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Direct partial oxidation of methane over ZSM-5 catalyst: Zn-ZSM-5 catalyst studies

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Extended studies on Zn-ZSM-5 catalyst for the production of liquid hydrocarbons in the direct partial oxidation (DPO) of CH_4 with O_2 are reported. Previously, it was reported that metal-containing ZSM-5 catalysts could produce C_{5+} hydrocarbons from pure CH_4/O_2 feeds without feed additives. Zn-ZSM-5 produced the highest C_{5+} yields of the catalysts tested. This work shows that the method of introducing Zn onto the catalyst, ion-exchange versus impregnation, does not significantly alter C_{5+} yields if low Zn content is maintained (~ 0.4–0.5 wt%). Liquid hydrocarbon yields in this system doubled after 8 h on stream while overall C_{2+} yields increased by over 300%. Mechanistic implications of these findings are discussed. Finally, processing a natural gas feed over Zn-ZSM-5 gave higher C_{5+} yields over CH_4 feed but these yields were not improved over previously published results using HZSM-5.

Keywords: methane; partial oxidation; catalyst; zinc; ZSM-5

1. Introduction

The successful production of C_{5+} hydrocarbons from CH_4 and O_2 over ZSM-5 catalyst has been recently reported [1–3]. This system, involving direct partial oxidation (DPO) of CH_4 to CH_3OH combined with methanol-to-gasoline (MTG) conversion, produces C_{5+} liquids in the presence of a feed additive [1,2] or when processing a CH_4/O_2 feed over a "coked" catalyst [3]. It was hypothesized that production of C_{5+} hydrocarbons was dependent on introducing an initial source of olefin in the reactor to assist in the slow step of the MTG reaction which allowed the reaction to proceed since studies with pure CH_4/O_2 feeds were unsuccessful [1,4–7].

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Subsequently, it was reported [8] that metal-containing ZSM-5 catalysts produced C_{5+} liquids from CH_4/O_2 in much the same manner as additized feeds. Among the various metal-ZSM-5 catalysts studied, Cu-, Ni-, Fe-, and Zn-ZSM-5 catalysts produced higher hydrocarbons from CH_4/O_2, whereas Co-, Cr-, and Mn-ZSM-5 catalysts did not. It was hypothesized that successful production of higher hydrocarbons resulted for metal oxide species having sufficiently high dehydrogenation activity combined with sufficiently low olefin oxidation activity. Further studies with Pt-, Ag-, and Ga-ZSM-5 catalysts gave results consistent with this hypothesis.

We report here the results of extended studies on Zn-ZSM-5, a metal-containing ZSM-5 catalyst which produced C_{5+} hydrocarbons. Catalyst parameters such as method of metal loading and metal concentration effects were investigated. In addition, the effect of time on stream with regard to higher hydrocarbon yields was examined. Finally, the influence of a natural gas feed containing C_{2+} additives with Zn-ZSM-5 catalyst was studied to see if C_{5+} selectivity or yield would improve by having increased amounts of olefin precursors in the feed.

2. Experimental

The preparation of ion-exchanged Zn-ZSM-5 has been published recently [8].

To examine the possible influence of the mode of sample preparation, a few versions of Zn-ZSM-5 catalyst were prepared by incipient wetness impregnation. Typically, about 15 g of HZSM-5 bound with Al_2O_3 (zeolite $SiO_2/Al_2O_3 = 70/1$, 35 wt% Al_2O_3) was used as the base catalyst. With a moderate amount of shaking, the catalyst was contacted with the proper amount of solution containing the desired level of dissolved metal. The catalyst was subsequently dried at 120°C for 3 h and then air-calcined at 538°C for 3 h.

The reactor system and procedures for $CH_4 + O_2$ conversion to higher hydrocarbons have been described previously [1–3]. The catalysts were tested at 960 psig, 4600 h^{-1} GHSV (on zeolite), 7 vol% O_2 in the feed, and temperatures ~ 5°C higher than that required for complete oxygen consumption. Ultrahigh purity CH_4 (>99.97%), C.P. grade O_2, and commercial natural gas, all supplied by Matheson, were used in this study. Analysis of the natural gas showed 96.6% CH_4, 1.9% C_2H_6, 0.3% C_3H_8, 0.1% C_4, 0.06% C_{5+}, 0.7% CO_2, and 0.3% N_2.

