

## CATALYTIC ACTIVITY OF Cu-ZSM-5 AND HZSM-5 ZEOLITE FOR SINGLE STEP CONVERSION OF METHANE TO LIQUID HYDROCARBON

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### ABSTRACT

The economical conversion of methane (CH<sub>4</sub>), the principal component of natural gas, to liquid fuels, particularly gasoline (C<sub>5</sub>-C<sub>10</sub>) is one of the main challenges in the gas to liquids (GTL) technology. The existing technology based on Fischer-Tropsch synthesis is adapted by SASOL in South Africa and SMDS in Malaysia. However, the process is energy intensified and costly. The research for the catalyst that is highly active to convert methane to higher hydrocarbons directly has mainly focused on microporous material such as the ZSM-5. The HZSM-5 and Cu-ZSM-5 zeolites were synthesized by hydrothermal crystallization at 170°C for seven days from mixtures containing sodium silicate, aluminium sulfate and tetrapropylammonium bromide (copper nitrate is added for the synthesis of Cu-ZSM-5). The catalysts were characterized using X-Ray Diffraction (XRD), Temperature-Programmed Desorption (TPD) and Nitrogen Adsorption. Methane with 99.9% purity was reacted with compressed air at atmospheric pressure and temperature, T = 800°C. The performance of the synthesized HZSM-5 and Cu-ZSM-5 was tested in a fixed-bed micro reactor at Weight Hour Space Velocity (WHSV) of 10440 ml.g<sup>-1</sup>.hr<sup>-1</sup> with CH<sub>4</sub>/O<sub>2</sub> ratio = 10:1. The percentage of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in the zeolite gel affected the surface area, micropore area, pore size and micropore volume as well as the acidity of the zeolite samples. While the conversion of methane decreased as a result of loading the Cu ions, the selectivities in the gasoline range hydrocarbon exhibit a considerable improvement over catalyst with moderate to high acidity range. For a catalyst with a weak acidity, loading metal ions into the framework may retard the formation of C<sub>5-10</sub> hydrocarbons.

Keyword : Cu-ZSM-5, Direct synthesis, Liquid hydrocarbon, HZSM-5, Methane

### INTRODUCTION

The economical conversion of methane (CH<sub>4</sub>), the principal component of natural gas, to liquid fuels, particularly gasoline (C<sub>5</sub>-C<sub>10</sub>) is one of the main issues in the solution of alternate energy. The existing technology based on Fischer-Tropsch synthesis is adapted by SASOL in South Africa and SMDS in Malaysia. However, the process is energy intensified, and is costly. At present many efforts are geared towards the development of catalysts that can convert methane to higher hydrocarbons over a catalyst such as the ZSM-5 zeolite [1].

ZSM-5 zeolites are shape-selective and acidic. Its high acidity, however, promotes the formation of CO<sub>x</sub> and H<sub>2</sub>O which are not desired for liquid fuels production. The acidity of the ZSM-5 zeolite can be modified by loading transition metals into its framework. ZSM-5 zeolites that are modified by the transition metals have exhibited encouraging performance in catalyzing the reaction between methane and O<sub>2</sub> to directly form gasoline [1-3].

The conversion of the oxidation product, methanol, to olefins and aromatics is probably acid catalyzed, although the olefin to aromatics step may also have an oxidation coupling component. However, the conversion of methane is low (2.7%) and the selectivities of methanol, C<sub>2</sub> and aromatics are low, 0.3%, 7.9% and 6.7%, respectively. Previously, it was reported [1] that selectivity of gasoline reached about 40% over Cu-ZSM-5 catalyst which has a moderate acidity. The acidity of the ZSM-5 zeolites is affected by the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios [4, 5]. In this work, the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios of HZSM-5 zeolites are varied to determine the influence of catalyst acidity in the formation of gasoline. The role of Cu, a strong oxidation component, on affecting the acidity of the zeolite and the oligomerization reaction is also investigated.

