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High yield synthesis of propanal from methane and air

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High yield synthesis of propanal from methane and air can be obtained in a single pass at atmospheric pressure. Three catalytic processes are combined to give 13% yield of propanal based on total methane input. Ethene is made from the oxidative coupling reaction and carbon monoxide and hydrogen is generated from partial oxygenation of methane. These gases are combined and passed to a hydroformylation catalyst to give liquid propanal. The unreacted methane is inert in the hydroformylation stage, while oxygen deactivates the catalyst readily. The results imply that propanal can be obtained, in good yield, from methane and air provided that total oxygen conversion is achieved. The yield of propanal from the three combined processes can be substantially higher than that of ethene from the oxidative coupling reaction. Thus, higher yields of a condensible and oxygenated product are obtained.

Keywords: Methane; oxidation; oxidative coupling; hydroformylation; propanal; catalysis

1. Introduction

The direct conversion of methane to chemicals such as methanol and/or formaldehyde [1,2] or ethene [3] via partial oxidation remains a most active research topic. However, despite the substantial effort applied towards these goals since the early 1980's, the capital intensive and somewhat cumbersome steam reforming reaction [4] of methane to carbon monoxide and hydrogen (synthesis gas) remains the only economically viable industrial process [5,6].

Of the direct conversion routes explored for methane, the partial oxidation to methanol and/or formaldehyde seems to be limited to yields of around 8% [7], although even this has proved to be difficult to reproduce [8], and is unable to compete economically with the presently used methanol synthesis via synthesis gas. Oxidative coupling to higher hydrocarbons, e.g. ethene, appears to offer slightly more promise, but a practical limit, for ethene, of about 20% yield seems

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to have been reached (over a number of different catalyst systems) without the aid of excessive dilution or added chlorine [9]. Partial oxygenation of methane with air to almost pure CO and H_2 has been achieved in > 90% yield at 780°C and 1 atm [10,11], but current synthesis gas technology requires compression to over 10 atm for further conversion, so a low pressure approach seems to have limited usage at present. Hydroformylation, however, the addition of CO and H_2 across an olefinic carbon–carbon double bond to yield aldehydes, can occur at atmospheric pressure with high yield and selectivity over, for example, the soluble rhodium catalyst, $RhH(CO)(PPh_3)_3$, in a homogeneous process, as developed by Union Carbide [12].

We have combined the three catalytic processes, namely, oxidative coupling of methane to ethene (OCC), partial oxygenation of methane to synthesis gas (POC) and hydroformylation of ethene, CO and H_2 (HFC), to give propanal, C_2H_5CHO. We have shown that we can achieve a continuous process at one atmosphere which gives pure liquid propanal in 13% yield from methane and air alone in a single pass. These results imply that the yield of propanal from the three combined processes can be substantially higher than the ethene yield in the OCC process with respect to methane conversion.

2. Experimental

The reactant gases (from Air Products plc) are greater than 99% purity and were used without further purification. The hydroformylation catalyst, $RhH(CO)(PPh_3)_3$, was prepared as described [13]. Table 1 shows that this catalyst can hydroformylate ethene to propanal at ambient pressure. The apparatus for converting methane to propanal is shown in fig. 1, and the corresponding gas flows and compositions at points (a) from the flow controllers, (b) before the OCC, (c) before the POC, (d) after the OCC, (e) after the POC, (f) the combination of the two effluents, (g) before the HFC, and (h) the final output,

Table 1
Ethene hydroformylation. $T = 115°C$, 1 atm, catalyst = $RhH(CO)(PPh_3)_3$, solvent = di-*n*-butylphthalate

Concentration of catalyst (g/ml)	Reactant ratio $C_2H_4:CO:H_2:(dil)$	Total flow rate (ml/min)	C_2H_4 conversion (%)	Product selectivities (%)	
				C_2H_5CHO	C_2H_6
0.008	1:2:2:0	15	65.6	99.1	0.9
0.008	1:2:2:5(N_2)	30	34.1	98.9	1.1
0.008	1:2:2:10(N_2)	45	21.4	99.0	1.0
0.008	1:2:2:10(CH_4)	45	21.1	99.1	0.9
0.008	1:2:2:10(O_2)	45	3.8	96.0	4.0
0.046	1:2:2:0	30	96.7	98.1	1.9

