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PARTIAL OXIDATION OF METHANE TO SYNTHESIS GAS

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Partial oxidation of methane to synthesis gas has been carried out over a number of transition metal catalysts under a range of conditions. It is found that the metals Ni, Ru, Rh, Pd, Ir and Pt, either supported on alumina or present in mixed metal oxide precursors, will bring the system to equilibrium. The yield of CO and H_2 improves with increasing temperature in the range 650–1050 K, and decreases with increasing pressure between 1 and 20 atm. An excellent yield (~ 92%) is obtained with a 4:2:1 $N_2:CH_4:O_2$ ratio at 1050 K and atmospheric pressure, with a space velocity of 4×10^4 hour^{-1}.

1. Introduction

Recent attempts to convert methane into more valuable chemicals have focused largely on oxidative coupling reactions to yield ethylene and ethane [1,2]. Unfortunately, under conditions where reactions of methane are fast enough to be of interest (say, > 1000 K), oxidation to C_2's appears to be difficult to achieve on an economical scale. An alternative strategy for the elaboration of methane is to convert it into synthesis gas (CO and H_2), either by steam reforming or partial oxidation. This, in turn, can be used as a feedstock for methanol or ammonia synthesis, or converted to higher hydrocarbons, alcohols or aldehydes by Fischer-Tropsch catalysis [3].

Steam reforming is a well established process [4] and is usually performed over nickel/alumina catalysts in the temperature range 975–1075 K according to:

$$CH_4 + H_2O–CO + 2H_2 \qquad (1)$$

The equilibrium constant is rather unfavourable (e.g. ~ 1 at 1000 K), and side reactions, including the water gas shift reaction, result in a product containing substantial proportions of CO_2, water, and unreacted CH_4. For this reason, it is common practice to employ a secondary reforming stage in which oxygen or CO_2 may be used as oxidants to improve the methane conversion and reduce the hydrogen content [5,6]. Nevertheless, steam reforming affords an inexpensive route for natural gas conversion and is widely used for methanol and ammonia synthesis.

Partial oxidation, by contrast, is relatively little used at the present time, even though it proceeds almost stoichiometrically at high temperatures according to:

$$2CH_4 + O_2 - 2CO + 4H_2 \tag{2}$$

It forms the basis of an industrial process [7] at high pressures and temperatures ($>$ 1300 K), where the reaction may be non-catalytic, but it has been known since the 1940's that it will proceed at lower temperatures over nickel metal [8,9]. In this context, we have recently established that excellent yields of synthesis gas ($>$ 90%) can be achieved at 1050 K over mixed metal oxides of ruthenium under carefully chosen conditions [10]. We now report further details of this reaction and establish that it can be carried out over a wide range of supported metal catalysts.

2. Experimental

The supported metal catalysts were prepared by an incipient wetness technique. The appropriate amount of metal chloride (Johnson Matthey plc) was dissolved in the minimum of dilute hydrochloric acid and added in aliquots to 1 g of 80–100 mesh alumina (Phase Sep.), removing the solvent under reduced pressure each time. The uniform dispersion was then reduced under flowing hydrogen for 24 hours at 1073 K. The nickel catalyst, CRG 'F', was supplied by the British Gas, London Research Station in 1/8 inch pellet form, and was lightly crushed by pestle and mortar before use. The mixed metal oxides were prepared from the correct stoichiometric ratios of the relevant oxides (Aldrich Chem. Co. Ltd.) which were intimately mixed, then pressed into pellets, before heating in air at 1273 K for 7 days ($Pr_2Ru_2O_7$ and $Eu_2Ir_2O_7$), in air at 1473 K for 14 days (La_2MgPtO_6), or in sealed evacuated silica tubes at 1323 K for 2 days ($Bi_2Ru_2O_7$, $Yb_2Ru_2O_7$, $Dy_2Ru_2O_7$).

Catalyst testing was performed on a Labcon microreactor. 50 mg of catalyst was lightly packed in between silica wool in a 4 mm internal diameter silica tube, then placed in a close-fitting steel block which was heated to the desired temperature. The reactant gases (methane from Union Carbide, Gas and Equipment Ltd.; oxygen and nitrogen from Air Products) were supplied at measured, constant rates between 1 and 150 ml/minute. Feed and product gas analyses were performed using an Hewlett Packard 5980A g.c., fitted with Porapak Q and 5 Å molecular sieve columns, using helium carrier gas and a TCD calibrated *in situ*.

3. Results and discussion

Results obtained for the partial oxidation of methane by air ($CH_4/O_2 = 2$) at 1050 K over a range of supported metals and mixed metal oxides are presented in table 1. The most striking feature of these results is the remarkably high yield that can be obtained under these conditions. Also notable is the consistency of the conversions and selectivities over most of the catalysts, a finding that clearly indicates that equilibrium is being established in these cases. We have already suggested [10] that the active catalyst is the supported metal, and the latest results corroborate this view. Correspondingly, the only poor catalysts in table 1 are La_2MgPtO_6, which would be expected to reduce only slowly to Pt metal due to the kinetic inertness of low-spin Pt^{IV}, and $Bi_2Ru_2O_7$, which reduces preferentially to Bi metal rather than Ru.

