Steady-state conversion of methane to aromatics in high yields using an integrated recycle reaction system

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Methane can be converted in high yields to aromatic products using an integrated recycle system containing both an oxidative coupling (OCM) reactor at 800°C, for conversion of CH_4 to C_2H_4, and a secondary reactor containing Ga/ZSM-5 at 520°C for subsequent conversion of ethylene to aromatics. Using this system, aromatic product yields of $> 70\%$ at CH_4 conversions of $\sim 100\%$, based on total CH_4 added, can be obtained.

Keywords: methane, oxidation, aromatics, Ga/ZSM-5, recycle reactor

1. Introduction

Although the oxidative coupling of methane (OCM) is one of the more promising methods for the conversion of methane to useful chemicals and fuels, the conversions and selectivities obtainable are such that C_2 (ethane + ethylene) yields are generally $< 25\%$, at least under steady-state conditions [1]. Moreover, after more than a decade of research on OCM catalysts and reactor designs, the empirical evidence suggests that this 25% C_2 yield may be a realistic upper limit [2], due, in part, to the fact that the C_{2+} products of the OCM reaction are themselves more reactive than is the CH_4 reactant. Thus, in order to achieve an economical process for the production of ethylene based on the OCM reaction, one must have an effective method for separating the olefinic products from dilute streams and for delivering the product in relatively pure form at a reasonable pressure.

Aris and co-workers, for example, developed a process for conducting the OCM reaction in a separative reactor system which simulated a countercurrent moving-bed chromatographic reactor [3]. Using this reaction system, the authors achieved a C_2 selectivity of 80% at a CH_4 conversion of 50%. Vayenas et al. utilized both a closed-loop recirculation-type reaction system, containing fixed initial amounts of CH_4 and O_2 [4], and a total recycle reactor, in which CH_4 and O_2 reactants were continuously added [5], and in which C_{2+} olefinic OCM products were continuously removed from the recirculating or recycle reaction streams by an in-line trap containing 5A molecular sieve at 30°C. The olefins were subsequently released by heating the trap to 400°C. Using this two-step technique, the authors obtained an ethylene yield of 85% in the recirculation reactor and of 50% at a CH_4 conversion of 76% in the recycle reactor. Hall and Myers have also employed a condensation/absorption technique to continuously remove C_{2+} and CO_2 products in a back-mixed batch reactor, and obtained a C_2 selectivity in excess of 80% at a CH_4 conversion of 80% [6]. Similarly, Mashocki has described a recycle-type reactor that contained an adsorbent for continuous removal of olefinic products, which were subsequently recovered by thermal treatment [7]. Using this system, he obtained a C_2 selectivity of 70% (consisting of 92% ethylene) at a total CH_4 conversion of 94%.

We have previously described an integrated system that can achieve high yields of ethylene from the OCM reaction, using a recycle reactor with continuous separation and removal of the olefinic products [8]. The system consisted of two principal components: (1) a recycling catalytic/thermal reaction system, in which methane is catalytically converted via oxidative coupling into ethane, and is subsequently dehydrogenated to ethylene, and (2) a separation system, in which ethylene is continuously removed from the circulating reactant/product gas stream by Ag^+-assisted transport across a polypropylene membrane. However, the overall rate of olefin production in such a system is inherently limited by the relatively low rate of transport of the desired products through the liquid-based Ag^+ complexation solution. As a result, despite C_2H_4 separation efficiencies approaching 90%, the absolute rate of olefin production is small in comparison to the total amount of recycle gas. At optimal overall operating conditions, the maximum rate of olefin ($C_2H_4 + C_3H_6$) production at a total CH_4 recycle rate of 100 ml/min, for example, is only ~5 ml/min [8].

Consequently, we have more recently begun investigating an alternative type of integrated system, in which the ethylene that is produced by the OCM/dehydrogenation/hydrogenation reactor sequence is continu-

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ously removed from the recycle stream by conversion in a subsequent sequential reactor into higher molecular weight products, preferably aromatics. In this modified system, the previously employed membrane contactor and Ag^+ solution recycling loop are replaced by a catalytic reactor and a cooled trap for continuous removal of condensible products. Such a system could be utilized at a remote natural gas-producing site, for example, to convert CH_4 into more economically transportable liquid products.

