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The Activity of Ni-Based Catalysts on Steam Reforming of Glycerol for Hydrogen Production

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Abstract: Glycerol, the readily available bio renewable material, is effectively utilized for hydrogen production by a steam reforming reaction. The experiments were carried out in a continuous flow fixed-bed reactor over Nickel supported alumina catalysts under atmospheric pressure at 600°C and three hours reaction time. 5%wt Ni was loaded over γ-Al_2O_3 and effect of promoter metals such as Fe and Co over Ni/γ-Al_2O_3 catalytic systems were evaluated. The catalysts were characterized by BET surface area, XRD and SEM techniques. The activity results showed that the addition of Co enhanced the catalyst performance. The catalysts exhibited a good activity and selectivity to hydrogen.

Keywords: Hydrogen production, impregnation method, glycerol reforming, nickel catalysts.

1. Introduction

Due to the reduction of fossil fuel reserves and the need to ensure the energy requirements for future generation, developing alternative sources of energy become a considerable attention to many researchers. Recently, the production of biomass and its use has received much interest as a renewable source of energy. During a bio-diesel production process, a glut of glycerol, which has a high content of hydrogen, is produced. Many efforts have been made in order to utilize glycerol for hydrogen production. One of the implemented processes to extract hydrogen from this biomass material is steam reforming process. In this process, glycerol-water solution is fed together to a fixed bed reactor under atmospheric pressure and at a relatively high reforming temperature. The glycerol steam reforming reaction is given in the following equation:

$$C_3H_8O_{3\,(g)} + 3H_2O_{\,(g)} \rightarrow 7H_{2\,(g)} + 3CO_{2\,(g)} \qquad (1)$$

From the reaction equation, seven moles of hydrogen can be produced from one mole glycerol reacted.

In order to maximize the hydrogen production, a few studies have been made on the optimization of reaction parameters for the steam reforming of glycerol. The substantial attention of these studies was focused on improving the catalyst activity by studying the effect of the metal used, the type of support, and the addition of promoters and the preparation methods on hydrogen production. Transition metals, specially nickel based-catalysts, over a variety of supports, such as Al_2O_3, CeO_2, MgO, TiO_2 and hydroxyapatite [1-4] had explored for the steam reforming of glycerol. Moreover, other studies have tested the activity of noble metal catalysts on the reforming process [5-8]. Sushil and Ivana applied a wet impregnation method for the catalyst preparation [1, 2], whereas Baocai used deposition-precipitation method [3].

In the present work, Ni and Ni promoted with Co, Na, Fe and Cu over γ-Al_2O_3 catalysts were prepared by a simple wet impregnation method. These catalysts were characterized and their activities were tested for hydrogen production in a continuous fixed-bed reactor.

2. Experimental

2.1 Catalyst Preparation

Catalysts consisting of 5wt% Ni and Ni promoted with 0.3wt% Co, Fe, Cu and Na supported on a commercial γ-Al_2O_3 were prepared by incipient wetness impregnation method. First, nickel nitrate hexahydrate [Ni $(NO_3)_2$. $6H_2O$] (Sigma Aldrich) solution was impregnated with γ-Al_2O_3 (Sigma Aldrich). The catalyst was then dried at 100°C over night and then calcined at 550°C for five hours.

For promoted catalysts' preparation, the promoters nitrate solution was added to the nickel nitrate solution, and then the mixture was impregnated with γ-Al_2O_3. Drying and calcinations steps were done same as above which was used to prepare Ni/ γ-Al_2O_3.

2.2 Catalyst Characterization

XRD analysis has been applied in order to identify the crystalline structure of the prepared catalysts. The experiments were performed on a Bruker AXS D8

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Advanced diffractometer using a Cukα (λ=1.5418) radiation source with a scanning rate of 0.02°/s. The XRD patterns were working at current and voltage of 30 mA and 40 kV respectively.

