PARTIAL OXIDATION OF METHANE TO SYNGAS IN DIFFERENT REACTOR TYPES.

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INTRODUCTION

Most of the reported work on catalytic partial oxidation (CPO) of methane to syngas has concentrated on catalyst development and testing in fixed bed reactors at atmospheric pressure (1). Very few workers have investigated CPO in fluidised bed reactors (2-4) or at elevated pressures (5,6). All results reported for high pressure experiments were obtained either with diluted (with excess steam or inert gas) or non-stoichiometric (low oxygen) feeds and are therefore not indicative of the performance under conditions required for a commercial plant. In this paper we report the results obtained in fixed and fluidised bed reactors at atmospheric and elevated pressures with a methane to oxygen ratio of 2. These results are discussed in the context of further development of the CPO process.

EXPERIMENTAL

The catalyst tested in this work was 0.25%Rh/5%ZnO/γ-Al_2O_3. The experiments were carried out using three reactors made of silica : fixed bed and fluidised bed, the latter type configured either in the conventional way with porous distribution plate or as a spouted reactor (Fig 1). The design of the spouted reactor was such that methane and oxygen were mixed immediately before entering the catalyst bed. The spouted reactor was designed specifically for experiments at high pressures where short mixing times were important to limit the contribution of non-catalytic gas phase reactions between methane and oxygen.

Typical experimental procedure was as follows. Prior to each experiment the catalyst was reduced in flowing hydrogen (CIG, >99%, 500 mL/min) at 500°C for 3 hrs and cooled to ambient temperature. Flows of methane (Matheson, >99%) and oxygen (CIG, 99.99%) into the reactor were adjusted to the desired level using mass flow controllers (Brooks 5850TR), keeping CH_4/O_2 ratio = 2. The reactor temperature was raised slowly until the reaction was initiated (300 - 500°C) and then stabilised at constant level. After the reaction reached steady state, the products were analysed several times under each set of conditions.

RESULTS AND DISCUSSION

The performance of the rhodium catalyst at different space velocities in the fixed bed reactor is shown in Figure 1. At temperature of 900°C methane conversion and syngas selectivity are close to equilibrium and do not vary with contact time. At 800°C the departure from this pattern becomes noticeable and both the conversion and the selectivity increases with decreasing contact time. This trend becomes even more pronounced at 700°C. At gas flows above 300 L/H/g it was impossible to maintain the reaction temperature at 700°C even after removal of the external heater. In some cases temperature differences across the catalyst bed exceeded 150°C.

This example is a good illustration of the autothermal character of the partial oxidation reaction. It also points to the major disadvantage of the fixed bed reactor, namely the heat transfer limitation leading to the formation of the " hot spot" in the upper zone of the catalyst bed. Even at lowest gas flows used overheating of the top layers of catalyst was noticeable.

Entirely different behavior was observed in fluidised bed reactor. Even though the range of space velocities feasible in this type of reactor was restricted by the terminal velocity, some valid conclusions can be drawn from the comparison.

First, methane conversions are generally lower compared with fixed bed reactor. This is most likely the result of much better heat dissipation within the catalyst bed. The highest observed temperature differences between the top an the bottom of the reactor were 40°C and in most cases fell below 20°C despite the fact that the diameter of the fluidised bed reactor was almost three times larger than the fixed bed reactor.

Second, both methane conversions and carbon monoxide selectivities tend to decrease with increasing gas flows indicating the lack of autothermal effect. Similar pattern was observed for hydrogen selectivities, except that they tend to increase at space velocities below 30 L/h/g before declining at higher gas flows. This effect is probably caused by secondary reactions (*i.e.* combustion of hydrogen) at longer contact times.

The greater thermal stability of a fluidised bed reactor makes it more suitable for carrying out the partial oxidation reaction on a larger scale. It also seems that the activity of the catalyst is not an important factor within the temperature range >900°C needed to achieve high methane conversions required by commercial application, since equilibrium is reached easily under wide range of conditions. This is well illustrated by the results shown in Figure 4. They show that variation in catalyst loading from 12g to 3g has no significant effect on performance.

It appears that apart from efficient handling of heat transfer the greatest challenge in practical implementation of partial oxidation as an alternative technology for syngas production will be successful

and safe operation of the reactor at elevated pressures. The requirement for the use of high pressure is driven mostly by economic factors. Operation at high pressure allows the use of a smaller reactor and reduces demand for syngas compression for downstream processes.

There are two major problems that arise when the reactor pressure increases. First, as pressure exceeds about 0.2 MPa, the mixture of CH_4/O_2 at ratio of 2 becomes explosive. Second, the rates of non-catalytic homogeneous gas phase reactions between methane and oxygen leading to the formation of a wide range of products (methanol, formaldehyde, light hydrocarbons, carbon monoxide) increase quickly making it difficult to preheat the reactor feed.

