# Partial Oxidation of Methane to Liquid Hydrocarbons over ZSM-5 Catalyst

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When a propane or propene additive is included in the feed, the partial oxidation of methane with oxygen over ZSM-5 catalyst yields aromatic-rich liquid hydrocarbons instead of methanol.

We report here the preparation of liquid hydrocarbons, and in particular aromatics, by direct partial oxidation (DPO) of methane with $O_2$ over zeolite catalysts. Although methanol is the primary non-$CO_X$ product in methane DPO at elevated pressures,[1] the subsequent transformation of methanol to measurable amounts of gasoline over ZSM-5 catalysts directly in the oxidation reactor has been essentially unsuccessful in the past.

In 1983, Shepelev and Ione first reported production of trace quantities of higher hydrocarbons from methane and $O_2$ in this system at atmospheric pressure and 0.9% yield of unspecified higher hydrocarbon product at elevated pressure.[2] Anderson and Tsai reported[3] the earlier work at atmospheric pressure as not reproducible. Recently, Shepelev and Ione[4] indicated only minute quantities of ethane and ethylene were produced in their system with $O_2$ as oxidant; the major products were $CO_X$. Young reported $CH_4$ oxidation with $O_2$ over zeolites produced only $CO_X$.[5] In general, production of liquid hydrocarbons from $CH_4$ over zeolites using $N_2O$ as oxidant has been more successful.[3–6]

We report the formation of aromatic-rich hydrocarbons from the DPO of $CH_4$ with $O_2$ over ZSM-5 zeolite in the presence of small amounts (~0.2–0.4 mol%) of a higher hydrocarbon additive such as propane or propene in the feed. The additive was added to initiate the methanol-to-gasoline (MTG) reaction as alkenes may be effective at eliminating the slow initiation phase observed with pure methanol feeds (propene is a postulated intermediate in the MTG reaction[7]).

Reactions were carried out in a pyrex-lined stainless steel reactor at 960 psig containing sand or an HZSM-5 catalyst having a hexane cracking activity, or 'alpha' value,[8] of ~ 90. The feeds used were of ultra-high purity $CH_4$, C.P. grade $O_2$ and $CH_4$–$C_3$ primary standards, all supplied by Matheson. With the ZSM-5 catalyst the gas hourly space velocity (GHSV) was 4600 $h^{-1}$ based on zeolite while the experiment with sand was performed at the same flow rates as the catalytic experiments. Temperatures were at 5–10 °C above that required for complete $O_2$ consumption. All runs employed 7 vol% $O_2$ in the feed.

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 ~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 $CH_4$ (and $C_3$ additive, as applicable). Carbon selectivities were based on grams of carbon in a given product as a percentage of feed carbon converted. Gas and liquid products were analysed by gas chromatography and GC–MS.†

The results are summarized in Table 1. A $CH_4$–$O_2$ feed processed over ZSM-5 produced exclusively $CO_X$ and $CH_3OH$; however, with $C_3$ additive in the feed over ZSM-5, product selectivities dramatically shifted towards the formation of liquid hydrocarbons. Chromatographic and mass spectral analyses show this $C_5^+$ hydrocarbon product to be aromatic-rich (>80 wt%).‡ Methanol selectivities for these systems were extremely low indicating conversion to gasoline over the zeolite. To verify the zeolite's role, a $CH_4$–propane–$O_2$ feed was passed over a sand-packed bed under the same conditions. The results showed that only products ($CH_3OH$ + oxygenates) with no liquid hydrocarbons were formed. Catalyst parameters (*e.g.* Al content) may impact the production level of higher hydrocarbons.