It has previously been suggested [8] that the partial oxidation process involves a series of steps:

$$CH_4 + 2O_2 – CO_2 + 2H_2O \tag{3}$$

$$CH_4 + H_2O – CO + 3H_2 \tag{4}$$

$$CO_2 + H_2 – CO + H_2O \tag{5}$$

$$CH_4 + CO_2 – 2CO + 2H_2 \tag{6}$$

Our findings are consistent with this view, at least to the extent that our active catalysts comprise those metals that are known to catalyse all of these reactions.

The influence of the CH_4/O_2 ratio of the feedstock on the partial oxidation reaction (table 2) is also consistent with the achievement of chemical equilibrium according to eqs. (3)–(6). Lean mixtures give enhanced methane conversion with

Table 1
Showing that a number of different supported metals and mixed metal oxides are efficient catalysts for the partial oxidation reaction. Gas feed, $CH_4:O_2:N_2 = 2:1:4$. GHSV $= 4 \times 10^4$ hour^{-1}. Temp = 1050 K.

Catalyst	% methane converted	% CH_4 converted to	
		CO	H_2
1% Ru/Al_2O_3	94	97	99
1% Rh/Al_2O_3	94	97	99
1% Pd/Al_2O_3	93	96	98
1% Pt/Al_2O_3	95	96	99
Ni/Al_2O_3*	94	97	99
$Pr_2Ru_2O_7$	94	97	99
$Eu_2Ir_2O_7$	94	96	98
La_2MgPtO_6	80	89	93
$Bi_2Ru_2O_7$ **	4	0	0

* CRG 'F' steam reforming catalyst, ex. British Gas.
** Only CO_2 (74%), C_2H_6 (21%) and C_2H_4 (5%) detected.

Table 2
Showing how the methane conversion and selectivity to partial oxidation products vary with methane:oxygen ratio. Gas feed contains approx. 57% N_2 diluent. GHSV = 4×10^4 hour^{-1}. Temp = 1050 K. Catalyst = $Pr_2Ru_2O_7$.

CH_4/O_2 ratio	% methane converted	% CH_4 converted to	
		CO	H_2
1.72	98	91	96
1.86	96	93	98
1.96	95	96	98
2.00	94	97	99
2.06	93	97	99
2.10	91	97	100
2.15	90	98	100

Table 3
Showing how the methane conversion and selectivity to partial oxidation products vary with reaction pressure. No N_2 diluent. GHSV = 4×10^4 hour^{-1}. Temp = 1050 K. Catalyst = $Dy_2Ru_2O_7$

Pressure (atm.)	CH_4/O_2 ratio	% methane converted	% CH_4 converted to	
			CO	H_2
1	3.4	56	99	100
5	3.8	39	91	91
10	4.1	38	90	90
15	4.5	33	86	88
20	4.5	30	85	88

Table 4
Showing how the methane conversion and selectivity to partial oxidation products vary with reaction temperature. Gas feed, $CH_4:O_2:N_2 = 2:1:0$. GHSV = 4×10^4 hour^{-1}. Catalyst = $Yb_2Ru_2O_7$

Temperature (K)	% methane converted	% CH_4 converted to	
		CO	H_2
1050	83	91	95
900	53	59	79
800	39	28	59
700	31	8	33
650	29	5	25

a higher proportion of combustion products whereas rich mixtures give better selectivity to synthesis gas with poorer methane conversions. The 2 : 1 stoichiometric ratio appears to give the optimum yields.

Table 5
Showing how the methane conversion and selectivity to partial oxidation products vary with reactant gas space velocity. Gas feed, $CH_4:O_2:N_2 = 2:1:0$. Temp = 1050 K. Catalyst = $Pr_2Ru_2O_7$

GHSY (hour^{-1})	% methane converted	% CH_4 converted to	
		CO	H_2
6×10^3	90	95	98
4×10^4	88	93	97
6×10^4	81	89	94
8×10^4	73	82	90
2×10^5	68	76	87

Measurements as a function of pressure (table 3) and temperature (table 4) demonstrate, as expected for the entropically favourable partial oxidation process, that both the methane conversion and the selectivity to synthesis gas are supressed at higher pressures and lower temperatures. For example, the reaction gives better yields in air than in oxygen (compare table 1, line 1, with table 4, line 1). Essentially, therefore, the use of the partial oxidation reaction at, say, 1050 K is an attractive route to synthesis gas only at pressures in the vicinity of 1 atmosphere; at higher pressures, the high selectivity must be retrieved by operating at higher temperatures, as in the existing industrial processes [7]. The need to use elevated pressures may stem from a desire to match the synthesis gas generation to a downstream process that requires high pressures, for example methanol synthesis, or it may arise from a need to maximise the product output. In the latter context, however, it should be noted that the space velocity of our low pressure, low temperature route is as high as 4×10^4 hr^{-1} with air as the oxidant (table 1), and in excess of 10^3 hr^{-1} in oxygen (table 5).

4. Conclusions

We have shown that the partial oxidation of methane to synthesis gas can be carried out with yields in excess of 90% at pressures of approximately 1 atmosphere and temperatures close to 1050 K. The yield of hydrogen is particularly good (91–94%) when air is used as the oxidant. Partial oxidation is more selective than conventional steam reforming, but it requires an oxygen plant if aerial oxidation is impracticable. In comparison with the existing high temperature partial oxidation processes, the low temperature route would involve considerably less capital outlay but cannot be operated efficiently at high pressures. At the present stage, a detailed process engineering study is required in order to ascertain whether it could usefully be employed in methanol or ammonia synthesis, or, for example, to provide hydrogen for a high temperature fuel cell.

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