## EXPERIMENTAL PROCEDURE

### Preparation of HZSM-5 & Cu-ZSM-5

HZSM-5 and Cu-ZSM-5 zeolites with different SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> ratios were synthesized by hydrothermal crystallization at 170°C for seven days from mixtures containing sodium silicate, aluminium sulfate and tetrapropylammonium bromide (copper nitrate is added for the synthesis of Cu-ZSM-5) based on the method described by Shariff Hussein [2]. The crystalline white solid product was filtered, washed thoroughly with deionised water and dried at 100°C for 12 hours. The resultant material was calcined at 550°C for five hours to remove the organic material and to obtain the sodium form of the ZSM-5. The Na-ZSM-5 form was converted into the NH<sub>4</sub>-form by ion exchange using 1M solution of ammonium nitrate. The procedure was repeated three times. Finally, the catalysts were dried and calcined at 550°C and marked as HZSM-5 (50, 70, 100) and Cu-ZSM-5 (50, 70, 100), accordingly. The catalysts were characterized using X-Ray Diffraction (XRD), Nitrogen Adsorption (NA) and Temperature Programmed Desorption (TPD).

### Reactivity Test

Methane with 99.9% purity was reacted with compressed air at atmospheric pressure and temperature,  $T = 800^\circ\text{C}$ . The performance of the synthesized HZSM-5 and Cu-ZSM-5 was tested in a stainless steel tube reactor (9 mm internal diameter and 300 mm in length) which was mounted vertically and heated by an electric furnace operating at Weight Hour Space Velocity (WHSV) of  $10440 \text{ ml.g}^{-1}.\text{hr}^{-1}$  with CH<sub>4</sub>/O<sub>2</sub> ratio = 10:1 as shown in Figure 1.

The products were separated into liquid and gas fractions through a series of two condensers cooled with ice. Samples of the gaseous product stream were filled and sealed in pre evacuated glass ampoules. The liquid and gaseous product were analyzed by gas chromatography (Perkin Elmer) using HP-1 capillary column.

The GC conditions for the gas fraction were : column temperature 75°C to 285°C with rate 15°C min<sup>-1</sup> then 10 min hold at 285°C, injection temperature 250°C, detector temperature 250°C, and helium flow rate 10 ml min<sup>-1</sup>. The samples were injected in the syringe mode at a column temperature of 75°C. Peaks were identified by matching their retention times with those of analyzed gases standards, Scott Specialty Gases, Supelco, USA (Cat. No. 2-2566).

