CHARACTERIZATION AND PERFORMANCE OF W-ZSM-5 AND W LOADED Cu/ZSM-5 CATALYSTS

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Abstract

The metal oxides with sufficiently high dehydrogenation and low olefin oxidation activities reduces the acidity of ZSM-5. As a result, the metal containing ZSM-5 can produce higher hydrocarbons in methane oxidation. Many researchers studied the applicability of HZSM-5 and modify ZSM-5 to methane conversion to liquid hydrocarbons but results of their research still lead to low conversion and selectivity. The modified HZSM-5 by loading with Tungsten (W) enhanced its heat resistant performance, and the high reaction temperature (800°C) did not lead to the loss of W component by sublimation. The loading of HZSM-5 with Tungsten and Copper (Cu) resulted in an increment in the methane conversion, CO_2 and C^{5+} selectivities. In contrast, CO, C^{2-3}, and H_2O selectivities were reduced. The process to convert methane to liquid hydrocarbons (C^{5+}) was dependent on the metal surface area and the acidity of the zeolite. The high methane conversion and C^{5+} selectivity, and low H_2O selectivity are obtained by using W/3.0Cu/HZSM-5.

Keywords: Characterization W-ZSM-5, Modified HZSM-5, Tungsten, Copper, Methane

Abstrak

Logam oksida dengan kemampuan dehidrogenasi yang tinggi dan aktifasi oksidasi olefin berkurang dengan sifat keasaman dari ZSM-5. Sebagai hasilnya, ZSM-5 yang mengandung logam dapat memproduksi hidrokarbon rantai panjang dari oksidasi gas metana. Telah banyak para peneliti mempelajari kemampuan HZSM-5 dan ZSM-5 yang telah dimodifikasi untuk mengubah gas metana menjadi hidrokarbon cair tetapi hasil konversi dan selektivitasnya masih rendah. Modifikasi HZSM-5 dengan penambahan logam Tungsten (W) meningkatkan daya tahan panas dan pada reaksi suhu tinggi (800°C) tidak menyebabkan hilangnya logam W dikarenakan proses sublimasi. Penambahan logam Tungsten dan Copper (Cu) menyebabkan meningkatnya konversi metana, selektifitas CO_2 and C^{5+}. Sebaliknya, selektifitas CO, C^{2-3}, and H_2O menurun. Proses konversi metana menjadi hidrokarbon cair (C^{5+}) ditentukan oleh luas permukaan logam dan sifat keasaman dari zeolit. Penggunaan katalis W/3.0Cu/HZSM-5 menghasilkan konversi metana dan selektifitas C^{5+} tinggi dan selektifitas H_2O rendah.

Kata Kunci: Karakterisasi W-ZSM-5, Modifikasi HZSM-5, Tungsten, Copper, Metana

1. Introduction

Ernst and Weitkamp (1989) reported in a paper on the conversion of methane over zeolite-based catalysts that the presence of strong acid sites in the zeolite catalyst is detrimental for the selective oxidation of methane to higher hydrocarbons; otherwise oxidized products, CO_x (CO, CO_2) predominate. When the acidity is reduced by exchanging the zeolite with alkali metal cations, the selectivity to higher hydrocarbons is slightly enhanced. Han et al. (1994 a,b) demonstrated the production of higher hydrocarbons from methane oxidation using a ZSM-5 zeolite catalyst containing metal oxides. The metal oxides with sufficiently high dehydrogenation and low olefin oxidation activities reduces the acidity of ZSM-5. As a result, the metal containing ZSM-5 can produce higher hydrocarbons in methane oxidation.

De Lucas et al. (1998, 1999, 2001) discovered that the introduction of Cu (II) ions by an ion-exchange method could remarkably increase the activity of Mo/HZSM-5 for methane aromatization and improve its stability to some extent. Mo species was the most active component for methane non-oxidative aromatization so far, but its activity and stability needed to be improved. Xiong et al. (2001 a,b) studied the incorporation of metals Zn, Mn, La, and Zr into the W/HZSM-5 catalyst. 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. (2001) reported the non-oxidative methane reaction over W/HZSM-5 that produced C2-C12 hydrocarbons. The C2-C12 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. Mo species was the most active component for methane non oxidative aromatization so far, but its activity and stability needed to be improved.

