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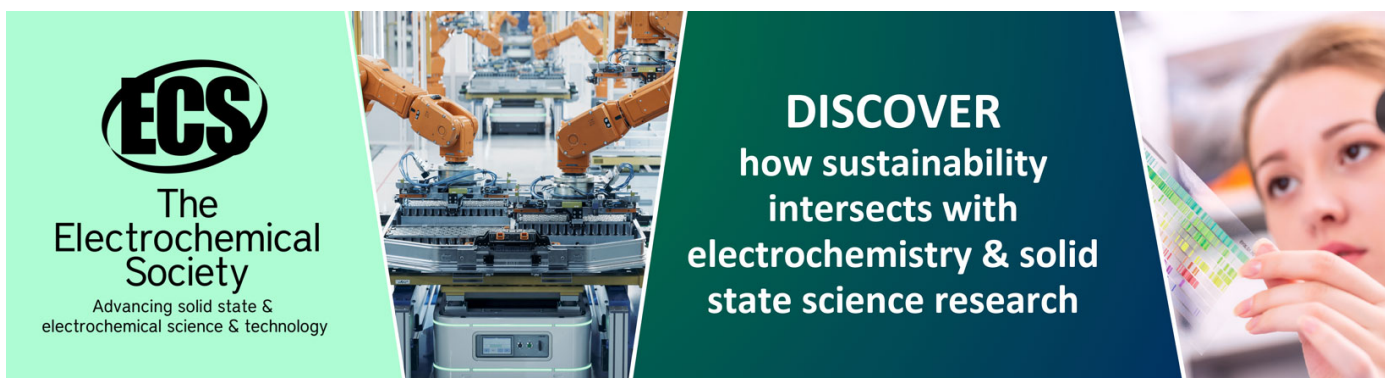
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Study of Catalyst Variation Effect in Glycerol Conversion Process to Hydrogen Gas by Steam Reforming

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Abstract. Along with the economic development, needs of energy being increase too. Hydrogen as alternative energy has many usages. Besides that, hydrogen is one source of energy that is a clean fuel, but process production of hydrogen from natural gas as a raw material has been used for a long time. Therefore, there is need new invention to produce hydrogen from the others raw material. Glycerol, a byproduct of biodiesel production, is a compound which can be used as a raw material for hydrogen production. By using glycerol as a raw material of hydrogen production, we can get added value of glycerol as well as an energy source solution. The process production of hydrogen by steam reforming is a thermochemical process with efficiency 70%. This process needs contribution of catalyst to improve its efficiency and selectivity of the process. In this study will be examined the effect variation of catalyst for glycerol conversion process to hydrogen by steam reforming. The method for catalyst preparation was variation of catalyst impregnation composition, catalyst calcined with difference concentration of hydrochloric acid and calcined with difference hydrochloric acid ratio. After that, all of catalyst which have been prepared, used for steam reforming process for hydrogen production from glycerol as a raw material. From the study, the highest yield of hydrogen gas showed in the process production by natural zeolite catalyst with 1:15 Hydrochloric acid ratio was 42.28%. Hydrogen yield for 2M calcined natural zeolite catalyst was 38.37%, for ZSM-5 catalyst was 15.83%, for 0.5M calcined natural zeolite was 13.09% and for ultrasonic natural zeolite was 11.43%. The lowest yield of hydrogen gas showed in catalyst 2Zn/ZSM-5 with 11.22%. This result showed that hydrogen yield product was affected by catalyst variation because of the catalyst has difference characteristic and difference catalytic activity after the catalyst preparation process.

1 Introduction

Nowadays, energy production is always linked with clean emissions by an environmentally friendly raw material, like hydrogen. The increasing of energy needs doesn't support by a suffice energy source which is from the fossil materials, so availability of energy is insufficient to satisfy human needs [1]. Hydrogen as alternative energy has many usages. Besides that, hydrogen is one source of energy that is a clean fuel, but process production of hydrogen from natural gas as a raw material has been used for a



long time. Therefore, there is need new invention to produce hydrogen from the others raw material [2]. Glycerol, a byproduct of biodiesel production, is a compound which can be used as a raw material for hydrogen production. Glycerol can converted to hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4) and the others trace of hydrocarbon. The products are used as an alternative fuel [3]. Considering of the increasing need for renewable fuels throughout the world, there is increasing production of biodiesel too. So, an excess of glycerol will be available in the world [4]. By using glycerol as a raw material of hydrogen production, we can get added value of glycerol as well as an energy source solution.