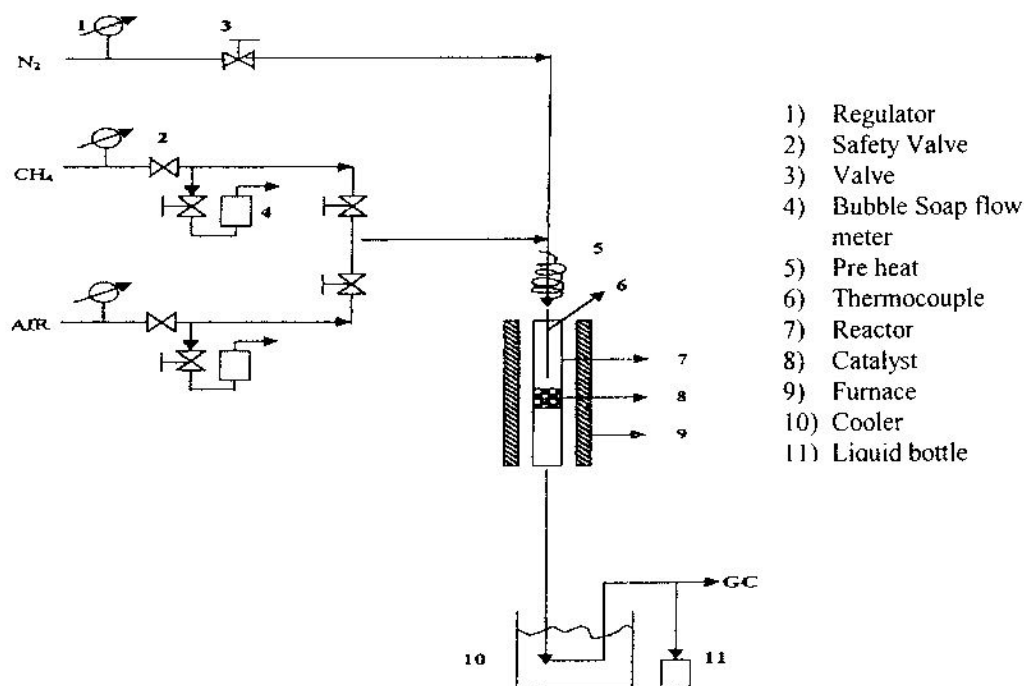


Figure 1 : Schematic diagram of the micro-reactor system used in this study

The GC conditions for liquid fraction were: column temperature 35°C to 203°C (2 min hold at 35°C then 14°C min<sup>-1</sup>), injection temperature 300°C, detector temperature 300°C, and helium flow rate 10 ml min<sup>-1</sup>. The samples were injected in the syringe mode at a column temperature of 35°C. Peaks were identified by matching their retention times with those of n-Parafins Mix standards, Supelco, USA (Cat No 4-4585).

The selectivity of hydrocarbon and methane conversion were calculated for all the catalysts. Percentage conversion is defined as mole of methane reacted divided by mole of methane fed multiplied by 100%. Percentage selectivity is defined as mole of hydrocarbon obtained divided by mole of total product multiplied by 100%.

## RESULTS AND DISCUSSION

### Catalysts properties

All HZSM-5 and Cu-ZSM-5 have XRD patterns similar to the commercial HZSM-5 (Figure 2) indicating that the structure of the zeolites did not collapse even after Cu ions were loaded into the framework. There is no evidence of Cu<sup>2+</sup> being incorporated in the framework from the XRD diffractograms presented. However, there are changes in the peak intensities and this could be due to the change in aluminium content and the presence of copper ions [1].

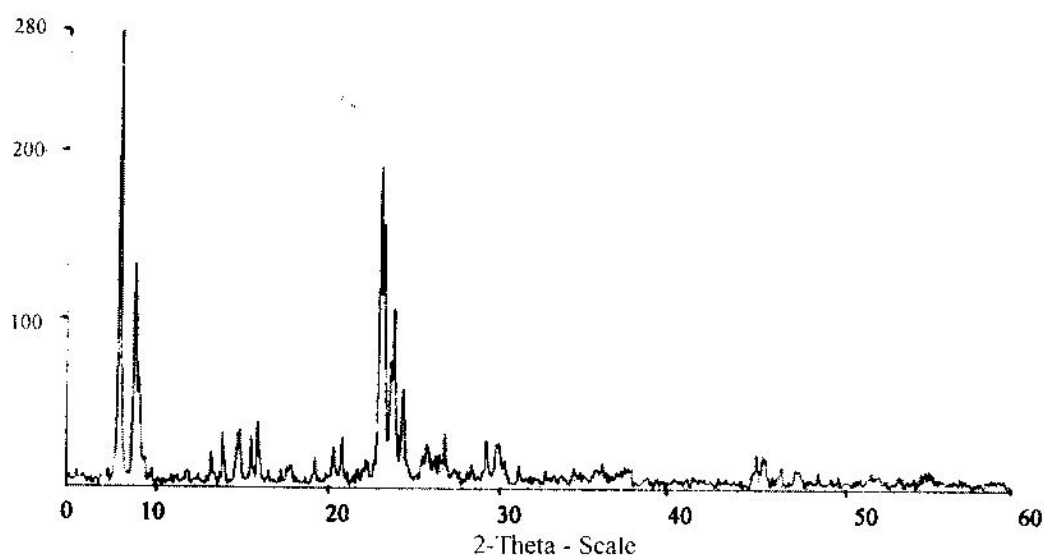


Figure 2: XRD Diffractogram of zeolite HZSM-5(100)

The variations in the micropore area and micropore volume of Cu-ZSM-5 and HZSM-5 are presented in Table 1. The results reveal that the micropore areas and micropore volumes for catalysts with 50 and 70 SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios did not differ largely after Cu is loaded into the framework. The CuZSM-5(100) catalyst exhibited a marked increment in the micropore area and micropore volume when compared to the HZSM-5 zeolite. Similarly, Figures 3 and 4 indicate that CuZSM-5(100) has a larger surface area and smaller pore size as a result of the Cu ion being loaded into the zeolite framework.

