

## Catalysts Screening for Catalytic Conversion of Glycerol to Olefins

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**Abstract:** Biodiesel is produced by trans esterification, in which the fats/oils react with methanol to form biodiesel methyl esters and glycerol, the latter being sold as byproduct. As biodiesel is rapidly produced, glycerol has become abundantly available and cheaper. The unique feature of glycerol and the cost advantage attracts researchers to seek for ways to utilize and transform glycerol to useful products. Among important chemicals that can be produced from glycerol is olefin. Olefin can be produced via catalytic reaction of glycerol with zeolite ZSM-5 based catalysts at high temperature. The zeolite catalysts were prepared by impregnation with several metals including chromium, calcium, copper, nickel and aluminium. From the experiment, CuZSM-5 has given the highest conversion and olefins yield with 17.72 and 3.55%, respectively.

**Key words:** Glycerol, olefin, catalytic conversion, zeolite, cracking, dehydrogenation

### INTRODUCTION

Biodiesel is an alternative fuel produced from renewable resources such as palm, canola, soya bean and rape seed oil (Hass, 2005). It is produced via transesterification reaction of fatty acid and alcohols. Approximately 10% of glycerol, an alcohol with three hydroxyl groups is produced as a byproduct in this reaction (Karinen and Krause, 2006; Chew and Bhatia, 2008; Huber *et al.*, 2007). The crude glycerol obtained is about 50% pure and is a huge potential as raw material to produce other valuable products (Chitra *et al.*, 2005; Pathak *et al.*, 2010) in manufacturing of drugs, cosmetics, synthetic resins, ester gums and gas production (Wolfson *et al.*, 2007). As more and more crude glycerol is generated as biodiesel by-product, efforts to seek for economical ways to convert glycerol to useful chemicals continue and this can indirectly minimize the cost of biodiesel production. One of the valuable chemicals that can be converted from glycerol is olefin (Zhou *et al.*, 2008; Pagliaro and Rossi, 2008), a petrochemical derivative conventionally produced by thermal cracking of natural gas and crude oil. Lower olefins have short chains with only two to four carbon atoms and the simplest one is ethylene. The higher olefins have chains of up to twenty or more carbon atoms. Main olefins products like ethylene, propylene, butadiene and C<sub>4</sub> derivatives are used to produce plastics, chemical intermediates, industrial solvents and others (Li *et al.*, 2007).

The objective of this study is to investigate the most suitable metal addition in zeolite HZSM-5 catalyst to increase the production of olefins via catalytic conversion of glycerol. In order to achieve the objective, a set of HZSM-5 zeolite based catalysts were impregnated with potential metals and tested. The structure of the modified catalysts was observed and the effect of the modified structure towards production of olefins from glycerol was studied. Parameters for this study include types of metal used to enhance active acid sites on the surface of the zeolite catalyst. Catalysts characterizations employed were X-ray Diffraction (XRD) and Fourier Transform Infra Red (FTIR). Products from the reaction were analyzed using gas chromatography (GC) from which the best catalyst was identified.

### MATERIALS AND METHOD

**Materials:** The main reagent used was HZSM-5 ( $n\text{SiO}_2/n\text{Al}_2\text{O}_3 = 30$ , molar ratio) which was purchased from Zeolist International and glycerol of 87.5% pure. The unmodified HZSM-5 catalyst was used as reference.

**Catalyst preparation:** The HZSM-5 catalyst was impregnated with different metals, namely chromium, aluminium, calcium, copper and nickel. The zeolite was added into 100 mL distilled water. Then the metals were added into the solution. For chromium metal, the zeolite was impregnated by 0.3 g of  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  with incipient-wetness impregnation method. For aluminium,

Table 1: Table of catalysts

| Catalysts | Weight% of active metal (g) | Before calcination (Crucible+sample)(g) | After calcination (Crucible+sample)(g) |
|-----------|-----------------------------|---|--|
| HZSM-5    | -                           | -                                       | -                                      |
| CrHZSM-5  | 10                          | 60.04                                   | 59.33                                  |
| AlHZSM-5  | 10                          | 59.03                                   | 58.12                                  |
| CaHZSM-5  | 10                          | 60.10                                   | 59.41                                  |
| CuHZSM-5  | 10                          | 58.67                                   | 57.12                                  |
| NiHZSM-5  | 10                          | 59.83                                   | 58.44                                  |

calcium, copper and nickel, the zeolite was impregnated with 0.3 g of aluminum nitrate, calcium chloride, copper (III) hydrate and nickel nitrate, respectively. The impregnation period lasted for half an hour at a temperature range of 30-40°C and then dried at 100°C and finally calcined at 550°C for 5 h (Murata *et al.*, 2008).