Recently, we found that the introduction of Cu(II) ions by an ion-exchange method can remarkably increase the activity of Mo/HZSM-5 for methane aromatization and can improve its stability to some extent. Cu loaded ZSM-5 catalyst via acidic ion exchange method has been identified to be the catalyst for conversion of methane to liquid fuels (Anggoro and Amin, 2001a, b). However, the infrared study of metal loaded ZSM-5 catalyst indicated that the catalysts were not resistant to high temperature.

Previous studies have indicated that metal loaded ZSM-5 did not exhibit vibration band at 3610 cm^{-1} and 3660 cm^{-1}, except for ZSM-5 which showed a weak vibration band at 3666 cm^{-1}. The result suggested that the framework and non-framework aluminum were either extracted to acidic solution or became silanol defect form when calcined at 800°C and made the catalysts inactive.

The scope of this paper ZSM-5 was modified with tungsten and copper and the catalyst performance was tested for the oxidation of methane to liquid hydrocarbons. The catalysts were characterized by XRD, TPR, TPD, and N_2 adsorption measurements. The illustrated of the process studied in this research is shown in this figure
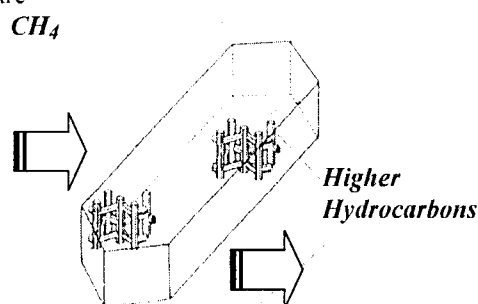

Figure 1. The Illustrated of The Studied Process

2. Fundamental

The applicability of HZSM-5 and modify ZSM-5 to methane conversion to liquid hydrocarbons were studied (Han, et al., 1994; Szoke and Solymos, 1996; Pierella, et al., 1997; Weckhuysen, et al., 1998; Didi, 1998; Sharif, 1999; Eliasson et al., 2000; Erena et al., 2000; Meriaudeau et al., 2000; and Pak et al., 2000) but the results of their research still lead to low conversion and yield as tabulated in Table 1.

The advantages of the modified HZSM-5 zeolite catalyst are metal loaded HZSM-5 can produce different gasoline components, the conversion of methane to gasoline in one step is possible but the selectivity obtained is still low, the cost of gasoline production from natural gas (methane) is substantially reduced because in this process only one reactor is needed while the operating pressure is atmospheric pressure.

ZSM-5 zeolite will be ion-exchanged with acidic metal ion solution. As a result of the modification it is envisaged that aluminium in the framework replaced with the metals. The activity of the HZSM-5 zeolite catalyst can be increased by the addition of metal ions while maintaining the high acidity of the zeolite.

Tabel 1. The Applicability of HZSM-5 and Modify ZSM-5 to Methane Conversion

Catalysts	Conv.CH₄ (%)	Selectivy of Products (%)			
		CO	CO₂	C₂₋₄ (GHC)	C₅⁺(LHC)
HZSM-5	5.0	42.5	50.0	3.5	4.0
Cu/HZSM-5	5.6	0.7	1.0	21.5	76.8
Mo/HZSM-5	5.3	0.6	0.4	21.6	77.4
Mo-HCl/HZSM-5	7.0	0.7	0.7	20.3	78.3
Mo-Co/HZSM-5	6.5	0.8	0.6	23.3	75.3
Mo-Co-HCl/HZSM-5	10.7	0.7	0.6	21.3	77.4

3. Methodology

ZSM-5 zeolite with a SiO_2/Al_2O_3 mole ratio of 30 was supplied by Zeolyst International Co. Ltd. Netherlands. The surface area of the zeolite was 400 m²/g. The W (3% weight) HZSM-5 catalyst was prepared by impregnating a certain amount of the HZSM-5 zeolite carrier with ammonium tungstate hydrate solution (Xiong et al., 2001).