3. Results and discussion

3.1. EFFECT OF LOADING METHOD AND ZINC CONTENT

The method of metal loading, i.e. ion-exchange versus impregnation, as well as amount of metal loading and its influence on gasoline production were examined for Zn-ZSM-5 in the DPO of CH_4 and O_2 to C_{5+} products. Catalytic data and results are given in table 1.

Previously, it was demonstrated [8] that a Zn-ZSM-5 catalyst prepared by ion-exchange and containing 0.44 wt% Zn produced liquid hydrocarbon products directly from CH_4 and O_2. The data in table 1 show that the method of loading Zn onto the catalyst is not critical for the system to produce C_{5+} hydrocarbons provided final Zn content remains similar. C_{5+} selectivities were modestly lower for the catalyst containing 0.48 wt% Zn prepared by impregnation (4.0% C_{5+} versus 7.7% C_{5+} for ion-exchanged Zn-ZSM-5). However, as the impregnated Zn loading was increased beyond 1 wt% metal, C_{5+} production stopped (table 1).

The lack of C_{5+} production from CH_4 and O_2 with Zn-ZSM-5 catalysts having high metal loadings may arise for several reasons. For this reaction, it was determined that significant ethylene oxidation activity on metal-containing ZSM-5 catalysts was deleterious to C_{5+} product formation [8]. Reaction of the desired MTG intermediate olefin would inhibit subsequent transformation of the CH_3OH formed in the system from CH_4 and O_2. Although Zn has low ethylene oxidation activity relative to other first row transition metals [9], high loadings would exert a strong concentration effect and work to reduce transient olefin levels in the system. Secondly, high metal loadings potentially reduce desired catalyst acidity needed for conversion of CH_3OH.

3.2. HIGHER HYDROCARBON YIELDS WITH TIME ON STREAM

The catalytic data and results for an ion-exchanged Zn-ZSM-5 catalyst at initial and >8 h time on stream are presented in table 2. At constant CH_4 conversion, C_{5+} selectivities increased dramatically with time on stream for this catalyst, more than doubling from 5.5 to 12.3%. In addition, C_2–C_4 yields also increased greatly

Table 1
Catalytic data and results for DPO of CH_4 over Zn-ZSM-5 – effect of loading amount and method (960 psig, 4600 h^{-1} GHSV on zeolite, 7 vol% feed O_2)

Zn loading (wt%)	0.44	0.48	1.42	3.98
method of loading	ion-exchange	impregnation	impregnation	impregnation
reaction temperature (°C)	460	465	465	465
CH_4 conversion (wt%)	5.3	5.2	5.3	5.5
carbon selectivities (wt%)				
CO	71.7	68.2	43.3	47.2
CO_2	16.2	22.0	35.9	31.1
CH_3OH	2.5	4.1	19.7	20.6
other oxygenates	0.2	0.5	0.4	0.8
C_2–C_4	1.7	1.2	0.7	0.3
C_{5+}	7.7	4.0	–	–

Table 2
Catalytic data and results for DPO of CH_4 with Zn-ZSM-5 (0.4 wt% Zn) – effect of time on stream with C_{5+} yields (960 psig, 4600 h^{-1} GHSV on zeolite, 7 vol% feed O_2)

	Catalyst	
	Zn-ZSM-5	Zn-ZSM-5
time on stream	fresh	>8 h
temperature (°C)	440	440
CH_4 conversion (wt%)	3.9	4.3
carbon selectivities (wt%)		
CO	46.1	50.5
CO_2	47.2	31.1
CH_3OH	0.1	0.1
other oxygenates	0.7	0.4
C_2–C_4	0.4	5.6
C_{5+}	5.5	12.3

with time on stream, giving a total higher hydrocarbon (C_{2+}) yield improvement of from 5.9 to 17.9%.

This unexpected result of higher desired product yields over processing time suggests an additional factor influencing the chemistry involved in this reaction. In the absence of any other obvious factor, it is believed increased initiation of the MTG reaction through sorbed aromatic hydrocarbons on the partially coked Zn-ZSM-5 catalyst is occurring. Previously, this phenomenon was observed [3] with HZSM-5 catalyst processing a CH_4/O_2 feed containing a small amount of C_3 initiator. In that work, C_{5+} production was maintained after subsequent removal of the C_3 feed additive. In the Zn-ZSM-5 system, the initiation effect is increased since partial coking increases heavy hydrocarbon concentration on the catalyst while the metal function increases intermediate olefin concentration. Both these factors would improve CH_3OH conversion to higher hydrocarbons in this system resulting in higher C_{2+} yields. No long term aging studies were performed to determine if yield gains would persist.