The process production of hydrogen by steam reforming is a thermochemical process that can produce up to 70% efficiency [6], but this process need contribution of catalyst to improve its efficiency. Catalyst for steam reforming process must have good catalytic activity, high selectivity to hydrogen, and resistance to coke formation [7]. The catalyst for steam reforming process has been investigated by [8]. An alumina supported Ni catalyst was used in catalytic steam reforming and get the hydrogen yield 30%. It was prepared by wet impregnation and result good structure for catalytic process [8]. In this research will be examined the effect of catalyst variation such as natural zeolite catalyst 1:15 HCL ratio [12], 2-Zn/ZSM-5 [9], 2M calcined natural zeolite [10], 0,5M calcined natural zeolite [10], ZSM5 and ultrasonic natural zeolite [11].

2 Methods

2.1 Material

Glycerol used as reactant in this research is in technical grade from Indrasari Chemical Store. Aquadest as reactant was bought from Membrane Research Center (MeR-C) Diponegoro University. Natural zeolite was bought from Wonosari Gunung Kidul and synthetic catalyst ZSM-5 was made by Latourette (1990) method used for catalytic processes. $ZnSO_4 \cdot 7H_2O$ in pro analysis grade used to add zinc metal component by impregnation ZSM-5. Hydrochloric acid in technical grade used for chemical treating the natural zeolite. Pure nitrogen gas used for a gas carrier of the process.

2.2 Catalyst preparation and characterization

The catalysts used in this research are based from natural zeolite and also synthetic catalyst ZSM-5. Firstly, the synthetic catalyst was made by Latourette (1990) method. Then 2Zn-ZSM5 was made by adding zinc component 2% weight/weight catalyst to ZSM-5 through wet impregnation method. The natural zeolite was being reduced into 100 mesh. Then hydrochloric acid solution with concentration 4M used as the solvent. Then, silver nitrate solution was also added for washing indicator. After that, by used three-neck flask then it was put in ultrasonic cleaner type JP-060S using 40 kHz frequency for the ultrasonic process [11]. Other variances of the natural zeolite are treated using the ratio of hydrochloric of 1:15, 0.5 M and also 2 M. After being chemically treated, the catalyst product was being filtered and washed using distillate water. At last, the catalysts were dried in $110^\circ C$ for 12 hours and calcined using furnace on the isothermal temperature at $500^\circ C$ for 5 hours in inert condition by adding nitrogen gas. Characterization of the catalyst has been done by [9] for 2Zn/ZSM-5 catalyst and by [11] for ultrasonic zeolite catalyst. The 2M calcined zeolite catalyst and 0.5M calcined zeolite catalyst [10] and zeolite 1:15 Hydrochloric acid catalyst was done by [12]

2.3 Catalytic testing for steam reforming process

The catalyst performances are being tested through steam reforming process. The catalyst was placed in catalytic fix bed reactor. At first, the feed was made by mixing glycerol and aquadest with the volume ratio of 1:9. Then, the feed was being vaporized in $200^\circ C$ before injected into the reactor. The nitrogen also injected to the reactor as the gas carrier. The reactor was previously heated to $500^\circ C$ as the operation

condition of the reactor for ten minutes of each process. Then, the product was passed through the cooler and the gas product being tested using gas analyzer and also hydrogen analyzer to get the gas composition.

Yield and the selectivity of each product being calculated by equation 2 and equation 3:

$$\text{Yield} = \frac{\text{hydrogen mass}}{\text{feed mass}} \times 100\% \quad (1)$$

$$\text{Selectivity} = \frac{\text{hydrogen mass}}{\text{gas product mass}} \times 100\% \quad (2)$$

3 Results and Discussions

3.1 Characterization of the catalyst

Characterization of the catalyst has been done by [9] for 2Zn/ZSM5 catalyst and by [11] for ultrasonic zeolite catalyst. The 2M calcined zeolite catalyst and 0.5M calcined zeolite catalyst by [10] and zeolite 1:15 Hydrochloric acid catalyst was done by [12].