The ammonium tungstate hydrate solution was prepared by dissolving $(NH_4)_2WO_4$ in deionized water. A small amount of H_2SO_4 was added to regulate the pH value of the solution to 2-3. The sample (10 mL of solution per gram zeolite) was dried in an oven at 120°C for two hours and then calcined at 500°C for four hours.

The W loaded Cu/HZSM-5 was prepared by first impregnating a certain amount of the HZSM-5 zeolite carrier with a calculated amount of copper nitrate in aqueous solutions, followed by drying at 120°C for two hours and calcining at 400°C for four hours, and subsequently 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 two hours and calcined at 500°C in air for five hours.

XRD, H_2-TPR, NH_3-TPD, N_2 adsorption, and FT-IR carried out the characterization of catalysts. The performance of the catalysts was tested for methane conversion to liquid hydrocarbons (LHC) via a single step reaction in a fixed-bed micro reactor (Anggoro and Amin, 2001a, b). Methane with 99.9% purity reacted at atmospheric pressure, various temperature and oxygen concentration. An on-line Gas Chromatography with TCD and Porapak-N column was utilized to analyze the gas. The liquid product was analyzed using GC FID and HP-1 column.

4. Results and Discussions

X-ray diffraction (XRD) and nitrogen adsorption (NA) were employed to determine the morphology of the catalysts. The XRD diffractograms of HZSM-5, W/HZSM-5, and Wloaded Cu/HZSM-5 catalysts with different Cu

loadings calcined at 550°C are shown in Figure 2. The peaks at $2\theta = 41$ indicated tungsten oxides (Logie et al., 2000) whilst copper oxides were indicated at $2\theta = 34$ (Li et al., 1999). The intensities of these peaks increased with increasing copper loading.
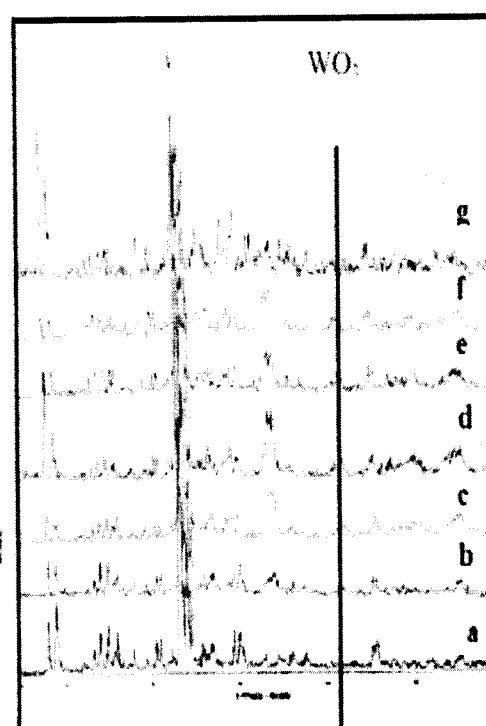
Figure 2. XRD Pattern of (a) HZSM-5; (b) W/HZ; (c) W/0.5Cu/HZ; (d)W/1.0Cu/HZ; (e) W/1.5Cu/HZ; (f) W/2.0Cu/HZ; (g) W/3.0Cu/HZ

The crystallinity values calculated from the XRD diffractograms and the areas of the samples from NA analysis are tabulated in Table 2. The crystallinities of W/1.0Cu/HZM-5, W/2.0Cu/HZSM-5, and W/3.0Cu/HZSM-5 were 89%, 88%, 69%, respectively. These values were lower compared to the values of other samples. All the metal and bi-metal ZSM-5 zeolite catalysts have surface and micropore areas smaller than the parent zeolite.

