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Partial oxidation of methane to formaldehyde with 50% yield in a continuous recycle reactor separator (CRRS)

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Abstract

The partial oxidation of methane (MPO) to formaldehyde by molecular oxygen has been studied in the temperature range 840–900 K and atmospheric pressure in a continuous gas recycle reactor separator using a supported V_2O_5–SiO_2 catalyst. The recycled gas passes continuously through a trap unit in the recycle loop and thus formaldehyde is protected from further oxidation. In this way high (up to 56%) selectivity is maintained for methane conversions up to 89%. This leads to formaldehyde yields up to 50 versus 2% for single pass operation. The effect is discussed of V_2O_5 catalyst loading, temperature, space velocity, inlet CH_4 to O_2 ratio and recycle flowrate on formaldehyde selectivity and yield. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Partial oxidation; Continuous gas recycle reactor separator; Flowrate

1. Introduction

Due to the worldwide abundance of natural gas the partial oxidation of methane to useful liquid chemicals, i.e. methanol and/or formaldehyde, has been a long sought goal [1–13]. Formaldehyde is currently manufactured from methane via a three-step process involving (i) high temperature steam reforming of methane to produce synthesis gas, (ii) methanol synthesis under high pressure, and (iii) oxidative dehydrogenation of methanol to formaldehyde:

$$CH_4 + H_2O \xrightarrow[\text{promoter } K_2O,\ T=800^\circ C]{NiO/\alpha\text{-}Al_2O_3} CO + 3H_2 \tag{1}$$

$$CO + 2H_2 \xrightarrow[P=50\,\text{atm},\ T=250^\circ C]{Cu/ZnO/Al_2O_3} CH_3OH \tag{2}$$

$$CH_3OH \xrightarrow[Fe_2(MoO_4)_3,\ T=425^\circ C]{Ag,\ T=600^o C} H_2CO + H_2 \tag{3}$$

Clearly a one-step partial oxidation process from methane to formaldehyde is highly desirable since it would, among others, eliminate the energy requirements of the endothermic steam reforming process and the high pressure operation and heat removal complexities of the strongly exothermic methanol synthesis.

While the partial oxidation of methane to H_2CO is thermodynamically favored, the total oxidation of methane to carbon oxides (CO_x) is even more favored [2].

Previous attempts to directly oxidize methane to methanol/formaldehyde have led to low yields due to the high reactivity of formaldehyde with oxygen to form CO and CO_2:

$$CH_4 \xrightarrow{O_2} H_2CO \xrightarrow{O_2} CO_x \tag{4}$$

which results in formaldehyde yield (Y_{H_2CO}) typically of the order of 2%, even when using catalysts, such as V_2O_5 which are selective at low CH_4 conversions [1–12]. Thus, the detailed kinetic studies of Spencer and Pereira [5] have shown that the kinetic constant for the consecutive undesirable H_2CO oxidation to CO_x is typically 50–100 times larger than the rate constant for the partial oxidation of CH_4 to H_2CO. As a result of that, high (~50%) selectivity to H_2CO (S_{H_2CO}) can be obtained only at low (<2%) methane conversion (C_{CH_4}) values leading to very few reports with Y_{H_2CO} values (Y_{H_2CO} equals $C_{CH_4} \times S_{H_2CO}$) higher than 2% [1–12].

Selectivity and yield are defined from

$$S_{H_2CO} = \frac{Q_{OUT} \times y_{H_2CO}}{Q_{IN}(y_{CH_4,IN} - y_{CH_4})} \tag{5}$$