2. Experimental

2.1. Catalyst preparations

The catalyst used in the OCM reactor in this study was Mn(2 wt%)/Na_2WO_4(5 wt%)/SiO_2. This catalyst was selected because it is capable of achieving a sustained C_{2+} selectivity of 80% at a CH_4 conversion of 20%, with virtually no loss of activity after more than 30 h on stream. The preparation and characterization of this catalyst have been described in detail previously [9]. Briefly, the silica gel support (Davison, 57-08-5) was impregnated to incipient wetness at 85°C with aqueous solutions having appropriate concentrations of $Mn(NO_3)_2$ and Na_2WO_4. The resulting material was then dried for 8 h at 130°C, calcined in air for 8 h at 800°C, and finally crushed and sieved to 20/45 mesh granules.

The catalyst used in the ethylene conversion reactor was a 5 wt% Ga/HZSM-5, and was prepared by impregnating NH_4-ZSM-5 (PQ Corp., Si/Al = 25) with an aqueous solution containing an appropriate concentration of $Ga(NO_3)_3$. Following impregnation, the catalyst was dried for 10 h at 120°C, calcined in air for 5 h at 550°C, and crushed to 20/45 mesh granules. A detailed kinetic and spectroscopic characterization of a series of Ga/ZSM-5 catalysts will be provided in a forthcoming communication [10].

2.2. Reactor system

The recycle reaction system utilized in this study is depicted schematically in figure 1. The system consisted of four separate sequential reactors, a metal bellows pump for gas recycle, inlets for continuous admission of CH_4 and O_2 reactants, as well as appropriate regulators, mass flow controllers, and sampling ports. The recycle and O_2 flow rates were adjusted using mass flow controllers, and the total pressure in the gas recycle loop was maintained with a regulator on the CH_4 inlet line. Since the recycle loop was maintained at a constant pressure, the CH_4 admission rate was determined by the rate of CH_4 conversion occurring in the OCM reactor. The latter was a 6 mm i.d. Al_2O_3 tube containing 0.5 g of the $Mn/Na_2WO_4/SiO_2$ catalyst and 1.1 g of quartz chips which served to preheat the gases. An electric furnace was used to heat the reactor to 800°C during steady-state operation. Under the OCM reaction conditions used in this study, the CH_4 and O_2 were converted principally to C_2H_4, C_2H_6, CO, CO_2, and H_2O. Conversion of O_2 in the OCM reactor was complete in all cases, so that no O_2 was present in the recycle stream. Following the OCM reactor, an open 1.5 cm i.d. quartz tube, heated to 800°C, was used to effect further dehydrogenation of C_2H_6 to C_2H_4 and H_2, plus a trace amount of C_2H_2. In the third reactor, a 0.5% Pd/α-Al_2O_3 catalyst at 80°C was used to convert the C_2H_2 to C_2H_4. A downstream in-line trap at 0°C maintained the maximum partial pressure of H_2O in the system at 2.4 Torr, while a second trap containing KOH at 25°C continuously removed the CO_2 by-product formed in the OCM reactor.

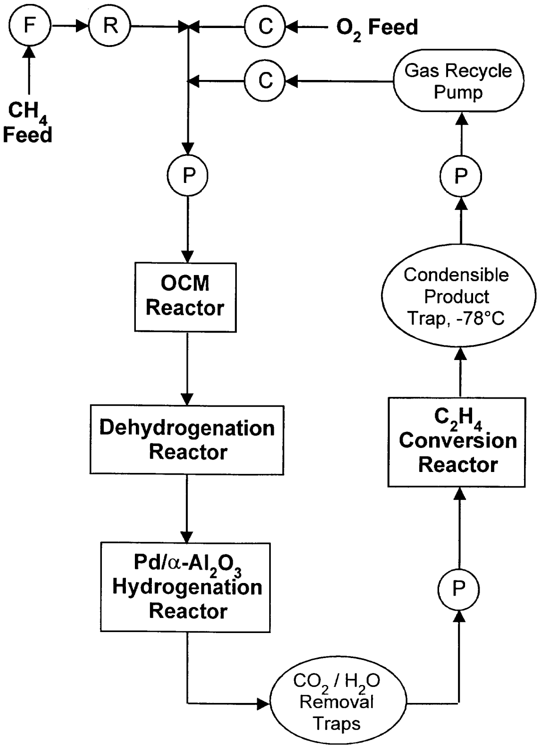

Figure 1. Schematic diagram of integrated recycle system for conversion of methane to aromatics. C = mass flow controller; F = flowmeter; P = gas sampling port; R = pressure regulator.