The weight of all catalysts was measured before and after impregnation in order to observe the weight loss during the process. The weight loss of the catalyst is listed in Table 1. One of the factors contributing to weight loss is the decomposition of metal precursors throughout the process.

Then, the catalysts were transferred into vials and marked as HZSM-5, CrHZSM-5, CuHZSM-5, AlHZSM-5, NiHZSM-5 and CaHZSM-5. Visually, catalysts with copper, calcium, nickel and aluminium metal were white in colour while slightly greenish powder was formed for catalyst with chromium.

X-Ray diffraction was performed using Siemens Diffractometer D5000 (Software Diffract Plus) with CuK  $\alpha$  radiation,  $\lambda = 1.54056\text{\AA}$  at 40 kV and 30 mA in the range of  $2\theta = 5^\circ$  to  $80^\circ$  at a screening speed of  $0.05^\circ$  per second, with a vertical goniometer at room temperature ( $20^\circ\text{C}$ ). The sample was held on mountain sample holder and then grounded before mounting on glass.

The existence of impregnated metal in zeolite catalysts was analyzed by Fourier Transform Infra Red (FTIR). Spectrum one FTIR Spectrometer and spectrum 20 explorer with instrumentation model spectrum one was used to characterize the catalysts. The sample was grounded with spectrograde KBr to form a mixture, which was pelletized using a hydraulic press. This pellet was used to record the infrared spectrum in a range of  $4000\text{-}375\text{ cm}^{-1}$ .

**Catalyst evaluation:** The catalysts performance testing was carried out in a fixed bed stainless steel reactor, with outside diameter of 13 mm and 35 cm length, positioned inside a Carbolite tubular furnace as illustrated in Fig. 1. Glycerol solution with 50% dilution was prepared as feed for the reaction. The prepared catalyst was sandwiched between quartz wools inside the reactor. Prior to starting the test, the catalyst was activated in a flow of helium gas for 1 h at  $500^\circ\text{C}$  to remove moisture and prepare the



Fig. 1: The reactor is heated inside this tubular furnace which is part of the experimental set-up of the reaction

catalyst for reaction. This was immediately followed by the reaction where temperature was set at  $700^\circ\text{C}$ , pressure 1 atm and lower space velocity with long residence times (20-80 sec) in order to obtain high olefins (Corma *et al.*, 2008). The products were then analyzed with gas chromatography equipped with both Thermal Conductive Detector (TCD) and Flame Ionization Detector (FID). The HP 6890N GC-TCD/FID is equipped with HP plot/Q, HP-Mole sieve, DB-1 and Hayasep-Q columns which are able to detect important compounds in this research such as olefins, paraffin and oxygenates.

## RESULTS AND DISCUSSION

**Catalyst characterization findings:** Figure 2 presents XRD patterns of HZSM-5 and the modified zeolite with different metals of nickel, aluminium, copper, chromium and calcium. The XRD patterns were analysed between  $5^\circ$  and  $45^\circ$  with  $2\theta$  scale. The X-ray diffraction pattern of the modified HZSM-5 completely matched with that of the parent HZSM-5, which indicates that the combined-modification measurement has no obvious effect on parent zeolite structure (Peiqing *et al.*, 2004). There was also no new phase formation during heat treatment and zeolite modification. The XRD pattern of the modified zeolite indicates that the structure of the zeolites remains intact after doping different metals over HZSM-5. No peak related to the metals was found on the diffractogram (Zaidi and Pant, 2005; Corma *et al.*, 2008).

This pattern reveals that the metals were highly dispersed on the HZSM-5. This finding is corroborated by the suggestions made by Jiangyin *et al.* (2006), where he stated that there are no diffraction peaks corresponding to the metal observed up to 40% loading in the XRD analysis. However the obtained intensities differ depending upon metals content. The highest intensity was observed for the CrHZSM-5, followed by AlHZSM-5, CaHZSM-5, NiHZSM-5, CuHZSM-5 and HZSM-5. The decrease in the intensities may due to the higher absorption coefficient of copper metals.

