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Oxidative Coupling of Methane Followed by Ethane Pyrolysis

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When mixtures of methane, ethane and oxygen are cofed over oxidative coupling of methane catalysts, oxygen is preferentially consumed for the oxidative dehydrogenation of ethane, resulting in low methane conversions and high carbon monoxide production. If, however, ethane is added to the post-oxidation zone of the reactor, methane conversion remains high and the calories generated from this exothermic reaction can be used for the endothermic pyrolysis of ethane to form ethylene plus hydrogen.

Although the oxidative coupling of methane (OCM) reaction over basic oxide catalysts has been shown to lead to the selective formation of ethane and ethylene,[1-4] it is poorly adapted for the conversion of mixtures of alkanes, such as would be found in natural gas. We have found that when mixtures of ethane, methane and oxygen are cofed over OCM catalysts, oxygen is preferentially consumed for the oxidative dehydrogenation of ethane to ethylene while leaving the methane largely untouched. If, however, the ethane is separated out of the reactant mixture, then added to the reactor after the selective oxidation of methane, the heat generated from the OCM reaction can be used to thermally covert ethane to ethylene plus hydrogen.[5,6]

The quartz reactor (effective cross sectional area = 1.04 cm^2) and assembly, shown in Figure 1, were used for the experiments. The reactant gases (either CH_4/O_2 or $CH_4/O_2/C_2H_6$ mixtures) were introduced into the bottom of the reactor where they were preheated on quartz grains before being contacted with the fixed bed catalysts. The small quartz side arm, located between the two tubular furnaces, was used to inject ethane into the product stream immediately after the oxidation step,(exp. **4**).

The results shown in Table 1 were obtained at fixed methane and oxygen flow rates of 1000 and 99 cm^3/min (STP) respectively. The temperature of the lower tubular furnace was adjusted to maintain a catalyst bed hot spot temperature of 880 °C. Maintaining an elevated bed temperature (>850 °C) and high space velocity (>0.45 m/s) are essential in order to limit backmixing of the products with the reactants and to assure an elevated and rapid oxygen conversion.[7]

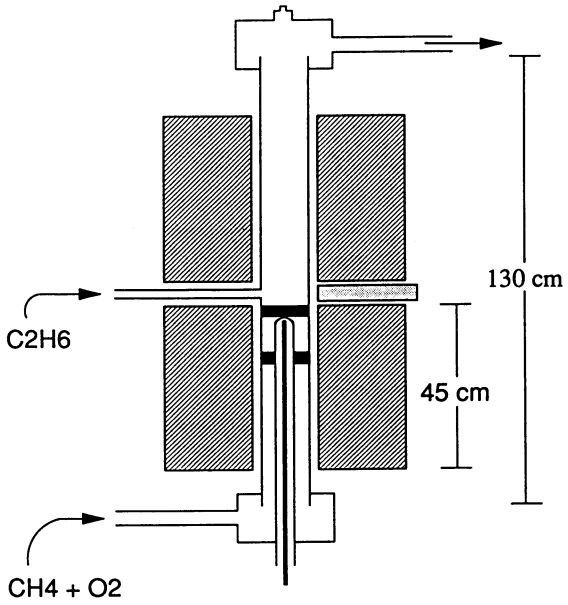

Fig. 1. The reactor assembly used for the OCM and Oxypyrolysis experiments was composed of: a tubular quartz reactor (length = 130 cm, internal diameter = 13 mm); a thermocouple well (outer diameter = 6 mm); two tubular furnaces (length = 45 cm), hatched region; two quartz wool plugs, black rectangles; thermal insulation material (between tubular furnaces), dotted region. The lower part of the reactor (below the quartz wool plugs) was filled with quartz grains, not shown. Methane and oxygen (and ethane, experiment **3**) were added into the bottom of the reactor. Ethane (experiment **4**) was added after the catalyst bed.

Chromatographic analyses of the effluent streams were performed using a 2m carbosphere column (80-100 mesh) with a micro TCD using either helium or argon (hydrogen analysis) carrier gas.