The fourth reactor, used for subsequent conversion of ethylene to aromatic products, was an 8 mm i.d. quartz tube, containing 1.0 g of the Ga/ZSM-5 catalyst and 4 ml of quartz chips located prior to the catalyst bed to preheat the incoming recycle gases. An electric furnace was used to heat the reactor to the desired temperature, normally 520°C. A third in-line trap, located downstream of the ethylene conversion reactor and maintained at −78°C, continuously removed condensible products generated by the Ga/ZSM-5 catalyst. Reaction mixtures were analyzed by gas chromatography using a TCD and a series-parallel arrangement of two packed columns: a 1/8 in. × 7 in. long column containing 5% AT-2000 + 1.75% Bentone 34 on Chromasorb WNW 100/120 for separation of C_{9+} aromatics, principally naphthalene, and a 1/8 in. × 10 ft. column containing HayeSep D 100/120 for separation of all other reactants and products. The formation of aromatic products was determined by analyzing both the gas stream exiting the ethylene conversion reactor and the trapped liquid condensate. Good agreement was typically observed between these two analyses.

Reactions were begun in the continuous flow single-pass mode, using the desired CH_4/O_2 flow ratio, and with the OCM and dehydrogenation reactors at 800°C and the Pd/Al_2O_3 hydrogenation reactor at 80°C. After the reaction had reached a steady-state condition over the OCM catalyst, the exiting reactant stream was introduced (still in single-pass mode) into the ethylene conversion reactor containing the Ga/ZSM-5 catalyst at 520°C. After the latter reactor had been purged by the reactant stream and a steady-state condition again achieved, the system was switched to the recycle mode of operation. With the O_2 flow rate fixed at the desired level, the CH_4 flow rate was adjusted to achieve complete conversion of O_2 at the exit of the OCM reactor and maintain steady-state operation.

3. Results and discussion

3.1. Single-pass behavior of OCM catalyst

The single-pass, non-recycle, activity/selectivity behavior of the $Mn/NaWO_4/SiO_2$ OCM catalyst at 800°C is shown in figure 2. At a fixed CH_4 flow rate of 120 ml/min, the CH_4 conversion increased from 8 to 31% as the O_2 flow rate was increased from 4.4 to 35 ml/min. But the increased formation of CO_x products resulting from this decreasing CH_4/O_2 reactant ratio caused the selectivity for C_{2+} hydrocarbon products (principally C_2H_4 and C_2H_6) to decrease linearly from 87 to 63%, resulting in a maximum C_{2+} yield of less than 20% at the highest O_2 flow rate, based on total CH_4 reactant feed rate. This overall behavior is in agreement with that reported previously for this OCM catalyst [9].

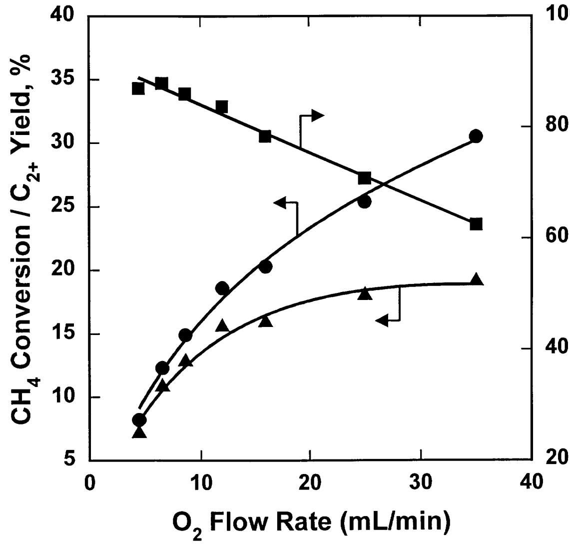

Figure 2. Catalytic behavior in single-pass mode of Mn(2 wt%)/Na_2WO_4(5 wt%)/SiO_2 catalyst for oxidative coupling of methane at 800°C. CH_4 flow rate = 120 ml/min. (●) CH_4 conversion; (■) C_{2+} selectivity; (▲) C_{2+} yield.

