Direct partial oxidation of methane over ZSM-5 catalyst: effects of additives

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Previously, it was reported that the direct partial oxidation (DPO) of CH_4 with O_2 over HZSM-5 catalysts produces C_{5+} hydrocarbon liquids when the feed contains a propane or propene additive. This work studies additive effects on C_{5+} production in this system by processing a CH_4/C_3H_8 feed with subsequent removal of the C_3 additive and by processing natural gas feed. Results show C_{5+} production is maintained at constant yields for HZSM-5 catalysts having different zeolitic Al contents after removal of the C_3 additive. Mechanistic implications are discussed. Natural gas DPO consistently produced C_{5+} liquids due to the presence of C_{2+} components in the feed. While C_{5+} yields from natural gas DPO are higher than those observed for CH_4/C_3 feeds, increasing feed O_2 concentration, and thus conversion, deleteriously affected C_{5+} selectivity.

Keywords: Methane; partial oxidation; additive; natural gas; ZSM-5

1. Introduction

The direct partial oxidation (DPO) of methane with O_2 at elevated pressures yields methanol as the primary non-CO_x product [1]. Attempts to shift product selectivity to liquid hydrocarbons via CH_3OH conversion in this system by introducing zeolite catalysts, particularly HZSM-5, were largely unsuccessful [2–5]. In general, the production of C_{5+} liquids over HZSM-5 by the DPO of CH_4 with N_2O has been more successful [3–6].

Recently, it was reported [7] significant quantities of aromatic C_{5+} products were observed in the CH_4/O_2 DPO over HZSM-5 system from the inclusion of minute amounts of propane or propene additive in the feed. CH_4 incorporation in this system was substantiated by selectivity calculations and isotopic labelling studies [7,8]. Two mechanisms were offered to explain the role of the C_3 additive [8]. One involved the presence of C_3 as an olefin or olefin precursor

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which initiated the conversion of methanol to gasoline (MTG) while the other suggested pathway involved C_3 aromatization over HZSM-5 followed by aromatic alkylation with CH_3OH.

We report here results obtained when the C_3 additive was removed from the feed *after* C_{5+} hydrocarbon production had begun; these findings hopefully shed light on which C_3 mechanism is dominant. Also, studies with natural gas feed containing larger quantities of C_{2+} feed additives are presented.

2. Experimental

The following feeds were used in the study: ultrahigh purity methane, methane/propane primary standards, commercial natural gas (analysis: 96.6% CH_4, 2.0% C_2H_6, 0.4% C_3H_8, 0.2% C_{4+}, and 0.8% CO_2), and CP grade oxygen. These feeds were supplied by Matheson. The catalysts used were bound HZSM-5 zeolites [9] containing 65 wt% zeolite/35 wt% Al_2O_3 binder. The natural gas experiments were performed with a catalyst having a zeolitic Al content of 2.37 wt% while the methane/propane additive studies were performed with catalysts having zeolitic Al contents of 0.170, and 6.13 wt%.

Reactions were carried out in a pyrex-lined stainless steel reactor at 960 psig. In a typical run, 8.0 cm^3 of a fresh Al_2O_3-bound HZSM-5 extrudate (65 wt% zeolite, 35 wt% binder) was mixed with an equal volume of sand and loaded into the reactor's 9/16″ i.d. pyrex glass liner insert. The sand-diluted catalyst bed was preceded and followed by sand-packed preheat and exit zones, respectively. Products exited through a back pressure regulator, a series of dry ice cooled-traps, gas sample bombs, and a wet test meter en route to vent. Exit lines were heat traced. The GHSV was 4600 h^{-1} based on zeolite for all runs and temperatures were at 5–10°C above that required for complete O_2 consumption. All runs employed either 7 or 14 vol% O_2 in the feed.

A calibration procedure involving the analysis of known amounts of various hydrocarbons permitted the determination of the absolute GC response per gram of carbon. With this calibration, absolute amounts of feed and product methane could be calculated directly. Multiple product gas samples (at least 5 and at least 1 every hour) were collected during each run and analyzed by GC to verify that unit operation was steady. Sample-to-sample variations were minimal and the average value for all samples was used to calculate the overall gas product composition for the run.