$$Y_{H_2CO} = \frac{Q_{OUT} \times y_{H_2CO}}{Q_{IN}\, y_{CH_4,IN}} \tag{6}$$

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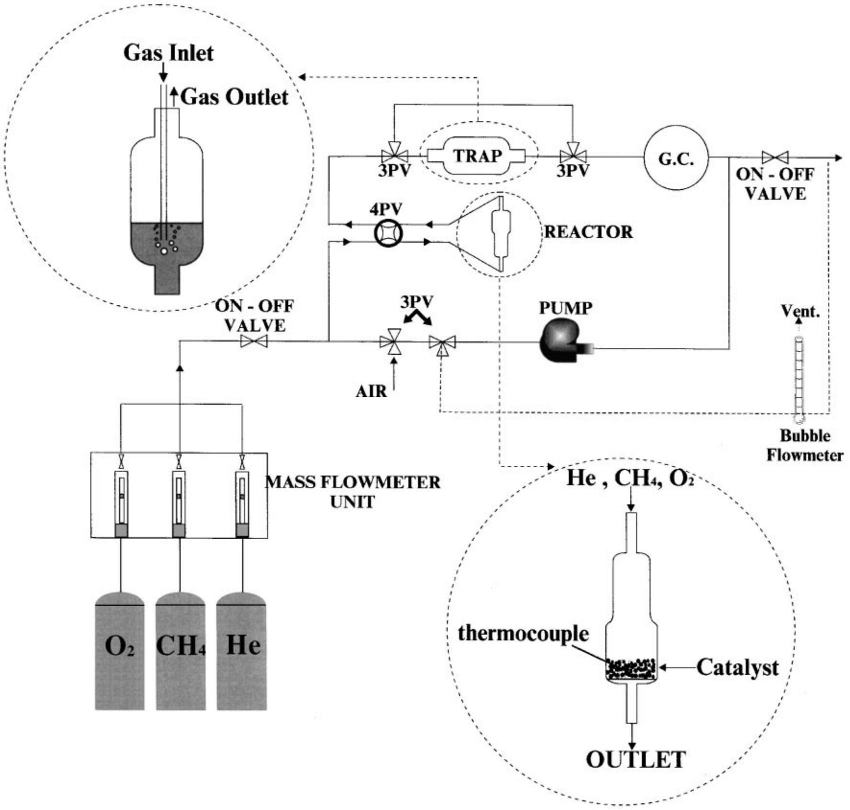

Fig. 1. Experimental setup; 3PV: three-port valve, 4PV: four-port valve, GC: gas chromatograph sampling port.

where Q_{OUT} and Q_{IN} stand for the inlet and outlet total volumetric flowrates, y stands for mole fraction and the subscript IN denotes inlet conditions. In the present study to a good approximation Q_{OUT} and Q_{IN} are equal

In an alternative approach Yu and coworkers [13] used a combination of a homogeneous catalyst (NO) and a heterogeneous one ($Na_2B_4O_2$) to achieve Y_{H_2CO} values up to 20.5 and 8.3% with O_2 and air as the oxidant in a catalytic reactor–condenser unit.

There are three more references where the yield of formaldehyde approaches or exceeds 10%. The first of these uses a manipulation of reactor design to increase the yield [14]. The catalysts are not specified explicitly but a relevant Patent [15] refers to AS-37, a commercial Russian aluminosilicate catalyst. The work would seem to be a follow up of a program carried out over many years [16]. Although conversion per pass is low, the products are extensively recycled but with CO and CO_2 being selectively removed, as these were shown to depress both conversion and yield. At the relatively high temperature of 973 K and an overall space velocity of 8000 h^{-1}, a recycle ratio of 50 increased the yield of H_2CO from ~2% to just under 30%. When CO and CO_2 were removed from the recycle gas, the yield of formaldehyde rose to 42% for the same recycle ratio, while the reactor productivity (gHCHO/volume catalyst/h) increased greatly.

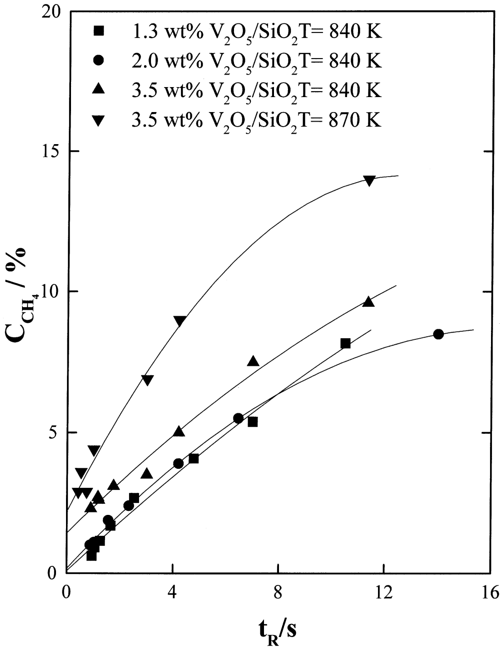

Fig. 2. Effect of reactor residence time (t_R) on methane conversion for various V_2O_5 catalyst loadings. Single pass operation.

A second reference to catalysts giving high yields of formaldehyde has appeared in a Japanese patent [17] which describes catalysts giving a selectivity of 66% at a methane conversion of 10.5% at 873 K and emphasizes the role that water plays in achieving high selectivities, without suggesting the possible mechanism. The best catalyst was found to be a mixture of the oxides (10% (w/w) of each) of Fe(III), Ni(III), Bi, Mg and Mo, the remainder of the catalyst (50% (w/w)) being a silica support. Mo oxides were implied to be the active phase since a similar catalyst without MoO_3 gave only 1.5% methane conversion at 90.3% selectivity under the same reaction conditions.

