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The Direct Partial Oxidation of Methane to Liquid Hydrocarbons over HZSM-5 Zeolite Catalyst

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The direct partial oxidation (DPO) of CH_4 with O_2 in the presence of a C_3 additive over HZSM-5 zeolite catalyst at 960 psig produced C_5^+ liquid hydrocarbons at the expense of the initially formed CH_3OH. Previous experiments with pure CH_4 and O_2 feed and with a sand-packed reactor conclusively showed the need for both the C_3 additive and the zeolite in the system to produce C_5^+ liquids. Evidence of CH_4 incorporation into the liquid products was given by selectivity calculations which indicated the C_3 alone could not account for the C_5^+ hydrocarbons. CH_4 incorporation has been conclusively confirmed by mass spectral analyses of tetramethylbenzene produced in a run with $^{13}CH_4$ under identical conditions which show significant ^{13}C enrichment in the $C_9H_{11}^+$ and $C_6H_5^+$ fragments. While CH_4 undergoes DPO to CH_3OH in the system, two possible reaction mechanisms can explain the role of C_3; one involves initiation of methanol conversion to gasoline (MTG) by alkenes and the second involves C_3 aromatization followed by aromatics alkylation with CH_3OH. Studies on this system with HZSM-5 catalysts having varying Al contents indicate a sensitivity to zeolite acidity except at high Al concentrations. © 1992 Academic Press, Inc.

INTRODUCTION

The utilization of natural gas, of which methane is the primary component, by direct conversion to liquid fuels or fuels precursors has been intensely studied due to its commercial potential. One direct conversion approach, the direct partial oxidation (DPO) of methane, produces methanol and formaldehyde as the main non-CO_x products. Methane DPO to methanol has been studied by a host of researchers for many years (*1*).

As CH_3OH is the primary oxygenate product in methane DPO at elevated pressures, a novel approach to this reaction has involved the use of HZSM-5 in the oxidation reactor to effect *in situ* conversion of the CH_3OH intermediate to gasoline range hydrocarbons. With molecular oxygen as oxidant, previous efforts to achieve this have been essentially unsuccessful.

In 1983, Shepelev and Ione first reported (*2*) observing trace quantities of a higher hydrocarbon product from CH_4 and O_2 in this system at atmospheric pressure, and 0.9% yield of unspecified higher hydrocarbon product at elevated pressure. Later, Anderson and Tsai (*3*) reported that the earlier Shepelev and Ione work at atmospheric pressure was not reproducible. Recently, Shepelev and Ione indicated (*4*) only small quantities of ethane and ethene were produced in their system with O_2 as oxidant; the major products were CO_x. In addition, Young has indicated that 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*).

Previously, we reported the production of C_5^+ hydrocarbon liquids from the DPO of CH_4 feeds containing C_3 additives with O_2

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over HZSM-5 (*7*). It was shown that HZSM-5 zeolite has little influence on product selectivity when a CH_4 feed containing no additive was reacted with O_2; methanol was the sole non-CO_x product observed in this system. Inclusion in the feed of 0.4 mol% propane or propene additives significantly shifted product selectivities toward higher hydrocarbons and, in particular, C_5^+ liquids at the expense of CH_3OH. The role of the zeolite was also verified using a sand-only packed reactor under identical conditions and flow rates. Methanol formation occurred but no hydrocarbon liquid products were observed in the absence of the zeolite. The propane or propene was believed to initiate the methanol-to-gasoline (MTG) reaction since alkenes (propane is an alkene precursor in the system) are potentially effective at eliminating the slow initiation phase observed with pure methanol feeds; alkenes are postulated intermediates in the MTG reaction (*8*).

The extension of earlier results on CH_4/O_2 DPO with C_3 feed additives are reported here. In particular, we report the use of $^{13}CH_4$ to conclusively confirm CH_4 incorporation into C_5^+ liquid products and present an alternative mechanism to alkene-initiated MTG. Initial studies on the effect of zeolite Al content, and hence, acidity on C_5^+ production were also performed.

METHODS

Methane/C_3 primary standards and C. P. grade oxygen feeds were used in this study. These feeds were supplied by Matheson. A CH_4/C_3H_8 feed containing 40.5 vol% ^{13}C-labelled CH_4 was obtained from Cambridge Isotope Laboratories.

The catalysts used were bound HZSM-5 zeolites (*9*) containing 65 wt% zeolite/35 wt% Al_2O_3 binder. The initial and isotopic experiments were performed with a zeolitic Al content of 2.37 wt%, while the catalyst variable studies were performed with zeolitic Al contents of 0.170, 2.37, and 6.13 wt% Al.

