The effect of fixed-bed reactor configuration on the oxidative coupling of methane over a Li/Pb/Ca catalyst

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Introduction of additional O_2 at the midpoint of the catalyst bed of a methane oxidative coupling, fixed bed reactor, increases the C_2 STY more than the CO_x STY over a Li/Pb/Ca catalyst. This observation is not only a consequence of kinetics but may also be attributed to increased methyl radical generation on the O_2 replenished catalyst surface.

Keywords: Methane; oxidative coupling; catalyst; reactor configuration

1. Introduction

Oxidative coupling of methane to C_2 hydrocarbons is still considered an industrially viable alternative for the direct conversion of methane to more valuable products. Although many different catalyst formulations have been investigated for this reaction [1–9], an apparent maximum in the C_2 yield of approximately 25% exists [5] which precludes the process to be commercially feasible. It was suggested [5] that this limitation in the C_2 yield cannot be circumvented catalytically due to the fact that, at high temperatures, the coupling reaction is controlled mainly by homogeneous processes occurring in the gas phase [5]. These homogeneous processes will occur in both the free volume of the reactor and the void space within the catalyst and their extent will likely depend on the reactor configuration.

The highest C_2 yields (although not exceeding 25%) in a catalyzed, single pass process of oxidative coupling of methane are obtainable by increasing the

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methane conversion or the C_2 selectivity or both. However, the selectivity is the most important factor in the practical application of the coupling reaction. If the selectivity is high, a higher than 25% total C_2 yield may be achieved by recycling the reactants. There is merit, therefore, to strive for an optimal process carried out in a better designed reactor on known catalysts showing stability and longevity of performance.

The fact that the C_2 selectivity of the methane oxidative coupling reaction increases with increasing CH_4/O_2 feed gas ratio is well established [5,6,10]. At high ratios, however, O_2 is rapidly depleted and the reaction becomes oxygen limited. Maintaining a relatively high CH_4/O_2 ratio throughout the reactor without O_2 depletion is therefore desirable to improve the selectivity to higher hydrocarbons. Reactor simulation studies on methane oxidative coupling have predicted [11] that improvements in conversion and selectivity at the reactor exit can be obtained by modifying the way in which oxygen is fed to the reactor. Recently, it has been shown by Choudhary et al. [7] that several reactors operated in series with oxygen addition between the reactors, resulted in higher methane conversion and C_2 selectivity compared with the same total CH_4/O_2 feed without interstage oxygen addition. It was suggested that this improvement was a result of better distribution of oxygen throughout the La/MgO catalyst. However, at the conditions of the study, the gas flow through each reactor was altered with the change in oxygen distribution, and it is not clear what influence this changing gas flow had on the selectivities and conversions reported.

In the present paper, we report the beneficial effect of introducing additional O_2 within the typical fixed-bed reactor, at conditions such that the superficial gas velocity in all cases remains constant and gas flow effects are eliminated from the data comparison. A Li/Pb/Ca catalyst has been used in the investigation as a result of a prior catalyst screening study reported elsewhere [12]. This previous study compared the performance of Pb, Sn, Bi and Mn oxide catalysts, supported on MgO, CaO, Al_2O_3 and zeolites. Some of the catalysts were also promoted with alkali metals and La. The Li/Pb/Ca catalyst gave the highest yields of C_2 hydrocarbons compared to any of the other catalysts in this altogether "medium" performing (C_2 yield $< 17\%$) group of catalysts [10].

2. Experimental

Li/Pb/Ca CATALYST PREPARATION

The Li/Pb/Ca catalyst was prepared by adding dropwise an appropriate amount of $Pb(NO_3)_2$ to $Ca(OH)_2$ (Fisher, Certified). The Li promoter was added as LiOH to the resulting paste which was subsequently extruded, dried at 120°C for 2 h in air and calcined at 800°C for 1 hour. After cooling in a desiccator, the 1/16 inch extrudates were crushed and sieved to $-20/+40$

mesh particles. Air contact was minimized following calcination by rapid cooling in the desiccator and storing the sized material in an air tight container. This procedure limited the amount of $Ca(OH)_2$ and $CaCO_3$ formed by moisture and CO_2 contact with the CaO.