Figure 3 illustrates the FTIR spectra when different metals were impregnated to the HZSM-5 catalysts. The spectra shows that the impregnated metals do not change the characteristic of zeolite catalysts. The broad peak was

observed at  $3600\text{ cm}^{-1}$  that consist of O-H bond for phenols functional groups. Another peak was present at  $1637\text{ cm}^{-1}$  for all catalyst, corresponding to the H-O-H bonding in the structure. All catalysts also show three other significant broad bands at 1230, 1100 and  $796\text{ cm}^{-1}$  which are associated with asymmetric and symmetric stretching vibrations of the Si-O-Si. These bands are also related to the internal linkages in  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  of zeolite lattice (Jiangyin *et al.*, 2006). The FTIR spectra for all modified catalysts were similar to each other except for AlZSM-5 that has a slightly different pattern. This may be due to the metal addition that alters the compositions of aluminium compound in zeolite structure, since the zeolite itself has certain aluminium ratio.

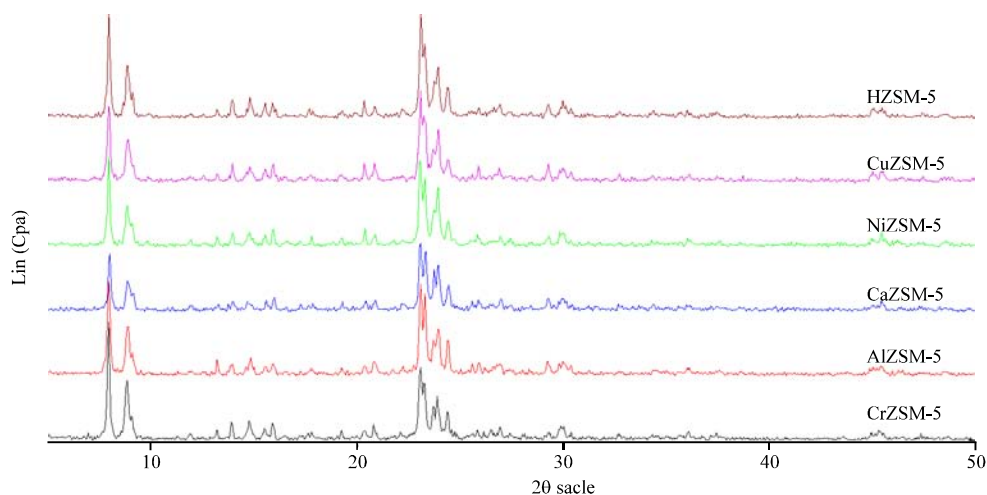


Fig. 2: XRD spectra for various impregnated metal ZSM-5 catalyst

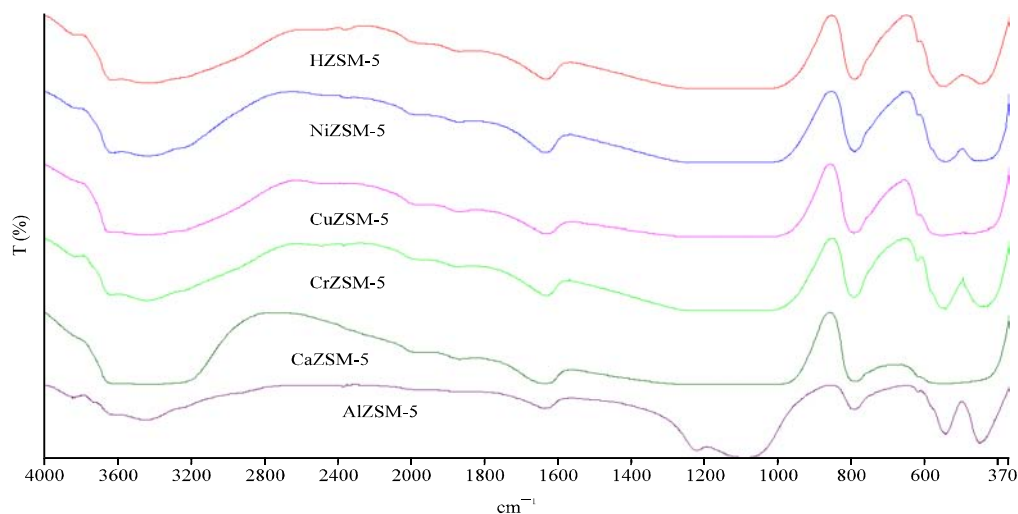


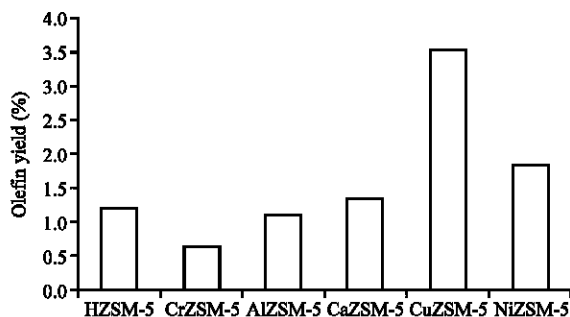
Fig. 3: FTIR spectra for various impregnated metal ZSM-5 catalyst

