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Study on Conversion of Glycerol to Light Olefins over Modified ZSM-5

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Abstract—*Due to large scale production of Biodiesel, glycerol (by-product) is produced in surplus amount. Glycerol has qualities to be converted into value-added products and chemicals. In this study, metals nickel, magnesium and copper doped over ZSM-5 catalyst were prepared and tested. The screening process for ZSM-5 and modified ZSM-5 catalysts have been investigated in this study. The reaction takes place in fixed bed reactor and temperature of the system is 450-600°C and atmospheric pressure. XRD and SEM characterization is done to study the structure and shape of the catalyst. GC TCD/FID analyze light olefins, paraffin, methane, CO and carbon dioxide in gaseous product stream. Cu/ZSM-5 gives 100% conversion and gives highest yield*

Keywords*: ZSM-5, Glycerol, Olefins.*

1. INTRODUCTION

The worldwide increase in production of biodiesel via renewable resources has gained more attention as it provides an alternative for renewable resources. Biodiesel is produced by transesterification of fatty acids & alcohols. In this process approximately 100kg of glycerol is produced as by-product per ton of biodiesel [1,3,6,8]. The continued production of biodiesel leads to surplus amount of glycerol which reduces its price in market. Glycerol has a huge potential to be converted into other valuable products like acrolein [7], gasoline [9] formaldehyde, acetol, propane [5], alkyl aromatics [2,4]. Now a days, some studies have been investigated to convert glycerol to one of the most valuable chemical i.e. olefin. Olefin is a petrochemical derivative which is also produced by thermal cracking of naphtha and crude oil which is a non-renewable process [6]. The two main olefins which are used in petrochemical industry are ethylene and propylene [1, 6]. They are mainly used in making plastics.

In this paper, we investigate the production of olefins via catalytic cracking of glycerol by using ZSM-5 and modified ZSM-5 as a catalyst. Here the ZSM-5 catalyst is doped with different metal via wet impregnation method. The parameters which affect the process or cracking of glycerol are acidic sites of catalyst and surface of zeolite. The modified zeolite catalyst promotes formation of olefins by increasing acidic sites of zeolite catalyst. The cyrstallinity of ZSM-5 before and after loading metals were analyzed by X-ray diffraction (XRD) technique. And the Morphology of the sample was determined by scanning electron microscope. The products evolved from the reaction were analyzed by Gas-chromatography.

2. EXPERIMENT

2.1 Catalyst preparation

The ZSM-5 catalyst was doped with metals (Ni, Mg, and Cu) via wet impregnation method. The ZSM-5 was impregnated with aqueous solution containing desired amount of nitrate solution of different metals. The impregnation period last for 30 min at temperature range of 40-50°C and then dried the sample at 100°C and then finally calcined the product at 600°C (heating rate of 10°C/min) for 5 hrs.

2.2 Catalyst activity testing

The glycerol to olefin (GTO) reaction was conducted at 600°C in fixed bed reactor using 1.5 g of the catalyst. The catalyst with different metal loading (wt %) were compared for their performance for glycerol conversion by conducting experiments under identical conditions. The reaction temperature was measured by K type thermocouple inserted in the reactor through thermocouple well. Prior to reaction, the sample of 1.5g was pre-treated in nitrogen at 400°C for 2 h. Liquid glycerol was evaporated by preheater at temperature 200°C. Glycerol was fed to reactor by a dosing pump and vaporized glycerol was made to enter in reactor at WHSV= 8.4 h^{-1}.The reactor effluent was analyzed by two gas chromatographs equipped with flame ionization detector and thermal conductivity detector. In flame ionization detector the capillary HP-INNOWAX column was used to detect liquid hydrocarbons and gas products were detected by FID column equipped with Propack Q column.

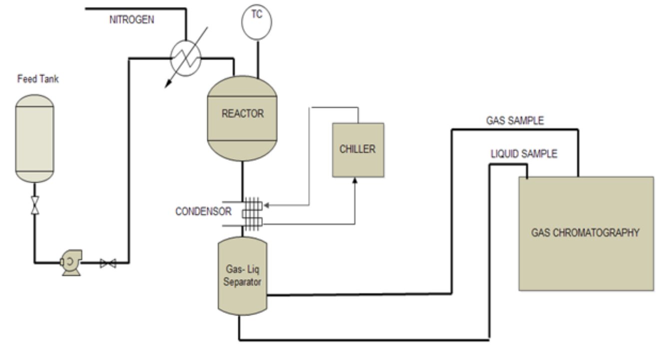

Fig. 1: Schematic Diagram

3. RESULTS AND DISCUSSIONS

3.1 XRD analysis

The XRD patterns are analyzed from 5^0 to 60^0 with 2ɵ scale. The maximum intensity peak of XRD is coming below 10^0 or 20^0-30^0. Pure ZSM-5 shows high intensity peak as compared to modified ZSM-5. The difference in intensity of pure ZSM-5 and metal loaded ZSM-5 depends upon the metal content. The XRD patterns show that there is no effect of metal loading on HZSM-5 as there is no other peak of metals were there which indicates well dispersion of metal on catalyst. The variation in intensity (peak) of different sample is due to high absorption coefficient of metals. Decrease in intensity of peak is due to decrease in crystallinity of catalyst which is due to presence of cationic sites.