In the third report Amir-Ebrahimi and Rooney [18] have examined the problem of developing the partial oxidation catalysts and combining the ideas of methyl radical generation from an Mo=O center with elements of olefin metathesis catalysts. The result was a series of catalysts, based on $MoCl_5/R_4Sn$, where R is an alkyl group, supported on silica that plays an important part in the reaction. The best of the series of catalysts had exceptional activity for formaldehyde formation from methane, giving 20% conversion with 80% selectivity at 973 K using 1:1 methane–air mixture.

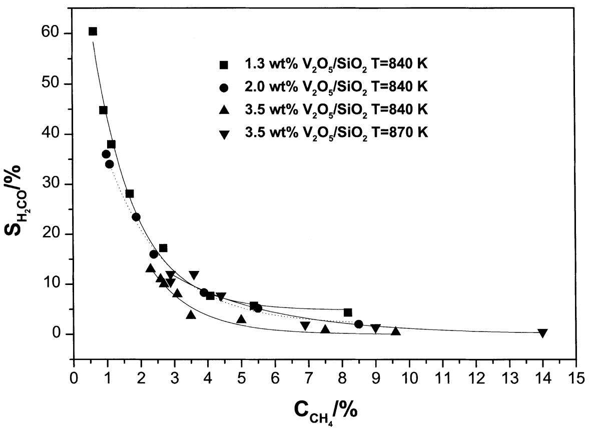

Fig. 3. Dependence of H_2CO selectivity on CH_4 conversion for various V_2O_5 catalyst loadings. Single pass operation. Outlet gas compositions given in Table 1.

The problem of the high reactivity of formaldehyde to CO_x formation during the methane partial oxidation (MPO) process is in a way similar to, and even more severe than, that of the high reactivity of C_2 hydrocarbons for CO_x

Table 1
Experimental conditions and outlet gas compositions of Figs. 2 and 3

Q_{IN}	t_R (s)	y_{CH_4} (%)	y_{O_2} (%)	y_{CH_4}/y_{O_2}	y_{CO} (%)	y_{CO_2} (%)	y_{H_2CO} (%)	C_{CH_4}	S_{H_2CO}	S_{CO}	S_{CO_2}
$m_c = 1.2$ g, $V_R = 7$ cm^3, 1.3 wt.% V_2O_5/SiO_2, $T = 840$ K. Single pass operation (■)											
40	10.5	42	2.5	16.8	2.9	0.64	0.16	8.18	4.4	78.3	17.3
60	7	47.1	0.4	118	2.15	0.38	0.15	5.38	5.7	80	14.3
88	4.7	46.8	0.18	260	1.66	0.18	0.15	4.08	7.7	83.4	8.9
166	2.53	55	1.1	50	1.15	0.11	0.26	2.68	17.2	75.6	7.2
255	1.65	55.4	2.53	22	0.62	0.06	0.27	1.69	28.1	65	6.9
335	1.25	52.9	2.78	19	0.34	0.036	0.23	1.15	38	56	6
400	1.05	44.3	2.48	17.9	0.2	0.025	0.18	0.92	44.8	49.4	5.8
446	0.94	38.7	3.26	11.9	0.095	0	0.15	0.62	60.4	39.6	0
$m_c = 1.2$ g, $V_R = 7$ cm^3, 2.0 wt.% V_2O_5/SiO_2, $T = 840$ K. Single pass operation (●)											
30	14	49	3	16.3	4	0.55	0.09	8.5	2	86.2	11.8
65	6.46	39	8.4	4.65	1.96	0.2	0.117	5.5	5.16	86.1	8.74
100	4.2	40.7	9.35	4.35	1.41	0.1	0.14	3.9	8.3	85.5	6.2
180	2.33	41.8	10.2	4	0.82	0.049	0.165	2.4	16	79.3	4.7
270	1.55	47.4	9.8	4.8	0.66	0.035	0.21	1.88	23.4	73	3.6
410	1.02	51.5	7.2	7	0.35	0.023	0.19	1.1	34	62	4
480	0.87	34	6.3	5.4	0.22	0.013	0.13	1	36	61	3
$m_c = 1.2$ g, $V_R = 7$ cm^3, 3.5 wt.% V_2O_5/SiO_2, $T = 840$ K. Single pass operation (▲)											
37	11.35	48.6	2.2	22	4.4	0.75	0.018	9.6	0.4	85	14.6
60	7	39	2.6	15	2.86	0.28	0.024	7.5	0.8	90.4	8.8
100	4.2	25.5	13.9	1.83	1.22	0.075	0.037	5	2.8	92	5.2
140	3	55	6.9	8	1.9	0.06	0.075	3.5	3.7	93.4	2.9
240	1.75	14.7	8.3	1.8	0.42	0.013	0.038	3.1	8	89.2	2.8
350	1.2	20	5.4	3.7	0.47	0.009	0.06	2.6	11	87	2
360	1.166	35	1.8	19.4	0.85	0.013	0.095	2.7	10	89	1
470	0.893	23.5	4	6	0.5	0	0.07	2.3	12	88	0
$m_c = 1.2$ g, $V_R = 7$ cm^3, 3.5 wt.% V_2O_5/SiO_2, $T = 870$ K. Single pass operation (▼)											
30	14	37	3.5	10.5	4.6	1.3	0.025	14	0.42	77.6	22
100	4.2	34.2	8.6	4	3	0.28	0.045	9	1.4	90.2	8.4
140	3	53	3.8	13.95	3.7	0.22	0.075	6.9	1.9	93	5.1
420	1	24	3.75	6.4	1	0.024	0.085	4.4	7.7	90.2	2.1
570	0.73	8.65	3.4	2.55	0.23	0	0.027	2.9	10.5	89.5	0
800	0.52	39	1.4	28	1.25	0.036	0.17	3.6	12	86	2
1000	0.42	22	1.7	13	0.56	0.01	0.078	2.9	12	86	2