Reactions were carried out in a pyrex-lined stainless steel reactor at 960 psig. In a typical run, 8.0 cc of fresh HZSM-5 catalyst 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. With the HZSM-5 catalyst, the GHSV was 4600 hr^{-1} based on zeolite. Temperatures were at 5–10°C above that required for complete O_2 consumption. All runs employed 7 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 five) 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 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 ~90%. Results were normalized on a no-loss-of-carbon basis. Individual component and total carbon conversions were calculated from the difference between the absolute amounts of feed and product component hydrocarbons. Selectivities are based on grams of carbon in a given product as a percent of feed carbon converted.

In the isotopic labeling studies, a reactor charged with fresh HZSM-5 was brought to run conditions with the CH_4/C_3 primary standard/O_2 feed. When steady operating conditions were reached, the $^{13}CH_4$ labelled feed was processed over HZSM-5 for 5 hr. The liquid hydrocarbon products were analyzed with an HP 5890 GC and an HP 5971 MS detector at 1440 Em volts in scan mode and selected ions were used for the analyses.

TABLE 1

Reaction Conditions and Results for CH_4 Direct Partial Oxidation with O_2 and Propane Feed Additive over HZSM-5 Catalyst

Run	1	2[a]
C_3 type	Propane	Propane
Catalyst	HZSM-5	HZSM-5
Temp. (°C)	450	440
Pressure (psig)	960	960
C_3 conc. (mol%)	0.4	0.4
O_2 conc. (mol%)	7.6	7.0
GHSV (hr^{-1})	4600	4600
O_2 conv. (%)	100	100
Total carbon conv. (%)	5.0	4.6
Product Selectivities Based on Total Carbon Conversion (%)		
CO_x	83.5	81.7
CH_3OH	0.2	0.1
Other aqueous phase oxygenates	0.3	0.5
C_2–C_4	2.4	4.0
Liquid hydrocarbon product	13.6	13.7

[a] Taken from Ref. (*7*).

RESULTS AND DISCUSSION

Methane/C_3 DPO over HZSM-5

A repeat of the CH_4/O_2/propane experiment reported previously (*7*) was performed using a separately prepared batch of HZSM-5 catalyst. Comparison of these two runs (Table 1) show good reproducibility in this system for carefully prepared HZSM-5 zeolite samples having consistent catalyst parameters.

Methane Incorporation into C_5^+ Liquids

An important issue considered in our experiments was whether CH_4, in the presence of more reactive C_3H_8, actually participated in the DPO reaction to hydrocarbon liquid products. Two approaches were used to substantiate CH_4 incorporation and are discussed here.

(*1*) *Selectivity calculations.* The participation of the converted CH_4 in the production of hydrocarbon products was indicated by selectivity calculations presented previously (*7*). Briefly, if it is assumed that all higher carbon number products (i.e., C_2^+, including non-CH_3OH aqueous phase oxygenates) were derived from the converted C_3 component, the selectivities so calculated summed to 150–200% for the zeolite catalyzed reactions. Consequently, the C_3 component alone could not account for the yield of higher hydrocarbons and thus CH_4 participation was evident. Calculations at the limiting cases of additive utilization suggested the selectivity to useful products (non-CO_x) for the CH_4 conversion is in the range of 7–19%.

(*2*) *DPO with $^{13}CH_4$.* A DPO run was conducted with ^{13}C-tagged CH_4 and O_2 over a fresh HZSM-5 catalyst. A feed containing 40.5 vol% $^{13}CH_4$ was diluted with a nonlabelled CH_4/C_3 feed and processed with O_2 over HZSM-5 under identical conditions for 5 hr. The feed composition passed over

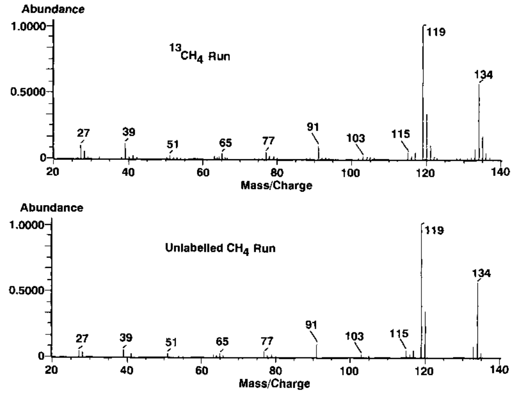

FIG. 1. Mass spectra for tetramethylbenzene product obtained from $^{13}CH_4$ and unlabelled CH_4 direct partial oxidation with O_2 over HZSM-5 catalyst.