Table 2. Crystallinity and Surface Area of The Catalysts

Catalysts	Crystallinity	BET surface area (m^2/g)	Micropore area (m^2/g)
HZSM-5	100%	403	373
W/HZSM-5	100%	280	257
W/0.5Cu/HZSM-5	94%	266	243
W/1.0Cu/HZSM-5	89%	286	261
W/1.5Cu/HZSM-5	101%	267	244
W/2.0Cu/HZSM-5	88%	285	260
W/3.0Cu/HZSM-5	69%	236	213

Table 3. Total Volume, Pore Distribution, and Acidity of The Catalysts

Catalysts	Total Vol. (cm^3/g)	Micropore Vol. (cm^3/g)	Ratio Microp. Vol./tot.vol.	Av.Pore Diam. (Å)	Acidity (mol/Kg)
HZSM-5	0.245	0.149	61%	5.2	0.87
W/HZSM-5	0.187	0.106	57%	5.4	0.81
W/0.5Cu/HZSM-5	0.176	0.101	57%	6.0	0.91
W/1.0Cu/HZSM-5	0.175	0.110	63%	6.0	1.01
W/1.5Cu/HZSM-5	0.179	0.101	56%	5.8	1.01
W/2.0Cu/HZSM-5	0.191	0.109	57%	6.0	0.98
W/3.0Cu/HZSM-5	0.176	0.088	50%	5.8	1.19

The reduction in the surface area of the metal-loaded HZSM-5 indicated a strong interaction between the surface of the zeolite and the copper and tungsten species, which enabled a good dispersion of metals on the surface (de Lucas et al., 2001). Among the samples, the BET surface area and the micropore area of W/3.0Cu/HZSM-5 were the lowest at 236 m^2/g and 213 m^2/g, respectively.

The results in Table 3 pertain to the total volume, micropore volume, average pore diameter and acidity of the catalysts. Tungsten and copper species easily entered or partially blocked 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 as revealed by the results in Table 3. The average pore diameter of W/3.0Cu/HZSM-5 was the largest, and as indicated in Table 3, the percentage of micropore volume in the catalyst surface was reduced to 50%.

The ammonia-TPD spectra of the catalyst provided useful information about the intensity and the concentration of the acid sites on the catalysts surface as tabulated in Table 3. The concentrations of the surface acid sites (acidity) of the metal-loaded HZSM-5 were higher than the ZSM-5 zeolite. This could probably be attributed to the average pore diameters of the metal-loaded HZSM-5 which were larger than the pore diameters of HZSM-5 zeolite itself, as shown in Table 3.

Figure 3 depicts the ammonia-TPD spectra of the HZSM-5, W/HZSM-5 and W loaded Cu/HZSM-5 with different amount of Cu loading. For the HZSM-5 and W/HZSM-5, the ammonia-TPD peaks appeared at $\approx 250°C$ and $\approx 430°C$, which may be ascribed to the desorption of two kinds of ammonia species adsorbed on weak acid (mostly Lewis acid) sites and strong acid (mostly Brönsted acid) sites respectively (Woolery et al., 1997).

The addition of 0.5% Cu to HZSM-5 led to the reduced intensity of the high temperature ($\approx 430°C$) peak and a small downshift of its position as revealed in Figure 3. When the amount of Cu loading increased to 1.0%, the high temperature peak disappeared, indicating that most of the surface Brönsted acid sites vanished.