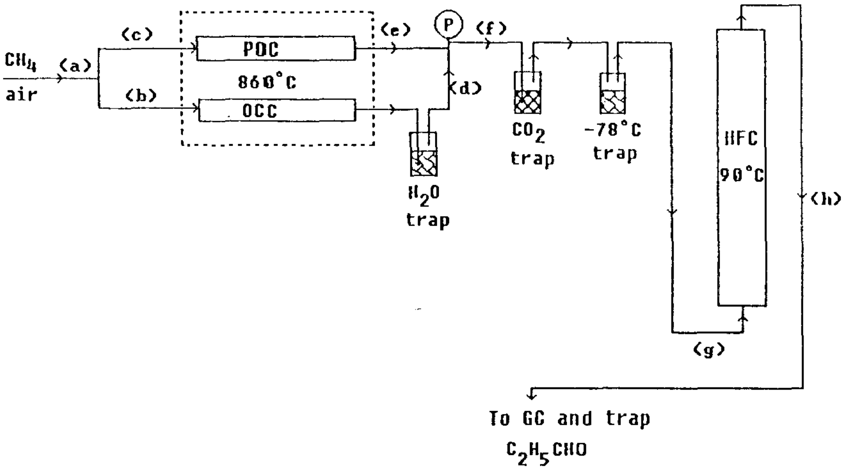

Fig. 1. Schematic diagram of apparatus used for single pass conversion of methane to propanal.

are given in table 2. Table 3 gives the catalytic conversions and product selectivities from the three individual steps.

The oxidative coupling was achieved in a 4 mm i.d. silica tube, in a 300 mm long tube furnace at a temperature of 860°C. 0.5 g of 2 mol% K/$BaCO_3$ was used due to its long term stability, and prepared by an incipient wetness impregnation method, then calcined in air for 8 h at 860°C [14].

The partial oxygenation was conducted in the same furnace in an identical, parallel, silica tube, but over 50 mg of a 1% w/w Rh/Al_2O_3 catalyst, prepared

Table 2
Gas flows (in ml/min) and compositions (in percent) at various points in the experimental production of propanal from methane and air (refers to fig. 1). OCC = oxidative coupling catalyst, POC = partial oxygenation catalyst, HFC = hydroformylation catalyst

	(a)	(b) pre OCC	(c) pre POC	(d) post OCC	(e) post POC	(f) combined	(g) pre HFC	(h) final
flow rate	36	30	6	25.7	8.4	34.1	32.6	31.6
volume								
N_2	57.1	57.1	57.1	66.7	40.8	60.3	63.2	65.1
O_2	14.3	14.3	14.3	0	0	0	0	0
CH_4	28.6	28.6	28.6	20.1	0.7	15.3	16.0	16.5
CO	0	0	0	1.4	19.5	5.9	6.1	4.9
CO_2	0	0	0	5.9	0.2	4.5	0	0
H_2	0	0	0	2.9	38.9	11.7	12.3	11.2
C_2H_4	0	0	0	2.4	0	1.8	1.9	0.5
C_2H_6	0	0	0	0.6	0	0.4	0.4	0.5
C_2H_5CHO	0	0	0	0	0	0	0	1.4

Table 3
Catalytic conversions and product selectivities over the three catalysts used in the production of propanal from methane

Conversion (%)	Product selectivities					
	C_2H_4	C_2H_6	CO_2	CO	H_2	C_2H_5CHO
2 mol% K / $BaCO_3$						
CH_4 39.7	36.1	8.5	44.8	10.6	9.7	
1% w / w Rh / Al_2O_3						
CH_4 96.5	0.0	0.0	1.0	99.0	99.2	
0.1 g / ml RhH(CO)(PPh_3)$_3$ in di-n-butylphthalate [a]						
C_2H_4 76		4				96
overall, for the three catalytic processes combined						
CH_4 49.2	5.9	6.4	30.2	30.7	32.6	26.8

[a] Inlet gases from (g) in fig. 1.

as before in this laboratory via a vacuum incipient wetness technique from $RhCl_3$, then reduced under flowing H_2 at 860°C for 24 h [11].

