Steady-state conversion of methane to C_{4+} aliphatic products in high yields using an integrated recycle reactor system

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Conversion of methane in high yields to C_{4+} nonaromatic hydrocarbons was demonstrated in a recycle system. The principal components of the recycle system included an oxidative coupling reactor with a $Mn/Na_2WO_4/SiO_2$ catalyst at 800 °C for conversion of methane to ethylene, and a reactor with an H-ZSM-5 zeolite at 275 °C for subsequent conversion of ethylene to higher hydrocarbons. Total yields of C_{4+} products were in the range of 60–80%, and yields of C_{4+} nonaromatic hydrocarbons were in the range of 50–60%.

Keywords: methane, oxidation, aliphatic hydrocarbons, zeolite, recycle reactor

1. Introduction

Several recent studies have demonstrated that product yields approaching 70% may be achieved during the oxidative coupling of methane (OCM) by employing a recycle reactor with continuous removal of ethylene [1–4]. The ethylene may either be directly separated from the recycle stream or it may be converted to another product, which is subsequently separated. As an example of the former, we have used Ag^+ ions to facilitate the transport of ethylene and a small amount of propylene through a membrane contactor. The olefins were recovered in nearly pure form by heating the aqueous silver–olefin complexes to 100 °C. As an example of the second alternative, the ethylene was converted to aromatics (mainly benzene and toluene) over a Ga/H-ZSM-5 zeolite. The aromatics were separated from the recycle stream by cryogenic means.

In both of these cases, chemicals rather than fuels were produced. But for utilization of methane in large remote gas fields, one would like to form a liquid transportation fuel that has a minimal amount of aromatics. To achieve this objective, the operating conditions were modified. The results described here show that high yields of hydrocarbons in the C_{4+} range can indeed be attained.

2. Experimental

2.1. Catalysts

For the OCM reaction, a Mn(2 wt%)/Na_2WO_4(5 wt%)/SiO_2 catalyst was used. The preparation of the catalyst was described in detail earlier [6]. From 400 to 600 mg of this material with 20–40 mesh size was placed in an alumina reactor with an ID of 6 mm. The temperature of the OCM reactor during the experiments was kept at 800 °C.

Ethylene conversion to higher hydrocarbons was carried out in a Pyrex reactor with an ID of 25 mm. Six grams of Mobil H-ZSM-5 zeolite (MZ-1224, Si/Al ratio = 28.5) was used for ethylene oligomerization. The temperature of the reactor was 275 °C. The zeolite gradually deactivated, and after 8 h, the conversion of ethylene from the OCM reactor was 90%. Following deactivation to this level, the zeolite was regenerated in flowing oxygen for 3 h at 450 °C, which completely restored the activity of the catalyst.

2.2. Analysis

Analysis of the products of the reaction was carried out by GC using two types of columns. The C_1–C_4 hydrocarbons were determined with a Hayesep D column, and the higher carbon number aliphatic and aromatic products were analyzed with a 10% 1,2,3-tris(2-cyanoethoxy)propane (TCEP) on 100/120 Chromosorb column. Thus, the complete product distribution was obtained, including high- and low-boiling compounds, as well as the selectivities for nonaromatic products.

2.3. Reactor system

The recycle system utilized in this study is depicted schematically in figure 1. It consisted of two sequential reactors, a metal bellows pump for gas recycle, inlets for continuous admission of CH_4 and O_2 reactants, sampling ports and traps for certain products of the reaction. The recycle and oxygen flow rates were controlled and maintained at a constant value by mass flow controllers. The rate of methane entering the system was controlled by a pressure regulator; i.e., the methane was added at a rate necessary to maintain a constant pressure. At a constant total pressure in the recycle system, the flow of methane was equal to the rate of methane conversion.