However, as the copper loading was further increased at 1.5% and 3.0%, the ammonia-TPD peaks appeared again at $\approx 430°C$. One interesting feature of Figure 3 is the ammonia-TPD spectra of W/2.0Cu/HZSM-5 which indicated a peak at 400°C (Figure 3(f)). This small peak may be attributed to the emergence of medium strength Brönsted acid sites. This is similar with the results found by previous researchers (Xiong et al., 2001), where the incorporation of Mg^{2+} and Zn^{2+} into the W/HZSM-5 host catalyst resulted in the elimination of strong surface Brönsted acid sites and the generation of new medium strength acid sites.
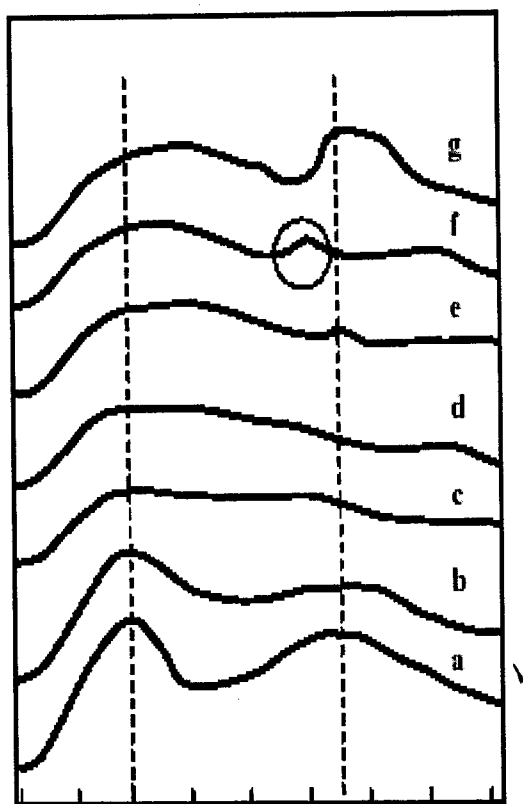
Figure 3. Ammonia-TPD Spectra of (a) HZSM-5; (b) W/HZ; (c) W/0.5Cu/HZ; (d) W/1.0Cu/HZ; (e) W/1.5Cu/HZ; (f) W/2.0Cu/HZ; (g) W/3.0Cu/HZ

The migration of W and Cu species was indirectly studied by infrared (IR) spectroscopy. W/HZSM-5 and W/Cu/HZSM-5 samples showed that in the OH stretching vibration three IR bands at ≈3610 cm⁻¹, due to bridge Si-OH (Al) acidic groups, at ≈ 3660 cm⁻¹ due to non-framework Al sites, or octahedral, and at ≈3740 cm⁻¹ were attributed to terminal Si-OH non-acidic groups (Amin and Anggoro, 2002).

The vibrations (OH) region of the IR spectra of W/HZSM-5 and W/3.0Cu/HZSM-5 zeolite catalysts are shown in Figure 4, where all the fresh samples have bands at ≈3,610 cm⁻¹, ≈ 3,660 cm⁻¹, and ≈ 3,740 cm⁻¹. The spectra indicated that all the samples have aluminum framework, silanol, and aluminum non framework groups. In addition, the IR spectra demonstrated that the intensity of the band at ≈ 3,610 cm⁻¹ of fresh W/HZSM-5 was stronger than fresh W/3.0Cu/HZSM-5. This is probably due to W or W and Cu species that have migrated in the zeolite framework and occupied the H⁺ position. It resulted in a large decrement of the 3610 cm⁻¹ IR
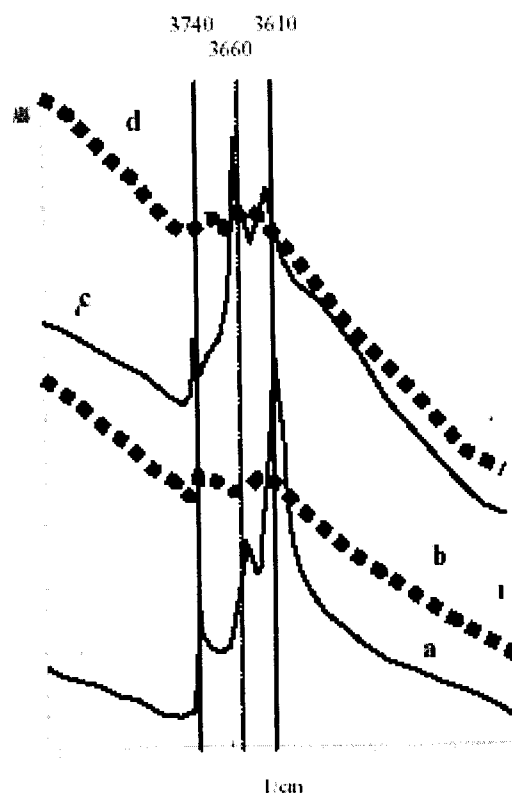