The results in Table 1 and Figure 3 indicate the micropore area and the micropore volume of Cu-ZSM-5 are higher than HZSM-5 with similar SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio. This implies that some of the copper ions were attached on the surface of the zeolites and some were trapped in the catalyst pores. As a result, the surface areas (Figure 3) of all Cu-ZSM-5 zeolites are higher than HZSM-5 and that the pore sizes (Figure 4) of Cu-

ZSM-5 are smaller than HZSM-5 for their respective SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios. Among all the zeolites, CuZSM-5(100) has the largest surface area while HZSM-5(70) has the smallest. The pore size of CuZSM-5(100) is the smallest while HZSM-5 (50) is the largest.

Table 1 : Results of Nitrogen Adsorption Analyst of Cu-ZSM-5 and HZSM-5 for different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio

Catalysts	Micropore Area (m <sup>2</sup> /g)	Micropore volume (cm <sup>3</sup> /g)	Ratio Micropore Area/BET S.Area
HZSM-5(50)	383.6	0.16	0.92
HZSM-5(70)	348.1	0.15	0.87
HZSM-5(100)	377.9	0.17	0.88
CuZSM-5(50)	387.6	0.17	0.92
CuZSM-5(70)	353.9	0.15	0.87
CuZSM-5(100)	431.2	0.18	0.90

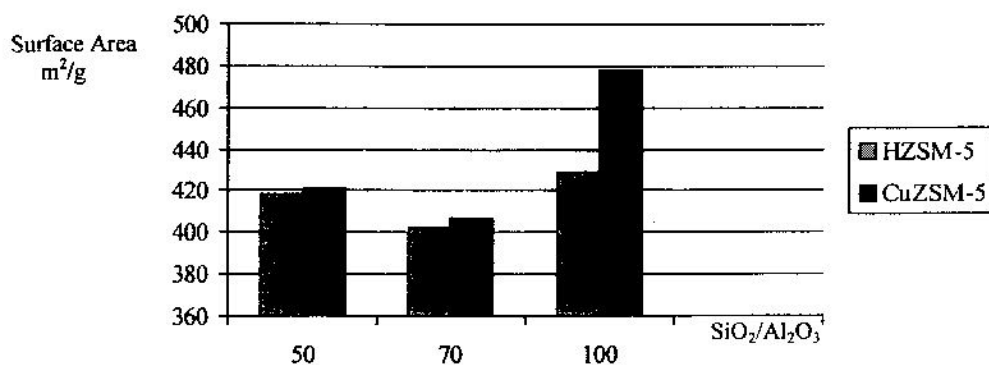


Figure 3 : Surface area pattern for HZSM-5 and Cu-ZSM-5 for different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio

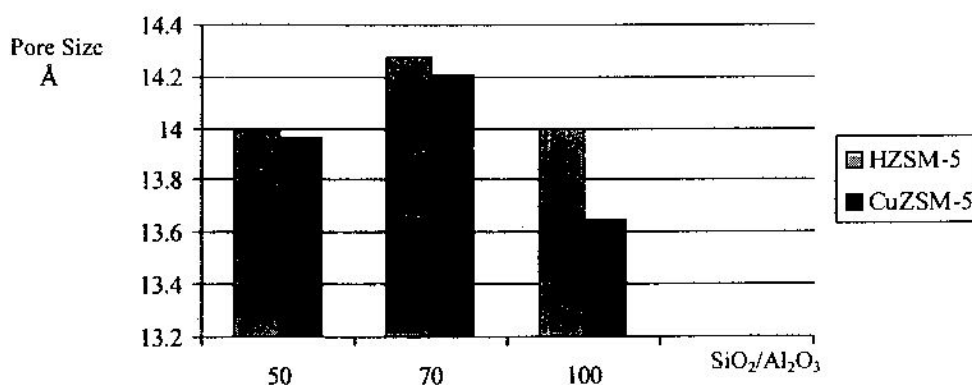


Figure 4 : Pore size pattern of HZSM-5 and Cu-ZSM-5 for different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>

The result from TPD provide information on the amount of chemisorbed (acidity) of the series of HZSM-5 and CuZSM-5. The amount of acidity on a solid is usually expressed as the number or mmol of acid sites per unit weight or per unit surface area of the solid. The amount of chemisorbed for Cu-ZSM-5 decreased in the following order: Cu-ZSM-5(50)>Cu-ZSM-5(70)>Cu-ZSM-5(100) whereas the amount of chemisorbed for HZSM-5 decreased in the following order: HZSM-5(50)>HZSM-5(70)>HZSM-5(100).

