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Direct Partial Oxidation of Methane over ZSM-5 Catalyst: Metals Effects on Higher Hydrocarbon Formation

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The direct partial oxidation (DPO) of CH_4 with O_2 to higher hydrocarbons, and in particular C_5^+ liquids, over metal-containing ZSM-5 catalysts is reported. At 960 psig, 4600 hr^{-1} GHSV, 7 vol% O_2, and temperatures sufficient for 100% O_2 conversion (440–465°C), our studies with first row transition metals supported on ZSM-5 showed that Cu, Ni, and Zn oxides produced C_5^+ liquids (Fe–ZSM-5 produced C_2–C_4 hydrocarbons) without the need for a feed additive. Co–, Cr–, and Mn–ZSM-5 catalysts under the same conditions produced no higher hydrocarbons. It is believed that conversion of the CH_3OH formed in the system to higher hydrocarbons over metal-containing ZSM-5 is made possible by two metal functions. Initial trace dehydrogenation of CH_4 (or of minute C_2^+ feed components) to olefins provides initiation of the methanol-to-gasoline (MTG) reaction but survival of olefins in the system is a function of the olefin oxidation activity of the metal oxide. Further experimentation using Ga–, Pt–, and Ag–ZSM-5 catalysts was consistent with this hypothesis. Thus, metal-containing ZSM-5 catalysts can produce C_5^+ liquids from CH_4 and O_2 if dehydrogenation and oxidation functions of the metal are in balance. © 1994 Academic Press, Inc.

INTRODUCTION

The production of higher hydrocarbons (C_5^+) directly from CH_4 and O_2 over HZSM-5 zeolite was initially reported by Shepelev and Ione in 1983 (1) but was subsequently determined not to be reproducible (2–4). Previously, we reported (5, 6) that this system could produce C_5^+ hydrocarbons if an olefin or olefin precursor such as propene or propane was present in small concentrations in the feed. CH_4 incorporation in this work was substantiated by selectivity calculations (5, 6) and ^{13}C isotopic labeling studies (6). Two mechanisms were proposed to explain the role of the C_3 additive, one involving an initiation of the methanol-to-gasoline (MTG) reaction and the other involving C_3 aromatization followed by CH_3OH alkylation (6).

Recently, we reported that production of C_5^+ liquids was possible in the system if the C_3 additive was removed after hydrocarbon production had begun (7). It was postulated that sorbed heavy aromatic hydrocarbons on the partially coked HZSM-5 could initiate the MTG reaction in much the same manner as C_3. Smaller olefins which serve as MTG initiators could be derived from removal of aromatic side chains by cracking or reaction with CH_3OH. It was suggested (7) that these observations supported the C_3 initiation mechanism of the previous studies (5, 6) more than the aromatization/alkylation pathway.

We report here studies on the $CH_4 + O_2$ to higher hydrocarbons system using ZSM-5 catalysts containing first row transition metal oxides. The rationale of this work was to investigate whether a dual-functional approach, i.e., CH_4 to CH_3OH over an oxidation component plus MTG over the zeolite catalyst, could provide advantageous effects such as lower reaction temperatures. In addition, the metal activity effect observed, e.g., oxidation versus dehydrogenation activity, would provide insight into the mechanistic chemistry of this system. In our studies with Cr–, Mn–, Fe–, Co–, Ni–, Cu–, and Zn–ZSM-5 catalysts for the direct partial oxidation of CH_4 with O_2, it was found that various metal-containing ZSM-5 catalysts could effect the direct transformation of CH_4 to C_5^+ hydrocarbons in the absence of a feed additive.

It is believed that the successful production of C_5^+ hydrocarbons in this system relies on the metal's ability to produce small amounts of olefins or aromatics from CH_4 to initiate the MTG reaction while having a sufficiently low olefin oxidation activity to minimize conversion of the desired intermediate to CO_x. To further support this hypothesis, we also studied ZSM-5 containing various non-first-row transition metal oxides (Ga, Pt, Ag) and those results are also reported here.

METHODS

The metal-containing ZSM-5 catalysts were prepared by ion exchange. Generally, about 15 g of HZSM-5 bound with Al_2O_3 (zeolite SiO_2/Al_2O_3 = 70/1, 35 wt% Al_2O_3

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TABLE 1

Metal Loading and Percent Theoretical Exchange for Ion Exchanged Metal-Containing ZSM-5 Catalyst Preparations

Metal	Loading (wt%)	% Theoretical Exchange
Cu	0.83	86
Fe	0.56	66
Ni	0.25	28
Zn	0.44	44
Co	0.26	30
Cr	0.52	100
Mn	0.33	40
Ga	2.24	100[a]
Pt	2.19	74
Ag	1.91	59

[a] Assumes Ga^+ was the primary exchange species (see text).

binder) was immersed in ~200 g of an aqueous solution containing an amount of metal such that the atomic ratio of metal to tetrahedral Al^{3+} was 2 to 2.5. Thus, metal was present in excess in the exchange solution. The metal source was generally the hydrated metal nitrate. Exceptions were iron and platinum, with which the chloride and tetraamine nitrate forms were used, respectively. The metals were all in the +2 oxidation state with the exception of silver (+1) and chromium (+3). Also, although gallium was supposed to be +3, the high loading achieved suggested appreciable contamination of the source material with the +1 form. Elemental analysis of the gallium nitrate starting reagent indicated the presence of copious Ga^+.

