AJChE 2006, Vol. 6, No. 2, 58–65

Methane Conversion to Liquid Hydrocarbons Over W-ZSM-5 and W-Loaded Cu/HZSM-5

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The direct conversion of natural gas—in particular, its principal component, methane—into useful products has been the subject of intense study over the past decades. However, commercialization of this process is still not viable because its conversion and selectivity potentials remain low. Thus, the search continues to come up with a suitable catalyst that allows methane to be oxidized in a controlled environment to yield a high percentage of higher hydrocarbons. ZSM-5 zeolite has been known to be a suitable catalyst for olefin oligomerization. Previous studies, however, have indicated that ZSM-5 zeolites are not resistant to high temperatures. In this work, ZSM-5 was modified with copper and tungsten to develop a highly active and heat-resistant bifunctional oxidative acid catalyst. The oxidation of methane was performed over W/Cu/HZSM-5 catalyst and the results compared with the catalytic performance of W/HZSM-5 and HZSM-5 catalysts. The metal oxide on the catalyst surface led to enhanced conversion of H_2 and CO to $C_{2\text{-}3}$ hydrocarbons and, hence, reduced H_2O selectivity. In the liquid hydrocarbons, C_5^+ selectivity increased with increasing amount of surface Brønsted acid sites. The experimental results indicated higher methane conversion and liquid hydrocarbon selectivity than that of W/3.0Cu/HZSM-5 catalyst.

Keywords: Copper, liquid hydrocarbons (LHs), methane, oxidation, tungsten, *and* ZSM-5 zeolite.

INTRODUCTION

In general, there are two routes for converting methane to gasoline, the indirect and direct routes. The *indirect route* is a two-step process where natural gas is first converted into synthesis gas, a mixture of H_2 and CO, and then into gasoline range. The *direct route* is a one-step process in which natural gas is reacted with oxygen, or another oxidizing species, to give the desired product directly.

Ernst and Weitkamp (1989) reported that the presence of strong acid sites in the zeolite catalyst is detrimental to the selective oxidation of methane to higher hydrocarbons; otherwise, oxidized products such as CO_x (CO, CO_2) predominate. When acidity is reduced by exchanging the zeolite with alkali metal cations, selectivity to higher hydrocarbons is slightly enhanced.

Han et al. (1994) demonstrated the successful production of higher hydrocarbons from methane oxidation using ZSM-5 zeolite containing metal oxide catalysts. Metal oxides with sufficiently high dehydrogenation and low olefin oxidation activities reduced the acidity of ZSM-5. As a result, metals containing ZSM-5 produced higher hydrocarbons in methane oxidation.

De Lucas et al. (1998, 1999, 2000) discovered that the introduction of Cu(II) ions by ion-exchange method could remarkably increase the activity of Mo/HZSM-5 for methane aromatization and improve its stability to some extent. Mo species is by far the most active component for methane nonoxidative aromatization, but its activity and stability needs to be improved.

Xiong et al. (2001a, 2001b) studied the incorporation of the metals Zn, Mn, La, and Zr into the W/HZSM-5 catalyst. Under reaction conditions of 0.1 Mpa, 1,073 K, and with the gas hourly space velocity (GHSV) of the feed gas CH_4+ 10% Argon at 960 h^{-1}, the conversion of methane reached 18-23% in the first two hours of reaction, and the corresponding selectivity to benzene, naphthalene, ethylene and coke was 48-56%, 18%, 5%, and 22%, respectively. Ding et al. [8] reported the nonoxidative methane reaction over W/HZSM-5 produced C_2–C_{12} hydrocarbons. Under condition of 700°C, flow rate CH_4 + Argon at 12.5 cm^3/min, the C_2-C_{12} selectivity was 70-80%. However, the methane conversion was small between 2% and 3%. On the basis of the chemical similarities between MoO_3 and WO_3 it seems reasonable to expect a parallelism in their catalytic properties.

Cu loaded ZSM-5 catalyst via acidic ion exchange method had been identified as the potential catalyst for the conversion of methane into liquid fuels (Anggoro and Amin 2001, Amin and Anggoro 2001). However, the infrared study on metal-loaded ZSM-5 catalyst indicated that the catalysts were not resistant to high temperatures. Previous studies also indicated that metal-loaded ZSM-5 do not exhibit vibration bands at 3,610 and 3,660 cm^{-1}, except for ZSM-5, which showed a weak vibration band at 3,666 cm^{-1}. The results likewise suggested that framework and nonframework aluminum, whether extracted to the acidic solution or became a silanol defect form when calcined at 800°C, made the catalysts inactive.