Table 1. BET Result Surface Area of the Catalyst

Catalyst	Surface Area (m ² /g)	Reference
ZSM-5	20	[13]
2-Zn/ZSM-5	0.402	[9]
0.5M Calcined Natural Zeolite	101.943	[10]
2M Calcined Natural Zeolite	130.657	[10]
Ultrasonic Natural Zeolite	79.09	[11]
Zeolite 1:15 HCl	199.760	[12]

3.2 Hydrogen yield for various catalyst types

Figure 1 shows the highest yield could be achieved by zeolite catalyst which had been calcined by HCl 1:15 molar ratio, with hydrogen yield 42.48%. This high yield could be achieved because the natural zeolite already being chemically treated. From the studies before, the zeolite framework could be changed along with the treatment. Acid treatment could cause dealumination of the zeolite sample, which means it leached Al framework from zeolite, and it could increase the catalyst Si/Al ratio [14]. Along with the increasing of the Si/Al ratio, a catalyst could be more stable at high temperature. Then, for another catalyst, the results are 38.75% for 2M Calcined Natural Zeolite, 15.83% for ZSM-5, 13.09% for 0.5M Calcined Natural Zeolite, 11.43% for Ultrasonic Natural Zeolite and 11.22% for 2-Zn/ZSM5. The performance of catalyst 2-Zn/ZSM5 is affected by its surface area. From BET data it shows that the surface area of 2-Zn/ZSM5 is only 0.402 m²/g, where it is much smaller than the surface area of natural zeolite that around 20 m²/g. From the study, yield of the process is increase during the increasing of the surface area of the catalyst.

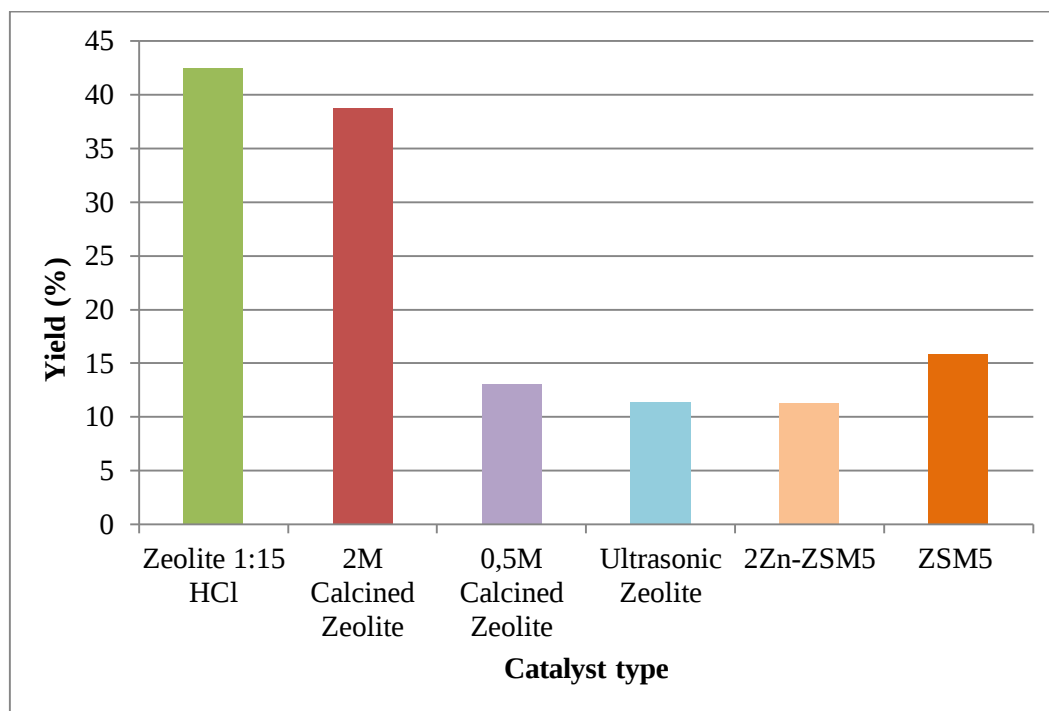


Figure 1.Yield of hydrogen for various catalyst types

3.3 Hydrogen selectivity for various catalyst types

Catalysts for steam reforming processes are currently a research subject, mainly focused on the improvement of the catalytic activity, the selectivity to hydrogen, and the resistance to coke formation [7].