3.2. Ethylene conversion over Ga/ZSM-5

Because of this apparent limitation on C_{2+} yield, when restricted only to the products of the OCM reaction, we have investigated the feasibility of secondary downstream processing of the ethylene OCM product as a means of increasing the overall yield of higher hydrocarbons. Ga/ZSM-5, for example, has been shown to exhibit excellent activity/selectivity behavior for the conversion of lower hydrocarbons to aromatic products [11,12]. Table 1 summarizes results obtained from a series of Ga/ZSM-5 catalysts at 520°C for the reaction of a 3% C_2H_4/CH_4 mixture, intended to simulate the typical composition of an OCM-based recycle stream. (The unreported selectivity for each catalyst consisted of CH_4 and a small amount of coke.) It is apparent that pure

Table 1
Ethylene conversion and product selectivity over Ga-containing HZSM-5 [a]

Ga (wt%)	C_2H_4 conv. (%)	Selectivity (%)								Aromatics select. (%)	Aromatics yield (%)
		non-aromatics			aromatics						
		C_2	C_3	C_{4+}	Bz	Tol	C_8	C_9	Naph		
0.0	40	12	58	10	6	9	0	0	0	15	6
0.1	65	8	20	0	32	28	10	0	0	69	45
0.5	91	4	5	0	38	31	7	1	3	79	72
2.0	92	4	3	0	35	31	7	4	6	82	75
5.0	93	2	4	0	34	31	8	4	4	80	74
10.0	92	8	4	0	34	31	7	5	3	80	73

[a] Si/Al = 25, 1.0 g of catalyst; reaction temp. = 520°C; CH_4 = 100 ml/min, C_2H_4 = 3 ml/min; data taken after 70 min on stream.

HZSM-5 is not an effective catalyst for the conversion of a dilute ethylene stream to aromatic products under gas flow rate conditions similar to those used in a recycle reactor system, producing primarily non-aromatic products, presumably resulting from oligomerization and recracking reactions. However, the addition of even 0.1 wt% of Ga significantly improves the yield of aromatics, and as little as 0.5 wt% of Ga results in the maximum attainable selectivity and aromatics yield, viz., ~80% and ~75%, respectively. The aromatic products obtained consisted of approximately equimolar amounts of benzene and toluene, with lesser amounts of C_{8+} compounds. Based on the results presented in table 1, the 5 wt% Ga/ZSM-5 catalyst was selected for further study as part of the integrated recycle system. A more complete catalytic and spectroscopic characterization of the entire series of Ga/ZSM-5 catalysts will be reported in a future communication [10].

3.3. Integrated recycle system performance

The effect of O_2 flow rate on overall system performance at a fixed CH_4 recycle flow rate of 120 ml/min is shown in figure 3. Although the overall rate of CH_4 conversion increases continuously with increasing O_2 flow rate, the rate of CH_4 conversion to aromatic products increases up to an O_2 flow rate of ~20 ml/min ($CH_4/O_2 = 6$), but then remains essentially constant at higher O_2 flow rates, resulting in a decline in aromatic product yield at high O_2 flow rates. This behavior is due to the fact that, with decreasing CH_4/O_2 reactant ratio, an increasing fraction of the recycled CH_4 (and unreacted C_2H_6) is converted into CO_x in the OCM reactor, causing the rates of production of C_2H_4 and, hence, of aromatics to level off. Thus, the O_2 flow rate needed to optimize aromatics production under these operating conditions is ~12 to 16 ml/min, for which the aromatic product yield exceeds 70%, and the rate of CH_4 conversion to aromatic products is > 10 ml/min. The CH_4 recycle ratio under these conditions is ~8–10.