The results in Table 2 reveal that the acidity of the zeolites decreased as the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of the zeolites increased, similar as the result postulated by Topsoe, Pederson and Derovane [6].

The relationship between zeolite acidity and the surface area is discussed next. The zeolite with the least acidity [(HZSM-5(100) and Cu-ZSM-5(100))] gave the largest surface area. The variation observed are attributable to the number of active acid sites in the intracrystalline volume. The ratio between the micropore area and the surface area tabulated in Table 1 show that the catalysts contain higher micropores than the mesopores.

Table 2: Acidity of zeolites

Catalysts	Acidity (moles/kg)	Catalysts	Acidity (moles/kg)
HZSM-5 (50)	0.96	Cu-ZSM-5 (50)	0.98
HZSM-5 (70)	0.71	Cu-ZSM-5 (70)	0.82
HZSM-5(100)	0.59	Cu-ZSM-5(100)	0.41

### Catalyst Activity

The results of the various catalytic performances for the reaction between methane and oxygen at 800°C and atmospheric pressure are given in Figure 5. The table summarizes the methane conversion and the liquid hydrocarbon compositions for C<sub>5-10</sub>, C<sub>11-15</sub> and >C<sub>16</sub> hydrocarbons for the catalyst tested.

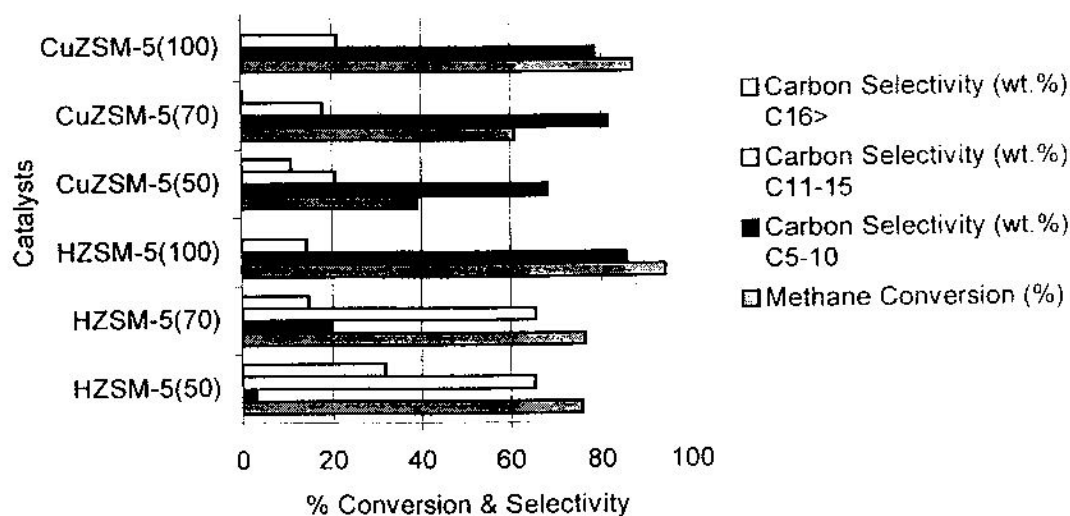


Figure 5 : Results of the catalyst testing on methane reaction with oxygen

The highest methane conversion came from the reaction over HZSM-5(100) catalyst followed by Cu-ZSM-5(100). With reference to Figure 3, the surface areas for both the catalysts are larger than the other samples. All HZSM-5 gave better conversion than their respective Cu-ZSM-5 for the same silica to alumina ratio. The relationship between catalysts acidity and methane conversion is shown in Figure 6. As the acidity decrease, methane conversion increase. This could be due to the lower moles of acid sites but higher in acid strength [5] which resulted in higher methane conversion.