The resulting Li/Pb/Ca catalyst had a surface area of 0.6 m^2/g and a composition of $Li_2O:PbO:CaO = 6.7:17.1:76.4$ wt%.

REACTOR CONFIGURATION STUDIES

Fig. 1 shows the reactor used in the present work, consisting of a 3 mm diameter quartz dip-tube placed co-axially within a 1 cm diameter quartz reactor tube. The exit of the inner tube could be positioned anywhere within the reactor and two locations used in the present study are specified in fig. 1. The auxiliary gas was fed through the 3 mm diameter tube into the reactor, whereas the primary feed gas entered at the top of the 1 cm diameter tube. The exit of the reactor tapered to a diameter of 0.5 cm. The catalyst (approximately 3 g) was placed in the middle of the tube and held in position with two quartz wool plugs placed on either side of the catalyst. The catalyst bed length was about 40 mm. The reactor was placed in a tubular furnace with the catalyst bed located in the centre of the furnace. The reactor temperature was controlled using an ERO Electronics Model S48 temperature controller. A thermocouple placed in the middle of the catalyst bed was used as the measuring and controlling element.

Inert He was mixed with CH_4 and O_2 using 3 Matheson mass flow controllers. The He/CH_4 and He/O_2 mixtures were mixed in the appropriate ratio and fed to the primary feed port of the reactor. A He/O_2 mixture was also fed to the auxiliary feed port. The feed gas was diluted in He (nominally 90%) to avoid potential explosion hazards with concentrated CH_4/O_2 mixtures [13]. The product and unreacted feed gases from the reactor were fed to two gas chromatographs via a condenser held in an ice bath. Gas samples were injected into the chromatographs, one with a thermal conductivity detector (TCD) the other with a flame ionization detector (FID). Concentrations of carbon monoxide, CO_2 and O_2 were monitored using the TCD and the product hydrocarbons and CH_4 were determined using the FID. Product separation was achieved using a 3 m Carbosieve SII column for the TCD and a 2 m Poropak Q column for the FID.

The analytical procedures quantified the hydrocarbons, CO, CO_2 and O_2 present in the exit gas. The feed composition was also routinely determined while the feed flowrate was controlled by the mass-flow controllers and the exit flow was measured using a bubble meter. These measurements were utilized to calculate carbon balances that were better than 98% for all the experiments reported here. The oxygen conversion was always below 100%. The experiments were all performed at 700°C, 101 kPa with 3 g of Li/Pb/Ca catalyst. Analysis of a series of repeat experiments performed over a range of conditions showed the