In this paper, HZSM-5 was modified with tungsten and copper and the catalyst performance tested for the oxidation of methane to liquid hydrocarbons. The catalysts were characterized by X-ray Diffraction (XRD), temperature-programmed reaction (TPR), temperature-programmed desorption (TPD), and N_2 adsorption measurements. Specifically, the research investigated the resistivity of tungsten-modified HZSM-5 to high temperatures and tested its catalytic activity for the conversion of methane.

EXPERIMENT

The ZSM-5 zeolite, which has an SiO_2/Al_2O_3 mole ratio of 30 and a surface area of 400 m^2/g, was supplied by Zeolyst International Co., Ltd., the Netherlands.

The W-HZSM-5 catalyst was prepared by impregnating a certain amount of HZSM-5 zeolite carrier with ammonium tungstate hydrate solution (Zhing et al. 2001a). The ammonium tungstate hydrate solution was prepared by dissolving $(NH_4)_2WO_4$ in deionized water and adding a small amount of H_2SO_4 to regulate the pH of the solution to 2–3. The sample (10 ml of solution per gram of zeolite) was dried in an oven at 120°C for 2 hours and then calcined at 500°C for 4 hours.

The tungsten-loaded Cu-HZSM-5 zeolite catalyst was prepared by first impregnating a certain amount of HZSM-5 zeolite carrier with a calculated amount of copper nitrate in aqueous solutions, followed by drying at 120°C for 2 hours, calcining at 400°C for 4 hours, and impregnating with a calculated amount of H_2SO_4 acidified $(NH_4)_2WO_4$ aqueous solution (pH= 2–3). Finally, the sample was dried at 120°C for 2 hours and calcined in air at 500°C for another 5 hours.

The catalysts were characterized by X-ray Diffraction, H_2-TPR, NH_3-TPD, and N_2 adsorption. The performance of the catalysts was tested for methane conversion to liquid hydrocarbons (LHCs) via single-step reaction in a fixed-bed microreactor. Methane with 99.9% purity was reacted at atmospheric pressure and at various temperatures and oxygen concentrations. Online Gas Chromatography, which had been equipped with TCD and Porapak-N column, was utilized to analyze the gas. The liquid product was analyzed using Gas

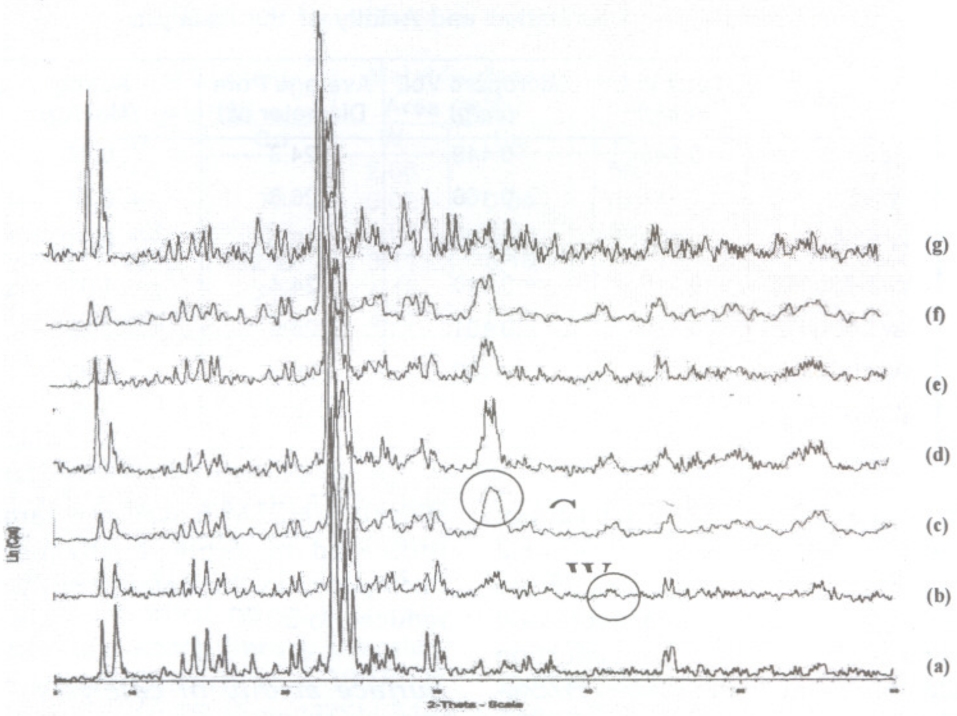

Figure 1. XRD Pattern of (a) HZSM-5, (b) W/HZ, (c) W/0.5Cu/HZ, (d) W/1.0Cu/HZ, (e) W/1.5Cu/HZ, (f) W/2.0Cu/HZ, and (g) W/3.0Cu/HZ

N column, was utilized to analyze the gas. The liquid product was analyzed using Gas Chromatography–Flame Ionization Detection (GC–FID) and HP-1 capillary column.