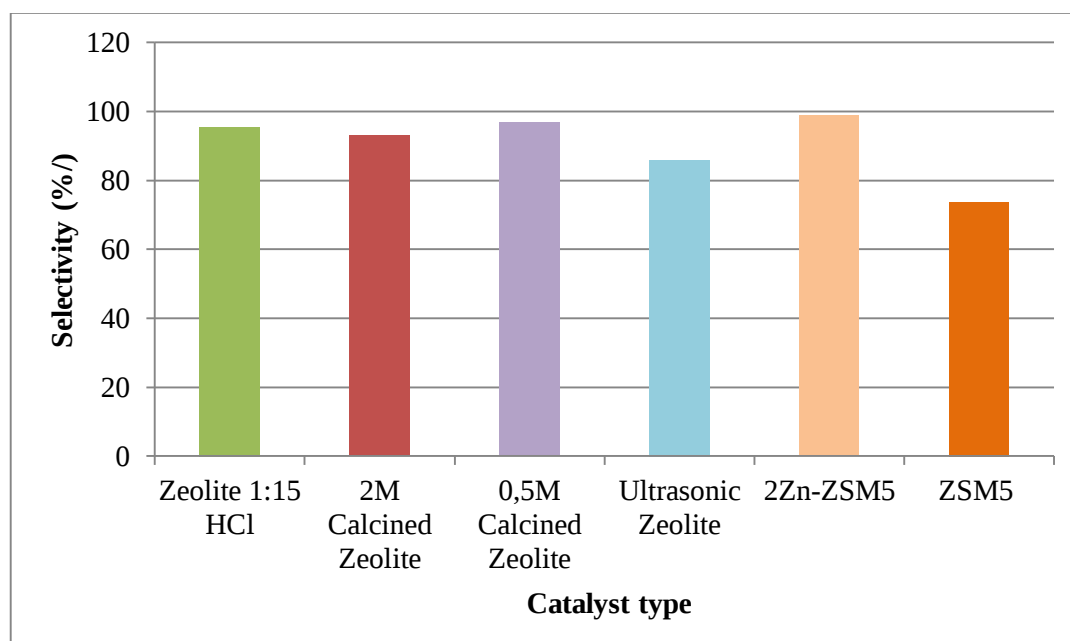


Figure 2. Selectivity of hydrogen for various catalyst types

From the water and glycerol compound reaction, can be produced H₂, CO, CO₂, CH₄, and hydrocarbon component and condensate product as this following reaction:

Steam reforming of glycerin:



Reverse water gas shift reaction:



With H₂, CO₂, CO, and CH₄ which can be obtained from steam reforming process, so this can influence the product selectivity, where the selectivity is variant along with the catalyst variances. The highest selectivity of the steam reforming process was by 2Zn-ZSM5 catalyst, with selectivity percentage 98.77%. The selectivity for 0.5M Calcined Natural Zeolite 96.75% and 95.51% for Natural Zeolite catalyst 1:15 HCl ratio. The selectivity for 2M Calcined Natural Zeolite 93% and 85.9% for Ultrasonic Natural Zeolite. The lowest selectivity of the catalyst was 73.81% for ZSM-5.

The highest selectivity is influenced by catalyst mechanism and properties. The stability state in high temperature for each catalyst is influenced by the Si/Al ratio, where commonly natural zeolite classified as intermediate Si/Al zeolites (~2-5), while the ZSM5 classified as high Si/Al zeolites (~10-100) [15]. Hence, 3Zn-ZSM5 catalyst shows the highest selectivity because of its ability to keep stable at high temperature. While the higher Si/Al ratio of a catalyst, the more stable it will be. Adding metal component into zeolite catalyst can change its structure and characteristic [16].

4 Conclusions

Glycerol steam reforming process to produce hydrogen was influenced by many factors, one of them is catalyst variances. According to the yield percentage, the result showed that Natural Zeolite catalyst 1:15 HCl ratio gave the highest yield because of its large active surface. But, according to the selectivity, 2Zn-ZSM5 catalyst gave the highest selectivity due to its small Si/Al ratio. Furthermore, metal impregnation can make that catalyst more stable because of the structure and characteristic change.

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