

CATALYTIC CRACKING OF GLYCEROL TO LIGHT OLEFINS OVER ZEOLITES

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ABSTRACT

The production of glycerol has increased greatly in last few years due to large demand of biodiesel. Glycerol has enormous potential to be converted into higher value-added fuels and chemicals. One of the products that can be converted from glycerol is olefin. The conversion of glycerol to light olefins has been studied in this paper using modified ZSM-5 as a catalyst. In this study, the catalyst was prepared by doping oxalic acid, tartaric acid & phosphoric acid to ZSM-5. The pH of catalyst was maintained at 3 and temperature of reaction is 600^oC as high temperature favour high olefin production. The catalysts were characterized to relate their properties with catalyst activity. XRD characterization results demonstrated that the structure of the catalysts remained intact while BET revealed the surface and micropore areas decreased after metal loading. The main products that are detected by gas chromatography were paraffin and light olefins (ethylene & propylene). Tartaric acid doped ZSM-5 catalyst shows highest conversion and yield towards olefins.

Keywords: Biodiesel, Cracking, Glycerol, Olefins, ZSM-5.

I. INTRODUCTION

Due to large emission of green house gases like Carbon dioxide which causes global warming it is important to find an alternative source such as biodiesel which is a renewable resource and has multiple uses. Biodiesel is produced from palm oil, soya bean and rape seed oil [1], animal fat [3] in the presence of alcohol (i.e. ethanol or methanol). The main benefit of using biodiesel is its “carbon neutral” in terms of releasing of carbon dioxide since the emission of carbon dioxide from combustion of biodiesel is considered to be recycled by planting [6]. Due to high demand and production of biodiesel, glycerol (by-product in biodiesel production) is also produces in surplus amount. In the transesterification reaction, approximately 100 kg of glycerol is produced per ton of biodiesel [5]. As production of biodiesel increases day by day, the price of glycerol is expected to drop to half in last few years [1, 3, 6]. Glycerol is also produced from fermentation process using glucose as a raw material and from hydrolysis of fats and oils which yields glycerol and crude soap. Glycerol is used as raw material for manufacturing of various fuels like olefin [3], aromatics [2], propane [4], gasoline [6]. Besides this glycerol can be converted to various chemicals like acrolein [7], glyceric acid [9], acetaldehyde [10].

Olefins, a petrochemical derivative which are produced by thermal cracking of crude oil, steam reforming of natural gas [1], non-renewable resources (naphtha) can also be produced from conversion of glycerol. Very limited research has been done in the field of conversion of glycerol to olefin. The main olefins products are

ethylene, propylene, and butadiene and used as building block for making other petrochemicals and polymers [1].

The main objective of this study is to find out the suitable metal loading over zeolite, to increase the productivity of olefins and also the suitable temperature at which the suitable conversion and yield is achieved. For this various catalyst characterization methods are used like X-ray diffraction (XRD), Scanning electron microscopy (SEM). The products from the reaction are analysed by Gas Chromatography from where we identify which catalyst is best.

II. EXPERIMENTAL SECTION

2.1 Materials Required

Chemicals used in this study were liquid glycerol, ZSM-5 zeolite catalyst, phosphoric acid, oxalic acid, tartaric acid and water. All the reagents were of analytical grade and purchased from Sigma-Aldrich Company.

Stainless steel reactor was used throughout the experiment. An electrical furnace, a 500 ml round bottom flask, thermometer, condenser and conical flask were also used in the experimental set-up.

2.2 Catalyst Preparation

Doping of acids i.e. Oxalic acid, Phosphoric acid, Tartaric acid on ZSM-5 was done by maintaining 3 pH in catalyst preparation method. Firstly take ZSM-5 catalyst in beaker and add 100 ml of water and stir it in magnetic stirrer. Now add different amount of acid in the solution drop wise and maintain the pH of the solution accordingly by pH meter. Now again stir the solution in magnetic stirrer and heat the sample up to 50°C. Then filter the solution & wash it with the water & put the sample in oven for 2 hours at 110°C for drying. Now put the sample in furnace for calcination at 550°C for 5 hours.