The two effluent gas streams were combined at (f), and passed through a Dreschel bottle containing diethylenetriamine ($NH(CH_2CH_2NH_2)_2$, $T_b = 207°C$) which effectively removed all of the CO_2 and H_2O. The gases were then passed through a cold trap at −78°C to remove the water and amine.

The remaining gases were passed through the hydroformylation catalyst which consisted of 2 g of $RhH(CO)(PPh_3)_3$ in 20 ml of di-*n*-butylphthalate (concentration 100 mM), a high boiling and polar solvent ($T_b = 340°C$) which gives high hydroformylation activity, while remaining inert to methane and nitrogen. The gases were passed through a sintered frit to disperse the bubbles through the catalyst solution which was held in a 50 cm high column at 90°C.

All product gas analyses were performed by GC, or GC-MS and, to confirm the whole process, experiments were run for a total of 18 h, the liquid product collected in a small trap at −78°C, and weighed.

3. Results and discussion

Table 1 shows that pure ethene mixed with CO/H_2 can be hydroformylated to propanal in a very high yield. It can be seen that the ethene conversion is dependent on residence time and, especially, on catalyst concentration. Methane has no significant effect on ethene hydroformylation, however, oxygen will deactivate the catalyst readily. These results show that it is possible to hydroformylate the ethene produced from the oxidative coupling reaction provided that no residue oxygen is allowed to enter the hydroformylation stage.

The results for the three individual catalysts are given in table 3. Over the oxidative coupling catalyst the oxygen conversion was essentially complete ($>99.9\%$) and the conversion of methane was 40%, at a selectivity to ethene of 36%, a total ethene yield of 14.4%. Over the partial oxygenation catalyst the oxygen conversion was again essentially complete ($>99.9\%$), and the methane conversion was 97%, at selectivities to H_2 and CO of 99%. In the final hydroformylation stage, 76% of the ethene is converted, together with 23% of the CO and 12% of the H_2 (both present in excess), to propanal, with small amounts of ethane being formed. The yield of propanal from ethene in this stage was 73%. The final output, then, given in table 3 and corresponding to (h) in table 2, is equivalent to a total CH_4 conversion of 49.2%, with selectivity to propanal of 26.7%, corresponding to a single pass yield of 13.2%.

The reaction product was collected during an 18 h period and analysed as essentially pure propanal (^1H NMR) together with a trace of benzene, arising from slight but insignificant degradation of the hydroformylation catalyst [15]. The mass of propanal obtained was 1.178 g (20.31 mmol), which corresponds to a 13.2% yield, the total amount of methane flowed being 463 mmol.

We have demonstrated that we can utilize the highly active and selective partial oxygenation process to boost the yield of useful products from the oxidative coupling reaction, by using the industrially proven hydroformylation reaction. The OCC reaction suffers from the high reactivity of the ethene product, which is destroyed at a rate competing with its formation, so that around 20% yield per single pass seems to be the highest attainable [3]. At this level, the ethene product, though valuable, is too expensive to compress and store, and is thus not an attractive process for methane conversion on its own. By converting it directly to propanal without the need for separation, the process becomes a simple route to a more useful product starting from methane. As noted, the propanal product formed is a liquid at room temperature and its separation from the gas stream is trivial. Further, this single pass three step process requires essentially no energy input since both the high temperature reactions are exothermic.

Theoretically, in a well designed (possibly multi-stage) methane coupling reactor, yields of 20% ethene should be possible in the initial stage, assuming optimum performance and total dehydrogenation of ethane to ethene. Passing the bare minimum of methane through the partial oxygenation catalyst to give just sufficient CO and H_2 for hydroformylation, and then total conversion of the ethene to propanal in the hydroformylation step would give a theoretical yield of around 28%, though this assumes a perfect plant.