One possible solution to these problems is to preheat methane and oxygen separately and to mix them immediately before introduction into the catalyst bed. To achieve this, a spouted reactor equipped with low residence time mixer (approx. 0.1 ms) was built (C, Figure 1). Ambient pressure tests have shown that its performance was identical to the conventional fluidised bed reactor. The results of high pressure operation of this reactor are presented in Figure 5. They show very minor drop in performance up to 0.6 MPa pressure. Several attempts to increase the pressure beyond 0.6 MPa were unsuccessful. They led to thermal instability indicated by temperature oscillations and resulted in damage to the reactor vessel in the region where methane and oxygen were mixed.

These results clearly indicate that further research aimed at development of a commercially viable partial oxidation process will have to concentrate on the reactor design to overcome problems associated with spontaneous ignition of the feed. Possible solutions may include multi-point oxygen injection, addition of steam to control the reaction exothermicity or the use of several reactors with heat recovery between stages.

CONCLUSIONS

The above results lead to the following conclusions :

1. Superior heat dissipation characteristics of fluidised bed reactors renders them most suitable for the partial oxidation reaction.

2. Further research should be aimed at overcoming problems associated with efficient heat removal from the reaction zone and elimination of autoignition of methane - oxygen mixtures.

ACKNOWLEDGMENT

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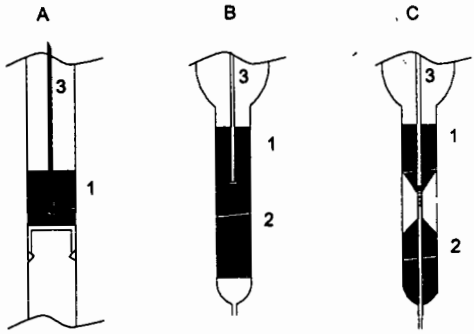

Figure 1. Design of the fixed bed (A, i.d. 10 mm), fluidised bed (B, i.d. 30 mm) and spouted (C, i.d. 30 mm) reactors. Catalyst (1), preheater (2), thermocouple well (3). All reactors made of silica.

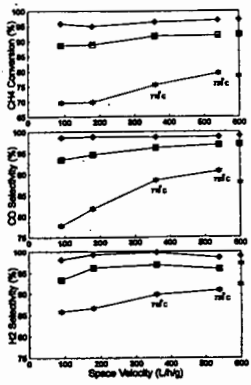

Figure 2. Space velocity vs. temperature profiles for the fixed bed reactor. (◆) 700°C, (■) 800°C, (✱) 900°C. Catalyst loading 0.25g, particle size +125-250 µm. Symbols on right axis indicate thermodynamic equilibrium.

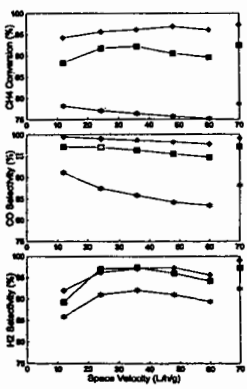

Figure 3. Space velocity vs. temperature profiles for the fluidised bed reactor. (◆) 700°C, (■) 800°C, (✱) 900°C. Catalyst loading 3.0g, particle size +180-250 µm. Symbols on right axis indicate thermodynamic equilibrium.

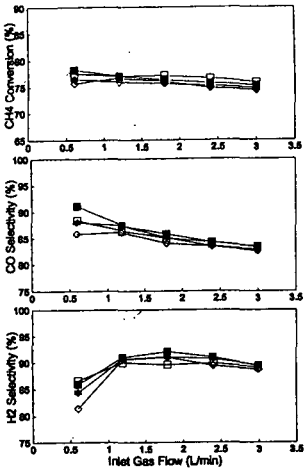

Figure 4. Effect of catalyst loading on performance in fluidised bed reactor at 700°C. (( ) 1.5g, (■) 3.0g, (✱) 6.0g, (□) 12.0g.

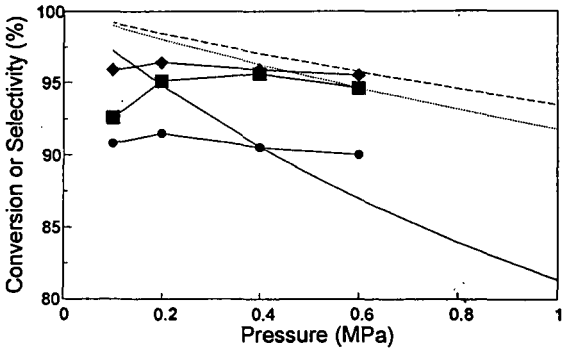

Figure 5. Performance of spouted reactor at high pressure at 900°C. Catalyst loading 3.0g, particle size +250-500 µm. (●) CH_4 conversion, (◆) CO and (■) H_2 selectivity observed.
(____) CH_4 conversion, (_ _ _) CO and (.....) H_2 selectivity predicted at equilibrium.