Liquid products were also analyzed by GC. Absolute methanol determinations were accomplished by doping the liquid product with a known amount of ethanol as an internal standard. Positive identification of the small amounts of C_{2+} water soluble organic products which were often present was not attempted. However, preliminary elemental, GC and MS analyses indicated that the average elemental composition of these species was approximately 42% C,

7% H, and 51% O ($C_2H_4O_{1.8}$). Since these species were generally present in very small amounts, any imprecision in these values had little impact on the overall results. Their overall yield was calculated subject to the assumption that their average relative GC response weight factor was the same as that of the ethanol internal standard. When a separate hydrocarbon layer was produced, it was analyzed by GC, GC/MS, and elemental determinations.

Carbon, hydrogen, and total material balances for the runs were $> 98\%$. The small amount of oxygen in the feed and associated low hydrocarbon conversions ("differential reactor" operation) resulted in oxygen balances of $\approx 90\%$. Results were normalized on a no-loss-of-carbon basis. Conversion was calculated from the difference between the absolute amounts of feed and product C_1–C_4 hydrocarbons. Selectivities are based on grams of carbon in a given product as a percent of feed carbon converted.

3. Results and discussion

3.1. $CH_4 + C_3$ ADDITIVE STUDIES

Previously, it was determined that C_3H_8 or C_3H_6 feed additives in the DPO of CH_4 with O_2 over HZSM-5 catalysts yielded C_{5+} hydrocarbon liquids [7]. In the present work, after production of the C_{5+} liquids was achieved using fresh catalyst and a C_3 feed additive, a subsequent run was performed using a pure CH_4/O_2 feed. Table 1 gives catalytic data and results for runs 1–4 which illustrate the effect of removing the C_3 additive. Runs 1 and 3 were performed with C_3 additive over HZSM-5 containing 0.170 and 6.13 wt% zeolitic Al, respectively. Runs 2 and 4 were performed over the same catalyst loadings in runs 1 and 3, respectively, but with no C_3H_8 additive (i.e. with pure CH_4 feed).

The data in table 1 indicate that C_{2+} hydrocarbon selectivities, and in particular the C_{5+} liquids selectivity, are maintained at similar hydrocarbon conversions when a CH_4/O_2 feed was processed after an initial run using $CH_4/C_3/O_2$. In the case of both HZSM-5 catalysts having a wide variation in framework Al content, C_{5+} selectivities are virtually identical before and after C_3H_8 additive was removed while C_2–C_4 selectivity increased after additive removal. Both HZSM-5 samples tested had similar reactivity patterns. Also, CO selectivity was high relative to CO_2 in all the runs. This result is consistent with our previous observations when C_{5+} was produced over ZSM-5 [7]. Higher CO_2 levels ($\approx 40\%$ selectivity at $\approx 5\%$ CH_4 conversion) were reported earlier for fresh ZSM-5 processing CH_4/O_2 feed without additive (i.e. when C_{5+} was not produced). That CO_2 selectivity remained low in the present study even when propane was removed from the feed indicates that an interval of C_{5+} production modifies the catalyst such that not only is the need for the C_3 additive eliminated but also the tendency to form CO_2 reduced as well.

Table 1
Catalytic data and results for direct partial oxidation over HZSM-5 with CH_4/C_3H_8 additive and pure CH_4 feeds

	Run 1	Run 2	Run 3	Run 4
HZSM-5 Al content (wt%)	0.170	0.170	6.13	6.13
pressure (psig)	960	960	960	960
temperature (°C)	450	465	450	450
GHSV (on zeolite) (h^{-1})	4600	4600	4600	4600
feed (vol%)				
CH_4	92.3	92.5	93.0	93.1
C_3H_8	0.4	–	0.4	–
O_2	7.3	7.5	6.6	6.9
feed carbon conversion (wt%)	5.6	5.8	5.9	5.4
selectivities (wt%)				
CO	71.2	67.7	65.9	66.3
CO_2	15.9	17.1	17.0	16.4
oxygenates	1.3	0.4	2.9	1.6
C_2–C_4	3.6	6.7	2.9	5.4
C_{5+}	8.0	8.1	11.3	10.3

Previous work [7,8] indicated CH_4 participated significantly in the formation of hydrocarbon products. In the propane-free experiments, higher hydrocarbons apparently are solely CH_4 derived, as opposed to a portion possibly being derived from C_3 feed additives during initial operation. The implications of this observation on previously discussed mechanisms [8] for the role of C_3 in the system are considered below.