Fig. 2a shows a possible process where the methane raw material will come from natural gas, and other strategies, albeit more complex and expensive, can be envisaged which could substantially increase the product yield; for example, by utilizing the unreacted methane from the oxidative coupling process. Also, where the natural gas contains 5% v/v ethane, an average value for, for

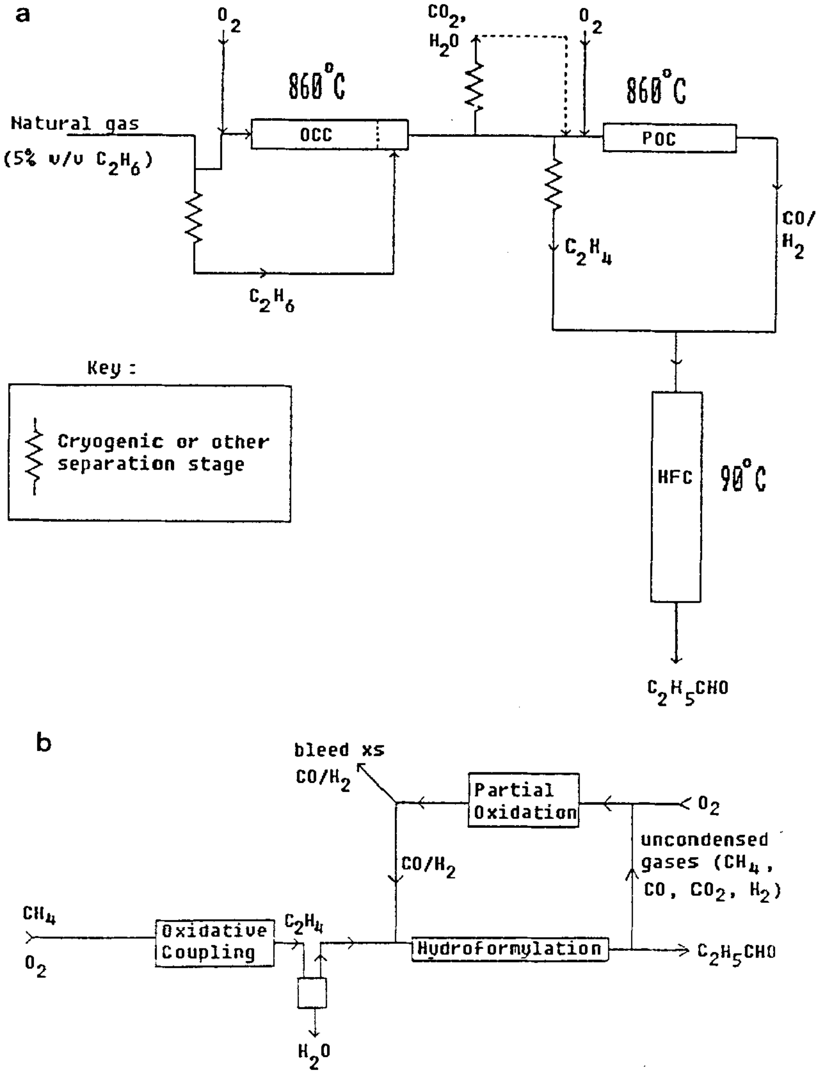

Fig. 2. (a) Schematic of proposed plant for high yield of propanal from natural gas. (b) Schematic route for propanal production without cryogenic stages.

example, North Sea gas, then this could be separated from the methane. The methane is then mixed with oxygen (an air separation plant is required) and passed over the oxidative coupling catalyst. The ethane separated from the natural gas can be added to the "afterburner", the hot post-catalytic volume, where it is thermally cracked to ethene in high yield. This is the basis of the IFP process [16]. The ethene, carbon dioxide and water may be cryogenically separated from the product stream, leaving methane, carbon monoxide and hydrogen. Oxygen is now added, in the correct proportion, to this stream which is passed over the partial oxygenation catalyst to give high yields of CO and H_2.

The separated CO_2 from the coupling reaction and any contained in the natural gas itself may also be added to the inlet of the partial oxygenation process to reduce the H_2/CO ratio to make it nearer 1 [17], which improves the selectivity in the hydroformylation step. The separated ethene may now be added to the effluent from the partial oxygenation (with the CO_2 and H_2O removed) and passed through the solvent containing the rhodium based hydroformylation catalyst.

Assuming 20% yield of ethene from the oxidative coupling of methane, and natural gas containing 5% v/v ethane, cracked to ethene, and 100% conversion of ethene to propanal in the hydroformylation step (achievable by increasing the catalyst concentration and/or residence time of the gases through the solvent), 42% yield of propanal is proposed at one atmosphere pressure, based on the total carbon atom % in the natural gas. However, the viability of this proposed process will depend on the relative cost of the cryogenic stages. Recycling of the reactant gases without cryogenic stages is also suggested in fig. 2b.

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