short contact time between the catalyst and reactants but due to the high surface temperature of the catalyst. At a reactor wall temperature of 600°C the conversion of methane and yields of carbon monoxide and hydrogen increased compared with the result at 400°C while the oxygen in the feedstream was comple-

Table 3
Methane or hydrogen oxidation with carbon dioxide as oxidant over 10 wt% Ru/SiO_2. Catalyst, 0.010 g; O_2 conversion 100% in runs 6 and 7

Run	Reactor wall temperature (°C)	Flow rate (dm^3 h^{-1})					CH_4 or H_2 conversion (%)	Yield[a] (%)				
		CH_4	O_2	CO_2	H_2	N_2		CO	CO_2	CH_4	H_2	H_2O
6	400	4.3	2.2	4.3	0	0	47	49			19	28
7	400	4.3	2.2	0	0	4.3	46	37	9		23	23
8	400	4.3	0	4.3	0	0	tr[b]	tr			nd[c]	
9	600	4.3	0	4.3	0	0	7	13			13	
10	800	4.3	0	4.3	0	0	16	32			16	
11	400	0	0	4.3	4.3	0	7	1		2		4
12	600	0	0	4.3	4.3	0	16	10		2		13

[a] Product yields for carbon monoxide and methane in runs 11 and 12 are calculated from the molar fractions of converted carbon dioxide and that for water is based on the molar fractions of hydrogen.

[b] Trace.

[c] No detection.

tely consumed even at 400°C (cf. runs 3 and 4 in table 2). No oxidation of methane was observed at a reactor temperature of 300°C (run 5 in table 2).

Although the conversion of oxygen was 100% with only 0.002 g of the catalyst, the conversion of methane increased with increase in the quantity of the catalyst (runs 1–3 in table 2). Hence, subsequent reactions without oxygen are evidently occurring after the supply of oxygen is depleted.

If carbon dioxide is an intermediate of the reaction, intentional addition of carbon dioxide to the feedstream should change the product distribution. Actually the yield of carbon monoxide was larger than the conversion of methane when carbon dioxide was added, that is, a portion of the carbon dioxide in the feedstream was apparently transformed to carbon monoxide. Two possibilities for the conversion of carbon dioxide to carbon monoxide appear to exist: one is the reaction between carbon dioxide and methane to form carbon monoxide and hydrogen and another is that between carbon dioxide and hydrogen to form carbon monoxide and water. Since the methane conversion was higher and the yield of hydrogen was lower than that in the reaction in which nitrogen was added to the feedstream instead of carbon dioxide (cf. runs 6 and 7 in table 3), both endothermic reactions appear to be occurring over the catalyst. Hence, methane or hydrogen was fed with carbon dioxide to the catalyst and the activity of the catalyst was evaluated. In the reaction between carbon dioxide and methane (runs 8–10 in table 3) carbon monoxide and hydrogen were produced while the yield of carbon monoxide was small at a reactor temperature of 400°C. On the other hand, oxidation of hydrogen took place in the reaction with carbon dioxide and products detected were carbon monoxide, methane and water (runs 11 and 12 in table 3). Formation of a small amount of methane may result from the exothermic reaction, $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$. At a reactor temperature of 400°C the yield of carbon monoxide was also small in the reaction between carbon dioxide and hydrogen. Thus there is evidence that, in addition to the direct oxidation of methane to carbon monoxide and hydrogen, the deep oxidation to carbon dioxide and water is also occurring. The heat generated in the process is apparently sufficient to increase the temperature of the catalyst bed to a level sufficient to permit the reforming of CH_4 with carbon dioxide and water to augment the yield of the desired products, CO and H_2.

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