**Table 2: The reactivity and selectivity (%) of M-ZSM-5 for the reaction of glycerol to olefin at T = 700°C**

| Catalysts | Glycerol conversion (%) | Olefins yield (%) | Liquid product selectivity (%) |                   |                        |               |
|-----------|-------------------------|-------------------|--------------------------------|-------------------|------------------------|---------------|
|           |                         |                   | Methanol                       | 3-methyl-1-butene | 2-methyl-1,3-butadiene | Other product |
| HZSM-5    | 11.62                   | 1.20              | 89.20                          | 10.80             | -                      | -             |
| CrZSM-5   | 10.85                   | 0.63              | 48.28                          | 51.72             | -                      | -             |
| AlZSM-5   | 10.44                   | 1.09              | -                              | 100               | -                      | -             |
| CaZSM-5   | 15.02                   | 1.34              | -                              | 19.05             | -                      | 80.95         |
| CuZSM-5   | 17.72                   | 3.55              | 19.12                          | 16.57             | 1.49                   | 62.82         |
| NiZSM-5   | 16.07                   | 1.84              | 2.78                           | 10.18             | -                      | 87.04         |

**Reactivity and selectivity:** The effect of different metals on the reactivity and selectivity of MZSM-5 (M = metal) catalysts for the reaction of glycerol at high temperature (700°C) with catalyst load mass 0.2 g is shown in Table 2. From the table, it is shown that the highest conversion of glycerol to olefins is with CuZSM-5 with 17.72% conversion. It is followed by the reaction of glycerol with NiZSM-5, CaHZSM-5, HZSM-5, CrHZSM-5 and AlHZSM-5 with percentage conversion of 16.07%, 15.02%, 11.62%, 10.85 and 10.44%, respectively. From the experiments it was found that the reaction produced methanol, olefins (3-methyl-butenes and 2-methyl-1, 2-butadiene) and other products. The highest selectivity of olefins is 100% with aluminium impregnated zeolites, evident by a GC report that shows only olefins peak is available for the reaction. Besides that, about 51.27% selectivity of olefins was recorded when glycerol was cracked with the assistance of CrHZSM-5 at 700°C. This agrees well with Lu *et al.* (2006) who has reported that the selectivity to butene smoothly increased with raising the loading amount of the Cr (III), when CrZSM-5 reacts in catalytic cracking of isobutane to produce light olefins. The analysis of the gaseous product was carried out using gas chromatography (GC-TCD) having a 10 ft column 80/100 Porapak N. From the chromatogram obtained no peaks were detected. This might be due to the small volume of the gaseous product. Besides, the low concentration of the gaseous product also makes it difficult for the GC to detect and identify the compound.

**Effect of metal impregnated ZSM-5 catalyst on product yield:** Compared with unmodified HZSM-5 zeolite, more olefins were comparatively produced from CaHZSM-5, CuHZSM-5 and NiHZSM-5. However, the yield of olefins decreased when chromium was used as active metal as shown in Fig. 4. Highest olefin yield was observed for reactions with copper impregnated zeolite. As stated by Zaidi and Pant (2005), copper oxide doped HZSM-5 catalyst result in an increased activity for conversion of methanol to liquid hydrocarbons of gasoline range. Compared to HZSM-5 catalyst there was a significant increase in conversion and hydrocarbon yield over CuO impregnated catalyst. The percentage of olefins yields using copper, nickel and calcium impregnated ZSM-5 is



**Fig. 4: Olefin yield for various active metal ZSM-5 catalysts**

high compared to unmodified zeolite. These results demonstrate that a small amount of metal inclusion like copper, calcium and nickel plays an important role of modification, not only did it enhance the reactivity for the glycerol conversion, but also increase the selectivity of olefins, especially the selectivity to 3-methyl-1,2-butadiene. CrZSM-5 and AlZSM-5 gave the lowest olefin yield. This might due to the metals altering the active sites of zeolite catalyst, hence resulting the catalyst to deactivate and not reactive. This is consistent with work reported by Jiangyin *et al.* (2006) and Lu *et al.* (2006) where one reason for the ineffective of chromium metal zeolite to yield high olefins is because the trace amount of Cr alters the acidity of the HZSM-5 catalysts. This shows that suitable strength and amount of acidity of the catalyst are important factors in favouring high olefin yields.