formation during the oxidative coupling of methane (OCM) to C_2 hydrocarbons [19]. In order to overcome this problem and obtain high C_2 yields in the OCM process two main reactor design strategies have been followed in recent years. The simulated countercurrent moving bed developed by Aris and coworkers [20] and the gas recycle reactor–separator developed by Jiang et al. [19] and further improved by Lunsford and coworkers [21,22] and Machocki [23].

In this work, we have used the continuous gas recycle reactor–separator concept in conjunction with a selective supported V_2O_5–SiO_2 catalyst in an effort to maximize formaldehyde yield during the MPO process.

2. Experimental

The experimental setup is shown schematically in Fig. 1. It consists of the gas feed unit and the recycle loop. The continuous recycle reactor–separator, CRRS [19] consists of a quartz fixed bed reactor, a formaldehyde absorption unit and a recycle pump. By appropriate setting of two on–off valves the reactor was operated either in a single-pass mode or in a recycle mode. The methane–air feed diluted in He was supplied to the CRRS unit at inlet flowrates (Q_{IN}) 10–700 cm^3 STP/min. The reactants were 20% methane diluted in He (used in the recycle experiments), or pure 99.99% CH_4 (used in the single pass experiments) 20% O_2 diluted in He and pure (99.99%) He used as diluent. The only detectable products were H_2CO, CO, CO_2 and H_2O. One significant advantage of the CRRS is that when operated at high recycle ratios as in the present study, it approaches the behavior of an ideal CSTR reactor–separator and thus the recirculating gas has the same composition as the exit stream, i.e. has low concentrations of unreacted methane and oxygen. In this way explosion hazards in the reactor can be avoided even when the overall gas feed composition is within the explosive region, i.e. 3–15% CH_4 in air.

Two quartz catalytic reactors, labeled R1 and R2, of volumes 7 and 25 cm^3, respectively, were used in the course of the experiments, the former mainly for catalyst and operating conditions screening, the latter for product yield maximization.

The reactor temperature was monitored and controlled via a quartz-enclosed K-type thermocouple fitted near the center of the catalyst bed. All gas lines in the recycle loop were heated at 400 K to avoid condensation of water and/or formaldehyde. Reactants and products were analyzed via on-line gas chromatography (Shimadzu 14A) equipped with two columns (Porapak N, molecular sieve) and two detectors (TCD, FID). The FID was used for the measurement of the H_2CO absorbed in the trap unit at the end of each run. The carbon mass balance closure was in practically all runs better than 8%.

The catalyst was V_2O_5 supported on commercial large pore silica (particle size 0.18–0.5 mm) prepared via wet impregnation of the support with an aqueous solution of ammonium metavanadate, followed by drying at 373 K for 10 h and calcination at 873 K for 5 h. The V_2O_5 loading was varied between 1 and 5.3 wt.%. Screening tests showed that the selectivity to formaldehyde decreases with increasing V_2O_5 loading, thus all results presented here were obtained with a vanadia loading of 1.3 wt.%. The maximum temperature rise in the reactor was 30 K.