3.3. NATURAL GAS STUDIES

Based on earlier studies [2,3], it was anticipated the combined benefits of processing natural gas with Zn-ZSM-5 would result in the highest yields of C_{5+} yet observed. The results with processing natural gas over ion-exchanged Zn-ZSM-5, compared with base case runs using HZSM-5 catalyst processing natural gas feed [3] and a C_3-containing feed [1,2], are given in table 3. The results indicate that the use of Zn-ZSM-5 with a natural gas feed resulted in no improvement in liquid hydrocarbon product selectivity compared to HZSM-5 with the same feed [3] or a CH_4 feed containing C_3 additive [1,2]. This result suggests a limit to benefits asso-

Table 3
Catalytic data and results for DPO of natural gas with Zn- ZSM-5 (960 psig, 4600 h^{-1} GHSV on zeolite, 7 vol% feed O_2)

	Catalyst		
	HZSM-5 [a]	HZSM-5 [b]	Zn-ZSM-5
temperature (°C)	410	440	400
conversions (wt%)			
CH_4	4.2	4.1	3.8
C_2	27.2	–	34.5
C_3	23.8	47.3	33.5
C_4	43.2	–	24.2
total hydrocarbon	5.6	4.6	5.6
carbon selectivities (wt%)			
CO_x	83.0	81.7	81.2
oxygenates	0.8	4.6 [c]	5.6
C_{5+}	16.2	13.7	13.2

[a] From ref. [3].
[b] Processing CH_4 feed containing 0.4% propane; from ref. [1].
[c] Total includes 0.6% oxygenates +4.0% C_2–C_4.

ciated with increasing higher hydrocarbons in the feed and indicates that Zn-ZSM-5 achieves a high C_{5+} yield plateau independent of C_{2+} feed concentration.

For both runs given in table 3, product selectivity to CO_x was essentially the same, as was selectivity for total products (C_5 + oxygenates). In both cases, net C_2–C_4 conversion was $\lesssim$40% or less. As has been demonstrated previously [1,2], CH_4 undergoes conversion to C_2–C_4 hydrocarbons during DPO of C_3-additized feeds. Thus, CH_4 derived C_2–C_4 products in the present runs reduce the net conversion levels of the C_2–C_4 feed components.

A marginal temperature reduction ($\sim$ 10°C) in the required operating temperature was observed for natural gas DPO for Zn-ZSM-5 versus HZSM-5. A similar result was observed previously for DPO of pure CH_4 over Zn-ZSM-5 [8]. The reduction in operating temperature (50–65°C) associated with the use of natural gas feed instead of pure CH_4 feed resulted from the recognized influence of the C_2–C_4 components present in natural gas. Activation energies for oxidation of the higher hydrocarbons species are generally lower than that of CH_4. In any case, the combined use of a metal-containing zeolite plus a natural gas feed did not reduce further temperature significantly nor influence selectivity.

References

[1] D.E. Walsh, S. Han and R.E. Palermo, J. Chem. Soc. Chem. Commun. (1991) 1259.
[2] S. Han, D.J. Martenak, R.E. Palermo, J.A. Pearson and D.E. Walsh, J. Catal. 136 (1992) 578.

[3] S. Han, R.E. Palermo, J.A. Pearson and D.E. Walsh, Catal. Lett. 16 (1992) 263.
[4] S.S. Shepelev and K.G. Ione, React. Kinet. Catal. Lett. 23 (1983) 323.
[5] J.R. Anderson and P. Tsai, Appl. Catal. 19 (1985) 141.
[6] D. Young, US Patent 4,497,970 (1985).
[7] S.S. Shepelev and K.G. Ione, J. Catal. 117 (1989) 362.
[8] S. Han, D.J. Martenak, R.E. Palermo, J.A. Pearson and D.E. Walsh, J. Catal. 148 (1994), in press.
[9] B. Dmuchovsky, M.C. Freerks and F.B. Zienty, J. Catal. 4 (1965) 577.