It is hypothesized that sorbed heavy hydrocarbons (likely aromatics) on the partially coked HZSM-5 catalyst initiate the MTG reaction in much the same manner as C_3. In this scheme, smaller olefins which serve as MTG initiators may be derived from removal of aromatic side chains in the coke precursors by either cracking or reaction with CH_3OH. Thus, we anticipate the reaction of pure CH_4 to C_{2+} and C_{5+} products persists without feed additives since higher hydrocarbons are continually formed in the system and sorbed on the catalyst.

The second suggested mechanistic pathway is more problematic in light of the current results. Since there is no additive present in the feed in runs 2 and 4, aromatic products are likely derived solely from CH_4 (via CH_3OH) in the absence of C_3 aromatization. However, since the catalysts used in runs 2 and 4 already contain hydrocarbon residues, it is possible that monoaromatics may be derived from the breakup of sorbed larger moieties on the catalyst which are subsequently alkylated with CH_3OH. While these series of reactions may occur in the system, we speculate that the dominant reaction likely involves MTG initiation via fragments derived from hydrocarbon residues on the catalyst.

3.2. NATURAL GAS STUDIES

An obvious extension of this work involving DPO of CH_4 with C_3 feed additives involves processing natural gas over HZSM-5 under similar conditions since C_{2+} hydrocarbons are present in small quantities in natural gas. Table 2 gives catalytic data and results for processing natural gas over ZSM-5 with O_2 with fresh and used HZSM-5 loadings and at higher oxygen feed concentration. Run 5 was a natural gas DPO run with ≈ 7 vol% feed O_2 over a fresh HZSM-5 catalyst and run 6 was a repeat run with the same catalyst loading (≈ 6 h aged HZSM-5). Run 7 involved natural gas DPO with fresh HZSM-5 but at ≈ 14 vol% feed O_2.

The data from table 2 show that C_{5+} liquid products were obtained from natural gas DPO over HZSM-5. In fact, run 5 produced a C_{5+} yield (0.91%) higher than any previously observed with C_3 feed additives [7,8]. C_{5+} selectivity was relatively constant with time on stream (run 6) showing less than 1% (absolute) variation for the 7 vol% feed O_2 run.

The data from run 7, an experiment with 14 vol% O_2/natural gas feed, show that, as expected, hydrocarbon conversion increased considerably over runs 5 and 6, but C_{5+} selectivity dropped dramatically ($< 5\%$). This selectivity penalty

Table 2
Catalytic data and results for natural gas direct partial oxidation with O_2 over HZSM-5 catalyst

	Run 5 fresh HZSM-5	Run 6 ≈ 6 h aged HZSM-5	Run 7 fresh HZSM-5
HZSM-5 Al content (wt%)	2.37	2.37	2.37
pressure (psig)	960	960	960
temperature (°C)	420	420	430
GHSV (on zeolite) (h^{-1})	4600	4600	4600
O_2 in feed (vol%)	6.7	6.7	13.9
conversions (wt%)			
CH_4	4.2	3.9	9.7
C_2	27.2	29.5	37.2
C_3	23.8	31.0	58.6
C_4	43.2	24.2	60.1
total hydrocarbon conversion	5.6	5.3	11.7
selectivities (wt%)			
CO_x	83.0	84.4	93.7
oxygenates	0.8	0.1	1.7
C_{5+}	16.2	15.5	4.6
selectivities based only on C_{2+} conversion [a] (wt%)			
oxygenates	1.0	0.6	1.4
C_{5+}	56.3	49.8	21.1

[a] See text.

at higher conversion (low net yields) is analogous to the selectivity/conversion relationship reported for literature data on CH_4 DPO to CH_3OH [10].

In all cases, net C_2–C_4 conversion was 60% or less. As has been reported previously [7,8], CH_4 converts to C_2–C_4 hydrocarbons during DPO with O_2 over HZSM-5 with C_3 additive in the feed. Thus, CH_4-derived C_2–C_4 products in the present runs reduced net conversion levels of the C_2–C_4 feed components. In addition, while selectivities to desired products (oxygenates + C_{2+} hydrocarbons) can be accounted for solely from conversion of the C_{2+} feed components in natural gas (table 2, bottom), previous work [7,8] with CH_4/C_3 additive feeds clearly demonstrated that such products can be extensively formed from CH_4.

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