2.3 Catalyst Performance Testing

The catalytic activity of the prepared Ni-based catalysts in hydrogen production by steam reforming of glycerol was investigated. All the experiments were carried out in a fixed bed micro-reactor (i.e. length: 39 mm, inside diameter: 6.35 mm, wall thickness: 0.9mm) under atmospheric pressure and 600°C. A HPLC pump (PHD 440, Harvard Apparatus) was used to introduce 0.05ml/min of glycerol-water solution into the reactor at a 1:6 glycerol to water molar ratio. The experiment started with placing a 0.5 g of the catalyst powder in the centre of the reactor supported by quartz wool. For all experiments, the catalysts were first heated at 350°C for 1hr and then activated in situ by reducing in a N_2 flow 40 ml/min with 10% H_2 for 1hr. After a 1hr reaction time, the outlet gases were analyzed every 30 min for 3hrs using online GC instrument (Clarus 500 Parkin Elmer with FID and TCD detector).

3. Result and Discussion

3.1 Catalyst Characterization

3.1.1 Brunauer, Elmmett And Teller (Bet) Surface Area

The measurements of surface area of Ni and Ni promoted with Co, Cu, Fe, and Na based catalysts using a Brunauer, Elmmett and Teller (BET) method are shown in the table below. Surprisingly there is an increase in the surface area after impregnation of Ni metal. Ni loading increases the surface area to 211m2/g which further show an increase to 216 upon addition of the promoters Cu and Fe. Co promoter shows a small decrease whereas Na promoter decreased the surface area to 185. The increased surface area may be a result of leaching out of some Al from the matrix during the treatment with Ni solution which may results in increased porosity. The decrease upon addition of some promoters may be due to the plugging of some of the pores [9].

Table 1 Surface Area of Ni/Al_2O_3 Catalysts.

Catalyst	Surface Area m^2/g
Al_2O_3	151.00
5wt% Ni/Al_2O_3	211.27
5wt% Ni/Al_2O_3 promoted with Co	210.87
5wt% Ni/Al_2O_3 promoted with Cu	216.98
5wt% Ni/Al_2O promoted with Fe	216.06
5wt% Ni/Al_2O_3 promoted with Na	185.97

3.1.2 X-Ray Diffraction (XRD)

Fig. 1 and 2 below shows the XRD patterns of Ni-based catalysts supported on alumina. The purpose of using XRD is to ensure whether the Ni phase is present in the sample or not. The characterization peaks of crystalline phase of γ-Al2O3 at 37.5°, 45.5° and 67.3° were observed. In addition, the diffraction lines at 19.5°, 43.2° and 63° associated to crystalline phases of NiO.[10]. The promoter oxide phases of Cu, Na, Fe and Co were presented at 16.23°, 20.5°, 32.7° and 59.9° respectively.

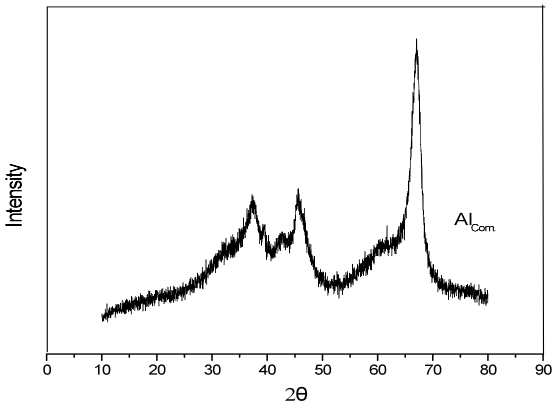


Fig. 1 XRD Patterns for Alumina (Al_2O_3).

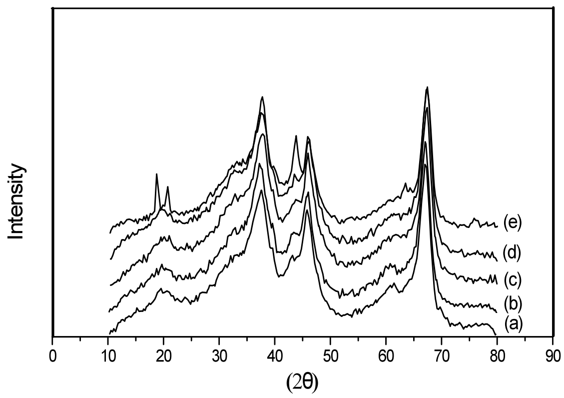


Fig. 2 XRD Patterns for (a) 5wt%Ni/Al_2O_3, (b) 5wt% Ni/Al_2O_3 promoted with Co, (c) 5wt% Ni/Al_2O_3 promoted with Cu, (d) 5wt% Ni/Al_2O_3 promoted with Fe, (e) 5wt% Ni/Al_2O_3 promoted with Na.