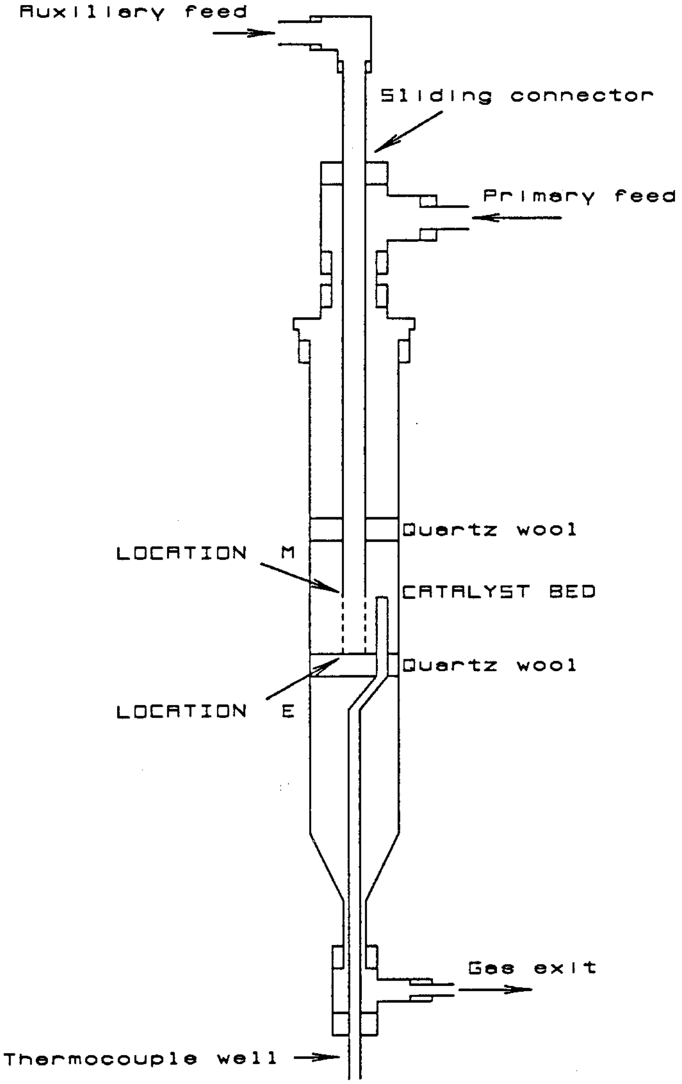

Fig. 1. Reactor configuration for auxiliary feed gas addition at the midpoint (location M) and the end (location E) of the catalyst bed.

repeatibility of the C_2 STY and the CO_x STY to be within 2% and 8% of the reported values, respectively.

The effect of reactor feed configuration was investigated by adding the auxiliary feed stream of O_2/He or He at the middle of the catalyst bed (Location M) and at the end of the catalyst bed (Location E), as illustrated in fig. 1. The auxiliary O_2/He addition experiments have been compared to the experiments where the O_2/He auxiliary stream was replaced by inert He at the same auxiliary feed gas flowrate. This ensures that the superficial gas velocity

Table 1
Effect of oxygen addition at the mid-point^M and at the end^E of the catalyst bed [a]

Auxiliary flow		Conversion		STY		$C_2^=/C_2$ ratio
Flow rate (mL/min)	O_2 content (%)	CH_4 (%)	O_2 (%)	CO_x (μmol g^{-1} s^{-1})	C_2	
50^M	–	29	74	0.270	0.096	0.8
50^M	6.7	37	42	0.336	0.136	1.2
50^E	–	34	88	0.321	0.113	1.2
50^E	6.7	34	50	0.319	0.119	1.2

[a] Primary flow = 50 mL/min (composition: CH_4 = 13%, O_2 = 6.7%, He = 80.3%).

through the catalyst bed is the same in the presence or absence of O_2 in the auxiliary feed stream.

3. Results and discussion

Table 1 shows that the addition of oxygen at the midpoint (see fig. 1) of the catalyst bed results in a 42% increase in the C_2 (ethane plus ethylene) space-time yield (STY) expressed in μmol · sec^{-1} · g^{-1} and a 24% increase in the STY of CO_x. Adding oxygen to the end of the catalyst bed causes an increase in C_2 STY of 5% whereas the CO_x STY remains unchanged within experimental error. Table 1 also shows that the ethylene/ethane ratio ($C_2^=/C_2$) increases when oxygen is added within the catalyst bed but is unchanged when oxygen is added at the end of the catalyst bed.

These results demonstrate that the C_2 STY can be significantly increased over the Li/Pb/Ca catalyst by auxiliary oxygen addition to the reactor. In particular, oxygen addition at the midpoint results in an increase in methane conversion with a slightly greater conversion of carbon to C_2 hydrocarbons than to carbon oxides, i.e., the methane conversion increases without loss of selectivity. In addition this reactor configuration increases the selectivity toward ethylene compared to ethane.