The results for the OCM experiment **1** are among the best reported to date: 80.8% C_2+ selectivity, 15.8% methane conversion, >99% oxygen conversion. The ethylene to ethane ratio can be increased by heating the second zone of the reactor (exp. **2**). Note that the reactor used in this experiment is not insulated and therefore substantial heat loss occurs through the reactor walls. The net effect of heating the second zone is to simulate the effect of an adiabatic reactor, and thus use the calories produced in the oxidation step to thermally convert ethane to ethylene and hydrogen. The conversion of methane is somewhat lower due to the regeneration of methane via the thermal cracking of ethane as described by the Rice mechanism.[8] It is worthwhile to note that the rates of production of the carbon oxides (experimental) and water (calculated) remain unchanged.

If we employ the same conditions used in the above oxidative coupling/pyrolysis experiment to a gas mixture of methane and oxygen containing 100 cm^3/min of ethane, the methane conversion decreases (+9.5 % CH_4 flow rate with respect to exp. **2**) and the carbon oxides production increases(+129 % CO and

Table 1. Product Flow Rates and Other Data for Oxidative Coupling and Oxypyrolysis Experiments[a)]

EXPERIMENT	1	2	3	4
Temperature of 2nd furnace (^{0}C)	20	850	850	850
Flow rate in (mol/h)				
CH_4	2.500	2.500	2.500	2.500
C_2H_6	0	0	0.250[b)]	0.250[c)]
O_2	0.248	0.248	0.248	0.248
Flow rate out (mol/h)				
H_2	0.064	0.124	0.222	0.303
O_2	0.001	0.001	0.002	0.001
CO	0.016	0.017	0.039	0.018
CO_2	0.060	0.059	0.064	0.059
C_2H_4	0.066	0.105	0.204	0.267
C_2H_6	0.082	0.036	0.067	0.094
C_3H_6	0.004	0.008	0.012	0.011
C_3H_8	0.004	0	0	0
CH_4[d)]	2.104	2.118	2.319	2.168
H_2O[e)]	0.358	0.359	0.325	0.358
CH_4 conversion (%)	15.8	15.3	7.2	13.3
O_2 conversion (%)	99.6	99.6	99.2	99.6
C_2H_6 conversion (%)[f)]	-	-	-[g)]	76.8
C_2H_4/C_2H_6	0.8	2.9	3.0	2.8

a) The catalyst bed hot point temperature was 880^{0}C for all experiments. The catalyst bed was composed of 300 mg of a mechanical mixture of $SrCO_3$ and $La_2O_2CO_3$ (La/Sr = 2) diluted with 3 ml of tabular alumina grains, (ref. 5a). b) Ethane added with methane and oxygen. c) Ethane added to the reactor after the catalyst bed. d) Methane flow rate out is calculated based on the sum of the carbon containing product gases. e) The quantity of water was calculated assuming that no other oxygen containing species were present in the effluent. f) The ethane conversion was calculated assuming that the differences in the results between experiments 2 and 4 were due to ethane (i.e. the increase in the CH_4 flow rate out is due to ethane pyrolysis). g) The ethane conversion cannot be directly calculated.

+8.5 % CO_2). The lower conversion of methane is understandable given that C-C bond dissociation energy of ethane is substantially lower than the C-H bond dissociation energy of methane. The high temperatures used in this study, although advantageous for the oxidative coupling of pure methane, probably lead to the thermal pyrolysis of ethane to methyl, ethyl and hydrogen radicals in the preheat zone before the catalyst bed. The significantly higher CO production is therefore due to homogeneous gas phase oxidation of the hydrocarbon radicals.

Experiment 4 is similar to the previous experiment with the exception that the ethane is injected **after** the catalyst bed (i.e. after the oxygen has already been consumed). The oxygen conversion and the CO and CO_2 flow rates were found to be virtually identical to those in experiment 2, while the rate of production of hydrogen was over 36 % higher than that in experiment 3. Although the overall methane conversion has dropped from 15.3 % (exp. 2) to 13.3 % (exp. 4), 76.8 % of the injected ethane has been converted, with over 85 % selectivity, to ethylene and propylene.

The selective oxidation of methane followed by the thermal pyrolysis of the OCM product stream and added ethane (oxypyrolysis) enables: 1) the oxygen to be used for the coupling of the methane and 2) part of the heat of reaction to be used for the thermal conversion of ethane to ethylene and hydrogen. If this hydrogen could eventually be used to hydrogenate some of the carbon oxides produced from non-selective oxidation (all of the CO and some of the CO_2), the overall selectivity of the oxypyrolysis reaction could conceivably surpass 90 %.

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