Figure 4. IR Spectra in the OH Region of (_) Fresh (a) W/HZSM-5 and (c) W/3.0Cu/HZSM-5, (---) used (b) W/HZSM-5 and (d) W/3.0Cu/HZSM-5 for Reaction at 800oC

It is clear that the roles of W on W/HZSM-5 and W and Cu on W/Cu/HZSM-5 were to reduce the amount of Brönsted acid sites. The amount of Brönsted acid sites (NBAC) was calculated by bridging OH groups (at 3,609 cm⁻¹ band) according to Amin and Anggoro, (2002) and Wichterlova et al. (1998). The NBAC for the HZSM-5, W/HZSM-5, and W/3.0Cu/HZSM-5 were 2.9 μmole/g, 0.5 μmole/g, and 0.3 μmole/g respectively.

Further reaction with methane and oxygen at 800°C for five hours resulted in the disappearance of the band at ≈ 3,610 cm⁻¹ for both W/HZSM-5 and W/Cu/HZSM-5 samples (Figures 3(b) and 3 (d)). This is probably due to the extraction of aluminum in the zeolitic framework into the non-framework or due to the deposition of carbonaceous residues. The deposition of the coke led to catalyst deactivation after five hours of reaction.

The TPR profiles of W/HZSM-5 and W loaded Cu/HZSM-5 catalysts are depicted in Figure 5. As observed, all the curves contain several peaks in the temperature range of 200-900°C.
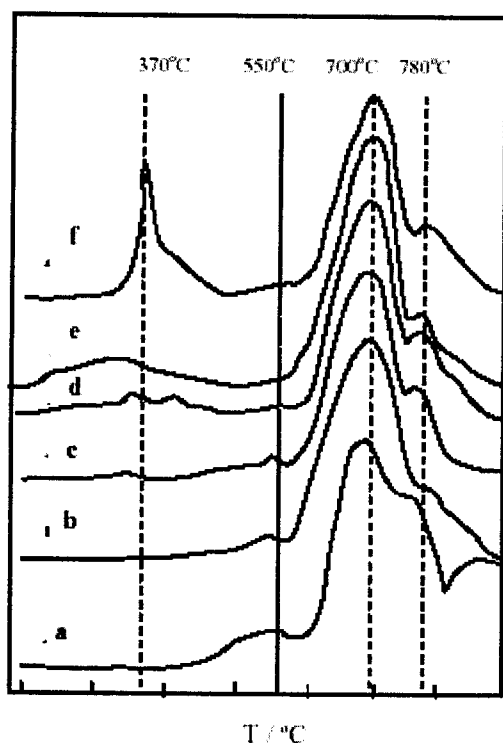
Figure 5. Hydrogen-TPR spectra of (a) W/HZSM-5; (b) W/0.5Cu/HZ; (c) W/1.0Cu/HZ; (d) W/1.5Cu/HZ; (e) W/2.0Cu/HZ; (f) W/3.0Cu/ HZ

The TPR patterns of all catalysts exhibited two peaks with the maximum at 700°C and 780°C. These peaks may be ascribed to the two subsequent steps of single electron reduction of the W^{6+} species derived from the $(WO_4)^{2-}$ precursor with tetrahedral coordination, $W^{6+} + e^- \rightarrow W^{5+}$ and $W^{5+} + e^- \rightarrow W^{4+}$ (Shu et al., 1997). The reducibility of this type of catalyst decreased as the strength of the interaction between the metal oxide species and the surface of the support increased.

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 be due to the single electron reduction of the W^{6+} species derived from the $(WO_6)^{n-}$ precursor with octahedral coordination, $W^{6+} + e^- \rightarrow W^{5+}$ (Xiong et al., 2001). This peak (at 550°C) disappeared if the amount of Cu loading on the HZSM-5 was more than 1.0 wt%. The observed hydrogen-TPR peak at 370°C could be due to the reduction of Cu^{n+} species and the intensity of the peak became stronger as the copper loading increased.