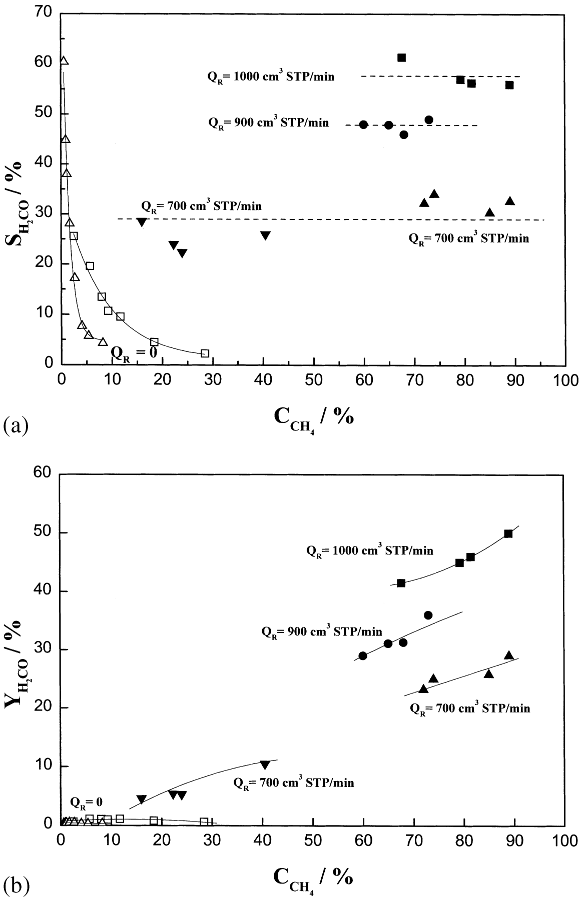

Fig. 4. Dependence of H_2CO selectivity (a) and yield (b) on CH_4 conversion for the two different modes of operation (open symbols: single pass operation, filled symbols: recycle operation). (△, $m_c = 1.2$ g, $V_R = 7\,cm^3$, $T = 840$ K), (□, $m_c = 1.9$ g, $V_R = 25\,cm^3$, $T = 880$ K), (■, $m_c = 1.9$ g, $V_R = 25\,cm^3$, $T = 890$ K, $Q_R = 1000$ cc/min, $Q_{IN} = 10$ cc/min), (▲, $m_c = 1.9$ g, $V_R = 25\,cm^3$, $T = 890$ K, $Q_R = 700$ cc/min, $Q_{IN} = 10$ cc/min), (▼, $m_c = 1.9$ g, $V_R = 25\,cm^3$, $T = 880$ K, $Q_R = 700$ cc/min, $Q_{IN} = 30$ cc/min), (●, $m_c = 1.9$ g, $V_R = 25\,cm^3$, $T = 880$ K, $Q_R = 900$ cc/min, $Q_{IN} = 10$ cc/min). In all cases the catalyst loading was 1.3 wt.%. Outlet gas composition given in Table 2.

Several trapping materials (Chromosorb 107, Porapak N, deionized H_2O) were tested for the efficient trapping of H_2CO and H_2O in the recycle loop. Deionized water gave the best results and was thus selected as the absorbent in the gas-bubble adsorption unit operating at 350 K. The pump provided recycle flowrates (Q_R) up to 1000 cc STP/min.

3. Results and discussion

3.1. Single-pass operation

At first, a set of experiments was carried out in the reactor R1 (7 cm^3) in order to optimize the vanadia loading of the catalyst. Four different catalyst loadings were investigated using the same total catalyst mass (1.2 g).

As shown in Fig. 2 increasing residence time (t_R) in the reactor causes a near-linear increase in methane conversion. The t_R is defined as the ratio of the reactor volume divided by the total volumetric flowrate. Increasing catalyst loading and increasing temperature enhance CH_4 conversion (Fig. 2), but at the same time cause a decrease in the selectivity to H_2CO (Fig. 3, Table 1). The 1.3 wt.% V_2O_5–SiO_2 catalyst gives S_{H_2CO} values up to 60% for CH_4 conversions, C_{CH_4}, below 1% (Fig. 3). This corresponds to residence times (t_R) of the order of 1s (Fig. 2). In view of the screening tests of Figs. 2 and 3 the 1.3 wt.% V_2O_5–SiO_2 catalyst was chosen for the continuous recycle operation experiments.

3.2. Recycle operation

Having chosen the most selective V_2O_5–SiO_2 catalyst the next step was to scale up the system by using a larger reactor. The reactor used (R2) had a volume of 25 cm^3. The mass of the catalyst was 1.9 g. At first, a set of single-pass experiments was performed and the dependence of formaldehyde selectivity upon methane conversion was investigated (Fig. 4a, open symbols, Table 2). Fig. 4a shows the effect of CH_4 conversion on H_2CO selectivity and compares single pass performance (open symbols) with