RESULTS AND DISCUSSIONS

Morphology of catalysts

XRD and N_2 adsorption were employed to determine the morphology of the catalysts. The XRD diffractograms of HZSM-5, W/HZSM-5, and W-loaded Cu/HZSM-5 catalysts, with different Cu loadings calcined at 550°C, are shown in Figure 1. The peak at $2q = 41$ indicates tungsten oxides (Logie et al. 2000), while the peak at $2q = 34$ peak indicates copper oxides (Li et al. 1999). The intensities of these peaks increased with copper loading increasing up to 2.0 wt% of copper. At higher copper loadings of 3.0 wt% of Cu, the peak is unclear and parts of the zeolitic frameworks have collapsed.

The results of the crystallinity calculated from the XRD diffractograms and the areas of the samples from the NA analysis are found in Table 1. The crystallinities of HZSM-5 and W/HZSM-5 are perfect while the crystallinities of W/1.0Cu/HZSM-5, W/2.0Cu/HZSM-5, and W/3.0Cu/HZSm-5 show low crystallinities at 89,

Table 1. Crystallinity and Surface Area of the Catalysts

Catalysts	Crystallinity *(%)*	BET Surface Area *(m^2/g)*	Micropore Area *(m^2/g)*	Ratio Micropore Area/Total Area *(%)*
HZSM-5	100	403	373	61
W/HZ	100	280	257	57
W/0.5Cu/HZ	94	266	243	57
W/1.0Cu/HZ	89	286	261	63
W/1.5Cu/HZ	101	267	244	56
W/2.0Cu/HZ	88	285	260	57
W/3.0Cu/HZ	69	236	213	50

Table 2. Pore Distribution and Acidity of the Catalysts

Catalysts	Total Vol. *(cc/g)*	Micropore Vol. *(cc/g)*	Average Pore Diameter *(Å)*	Acidity *(Mol/Kg)*
HZSM-5	0.245	0.149	24.3	0.87
W/HZ	0.187	0.106	26.8	0.81
W/0.5Cu/HZ	0.176	0.101	26.5	0.91
W/1.0Cu/HZ	0.175	0.110	24.4	1.01
W/1.5Cu/HZ	0.179	0.101	26.9	1.01
W/2.0Cu/HZ	0.191	0.109	26.6	0.98
W/3.0Cu/HZ	0.176	0.088	29.8	1.19

88, and 69 %, respectively. The BET surface area and the micropore area of W/3.0Cu/HZ are 236 and 213 m^2/g, respectively. Both surface area and micropore area decreased with increasing copper loading. The reduction in the surface area of the metal-loaded HZSM-5 indicated strong interaction between the surface of the zeolite and the copper and tungsten species that enabled good dispersion of metals on the surface.

The results in Table 2 pertain to the total volume, micropore volume, average pore diameter, and acidity of the catalysts. Tungsten and copper species might have entered easily or blocked partially the channels of the ZSM-5 zeolite pores and, thus, reduced the volume of the catalysts.

The average pore diameters of the metal-loaded HZSM-5 zeolites were larger than the parent zeolite. The average pore diameter of W/3.0Cu/HZSM-5 was the largest and, as indicated in Table 1, the percentage of micropores in the catalyst surface had been reduced to 50%.

Surface acidity of catalysts

The NH$_3$-TPD spectra of the catalysts provided useful information about the intensity and the concentration of the acid sites on the catalyst's surface as shown in Table 2. The concentrations of the surface acid sites (acidity) of metal-loaded HZSM-5 are higher than those of ZSM-5 zeolite. This is probably because the average pore diameters of the metal-loaded HZSM-5 are larger than the HZSM-5 zeolite itself. As revealed by the results found in Table 2, the strongest acidity shown by the W/3.0Cu/HZSM-5 zeolite coincided with the fact that it had the largest pore diameter (29.8 Å).