2.2 Catalytic Evaluation

A fixed bed continuous flow tubular reactor is used for the reaction to be carried out. The reactor was heated by a split-tube furnace with a digital feedback temperature controller. The catalyst (40-60 mesh) was treated in situ with nitrogen. Glycerol was fed using a syringe pump or high-pressure piston pump. The preheater was also used to preheat or vaporize the glycerol before entering to the reactor. The reaction was carried out over a range of temperatures from at 600°C and at 1 atm pressure. The carrier gas flow rate was about 26-30 ml/min and feed flow rate was about 8-10 ml/hr. The gas and liquid products are then separated from gas-liquid separator and are sent to gas chromatography (GC) for further analyzing the products. The liquid products including water were collected in a cold trap after accumulating for each hour of time on stream. The liquid products were found to settle down into two phases: a hydrocarbon phase containing aromatics and an aqueous phase containing oxygenates with product water. Each phase was then individually analyzed using a GC- flame ionization detector (FID) equipped with a capillary HP-INNOWAX column, and products were identified using GC/MS. The gas products are analyzed using a GC- flame ionization detector (FID) equipped with a Propack Q column.

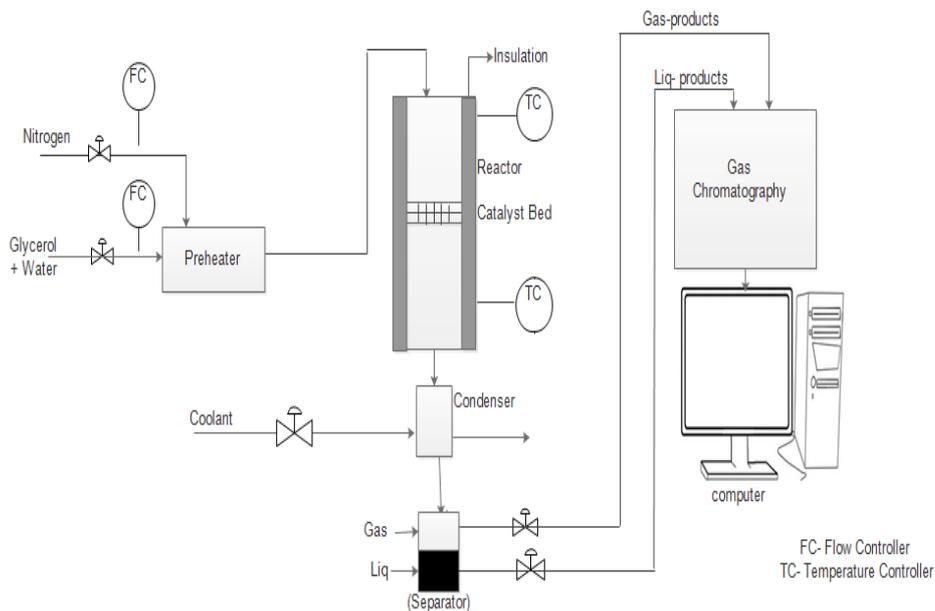


Fig 1. Experimental Set-Up

III. RESULTS AND DISCUSSIONS

3.1 Catalyst Characterization

Figure 2 represents the XRD patterns of ZSM-5 and the modified ZSM-5. The XRD patterns were analyzed between 5° to 60° with 2θ scale. The difference in intensity of peak of pure ZSM-5 & modified ZSM-5 depends upon the loading of acids over ZSM-5. The XRD patterns show that there is no effect of doping over ZSM-5 as no other peak of acids were coming which means well dispersion of acids over catalyst. The variation in intensity of peak of different sample is due to high absorption coefficient of acids (Zakaria et al., 2012).

To investigate the morphology of sample, SEM micrographs have been obtained. SEM images show that crystal grows into spherical polycrystalline aggregates and particle of undefined shape was also present as shown in Fig.3. In fig 3 the SEM images of pure and modified ZSM-5 are shown.