Normally, the exchange was conducted for 16–24 h at room temperature with periodic agitation, after which the sample was filtered, washed thoroughly with demineralized water, and dried at 120°C for 3 h. It was then air-calcined at 538°C for 3 h.

Table 1 shows the range of measured metal loadings in weight percent which reflect differences in the metals' atomic weights as well as in extents of exchange. The calculated percentages of theoretical exchange vary from ~30 to 100% and are generally in the 40–80% range.

The reactor system and procedures for $CH_4 + O_2$ conversion to higher hydrocarbons have been reported previously (5–7). All catalysts were tested at 960 psig, 4600 hr^{-1} GHSV (on zeolite), with 7 vol% O_2 in the feed. Temperature was adjusted for each catalyst to a point ~5°C above that required to achieve complete oxygen consumption. Ultrahigh purity CH_4 (99.97%) and C. P. grade O_2 were used.

RESULTS AND DISCUSSION

Under our standard test conditions, Ni–, Cu–, and Zn–ZSM-5 produced C_5^+ hydrocarbons from a CH_4/O_2 feed containing no additives. Table 2 gives catalytic data and results for these runs. The production of liquid hydrocarbons has been observed previously only for feeds containing a C_3 feed additive (5, 6) or for an unadditized CH_4/O_2 feed over a catalyst previously used to process a CH_4/C_3 feed (7). Fe–ZSM-5 produced appreciable quantities of C_2–C_4 hydrocarbon products exclusively (Table 2). This was not observed with any of the other metal-containing catalysts or in previous works on this system (5–7). Cr–, Mn–, and Co–ZSM-5 catalysts yielded exclusively oxygenate and C_2–C_4 products in the non-CO_x fraction. The catalytic data and results from these runs are given in Table 3.

We propose the following hypothesis to explain why certain metal-containing ZSM-5 catalysts can produce C_5^+ hydrocarbons directly from CH_4 and O_2 in the absence of a feed additive. The original mechanism proposed for production of C_5^+ hydrocarbons from CH_4/C_3 feeds (6)

TABLE 2

Catalytic Results for CH_4 Direct Partial Oxidation with O_2 over Metal-Containing ZSM-5 Catalysts—Catalysts Which Produced Higher Hydrocarbons (960 psig, 7 vol% O_2, 4600 hr^{-1} GHSV)

Catalyst	Cu–ZSM-5	Fe–ZSM-5	Ni–ZSM-5	Zn–ZSM-5
Temperature (°C)	465	465	465	460
Overall balance (%)	100.1	97.5	100.0	98.5
CH_4 conversion (%)	5.6	5.0	6.3	5.3
Product selectivities (%)				
CO	69.7	76.3	65.7	71.7
CO_2	17.0	13.2	18.1	16.2
CH_3OH	1.1	3.3	6.3	2.5
Other aqueous phase oxygenates	2.8	—	0.6	0.2
C_2–C_4	2.5	7.2	5.0	1.7
C_5^+	6.9	—	4.3	7.7

TABLE 3

Catalytic Results for CH_4 Direct Partial Oxidation with O_2 over Metal-Containing ZSM-5 Catalysts—Catalysts Which Did Not Produce Higher Hydrocarbons (960 psig, 7 vol% O_2, 4600 hr^{-1} GHSV)

Catalyst	Co–ZSM-5	Cr–ZSM-5	Mn–ZSM-5
Temperature (°C)	465	440	465
Overall balance (%)	99.4	100.1	98.9
CH_4 conversion (%)	5.2	5.2	4.8
Product selectivities (%)			
CO	69.0	71.5	71.7
CO_2	29.2	27.7	26.1
CH_3OH	1.2	0.8	1.2
Other aqueous phase oxygenates	0.2	—	1.0
C_2–C_4	0.4	—	—
C_5^+	—	—	—

via an MTG mechanism (8) relied on the C_3 additive as initiator in the system. After gas-phase oxidation of CH_4 to CH_3OH, the difficult step of olefin formation from dimethylether in the subsequent MTG reaction is assisted by a C_3 olefin source present in the feed. Metal-containing ZSM-5 catalysts, e.g., Ga–, Ga/Re–, Mo–, and Zn–ZSM-5, have been shown to convert CH_4 to aromatics at elevated temperatures (9–11). Since aromatics and intermediate olefins are formed from CH_4 over metal-containing ZSM-5 catalysts, the MTG initiator needed for the reaction to occur is present. Certainly, the function of an MTG initiator would not require it to be present in large amounts, and thus, minute conversion of CH_4 to olefins or aromatics under these conditions could result in C_5^+ product formation.