Table 2
Experimental conditions and outlet gas compositions of Fig. 4

$y_{CH_4,IN}$ (%)	$y_{O_2,IN}$ (%)	y_{CH_4} (%)	y_{O_2} (%)	$y_{CH_4,IN}/y_{O_2,IN}$	y_{CH_4}/y_{O_2}	y_{CO} (%)	y_{CO_2} (%)	C_{CH_4}	C_{O_2}	S_{H_2CO}	S_{CO}	S_{CO_2}	Y_{H_2CO}
m_c = 1.9 g, Q_{IN} = 10 cc/min V_R = 25 cm^3, 1.3 wt.% V_2O_5/SiO_2, T = 890 K. Q_R = 700 cc/min. Recycle operation (▲)													
3.9	18.5	0.6	12.5	0.21	0.05	0.26	2.2	89	35	33	7	60	29.4
4.5	18	0.75	11	0.25	0.07	0.3	2.35	85	42	30	8	62	25.5
6	14.6	1.7	8.1	0.41	0.21	0.4	2.7	74	50	34	8	58	25.1
7.6	13.5	2.4	4.5	0.56	0.53	0.46	3.4	72	70	32	8	60	23
m_c = 1.9 g, Q_{IN} = 10 cc/min, V_R = 25 cm^3, 1.3 wt.% V_2O_5/SiO_2, T = 890 K. Q_R = 1000 cc/min. Recycle operation (■)													
3	18.8	0.87	14.5	0.16	0.06	0.32	1.08	79	30	57	11	32	45
3.3	17.4	0.99	13	0.19	0.08	0.37	1.4	81	30	56	9	35	45.4
2.3	19.2	0.5	16.3	0.12	0.03	0.23	0.85	89	22	56	9.5	34.5	50
7.2	14	3.1	6.8	0.52	0.45	0.65	1.96	68	55	61	10	29	41.5
m_c = 1.9 g, Q_{IN} = 30 cc/min, V_R = 25 cm^3, 1.3 wt.% V_2O_5/SiO_2, T = 880 K. Q_R = 700 cc/min. Recycle operation (▼)													
12.6	10.5	7.5	2.2	1.2	3.4	1.3	2	40.5	79	26	29	45	10.5
33	20	25	6	1.75	4.2	2.7	2.5	24	70	22.4	40	37.6	5.4
40	17	31.1	2.5	2.4	12.4	3.1	3	22.3	85	24	39	37	5.4
52	14	43.7	0.9	3.7	48.5	2.9	2.5	16	94	28.6	39	32.4	4.6
m_c = 1.9 g, Q_{IN} = 10 cc/min, V_R = 25 cm^3, 1.3 wt.% V_2O_5/SiO_2, T = 880 K. Q_R = 900 cc/min. Recycle operation (●)													
5.1	17.6	1.3	11.2	0.29	0.12	0.51	1.7	73	37	49	12	39	35.8
6	17.6	1.9	9.7	0.34	0.2	0.6	1.7	68	45	46	14	40	31.3
6.5	14.5	2.3	7.5	0.45	0.3	0.68	1.8	65	50	47.9	14.2	37.6	31.1
7.7	14	3.1	6	0.55	0.52	0.88	2	60	57	48	16	36	28.8
Q_{IN}	t_R (s)	y_{CH_4} (%)	y_{O_2} (%)	y_{CH_4}/y_{O_2}	y_{CO} (%)	y_{CO_2} (%)	y_{H_2CO} (%)	C_{CH_4}	S_{H_2CO}	S_{CO}	S_{CO_2}		
m_c = 1.2 g, V_R = 7 cm^3, 1.3 wt.% V_2O_5/SiO_2, T = 840 K. Single pass operation (△)													
40	10.5	42	2.5	16.8	2.9	0.64	0.16	8.18	4.4	78.3	17.3		
60	7	47.1	0.4	118	2.15	0.38	0.15	5.38	5.7	80	14.3		
88	4.7	46.8	0.18	260	1.66	0.18	0.15	4.08	7.7	83.4	8.9		
166	2.53	55	1.1	50	1.15	0.11	0.26	2.68	17.2	75.6	7.2		
255	1.65	55.4	2.53	22	0.62	0.06	0.27	1.69	28.1	65	6.9		
335	1.25	52.9	2.78	19	0.34	0.036	0.23	1.15	38	56	6		
400	1.05	44.3	2.48	17.9	0.2	0.025	0.18	0.92	44.8	49.4	5.8		
446	0.94	38.7	3.26	11.9	0.095	0	0.15	0.62	60.4	39.6	0		
m_c = 1.9 g, V_R = 25 cm^3, 1.3 wt.% V_2O_5/SiO_2, T = 880 K. Single pass operation (□)													
25	60	16	1.5	10.7	3.5	2.1	0.13	28.4	2.3	61	36.7		
109	13.8	16.1	12.5	1.29	2.4	0.56	0.14	18.4	4.5	77	18.5		
230	6.52	18.2	11.7	1.6	1.7	0.32	0.21	11.68	9.57	76	14.4		
315	4.76	16.3	10.7	1.52	1.32	0.22	0.18	9.25	10.66	77	12.34		
410	3.66	14.5	9.7	1.5	1	0.17	0.18	8	13.5	74	12.5		
600	2.5	12.2	8.7	1.4	0.74	0.094	0.2	5.67	19.4	72	8.6		
700	2.14	25.6	7.4	3.5	1.27	0.155	0.5	2.5	25.9	66	8.1		