The effect of CH_4 recycle flow rate on system performance is less pronounced than that of O_2 flow rate, as shown in figure 4. At a fixed O_2 flow rate of 12 ml/min, the overall rate of CH_4 conversion is virtually unaffected by changes in the CH_4 recycle rate in the range 70 to 160 ml/min. Increasing CH_4 recycle rates, however, correspond to increasing CH_4/O_2 reactant ratios, resulting in improved C_2 selectivity in the OCM reactor and corresponding increases in the rate of CH_4 conversion to aromatics and the yield of aromatic products. At a methane recycle flow of 70 ml/min, for example, the rate of CH_4 conversion to aromatics was 10 ml/min, and the aromatic product yield was 72%, while at a CH_4 flow of 160 ml/min, the corresponding values are 12 ml/min and 83%. The corresponding CH_4 recycle ratios are 7 at a CH_4 flow of 70 ml/min and 13 at a CH_4 flow of 160 ml/min.

3.4. Effect of dehydrogenation reactor

All of the results described above for the integrated system were obtained using the four-reactor configuration shown in figure 1. In order to assess the importance of the homogeneous dehydrogenation reactor, located downstream of the OCM reactor, in increasing the overall production of C_2H_4 and, hence, of aromatics, several additional experiments were performed in which this reactor was omitted. (The accompanying subsequent

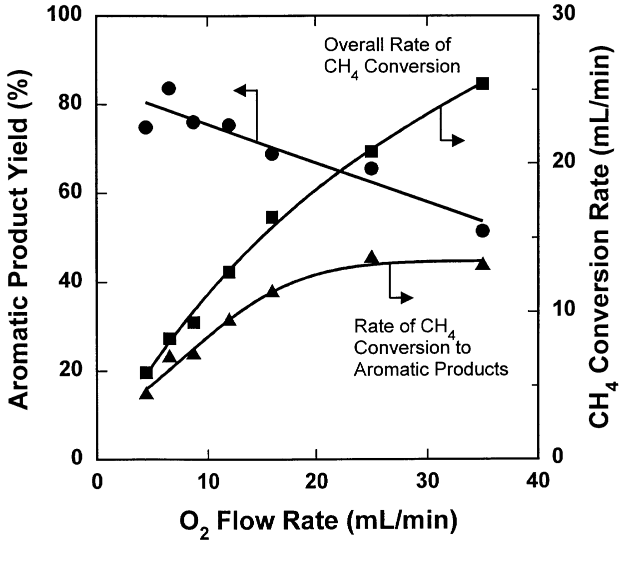

Figure 3. Effect of O_2 flow rate on CH_4 conversion rates and aromatic product yield at a CH_4 recycle flow rate of 120 ml/min: OCM temp. = 800°C; dehydrogenator temp. = 800°C; Pd/Al_2O_3 hydrogenator temp. = 80°C; C_2H_4 conversion reactor temp. = 520°C.

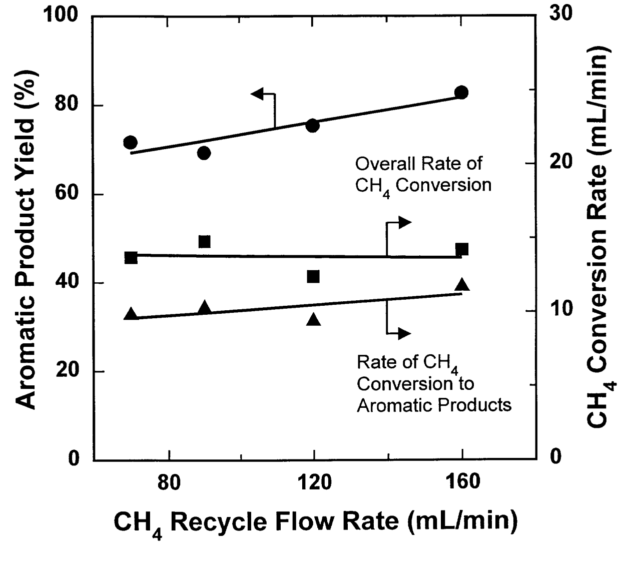

Figure 4. Effect of CH_4 recycle flow rate on CH_4 conversion rates and aromatic product yield at an O_2 flow rate of 12 ml/min: OCM temp. = 800°C; dehydrogenator temp. = 800°C; Pd/Al_2O_3 hydrogenator temp. = 80°C; C_2H_4 conversion reactor temp. = 520°C.