Several in-line traps were used to remove various reaction products. A trap at 0 °C, located downstream from the OCM reactor, decreased the water partial pressure to

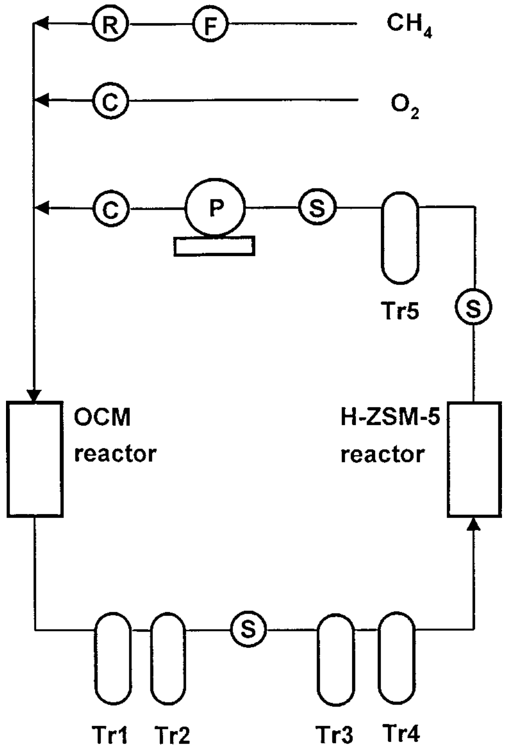

Figure 1. Schematic diagram of an integrated recycle system. C – flow controller, F – flowmeter, P – gas recycle pump, R – pressure regulator, S – gas sampling port, Tr1 – H_2O removal trap, Tr2 – CO_2 removal trap, Tr3 – silica trap, Tr4 – ethanol/dry ice trap (−72 °C), Tr5 – hexane slush trap (−94 °C).

2.4 Torr. A second trap containing KOH at room temperature continuously removed the CO_2 byproduct. A third trap containing silica gel, followed by one at −72 °C (ethanol/CO_2 slush), removed minor byproducts of the OCM reaction. The concentration of these products was below detection limits, but they affected the stability of the zeolite catalyst. Without these traps, the conversion of ethylene over the H-ZSM-5 zeolite decreased to less than 90% within 4 h. With the traps in place, however, the conversion of ethylene remained greater than 90% for up to 10 h. A fifth trap, maintained at −94 °C by hexane slush, located downstream from the H-ZSM-5 catalyst to condense C_{4+} hydrocarbons. The effectiveness for removal of C_{4+} products depended on the recycle flow rate and the overall condensation rate. In the experiments reported here, the efficiency for C_{4+} removal ranged from 45 to 75%.

3. Results and discussion

The conversions and selectivities obtained over the $Mn/Na_2WO_4/SiO_2$ OCM catalyst in a single-pass reactor have been described in detail in previous reports [3,5,6]. The reaction involves the formation of methyl radicals, which couple in the gas phase over the catalyst to produce ethane. The ethane is oxidatively dehydrogenated to yield ethylene [7]. In the single-pass (non-recycle) mode, a CH_4 conversion level of 20% and a C_{2+} product selectivity of 80% can be attained for periods up to 100 h when the reaction is carried out at 800 °C with a CH_4/O_2 ratio of 7.4. This conversion and selectivity corresponds to a C_{2+} yield of 16%. The ethylene-to-ethane ratio is 1.3.

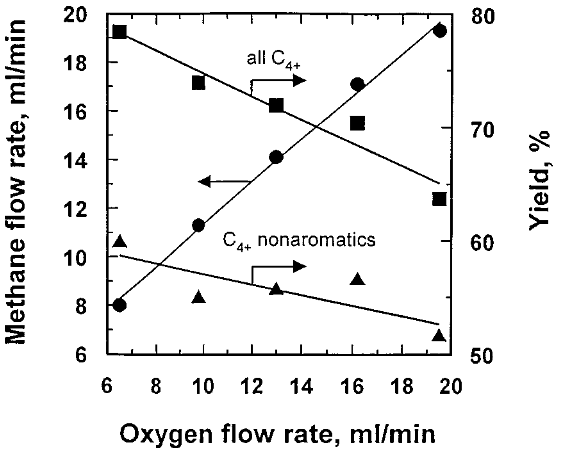

Figure 2. Effect of oxygen flow rate on methane reaction rate (methane flow rate) and yield of products at a total recycle rate of 116 ml/min.