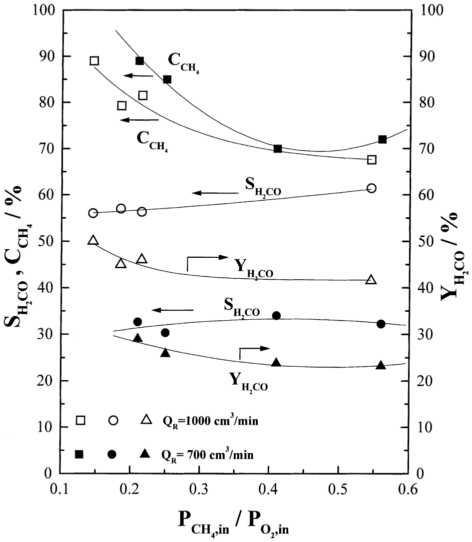

Fig. 5. Effect of inlet methane to oxygen ratio, $P_{CH_4,IN}/P_{O_2,IN}$ and of recycle flowrate (Q_R) on methane conversion (■, □), H_2CO selectivity (●, ○) and yield (▲, △). $m_{cat} = 1.9$ g, 1.3 wt.% V_2O_5–SiO_2, $T = 890$ K, $F_{IN} = 10$ cc/min, $V_R = 25$ cm^3. Open symbols: $Q_R = 1000$ cc/min, filled symbols: $Q_R = 700$ cm^3/min. Outlet gas compositions given in Table 3.

recycle performance (filled symbols). It is clear that although in single-pass operation high selectivity can be achieved only at very low methane conversions, recycle operation enhances dramatically the CH_4 conversion range of high selectivity and, at sufficiently high recycle flowrates (Q_R), enables one to maintain selectivities of the order of 55% at conversions approaching 90%. This enhances the formaldehyde yield from values of the order of 1% in single pass operation to values of the order of 30% and as high as 50% in recycle operation (Fig. 4b).

The formaldehyde selectivity and maximum yield were found to be weakly dependent on temperature in the range 840–880 K. Higher temperatures were found to cause a pronounced decrease in selectivity. Also, as shown in Fig. 5 (Table 3), the formaldehyde selectivity and yield are weakly dependent on the inlet methane to oxygen ratio over the range 0.15–0.55. The same figure shows that both selectivity and yield increase strongly with increasing recycle flowrate (Q_R).

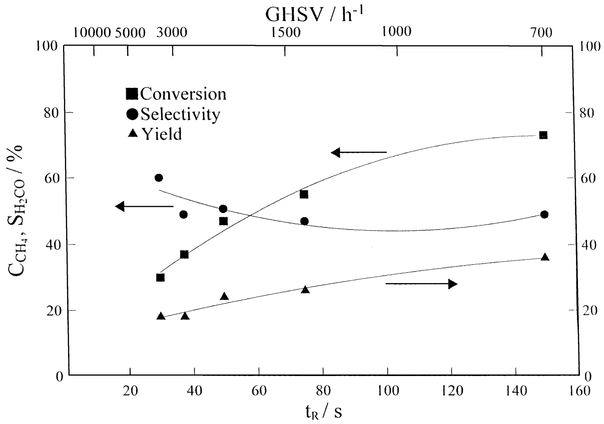

Fig. 6. Effect of reactor residence time and gas hourly space velocity (GHSV), based on catalyst volume, on methane conversion (■), H_2CO selectivity (●) and yield (▲). $m_{cat} = 1.9$ g, 1.3 wt.% V_2O_5–SiO_2, $T = 880$ K. $Q_R = 900$ cm^3/min, $(P_{CH_4}/P_{O_2})_{IN} = 0.3$, $V_R = 25$ cm^3. Outlet gas compositions given in Table 4.

Fig. 6 shows that the selectivity to formaldehyde remains practically constant with varying total residence time (t_R) or gas hourly space velocity (GHSV). The latter is based on the V_2O_5–SiO_2 catalyst volume. This constancy in selectivity value, in conjunction with the observed near-linear increase in methane conversion causes a near-linear increase in formaldehyde yield with increasing total residence time (Fig. 6, Table 4).

The formaldehyde yield values of 50% obtained in the present study are significantly higher than those previously reported in the literature. This pronounced improvement is not attributable to the properties of the V_2O_5–SiO_2 catalyst, which simply provides selectivities of the order of 55–60% at very low methane conversion, but is a result of the reactor–separator design and recycle operation which makes a predominantly consecutive reaction network (4) behave as a parallel reaction network would in a single-pass reactor, i.e. the selectivity to the desired product remains constant with increasing conversion (Fig. 4).