In Table 4 the quantitative results of the TPR is summarized. The tungsten content for all catalysts was constant. The copper content and % of copper dispersed for W/Cu/HZSM-5 catalysts increased with increasing copper concentration

Table 4. Metal State in The Reduced Catalyst Metal

Catalysts	Metal Content (μmol/g)		Metal Surface Area (m²/g)		Dispersion of Metal (%)		Mean Particle Diameter (nm)	
	W	Cu	W	Cu	W	Cu	W	Cu
W/HZSM-5	163	-	2.66	-	55	-	0.0518	-
W/0.5Cu/HZSM-5	163	79	6.02	0.04	100	24	0.0287	1.559
W/1.0Cu/HZSM-5	163	157	4.00	0.07	68	22	0.0419	1.721
W/1.5Cu/HZSM-5	163	236	3.11	0.16	65	40	0.0444	0.930
W/2.0Cu/HZSM-5	163	315	4.18	0.48	76	79	0.0379	0.475
W/3.0Cu/HZSM-5	163	472	4.77	0.92	86	100	0.0332	0.373

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

The results in Table 4 indicated the dispersion of Cu on W/1.0Cu/HZSM-5 was the smallest (about 22%) compared to the other samples, owing to the largest mean particle diameter of Cu (1.721 nm) on W/1.0Cu/HZSM-5. The small percentage of Cu being dispersed on W/1.0/HZSM-5 catalyst led to only a small amount of Cu ions being exchanged with H^+. As a consequence, the acidity of W/1.0/HZSM-5 was

high (1.01 mol/kg), although its pore size was small (24.4 Å). It is clear that the role of Cu on W/Cu/HZSM-5 was not only to reduce W^{6+} species derived from the $(WO_6)^{n-}$ precursor with octahedral coordination, but also to have an effect on the acidity of the ZSM-5 zeolite as revealed by the ammonia-TPD result.

The TPR profiles of W loaded 3.0Cu/HZSM-5 catalysts before and after reaction are depicted in Figure 6. The spectra demonstrated the existence of a single reduction peak of Cu oxide at 370°C. However, after reaction at 800°C the peak disappeared, probably due to the reduction of Cu^{n+}. Nevertheless, the peak of W^{n+} did not change

before and after the reaction. The TPR profile for tungsten revealed that the addition of tungsten has increased the thermal stability of the catalyst, as the W component was not lost by sublimation after reaction at 800°C.
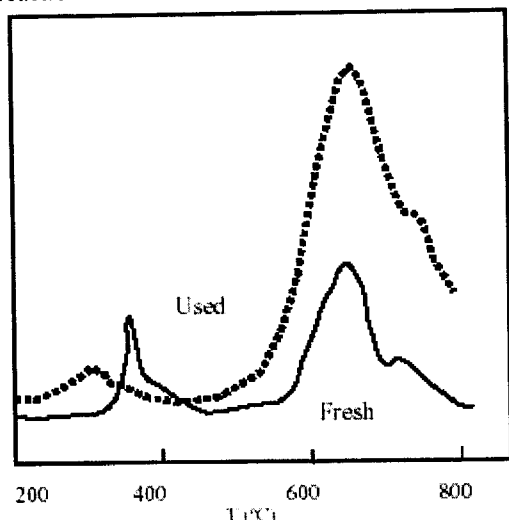

Figure 6. Hydrogen-TPR Spectra of W/3.0Cu/HZSM-5 Catalyst Before and After Reaction at 800°C

The methane conversion increased due to the increasing copper content and copper surface area, as shown in Figure 7. This result demonstrated that the methane conversion was related to the copper surface area.
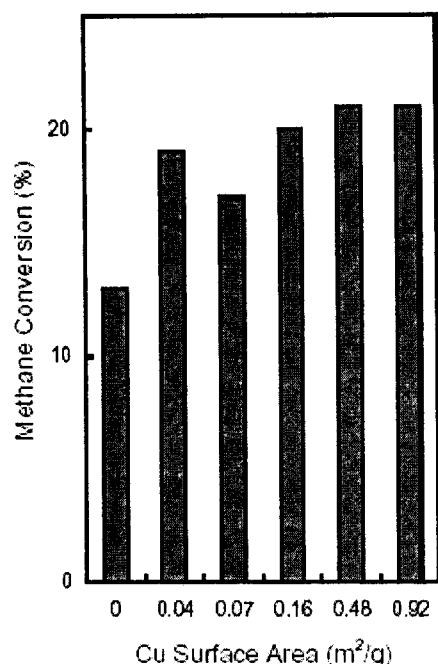