The oligomerization of olefins at moderate temperatures over an acidic ZSM-5 zeolite is a well known reaction that forms the basis for the Mobil olefin to gasoline and distillates (MOGD) process [8]. Among several H-ZSM-5 zeolites provided by different suppliers, the Mobil catalyst gave the best combined activity and selectivity for ethylene oligomerization to higher molecular weight aliphatic products. Using a model mixture of 3.3% ethylene in nitrogen, optimum conditions were determined for the production of C_{4+} aliphatics. In a temperature range of 271–279 °C, the conversion was 85–88% with a maximum selectivity of approximately 86% towards nonaromatic hydrocarbons. At higher temperatures, aromatics are favored. As noted earlier, the partially deactivated catalyst was also easily regenerated by treatment in O_2 at 450 °C.

Two types of experiments were conducted in the recycle system. While keeping the temperature of the OCM catalyst at 800 °C and the zeolite catalyst at 275 °C, the effects of varying the oxygen concentration and recycle rate were studied. The results obtained by varying the oxygen inlet flow rate at a fixed recycle rate of 116 ml/min are given in figure 2 and table 1. The overall effect is that the methane conversion rate, which is equivalent to the methane flow rate, increases, but the yield of condensed hydrocarbons, including nonaromatics, decreases. The decrease in the yield of desired products results from the fact that more methane was converted to CO_2 as the oxygen concentration increased. Since all oxygen was consumed in the OCM reactor, it did not influence the ratio of nonaromatics to aromatics formed in the second reactor. The rates at which CH_4 was converted to CO_2 and to the desired hydrocarbons are given in table 1. Among the C_4 products, the ratio of isobutane : n-butane : 1-butene + 1,3-butadiene was approximately $1:0.59:0.26$. The aromatic portion was mainly composed of toluene, xylenes and C_{10} aromatic compounds, with only trace amounts of benzene.

Table 1
Effect of oxygen flow rate.[a]

O_2 rate[b]	CH_4 rate (ml/min) to										C_{4+} nonarom./arom.
(ml/min)	CO_2	C_4	C_5	C_6[c]	C_{7+}[c]	Benz.	Tol.	Xyl.	C_{10} arom.	Total arom.	selectivity ratio
6.5	1.73	1.61	1.45	0.78	0.90	0.04	0.35	0.45	0.63	1.39	3.2
9.8	2.95	2.29	2.07	1.11	0.72	0.04	0.36	0.60	1.02	2.15	2.9
13.0	3.97	2.91	2.65	0.96	1.31	0.03	0.43	0.67	1.07	2.30	3.4
16.2	5.04	3.92	3.34	1.80	0.59	0.04	0.41	0.67	1.06	2.36	4.1
19.5	7.01	3.98	3.41	1.75	0.79	0.04	0.38	0.65	1.12	2.37	4.2

[a] Recycle rate – 116 ml/min, 0.69 g of $Mn/Na_2WO_4/SiO_2$ at 800 °C, 6 g of H-ZSM-5 at 275 °C.
[b] 1 ml/min (STP) corresponds to 44.6 μmol/min.
[c] Nonaromatic C_6 and C_{7+}.