**Table 1** Reaction conditions and results for methane direct partial oxidation with $O_2$ over ZSM-5 catalyst

| | Feed | | | |
|---|---|---|---|---|
| | $CH_4/O_2$ | $CH_4/C_3/O_2$ | $CH_4/C_3/O_2$ | $CH_4/C_3/O_2$ |
| $C_3$ type | — | propane | propene | propane |
| Catalyst | HZSM-5 | HZSM-5 | HZSM-5 | sand |
| Temp./°C | 450 | 440 | 440 | 450 |
| Pressure/psig | 960 | 960 | 960 | 960 |
| $C_3$ conc./mol% | — | 0.4 | 0.2 | 0.4 |
| $O_2$ conc./mol% | 7.0 | 7.0 | 7.0 | 7.2 |
| GHSV/$h^{-1}$ | 4600 | 4600 | 4600 | 4600[a] |
| $CH_4$ conv. (%) | 5.2 | 4.1 | 4.5 | 5.0 |
| $C_3$ conv. (%) | — | 47.3 | 64.1 | 68.9 |
| $O_2$ conv. (%) | 100 | 100 | 100 | 100 |
| Total carbon conv. (%) | 5.2 | 4.6 | 4.8 | 5.8 |
| Product selectivities based on total carbon conversion (%) | | | | |
| CO | 43.1 | 70.3 | 70.5 | 62.6 |
| $CO_2$ | 40.2 | 11.4 | 13.7 | 11.6 |
| $CH_3OH$ | 16.7 | 0.1 | 0.1 | 22.7 |
| Other aq. phase oxygenates | — | 0.5 | 1.8 | 3.0 |
| $C_2$'s | — | 0.5 | — | <0.1 |
| $C_4$'s | — | 3.5 | 3.4 | — |
| Liquid hydrocarbon product | — | 13.7 | 10.5 | — |
| Product selectivities based on $C_3$ conversion only (%)[b] | | | | |
| Other aq. phase oxygenates | — | 3.8 | 22.0 | 21.8 |
| $C_2$'s | — | 3.8 | — | 0.4 |
| $C_4$'s | — | 28.8 | 41.7 | — |
| Liquid hydrocarbon product | — | 112.0 | 130.7 | — |

[a] Pseudo GHSV-run performed at same flow rates as catalytic experiments. [b] $CH_3OH$ assumed to come solely from $CH_4$.

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† In the GC analyses, absolute methanol determinations were accomplished by adding a known amount of ethanol as an internal standard to the liquid product. 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 of the aqueous product indicated that the average elemental composition for these species was approximately 42 wt% C, 7 wt% H and 51wt% 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 reasonable assumption that their average relative GC response weight factor was the same as that of the ethanol internal standard.

‡ Liquid hydrocarbon product compositional information: $C_5$–$C_8$ paraffins and alkenes, 1.4 wt%; benzene, toluene and xylenes, 56.8 wt%; $C_9^+$ paraffins and alkenes, 0.1 wt%; $C_9^+$ aromatics, 23.7 wt%; unidentified, 18.0 wt%. Carbon and hydrogen analyses: C, 87.91 wt%; H, 10.30 wt%.

The participation of the converted $CH_4$ in the production of hydrocarbon products is indicated by selectivity calculations presented at the bottom of Table 1. If it is assumed that all higher carbon number products (*i.e.* $C_2^+$, including non-methanol aqueous phase oxygenates) were derived from the converted $C_3$ component, the selectivities so calculated sum to 150–200% for the zeolite catalysed reactions. Consequently the $C_3$ component alone cannot account for the yield of higher hydrocarbons and thus $CH_4$ participation is evident. Calculations at the limiting cases of additive utilization suggest the selectivity to useful products (non-$CO_X$) for the $CH_4$ conversion is in the range of 7–19%.§ Isotopic labelling studies are in progress to substantiate further methane incorporation into the $C_5^+$ product; these results will be reported in the future.

To the best of our knowledge, this is the first instance in which significant quantities of $C_5^+$ liquid hydrocarbons are produced directly from methane by direct partial oxidation with $O_2$. We believe the reaction sequence involves DPO of $CH_4$ to $CH_3OH$ followed by the methanol-to-gasoline reaction and the hydrocarbons are formed because alkenes (or alkene precursors) are present in the feed to initiate the MTG reaction. We are currently investigating the effects of other process variables, as well as the behaviour of other hydrocarbon additives.

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§ In the run with $CH_4$–propane–$O_2$ over ZSM-5, the selectivity of the $CH_4$ can be considered by examining two extremes. At the limit where $C_3$ is converted with 100% selectivity to 'desirable' products (oxygenates + $C_2^+$ hydrocarbons), the selectivity of $CH_4$ conversion to the remaining portion of such products is 6.8%. If the entire yield of useful products is derived from converted $CH_4$, the selectivity of the $CH_4$ conversion is 19.1%.

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