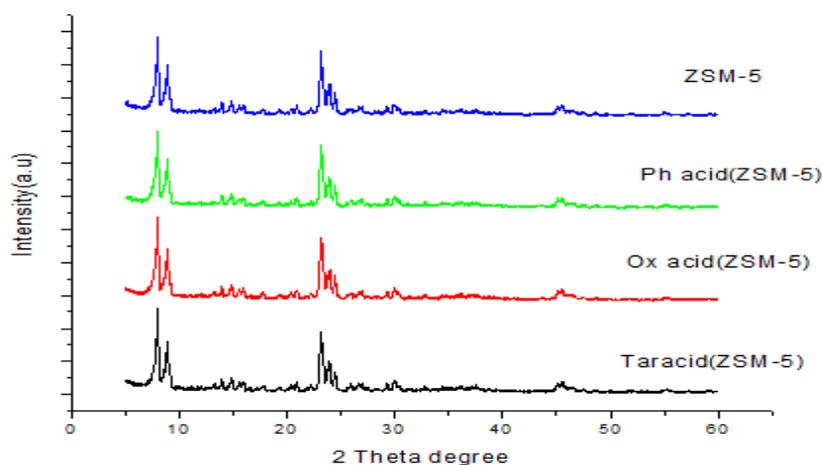


Fig 2. XRD patterns of parent & modified ZSM-5

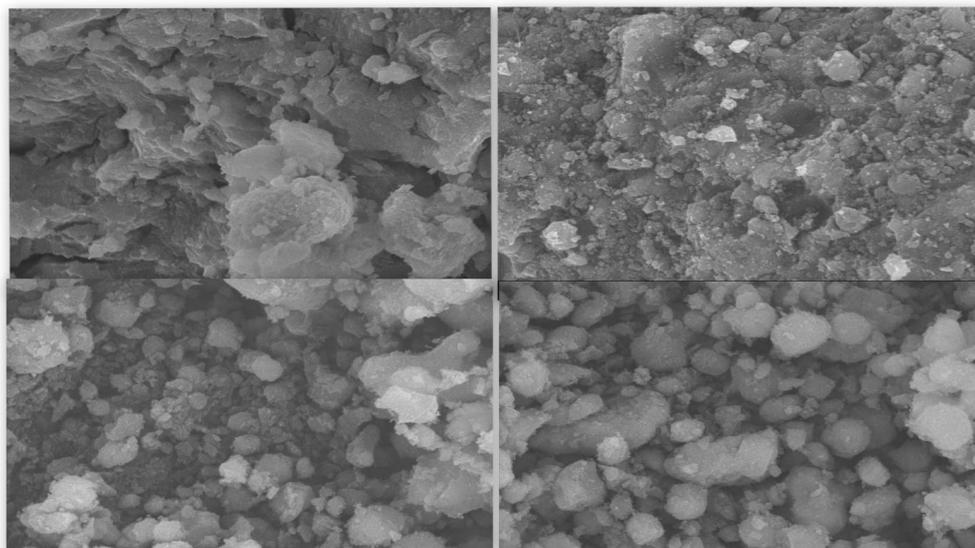


Fig 3. SEM images of ZSM-5 (i) pure ZSM-5 (ii) phosphoric acid doped ZSM-5 (iii) Oxalic acid doped ZSM-5 (iv) tartaric acid doped ZSM-5

3.2 Reactivity and Yield

In figure 4 maximum conversion is shown by ZSM-5(Tartaric acid) whose pH is 3 is 100%. Conversion decreases with increase in time as deactivation of catalyst starts takes place. And the yield % of olefins is also maximum for ZSM-5 (Tartaric acid) is 15.6% for Ethylene and 11.4 % for Propylene in figure 5. In starting yield of HZSM-5 will increases but with time it will decreases as deactivation of catalyst takes place or coking of catalyst will increase which then decreases the yield. This is due to presence of more acidic sites on catalyst which causes deactivation of catalyst.