The selectivities for C<sub>5-10</sub> for all HZSM-5 ratios increased with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios. The oxidation and dehydrogenation functions of Cu<sup>2+</sup> ions are evident from the selectivities of gasoline which increase from 3.13% to 68.3% and 19.8% to 81.6% over CuZSM-5 (50) and CuZSM-5(70), respectively. By the same token, the selectivities of C<sub>11-15</sub> and C<sub>16+</sub> decrease. The results over HZSM-5(100) and CuZSM-5(100) are quite different. Rather than showing an improvement in the catalytic performance when Cu ions are present the selectivities for C<sub>5-10</sub> hydrocarbons decrease from 85.6% to 78.7% while the selectivities for C<sub>11-15</sub>

hydrocarbons increased from 14.4% to 21.3%. From Figure 6, when acidity decrease, C<sub>5-10</sub> selectivity increase. Again, this might be because of the lower moles of acid sites but higher in acid strength for the catalysts with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 100. The functions of the metal to oligomerize is somehow triggered and longer hydrocarbon chains were propagated. The trend inferred that the acidity influence from the zeolite and the functions of the metals in the bifunctional catalysts need to be further studied. The results in Figure 5 also indicated that no hydrocarbon >C<sub>16</sub> is formed. The results suggested the pore sizes of the catalyst are big enough for <C<sub>15</sub> hydrocarbons only.

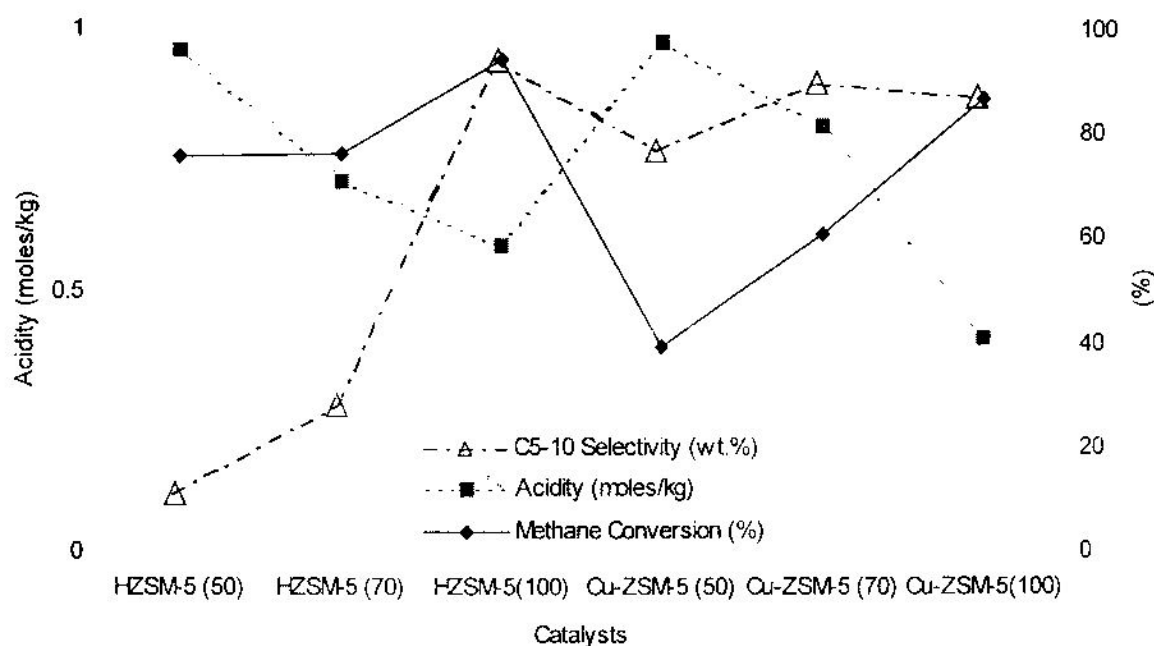


Figure 6 : Relationship of catalyst acidity, methane conversion and C<sub>5-10</sub> selectivity

## CONCLUSIONS

The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio affected the surface area, micropore area, pore size and micropore volume as well as the acidity of the zeolite samples. While the conversion of methane decreased as a result of loading the Cu ions, the selectivities in the gasoline range hydrocarbon exhibits a considerable improvement for catalyst with moderate to high acidity range. For a catalyst with a weak acidity, loading metal ions into the framework may retard the formation of C<sub>5-10</sub> hydrocarbons.

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