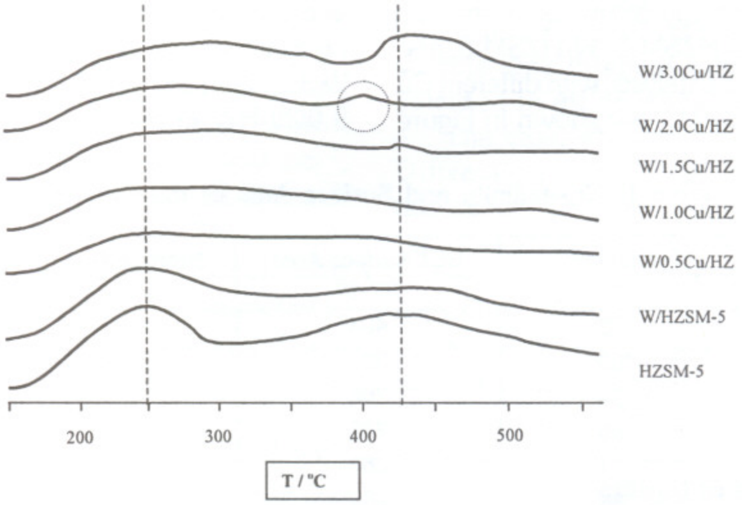

Figure 2. NH$_3$–TPD Spectra of Catalysts

Table 3. Metal State in the Reduced Catalysts

Catalyst	Metal Content (μmol/g)		Metal Surface Area (m^2/g)		Dispersion of Metal (%)		Mean Particle Diameter (nm)	
	W	Cu	W	Cu	W	Cu	W	Cu
W/HZ	163	-	2.66	-	55	-	0.0518	-
W/0.5Cu/HZ	163	79	6.02	0.04	100	24	0.0287	1.559
W/1.0Cu/HZ	163	157	4.00	0.07	68	22	0.0419	1.721
W/1.5Cu/HZ	163	236	3.11	0.16	65	40	0.0444	0.930
W/2.0Cu/HZ	163	315	4.18	0.48	76	79	0.0379	0.475
W/3.0Cu/HZ	163	472	4.77	0.92	86	100	0.0332	0.373

Figure 2 depicts the NH_3-TPD spectra of HZSM-5, W/HZSM-5, and W-loaded Cu/HZSM-5 with different amounts of Cu loading. For HZSM-5 and W/HZSM-5, the NH_3-TPD peaks appeared at around 250–430°C, which may be ascribed to the desorption of two kinds of ammonia species adsorbed on weak (mostly Lewis) acid sites and strong (mostly Brønsted) acid sites, respectively (Woolery et al. 1997).

The modification of 0.5% Cu to HZSM-5 led to the reduced intensity of the high temperature (~430°C) peak and to a small downshift in its position. When the amount of Cu loading increased to 1%, the high temperature peak disappeared, indicating that most of the surface Brønsted acid sites had vanished.

As the Cu loading further increased, however, the NH_3-TPD peaks reappeared at ~430°C. One interesting feature of Figure 2 is an NH_3-TPD spectra of W/2.0Cu/HZSM-5 indicating a peak at 400°C, which revealed that the catalyst may possibly have medium-strength Brønsted acid sites.

Reducibility of catalysts

The TPR profiles of W/HZSM-5 and W-loaded Copper/HZSM-5 catalysts are shown in Figure 3. As observed, all the curves contained several peaks in the temperature range of 200–900 °C. The TPR patterns of all catalysts exhibited two peaks with the maximum at 700 and 780 °C. These peaks may be assigned to the two step-wise reduction of WO_3 to W(IV) W(0) [De Lucas et al. 1999].

The reducibility of this type of catalyst decreases as the strength of interaction between the metal oxide species and the