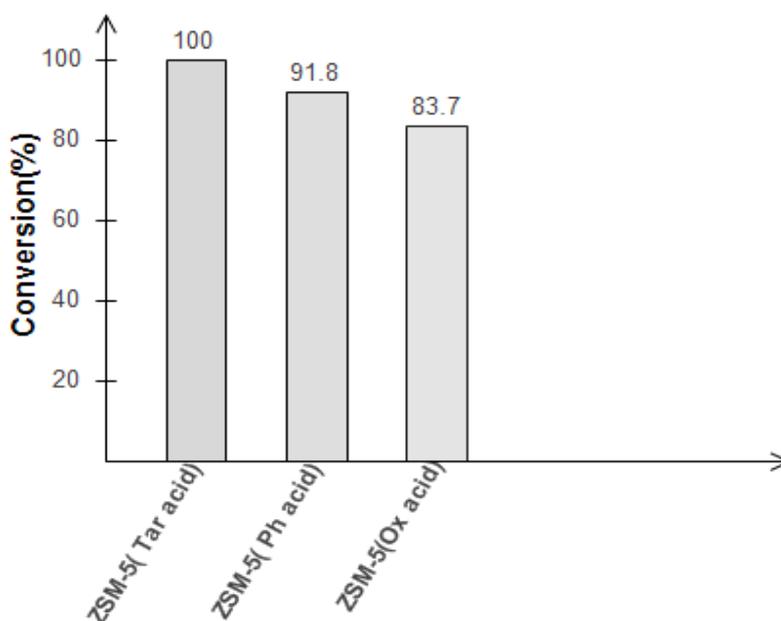


Fig 4. Conversion % of glycerol Over ZSM-5 catalyst

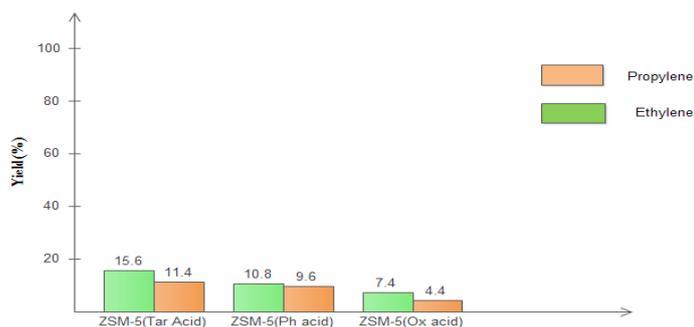


Fig 5. Yield % of Olefins

3.3 Effect of coke on deactivation of catalyst

As the reaction time increases, the coke content will start depositing on surface of catalyst. This is due to the presence of more acidic sites on the surface of that particular catalyst. In starting of the reaction the coke content present of catalyst surface was nil but as reaction will start amount of coke content on catalyst surface also increases. The more the coke content, the fast the catalyst will deactivate. If we see in the figure in starting coke present on ZSM-5(Tartaric acid (pH-3)) is about 0.5 gm and after 36 hours it reaches up to 2.5 gm. The coke content deposited over ZSM-5(Tartaric acid (pH-3)) is more as the acidic sites present on it are more as compared to other catalyst which in starting increasing the conversion & yield but also deactivates the catalyst fastly.

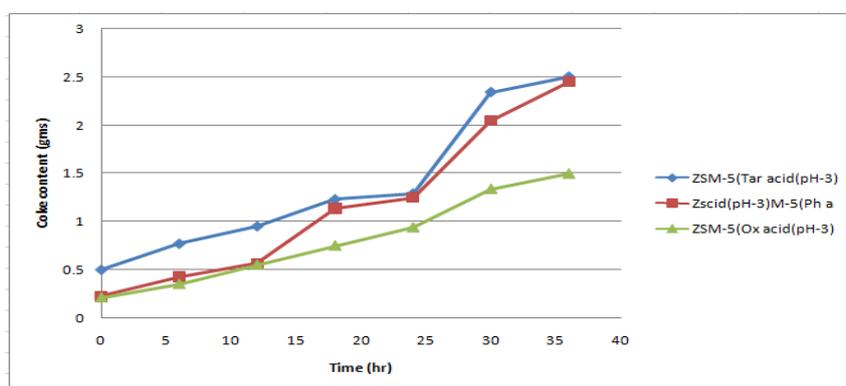


Fig 6. Effect of coke on deactivation of catalyst

IV. CONCLUSION

High reaction temperature of glycerol with zeolite gave maximum conversion. The loading of different acid on zeolite catalyst increases the acid site which were needed for cracking of glycerol. Among [ZSM-5(Phosphoric acid(pH-3)), ZSM-5(Oxalic acid(pH-3)), ZSM-5(Tartaric acid(pH-3))], ZSM-5(Tartaric acid(pH-3)) shows better results. It gives maximum conversion of 100%. It shows yield % of ethylene- 15.6 and yield % of propylene- 11.4. The loading of acid on parent ZSM-5 increases the activity & conversion of catalyst but increases the deactivation of catalyst with time as coking was taking place on catalyst. The high temperature makes the catalyst more active.

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