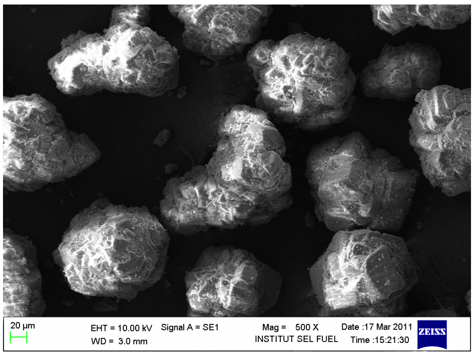
3.1.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) of prepared catalysts as well as γ-Al_2O_3 phase is illustrated in Fig. 3. In all samples, the crystal growth on large particles of alumina is clearly seen. It is visible that nickel particles are dispersed on the support in the spots of crystal growth. For the promoter catalysts, the dispersion of these promoters is not clear which may be due to the small percentage used and also may need more accurate scanning device such a Transmission Electron Microscopy (TEM).

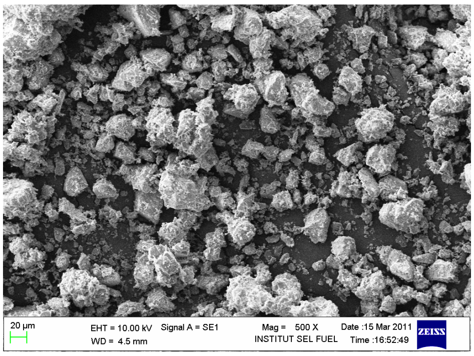
3.2 Catalyst Activity

The activity of all prepared catalysts was evaluated in term of hydrogen production by steam reforming of glycerol. As depicted in Fig. 4, the addition of Co and Na to the Ni catalyst enhanced its activity with respect to hydrogen production. For Co promoter catalyst the enhancement could be attributed to the improvement of metal dispersion and thermal stability[1, 3], whereas in the Na promoter, the improvement is due to the acidity reduction of the support which can prevent metal sintering[1, 11]. The deactivation of Ni/Al_2O_3 promoted with Co after 2hr collection time may due to the sintering and surface cobalt oxidation as reported elsewhere [3].

The deactivation of Ni catalysts promoted with Cu and Fe could attribute to the higher carbon deposition rate with respect to non-promoted Ni/Al_2O_3. In general, the best thermodynamic condition for hydrogen production by steam reforming of glycerol is at a temperature above 627°C [12] and since the micro-reactor used for this process is limited to 600°C, the hydrogen production can be improved by operating the reaction under a temperature higher than 600°C.



(a)



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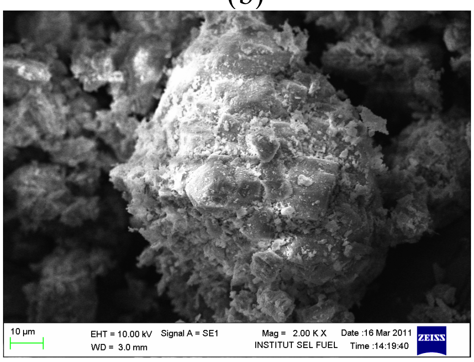

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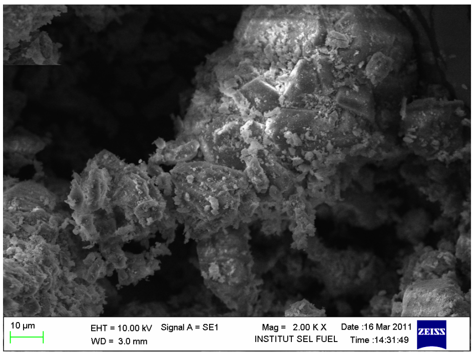