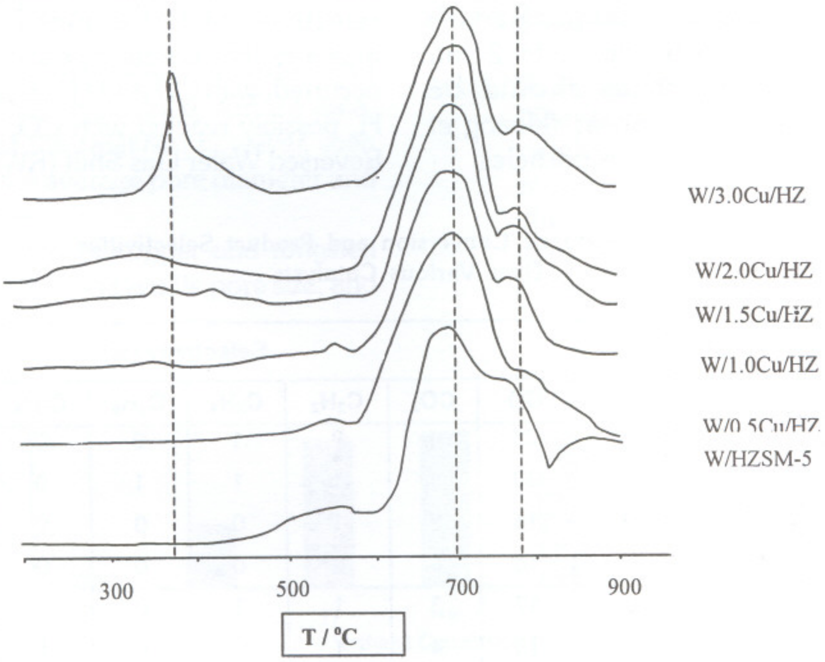

Figure 3. H_2–TPR Spectra of Catalysts

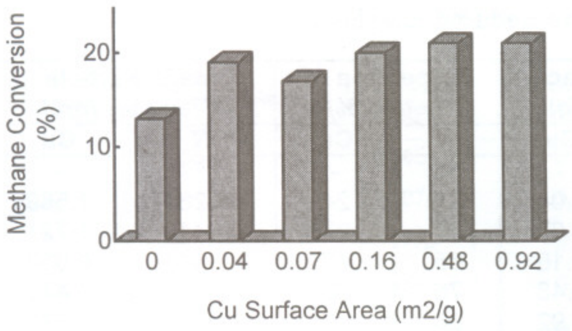

Figure 4. Effect of Cu Surface Area on CH_4 Conversion

surface of the support increases. The existence of a single reduction peak at 550°C for W/HZSM-5, W/0.5Cu/HZSM-5, and W/1.0Cu/HZSM-5 samples may indicate the presence of partially reducible polymeric tungsten species to some extent (Xiong et al. 2002).

The observed H_2-TPR peak at 370°C should be due to the reduction of Cu^{n+} species. As the Cu loading increased, the intensity of the peak became stronger.

In Table 3, the quantitative results of the TPR is summarized. The tungsten content for all catalysts is constant at 163 mmol/g. The copper content and percent of copper dispersed for W/Cu/HZSM-5 catalysts increased with increasing copper concentration.

The mean tungsten and copper particle sizes were estimated to be down to 2 nm (20Å). Such small particles should be localized inside the zeolite pores (Hoang et al. 1994), especially for tungsten particles.

Relationship between catalyst properties and catalytic activity

The products of the reaction between methane and oxygen over HZSM-5, W/HZSM-5, and W/Cu/HZSM-5 with different concentrations of copper are C_2H_2, C_2H_4, C_2H_6, C_3H_6, CO, CO_2, H_2O, and liquid hydrocarbons. Table 4 summarizes the performance of the catalysts.

By stoichiometry calculation the oxygen conversion is 100%. The methane conversion and product selectivities are calculated by:

$$CH_4\ \text{Conversion} = \frac{\text{mole } CH_4 \text{ input} - \text{mole } CH_4 \text{ output}}{\text{mole } CH_4 \text{ input}} \times 100\%$$

$$\text{Selectivity for Product (i)} = \frac{\text{mole Product (i)}}{\text{mole } CH_4 \text{ input} - \text{mole } CH_4 \text{ output}} \times 100\%$$

$i = CO, CO_2, C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_5^+$, and H_2O

Methane conversion increases due to the increase in both copper content and copper surface area, as shown in Tables 3 and 4. This trend is also evident in Figure 4. Methane conversion over HZSM-5 is about 13% but it increases to 21% at a copper surface area of 0.92 m^2/g for W/3.0Cu/HZSM-5.

The results in Table 4 show that over both HZSM-5 and metal-loaded HZSM-5, the selectivity of CO is higher than CO_2. This indicates that partial oxidation of methane has occurred, with CO and H_2 as products. However, H_2 possibly reacted with CO_2 to form H_2O in a Reversed Water Gas Shift (RWGS) reaction and,

Table 4. Methane Conversion and Product Selectivities Over Various Catalysts

Catalysts	Conversion (%)		Selectivity (%)							
	O_2	CH_4	CO	CO_2	C_2H_2	C_2H_4	C_2H_6	C_3H_6	C_5^+	H_2O
HZSM-5	100	13	25	1	2	1	0	0	3	68
W/HZ	100	15	39	1	1	1	1	0	12	45
W/0.5Cu/HZ	100	19	16	5	1	0	0	0	28	50
W/1.0Cu/HZ	100	17	16	8	0	0	0	0	29	47
W/1.5Cu/HZ	100	20	17	3	1	1	0	1	28	49
W/2.0Cu/HZ	100	21	13	4	1	0	0	1	32	49
W/3.0Cu/HZ	100	21	13	5	0	0	0	1	34	47

reaction, the complete oxidation of methane also occurred and produced CO_2 and H_2O.