Table 2
Effect of recycle rate.[a]

Recycle rate	CH_4 rate[b] (ml/min) to										C_{4+} nonarom./arom.
(ml/min)	CO_2	C_4	C_5	C_6[c]	C_{7+}[c]	Benz.	Tol.	Xyl.	C_{10} arom.	Total arom.	selectivity ratio
58	4.14	2.86	1.63	1.02	0.79	0.06	0.54	0.53	0.75	2.05	3.1
87	4.08	2.82	2.45	1.46	0.63	0.03	0.40	0.62	1.06	2.31	3.2
116	3.97	2.91	2.65	0.96	1.31	0.03	0.43	0.67	1.07	2.30	3.4
145	3.73	2.16	2.61	1.30	1.79	0.04	0.37	0.64	1.06	2.21	3.6

[a] O_2 flow rate – 13.0 ml/min, 0.69 g of $Mn/Na_2WO_4/SiO_2$ at 800 °C, 6 g of H-ZSM-5 at 275 °C.
[b] 1 ml/min (STP) corresponds to 44.6 μmol/min.
[c] Nonaromatic C_6 and C_{7+}.

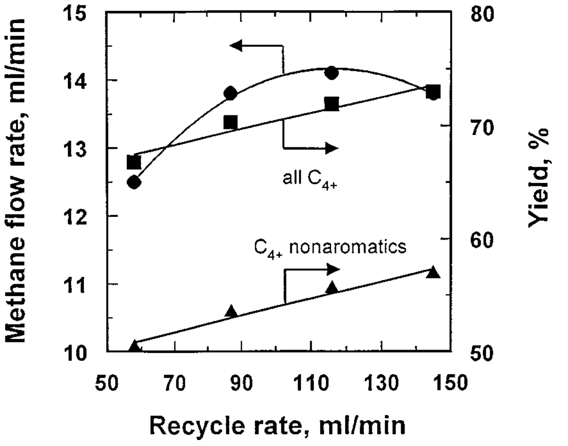

Figure 3. Effect of recycle rate on methane reaction rate (methane flow rate) and yield of products at an O_2 flow rate of 13.0 ml/min.

The most significant result shown in figure 2 is that C_{4+} nonaromatic yields approaching 60% and total C_{4+} yields approaching 80% can be achieved with the recycle reactor. These yields should be compared with an ethylene yield of about 8% in the single-pass reactor over the same catalyst. The ethylene yield may be improved somewhat by using a second dehydrogenation catalyst, but it never reaches more than about 14%.

The effect of the recycle rate on system performance is shown in figure 3 and in table 2. It appears that the methane conversion rate reaches a maximum at a recycle rate of ca. 120 ml/min, which corresponds to a recycle ratio of 8.6. The occurrence of a maximum may be related to the fact that an increase in the recycle rate influenced very significantly the condensation efficiency of the light hydrocarbons, especially the C_4 products, as can be seen from table 2. Untrapped hydrocarbons are returned to the OCM reactor where they consume O_2 as they are dehydrogenated or converted to CO_2. As a result, the consumption of methane decreases since O_2 is the limiting reagent. Although part of the C_4 hydrocarbons and all of the unreacted C_2 and C_3 hydrocarbons were recycled through the OCM catalyst, the yields of C_{4+} hydrocarbons continue to increase with increasing recycle rate. This observation implies that the selectivity for the oxidative dehydrogenation of paraffins to olefins, particularly the selectivity for ethylene formation from ethane, is very high over the OCM catalyst. Li et al. [9] have shown that $Mn/Na_2WO_4/SiO_2$ is indeed a very effective catalyst for the oxidative dehydrogenation of ethane. As shown in table 2, the ratios of nonaromatics to aromatics were within the same range as those observed when the oxygen inlet flow was varied (table 1).

4. Conclusions

The results presented here demonstrate that a recycle system may be successfully utilized for the production of nonaromatic hydrocarbons in the C_{4+} range. The data show that 100% methane conversion may be achieved with up to 60% C_{4+} nonaromatic product yield. Application of a more suitable condenser could improve the removal of light hydrocarbons from the stream, and, as a result, the productivity should increase. Furthermore, with a more effective condensing system, one could think about increasing the productivity by increasing the loading of the catalysts. Alternatively, by significantly increasing the pressure of the system, the molar conversion should increase and the partial pressures of the products should increase. This would greatly facilitate separation processes. In principle, the system could be scaled up to produce gasoline range products from methane (natural gas) in remote locations.

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