**CONCLUSION**

Catalysts screening of various metal impregnated ZSM-5 for catalytic conversion of glycerol to olefins has been carried out by testing its performance in a fixed bed reactor. Evidently, metal doped ZSM-5 resulted in an increase of activity and improved conversion of glycerol as well as the olefins yields. The products obtained were methanol, olefins and other unidentified compounds. CuZSM-5 has shown the best glycerol conversion and yield with 17.76% and 3.55%, respectively. The high reaction temperature makes the catalyst more active and favours the yield of light olefins.

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## REFERENCES

- Chew, T.L. and S. Bhatia, 2008. Catalytic processes towards the production of biofuels in a palm oil and oil palm biomass-based biorefinery. *Bioresour. Technol.*, 99: 7911-7922.
- Chitra, P., P. Venkatachalam and A. Sampatharajan, 2005. Characterization and purification of crude glycerol recovered from transesterification of jatropha curcus oil. *Madras Agric. J.*, 9: 241-243.
- Corma, A., G.W. Huber, L. Sauvanaud and P. O'Connor, 2008. Biomass to chemicals: Catalytic conversion of glycerol/water mixture into acrolein, reaction network. *J. Catalysis*, 257: 163-171.
- Hass, M.J., 2005. Improving economics of biodiesel production through the use of low value lipids as feedstocks: Vegetable oil soapstocks. *Fuel Process. Technol.*, 86: 1087-1096.
- Huber, G.W., P.O. Connor and A. Corma, 2007. Processing biomass in conventional oil refineries: Production of high quality diesel by hydrotreating vegetable oils in heavy vacuum oil mixtures. *Applied Catalysis A: Gen.*, 329: 120-129.
- Jiangyin, L., Z. Zhao, C. Xu, A. Duan and P. Zhang, 2006. CrHZSM-5 zeolites-highly efficient catalysts for catalytic cracking of isobutene to produce light olefins. *Catalysis Lett.*, 109: 65-70.
- Karinen, R.S. and A.O.I. Krause, 2006. New biocomponent from glycerol. *Applied Catalysis A: Gen.*, 306: 128-133.
- Li, X., B. Shen, Q. Guo and J. Gao, 2007. Effects of large pore zeolite additions in the catalytic pyrolysis catalyst on the light olefins production. *Catalysis Today*, 125: 270-277.
- Lu, J., Z. Zhao, C. Xu, A. Duan and P. Zhang, 2006. CrHZSM-5 zeolites-Highly efficient catalysts for catalytic cracking of isobutene to produce light olefins. *Catalysis Lett.*, 109: 65-70.
- Murata, K., I. Takahara and M. Inaba, 2008. Propane formation by aqueous-phase reforming of glycerol over Pt/H-ZSM-5, catalysts. *Reaction Kinetics Catalysis Lett.*, 93: 59-66.
- Pagliaro, M. and M. Rossi, 2008. *The Future of Glycerol: New Usages for a Versatile Raw Material*. 2nd Edn., The Royal Society of Chemistry, Cambridge, ISBN: 978-1-84973-046-4.
- Pathak, K., K.M. Reddy, N.N. Bakhshi and A.K. Dalai, 2010. Catalytic conversion of glycerol to value added liquid products. *Applied Catalysis A: Gen.*, 372: 224-238.
- Peiqing, Z., W. Xiangsheng, G. Xinwen, G. Hongchen, Z. Leping and H. Yongkang, 2004. Characterization of modified nanoscale ZSM-5 zeolite and its application in the olefins reduction in FCC gasoline. *Catalysis Lett.*, 92: 63-68.
- Wolfson, A., C. Dlugy and Y. Shotland, 2007. Glycerol as a green solvent for high product yields and selectivities. *Environ. Chem. Lett.*, 5: 67-71.
- Zaidi, H.A. and K.K. Pant, 2005. Catalytic activity of copper oxide impregnated HZSM-5 in methanol conversion to liquid hydrocarbons. *Can. J. Chem. Eng.*, 83: 970-977.
- Zhou, C.H., J.N. Beltramini, Y.X. Fan and G.Q. Lu, 2008. Chemoselective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals. *Chem. Soc. Rev.*, 37: 527-549.