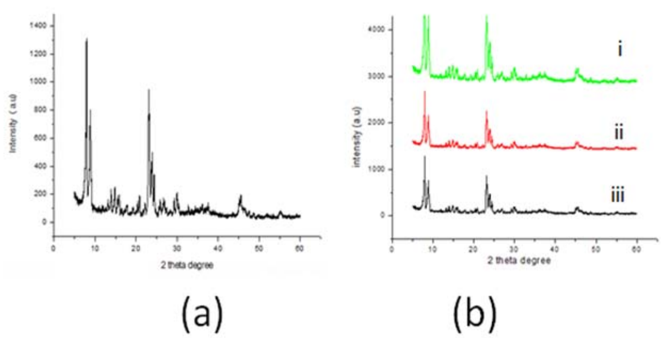

Fig. 2: XRD patterns of (a) ZSM-5 (b) modified ZSM-5 (i) Mg/ZSM-5 (ii) Ni/ZSM-5 (iii) Cu/ZSM-5

3.2 SEM analysis

The morphology of Zeolite and modified Zeolite was studied by scanning electron microscopy. The crystals or particles are spherical in shape. There is no significant change is seen after doping of metal to parent zeolite.

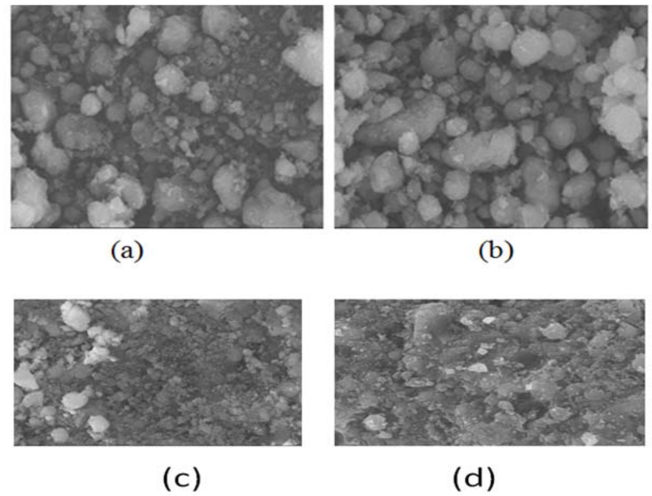

Fig. 3: SEM analysis of Zeolite and modified Zeolite (a) ZSM-5 (b) Cu/ZSM-5 (c) Ni/ZSM-5 (d) Mg/ZSM-5

3.3 Conversion and yield

Among all the catalyst, the maximum conversion is shown by Cu/ZSM-5 is 100%. It is mainly depends on the acidic sites available on surface of catalyst. But with the time as coke starts deposit on catalyst conversion starts decreasing. The maximum coke deposit on metals doped over ZSM-5 as they have more acidic sites than parent ZSM-5. The graph of conversion with time is shown in fig 3. The yield % of olefins with respect to time is shown in fig 4. The yield of olefins increases with increase in time but then there is declination in yield of olefins due to deactivation of olefins. Among all, Cu/ZSM-5 shows maximum yield.

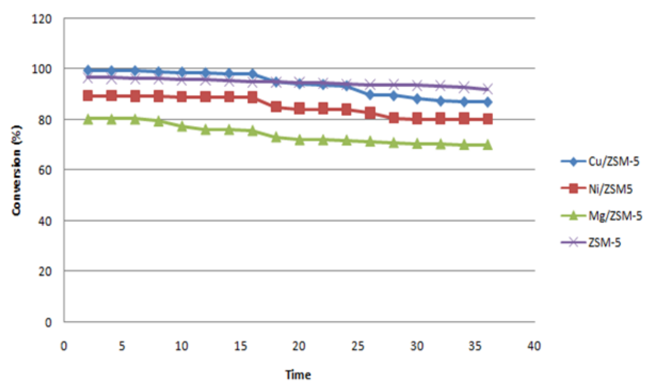

Fig. 4: Effect of time on conversion and deactivation of catalyst

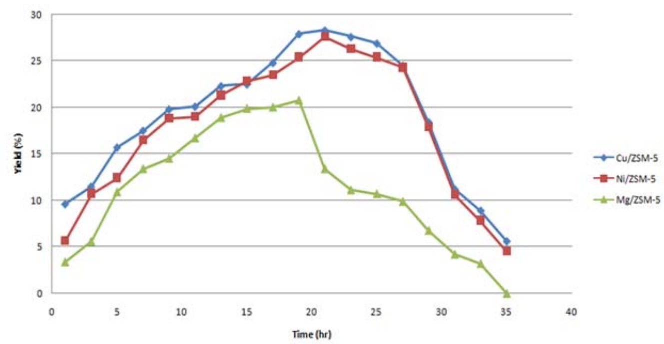

Fig. 5: Time vs. Yield graph of olefins

4. CONCLUSION

The catalytic screening of metal impregnated ZSM-5 was done for conversion of glycerol to light olefins. The synthesis of metal loading over ZSM-5 was took place via wet impregnation technique. This loading of metal over zeolite increases the acidic sites on surface of zeolite. The above study suggests that Cu/ZSM-5 shows maximum conversion and yield and is suited for light olefin production.

5. ACKNOWLEDGEMENT

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