Table 3
Experimental conditions and outlet gas compositions of Fig. 5

$y_{CH_4,IN}$ (%)	$y_{O_2,IN}$ (%)	y_{CH_4} (%)	y_{O_2} (%)	$y_{CH_4,IN}/y_{O_2,IN}$	y_{CH_4}/y_{O_2}	y_{CO} (%)	y_{CO_2} (%)	c_{CH_4} (%)	c_{O_2} (%)	S_{H_2CO} (%)	S_{CO}	S_{CO_2} (%)	Y_{H_2CO}
$m_c = 1.9$ g, $Q_{IN} = 10$ cc/min, $V_R = 25$ cm^3, 1.3 wt.% V_2O_5/SiO_2, $T = 890$ K. $Q_R = 700$ cc/min. Recycle operation (●, ■, ▲)													
3.9	18.5	0.6	12.5	0.21	0.05	0.26	2.2	89	35	33	7	60	29.4
4.5	18	0.75	11	0.25	0.07	0.3	2.35	85	42	30	8	62	25.5
6	14.6	1.7	8.1	0.41	0.21	0.4	2.7	74	50	34	8	58	25.1
7.6	13.5	2.4	4.5	0.56	0.53	0.46	3.4	72	70	32	8	60	23
$m_c = 1.9$ g, $Q_{IN} = 10$ cc/min, $V_R = 25$ cm^3, 1.3 wt.% V_2O_5/SiO_2, $T = 890$ K. $Q_R = 1000$ cc/min. Recycle operation (○, □, △)													
3	18.8	0.87	14.5	0.16	0.06	0.32	1.08	79	30	57	11	32	45
3.3	17.4	0.99	13	0.19	0.08	0.37	1.4	81	30	56	9	35	45.4
2.3	19.2	0.5	16.3	0.12	0.03	0.23	0.85	89	22	56	9.5	34.5	50
7.2	14	3.1	6.8	0.52	0.45	0.65	1.96	68	55	61	10	29	41.5

Table 4
Experimental conditions and outlet gas composition of Fig. 6

Q_{IN}	$y_{CH_4,IN}$ (%)	$y_{O_2,IN}$ (%)	y_{CH_4} (%)	y_{O_2} (%)	y_{CH_4}/y_{O_2}	y_{CO} (%)	y_{CO_2} (%)	c_{CH_4} (%)	c_{O_2} (%)	S_{H_2CO} (%)	S_{CO}	S_{CO_2} (%)	Y_{H_2CO}
$m_c = 1.9$ g, $y_{CH_4,IN}/y_{O_2,IN} = 0.3 = 0.3$, $V_R = 25\,cm^3$, 1.3 wt.% V_2O_5/SiO_2, $T = 880$ K. $Q_R = 900$ cc/min. Recycle operation													
10	6	20	1.9	9.7	0.2	0.6	1.7	73	45	49	13.5	37.5	35.8
20	5.9	20	3.1	12.9	0.24	0.78	0.9	55	40	47	25	28	25.9
30	5.4	18	3.2	14.7	0.22	0.68	0.58	47	25	50.7	26.5	22.8	23.8
40	6.1	20	4.3	14.6	0.29	0.7	0.4	37	32	49	33	18	18.1
50	5.6	18.7	4.1	15.6	0.26	0.55	0.27	30	20	60	27	13	18

The continuous recycle reactor–separator used here to convert methane to formaldehyde is similar to and simpler than the one recently developed for the OCM process [19,21–23], which requires a swing adsorption arrangement for C_2 trapping, and is also simpler than the simulated countercurrent moving bed developed by Aris and coworkers for the OCM system [20]. The underlying idea is, however, similar, i.e. protection of the highly reactive desired product by means of selective adsorption or absorption.

One significant problem for the successful scale-up of the present process can be the high recycle ratio and high heat exchange area needed to cool and heat the gases between the reactor and absorption units. Use of some of the recently reported state-of-the-art catalysts may lead to further improvements in yield and further reduction in the required recycle ratio.

4. Conclusions

A new continuous recycle reactor separator (CRRS) was used in order to investigate the partial oxidation of methane to formaldehyde. The system could perform two different modes of operation (single-pass and recycle operation). During the recycle operation a significant increase in the formaldehyde yield was observed. It reached the value of 50% while in the single-pass operation it was only up to about 2%. This yield value is the highest reported for the methane partial oxidation to formaldehyde with molecular oxygen at atmospheric pressure. The large increase in formaldehyde yield is mainly due to the design of the reactor–separator which combines the (high selectivity–low conversion) characteristics of the V_2O_5–SiO_2 catalyst with a formaldehyde trap unit which protects formaldehyde from further oxidation to CO_x.

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