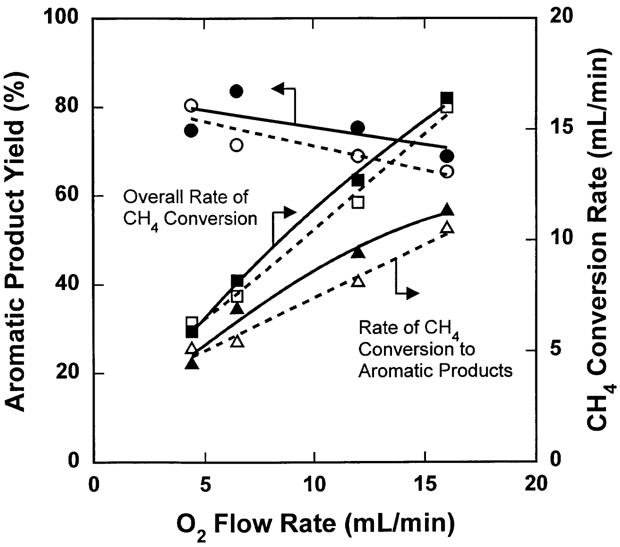

Figure 5. Effect of dehydrogenation reactor on CH_4 conversion rates and aromatic product yield at a CH_4 recycle flow rate of 120 ml/min and various O_2 flow rates: OCM temp. = 800°C; dehydrogenator temp. = 800°C; Pd/Al_2O_3 hydrogenator temp. = 80°C; C_2H_4 conversion reactor temp. = 520°C. Solid data points and solid curves are for system with dehydrogenation reactor; open data points and dashed curves are for system without dehydrogenation reactor.

reactor, containing a Pd/Al_2O_3 catalyst for hydrogenation of trace amounts of C_2H_2 exiting from the dehydrogenation reactor, was also by-passed in these experiments.) Figure 5 compares the results obtained at various O_2 flow rates without the dehydrogenation reactor to those obtained with the dehydrogenation reactor in the system. The effect of omitting the dehydrogenation reactor is to increase the amount of C_2H_6 in the recycle stream. The recirculating C_2H_6 passes unaffected through the Ga/ZSM-5 reactor and subsequently undergoes both oxidative dehydrogenation to C_2H_4 and conversion to CO_x in the OCM reactor. The result of increased CO_x formation is to slightly decrease both the net rate of CH_4 conversion to aromatics and the overall aromatic product yield, compared to those obtained with the dehydrogenation reactor in the system. The effect increases slightly with increasing O_2 flow rate at a fixed CH_4 recycle rate, resulting in about a 10% decrease in the rate of CH_4 conversion to aromatic products at an O_2 flow rate of 16 ml/min.

4. Conclusions

These initial results demonstrate that a relatively high yield of aromatic products can be attained from methane reactant by use of a catalytic C_2H_4 conversion reactor. Moreover, such use of a chemical, rather than a physical, technique can more efficiently remove ethylene from the circulating reactant/product gas stream in an OCM recycle reactor than can the liquid-based membrane contactor separation system that we have previously studied [8]. The advantage of this catalytic reactor is that there is no inherent limitation on the rate of ethylene removal because the amount of catalyst can, in principle, be easily adjusted to obtain a sufficient ethylene conversion rate. The catalyst can be used for several hours, and can then be regenerated to restore its original activity. Based on the results obtained with the reaction conditions employed thus far, 100% methane conversion and about 70% aromatic product yield can be achieved with this system, as well as ethylene removal rates that exceed those attainable with the liquid-based separation system. From an application standpoint, it is not yet clear whether the cost of cryogenically removing the aromatics produced in the Ga/ZSM-5 reactor can be sufficiently offset by the added value of these products to enable commercial use of this type of reaction system.

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