It is possible that trace amounts of C_2^+ components in the feed could have formed olefins over the metal–ZSM-5 catalysts studied. This would have produced the necessary initiator species for the MTG reaction to begin. Our CH_4 feed used, UHP grade with >99.97% CH_4 purity, potentially includes up to 300 ppm C_2–C_3 trace impurity. Dehydrogenation of these trace higher hydrocarbons could form olefins in high enough concentration to provide MTG initiation, although this hypothesis would be difficult to prove or disprove, even with higher purity grades of feed.

Why are there variations in product selectivities for different metal-containing ZSM-5 catalysts? Since ethylene is believed to be the initial olefin formed in the MTG reaction (8), a consideration of ethylene reactivity to O_2 in the presence of various metal oxides is appropriate. Metal oxides with high activity for ethylene oxidation (or that of olefins in general) would destroy the necessary intermediate in the most difficult step of the MTG reaction. Dmuchovsky *et al.* have reported (12) the following activity sequence for ethylene oxidation over various metal oxides: Co > Cr > Ag > Mn > Cu > Ni > V > Cd > Fe > Mo > W > Ti > Zn. In our studies, the metal oxides with lower ethylene oxidation activities, i.e., Cu, Ni, Fe, and Zn, all produced higher hydrocarbon products. The ZSM-5 catalysts containing Co, Cr, and Mn produced small, if any, amounts of higher hydrocarbons from CH_4 and O_2. This work suggests that the cutoff point where ethylene oxidation activity becomes deleterious to forming higher hydrocarbons occurs somewhere between Cu and Mn oxides.

In the case of Fe–ZSM-5, no C_5^+ products were observed; however, significant yields of C_2–C_4 products were seen. This implies that CH_3OH conversion did occur in the Fe–ZSM-5 case but the reaction terminated earlier along the MTG reaction pathway, perhaps due to reduced catalyst acidity. No further studies on why Fe–ZSM-5 gave C_2–C_4 rather than C_5^+ products were performed, since CH_3OH conversion to higher hydrocarbons was the primary concern and this was observed.

To further explore the above hypothesis, three additional non-first-row transition metal-ZSM-5 catalysts were examined. Gallium oxide was suspected to have similar properties to ZnO, i.e., some CH_4 dehydrogenation activity (9–11) but low ethylene oxidation activity, and thus should produce higher hydrocarbons in our system. The data in Table 4 show that Ga–ZSM-5 yielded C_5^+ products analogously to Zn–ZSM-5. Additionally, Pt- and Ag-containing catalysts were tested and compared as examples of metals with high olefin oxidation activities. Due to the unexpected high loading of Ga in Ga–ZSM-5 (cf. discussion in Methods), the Pt- and Ag–ZSM-5 catalysts were tested at comparably high metal loadings. Additional work on metal loading effects in this system are underway and will be published at a future date.

As expected, the Pt- and Ag–ZSM-5 catalysts did not produce significant quantities of higher hydrocarbons from CH_4 and O_2 (Table 4). In general, noble metal catalysts would be expected to have high oxidation activities,

TABLE 4

Catalytic Results for CH_4 Direct Partial Oxidation with O_2 over Metal-Containing ZSM-5 Catalysts—Catalysts Containing Non-first Row Transition Metals (960 psig, 7 vol% O_2, 4600 hr^{-1} GHSV)

Catalyst	Ga–ZSM-5	Pt–ZSM-5	Ag–ZSM-5
Temperature (°C)	465	450	440
Overall balance (%)	100.1	91.5	95.9
CH_4 conversion (%)	5.4	4.7	5.0
Product selectivities (%)			
CO	67.4	2.4	62.6
CO_2	15.6	94.8	11.6
CH_3OH	10.8	1.8	22.7
Other aqueous phase oxygenates	0.8	—	3.0
C_2–C_4	2.2	1.0	0.1
C_5^+	3.2	—	—

and as shown in the above list, Ag has relatively high ethylene oxidation activity (between Cr and Mn oxides). These results, along with that observed for Ga–ZSM-5, are consistent with our hypothesis that dehydrogenation and oxidation activities of metal oxides need to be balanced for C_5^+ production to occur via the CH_4 oxidation/MTG reaction sequence over metal-containing ZSM-5 catalysts.

CONCLUSIONS

The direct partial oxidation of CH_4 with O_2 to higher hydrocarbons, and in particular, C_5^+ liquids, occurs over ZSM-5 catalysts containing various first row transition metal oxides. C_5^+ production was observed with Cu–, Ni–, and Zn–ZSM-5 catalysts, while Fe–ZSM-5 produced significant quantities of C_2–C_4 products. Earlier transition metal oxides of Co, Cr, and Mn did not produce higher hydrocarbons in significant quantities. These findings suggest that successful CH_4 conversion (via CH_3OH transformation) to higher hydrocarbons over metal-containing ZSM-5 catalysts is due to two effects: (1) the ability of the metal to show some limited activity to generate olefins from CH_4 (or trace C_2^+ impurities in the feed) to act as initiator for the MTG reaction, and (2) having a sufficiently low olefin activity to allow the olefins produced to survive in the system. Additional studies using Ga–, Pt–, and Ag–ZSM-5 catalysts gave results consistent with this hypothesis.

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