Under standard reactor conditions, the oxygen is depleted through the catalyst bed and O_2 conversion reaches 100% under some conditions. For the data presented here, however, the oxygen conversion was always below 100%. The increase in oxygen concentration that results from the auxiliary oxygen addition at the midpoint of the reactor would therefore be expected to affect the reaction rates. From kinetic data reported on oxidative coupling catalysts, particularly those based on Pb, the reaction order in oxygen is known to be greater for CO_x formation than for C_2 formation [5]. In addition, increasing oxygen partial pressure increases CH_4 conversion and reduces the C_2 selectivity on the Li/Pb/Ca catalyst [14]. Thus, increasing oxygen partial pressure should result in a greater increase in CO_x STY than in C_2 STY. The observed greater increase in C_2 STY than CO_x STY with oxygen addition at the midpoint is opposite to what one predicts from the known kinetics. Therefore, it is suggested that the added oxygen does not only affect the rates of reaction by simple increased reagent concentration effect but that the oxygen must interact with and modify the catalyst surface. The oxygen interaction with the catalyst surface may follow that proposed by Lunsford and co-workers [2] and result in an increase in the number of $[Li^+O^-]$ methyl radical generating sites. As a matter of fact it has been reported [15] that the active sites generated in the presence of gaseous oxygen, disappear upon its removal. These arguments suggest that our observation with the Li/Pb/Ca catalyst is not necessarily typical of other catalysts.

The above arguments are also consistent with the generally accepted reaction mechanism for oxidative coupling of methane in which CO_x and C_2 are produced from methyl radicals primarily by two parallel reactions [5]. The fact that upon oxygen addition the increase in carbon conversion to C_2 is only slightly greater than to CO_x supports the argument that the effect of the oxygen addition is primarily to increase the rate of methyl radical generation.

The results of the experiments with oxygen addition at the end of the catalyst bed suggest that the rate of gas phase processes that result in higher hydrocarbons increase with an increase in O_2 partial pressure whereas the CO_x forming reactions remain unchanged. Although the difference in STY with and without oxygen addition at the end is small, the difference is greater than the estimated experimental error in C_2 STY of 2%. Similar trends in STY changes have been observed [12] over a series of other Pb catalysts. One possible explanation for the small increase in C_2 STY can be made based on the fact that it has been shown that the Li/Pb/Ca catalyst loses Li during operation due to the volatility of Li_2CO_3 and LiOH [10]. Adding oxygen in the gas phase may promote catalytic reactions with these volatile compounds resulting in an increase C_2 STY. The possibility of some backmixing of the added oxygen to the catalyst bed and subsequent increase in reaction rate could also explain the small increase in C_2 STY observed.

The ethylene/ethane ratio also increased with oxygen addition within the catalyst bed whereas oxygen addition at the end of the catalyst bed did not affect this ratio. These observations are in agreement with the proposal that ethylene is produced primarily by catalytic oxidative dehydrogenation of ethane [5] and that the oxygen addition increases the rate of this reaction only within the catalyst bed.

The results presented here provide good evidence that the beneficial effect of oxygen distribution on the C_2 selectivity reported by Choudhary et al. [7] is mechanistically complex. A simple assumption that the avoidance of contact of the hydrocarbon products with high oxygen concentrations precludes their deep oxidation [11] does not seem to be sufficient to account for all effects.

4. Conclusions

A greater increase in the C_2 STY compared with CO_x STY can be achieved by addition of auxiliary oxygen within the oxidative coupling reactor and this effect is demonstrated for O_2 addition at the midpoint of the catalyst bed. The observed increase is not only a result of kinetics but is attributed to the catalyst's effectiveness as a methyl radical generator which is improved by distribution of the oxygen in the catalyst bed which increases the O_2 interaction with the catalyst surface.

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