The H_2O selectivity of HZSM-5 is higher than that of metal-loaded HZSM-5 because HZSM-5 catalyst has neither metal content nor metal surface area, while metal-loaded HZSM-5 catalysts has both tungsten oxide and copper oxide content.

These results demonstrate that H_2O selectivity is related to the presence of tungsten oxide or copper oxide. Over tungsten or copper oxide oxide the reaction of H_2 and CO produces hydrocarbon (C_2 and C_3) gases, which can be oligomerized to liquid hydrocarbons (C_5^+) by the presence of an HZSM-5 zeolite catalyst.

The selectivity of C_2–C_3 for all catalysts is very low, only 1–2%, due to the medium acidity strength of all catalysts, which enhances the oligomerization of C_2 to C_5^+ liquid hydrocarbons and reduces the amount of C_2-C_3.

Figure 5 shows how C_5^+ selectivity increases when acidity increases; while Figure 6 illustrates how both CH_4 conversion and C_5^+ selectivity relate over all the catalyst samples used. The selectivity of C_5^+ using W/3.0Cu/HZSM-5 is the highest (34%) because it has the highest acidity (1.19 Mol/Kg) and the largest copper surface area (0.92 m²/g) among the samples used.

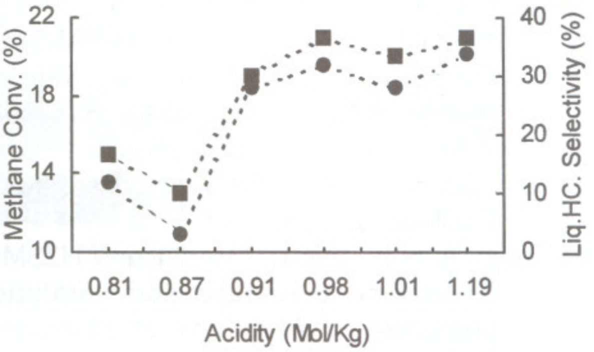

Figure 5. Effect of Acidity on Methane Conversion and Liquid Hydrocarbon Selectivity

CONCLUSIONS

The loading of HZSM-5 with tungsten and copper decreased the crystallinity, surface area, and total volume of the catalysts; however, such loading increased the average pore diameter and acidity of the zeolites.

The metal particles of copper and tungsten are smaller than the average zeolite pore size, and the metal particles may be localized to the inner side of the zeolite pores.

While loading HZSM-5 with tungsten and copper resulted in an increment in methane conversion and in CO_2 and C_5^+ selectivities, the CO, $C_{2\text{-}3}$, and H_2O selectivities were reduced. This shows that the process to convert methane to liquid hydrocarbons (C_5^+) is dependent on both the metal surface area and the acidity of the zeolite.

Hence, W/3.0Cu/HZSM-5 is a potential catalyst because over this catalyst (a) high methane conversion and C_5^+ selectivity as well as (b) low H_2O selectivity are obtained.

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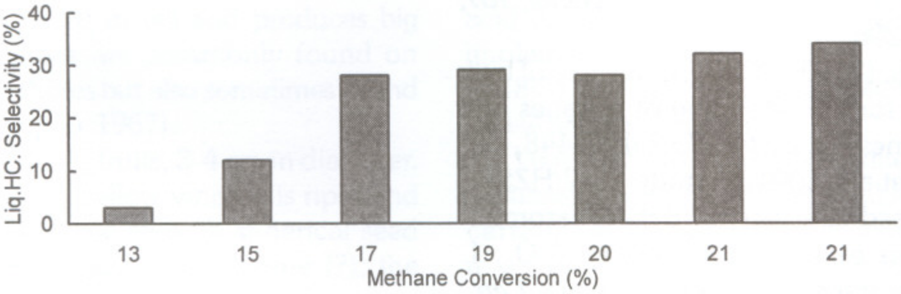

Figure 6. Liquid Hydrocarbon Selectivity vs. CH_4 Conversion

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