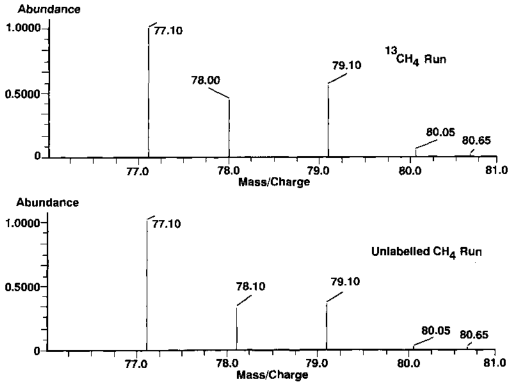

FIG. 2. Mass spectra (enlarged region) for the $C_6H_5^+$ fragment of tetramethylbenzene product obtained from $^{13}CH_4$ and unlabelled CH_4 direct partial oxidation with O_2 over HZSM-5 catalyst.

HZSM-5 was: CH_4, 82.55 mol%; $^{13}CH_4$, 9.95 mol%; C_3H_8, 0.34 mol%; O_2, 7.16 mol%.

Figure 1 shows the mass spectra for tetramethylbenzene products observed for the isotopically labelled run and an untagged run (Run 1, Table 1). Table 2 shows the abundances and calculated relative abundances observed for the MS fragments $C_9H_{11}^+$ and $C_6H_5^+$ of tetramethylbenzene in both runs. Figure 2 gives an enlarged view of the $C_6H_5^+$ MS peaks. The relative abundance of each fragment is defined here as the sum of the ^{13}C isotopic abundances (up to 3 amu increase) divided by the ^{12}C parent abundance. This measures the fraction of ^{13}C in a given fragment. For example, from Table 2, the relative abundance of the $C_9H_{11}^+$ fragment is

$$[\mathrm{Abund}_{120\,\mathrm{amu}} + (2 \times \mathrm{Abund}_{121\,\mathrm{amu}}) + (3 \times \mathrm{Abund}_{122\,\mathrm{amu}})]/\mathrm{Abund}_{119\,\mathrm{amu}}. \quad (1)$$

The results from Table 2 show substantial ^{13}C incorporation in the $C_9H_{11}^+$ fragment of the tetramethylbenzene product. The relative abundance for the tagged experiment shows a >6-fold increase in ^{13}C carbons in the product over the untagged reference case. Relative abundance calculations of the $C_6H_5^+$ fragment at 77 to 80 amu show incorporation of ^{13}C into the aromatic ring by 50% enrichment over the untagged reference case. Comparison of ^{13}C abundance value (derived from the summation of the pertinent abundances) in the untagged reference case shows close agreement with ^{13}C natural abundance (1.09% vs 1.11%, respectively) for the $C_9H_{11}^+$ fragment, whereas the ^{13}C abundance value obtained for the $C_6H_5^+$ fragment is high (1.69%) due to peak overlap from other fragments.

TABLE 2

Mass Spectral Data for Tetramethylbenzene Product from $^{13}CH_4$ and Unlabelled CH_4 DPO Experiments with O_2 and Propane Additive over HZSM-5

Fragment	$C_9H_{11}^+$		$C_6H_5^+$	
	m/z (amu)	Abundance	m/z (amu)	Abundance
	$^{13}CH_4$ Run			
	119.10	1.0000	77.10	1.0000
	120.10	0.3295	78.00	0.5288
	121.05	0.08256	79.20	0.3695
	122.15	0.01100	80.15	0.1027
Relative Abundance[a]		0.53		1.58
	Unlabelled CH_4Run			
	119.10	1.0000	77.10	1.0000
	120.10	0.08295	78.10	0.3392
	121.05	0.001813	79.10	0.3392
	122.35	0.0002711	80.05	0.008795
Relative Abundance[a]		0.087		1.04

[a] See text.

[b] Product from Run 2, Table 1.

Mechanistic Considerations

Methane has been clearly shown to be incorporated into the C_5^+ liquid products by DPO with O_2 over HZSM-5 and in the presence of C_3 additives. While CH_4 undoubtedly undergoes DPO to CH_3OH in this system, the role of the C_3 additive and its effect on the CH_3OH produced is less clear. Two mechanisms which may account for the formation of the predominantly aromatic hydrocarbon product in this system are presented.