Figure 7. Effect of Cu BET Surface Area on Methane Conversion

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 were C_2H_2, C_2H_4, C_2H_6, C_3H_6, CO, CO_2, H_2O, and liquid hydrocarbons. Figure 8 summarizes the product selectivities of all the catalysts.
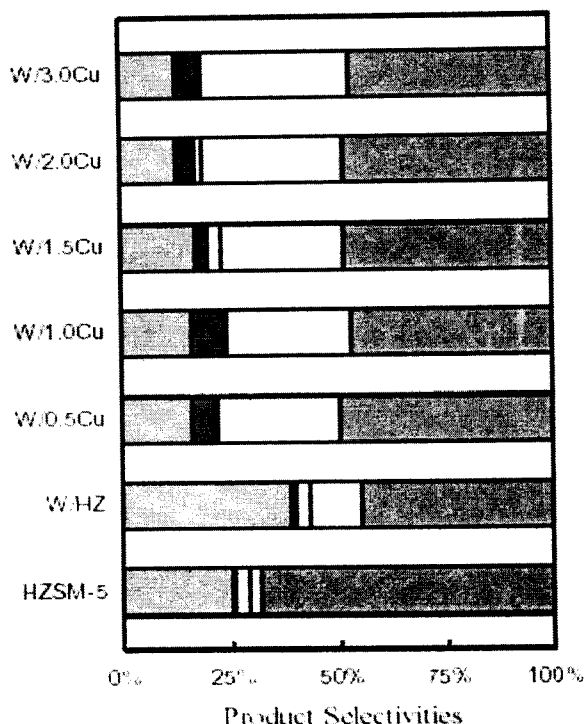

Figure 8. The Distribution of Product Selectivities over Different Catalysts

(▨) CO (■) CO₂ (□) C₂ hydrocarbons (☐) C₂ liquid hydrocarbons (▨) water

The result in Figure 8 shows that over HZSM-5 and metal loaded HZSM-5, the selectivity of carbon monoxide was higher than carbon dioxide. This indicates that the partial oxidation of methane occurred with carbon monoxide and hydrogen as the products. However, hydrogen possibly reacted with carbon dioxide to form water in the Reversed Water Gas Shift (RWGS) reaction.

From the ammonia-TPD (Figure 3) spectra the strength of Brönsted acid sites of W/3.0Cu/ZSM-5 was the strongest among others. These results suggest that production of gasoline form from methane depend on the number and the strength of Brönsted acid sites as well as the total acidity of the catalyst surface. The optimization this reaction was studied using *Statsoft Statistica* (Amin and Anggoro, 2004).

5. Conclusions

The loading of HZSM-5 with tungsten and copper decreased the crystallinity, surface area, and also the total volume of the catalysts. However, the average pore diameter and the acidity of the zeolites increased as a result of the modification with the metals. Such metal particles were smaller than the mesopore size, and the metal particles should be localized to the inner side of the zeolite mesopores. TPR analysis indicated that modified HZSM-5 by loading with Tungsten enhanced its heat resistant performance, and the high reaction temperature (800°C) did not lead to the loss of W component by sublimation.

While loading HZSM-5 with tungsten and copper resulted in an increment in the methane conversion, CO_2 and C_5^+ selectivities, the CO, C^{2-3}, and H_2O selectivities were reduced. The process to convert methane to liquid hydrocarbons (C^{5+}) was dependent on the metal surface area and the acidity of the zeolite. The high methane conversion and C_5^+ selectivity, and low H_2O selectivity are obtained by using W/3.0Cu/HZSM-5 catalyst.

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