The first route to explain CH_4 incorporation into the C_5^+ products in the presence of C_3 additive has been previously presented (*7*). The hypothesis that small concentrations of alkenes in the feed can initiate the MTG reaction was suggested since alkenes may be effective at eliminating the slow initiation phase observed with pure CH_3OH feeds. Propane additive behaves similar to an alkene precursor upon reaction over acidic HZSM-5. Recent work on aromatization of C_3H_8 over HZSM-5 catalysts (*10*) showed that C_3H_8 is converted to aromatics over HZSM-5 via an alkene intermediate at temperatures of 400–650°C and atmospheric pressure. The elevated pressure employed in our studies should enhance the formation of alkene intermediates. Initiation of MTG is thus possible particularly since the alkene need not be present in large amounts. Aromatics alkylation with CH_3OH would also be expected to occur, particularly at the elevated pressures used (*8*).

TABLE 3

Catalytic Results for $CH_4 + C_3H_8$ Additive/O_2 Direct Partial Oxidation over HZSM-5 with Varying Al Contents

HZSM-5 Al Content (wt%)	0.170	2.37	6.13
Temp. (°C)	450	450	450
Pressure (psig)	960	960	960
GHSV (on zeolite) (hr^{-1})	4600	4600	4600
C_3H_8 Conc. (vol%)	0.4	0.4	0.4
O_2 Conc. (vol%)	7.3	7.6	6.6
Total Hydrocarbon Conversion (wt%)	5.6	5.0	5.9
Selectivities (wt%)			
CO_x	87.1	83.5	82.9
CH_3OH	0.7	0.2	2.5
Other oxygenates	0.6	0.3	0.4
C_2–C_4	3.6	2.4	2.9
C_5^+	8.0	13.6	11.3
Yields (%)			
C_2^+	0.65	0.80	0.84
C_5^+	0.45	0.68	0.67

An alternative mechanism would involve C_3H_8 or C_3H_6 aromatization over HZSM-5 ["M-2 forming" (*10, 11*)] followed by aromatics alkylation with CH_3OH. The result of this reaction pathway would be that carbons derived from CH_4 would be expected to solely exist as alkylcarbons on the aromatic rings. This is in apparent contradiction with the $^{13}CH_4$ experiments which showed that CH_4-derived carbons were present in the aromatic rings. However, mechanisms involving intramolecular disproportionation of alkylaromatics, e.g., *m*-xylene, suggest that some reversible isomerization reactions over acidic catalysts at 400°C proceed via interconversion of C_6 and C_5 ring cations (*12*). Such reaction pathways (or those involving ring expansion to tropylium cations ($C_7H_7^+$) would result in alkyl carbons derived from CH_4 incorporating into the aromatic rings. Thus, the isotopic experiments showing ^{13}C in the aromatic rings are inconclusive in ruling out this mechanism due to the possibility of intramolecular scrambling. In either case, CH_4 is incorporated into the C_5^+ liquid product.

Effect of Zeolite Acidity

Three HZSM-5 catalysts with varying Al contents were used in the CH_4/C_3H_8 additive/O_2 DPO system to determine effect of acidity on C_2^+ and C_5^+ production. The data obtained for HZSM-5 zeolites with 0.170, 2.37, and 6.13 wt% zeolitic Al are given in Table 3. From Table 3, similar yields of C_2^+ and C_5^+ products were observed for the two HZSM-5 catalysts at higher Al content and these yields were higher than those observed for the zeolite with 0.170 wt% Al. For the 0.170 wt% Al HZSM-5, >90% of the C_2–C_4 product was ethene. Overall selectivities to non-CO_x products were similar for 2.37 wt% Al and 6.13 wt% Al HZSM-5 catalysts (16.5 wt% and 17.1 wt% oxygenates + C_2^+ product selectivities, respectively). CO_x selectivities appeared to be fairly constant, with a possible modest decline with increasing acidity. These data suggest that increasing zeolite acidity increases desired product selectivities but the benefits diminish with increasing Al content.

CONCLUSIONS

The production of C_5^+ hydrocarbons from the direct partial oxidation (DPO) of CH_4 with O_2 over HZSM-5 at 960 psig is reported. The shift in product selectivity from CH_3OH to aromatic hydrocarbon liquids results from the inclusion of a propane or propene additive in the feed. Methane incorporation into the C_5^+ products has been conclusively verified by experiments with $^{13}CH_4$. Two possible reaction pathways involving CH_4 incorporation (via the DPO reaction to CH_3OH) in the presence of the C_3 additive over HZSM-5 are considered. Presently, it is unclear whether alkene initiation of the methanol-to-gasoline (MTG) or C_3 aromatization followed by CH_3OH alkylation is the dominant mechanism. Experiments with HZSM-5 having varying Al contents suggest a limit to increased C_2^+ and C_5^+ product selectivities at higher zeolite acidities.

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