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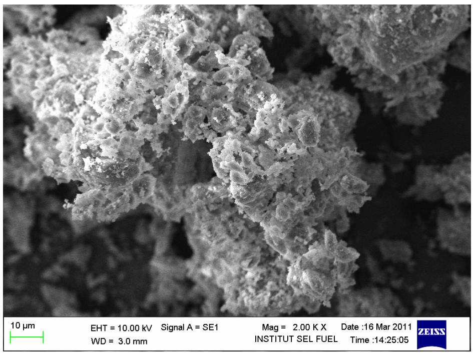
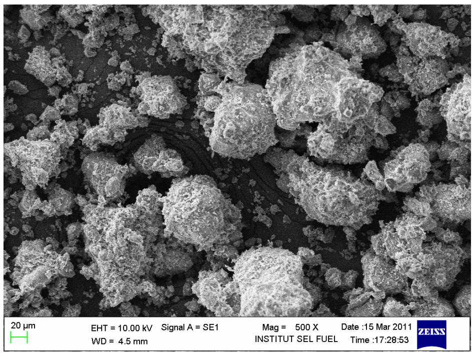


(e)



(f)

Fig. 3 SEM for (a) Al_2O_3, (b) 5wt% Ni/Al_2O_3, (c) 5wt% Ni/Al_2O_3 promoted with 0.3wt% Co , (d) 5wt% Ni/Al_2O_3 promoted with 0.3wt% Cu , (e) 5wt% Ni/Al_2O_3 promoted with 0.3wt% Fe , (f) 5wt% Ni/Al_2O_3 promoted with 0.3wt% Na

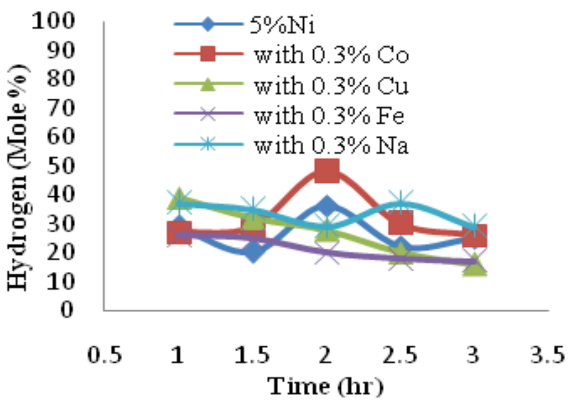


Fig. 4 Hydrogen Production by Steam Reforming of Glycerol

4. Conclusion

The steam reforming process for hydrogen production from glycerol was carried out over Ni/Al_2O_3 and Ni/Al_2O_3 promoted with Co, Cu, Fe and Na catalysts. Various techniques were applied for catalysts characterization. XRD analysis showed that all types of catalysts have similar phase structure. The positive effect on the Ni/ Al_2O_3 catalyst performance was noticed when it was promoted with Co and Na.

REFERENCES

[1] Ivana N. B., Francisco P., Gerardo F. S., N.N. Nichio, (2009), Nickel Catalysts Applied in Steam Reforming of Glycerol for Hydrogen Production. Catalysis Communications, 10(13), p. 1656–1660.

[2] Adhikari S., Fernando S. D., Haryanto A., (2008), Hydrogen Production from Glycerin by Steam Reforming over Nickel Catalysts. Renewable Energy, 33(5), p. 1097–1100.

[3] Zhang B., Tang X., Li Y., Xu Y., Shen W., (2007), Hydrogen Production from Steam Reforming of Ethanol and Glycerol over Ceria-Supported Metal Catalysts. International Journal of Hydrogen Energy, 32(13), p. 2367 – 2373.

[4] Lukman H., Zahira Y., Manal I., Daud W.R.W., (2010), Nickel-Hydroxyapatite as Biomaterial Catalysts for Hydrogen Production via Glycerol Steam Reforming Key. Engineering Materials, 447-448, p. 770-774.

[5] Iriondo A., Barrio V.L., Cambra J.F., Arias P.L., Güemez M.B., Navarro R.M., Sanchez-Sanchez M. C., Fierro J. L. G., (2009), Influence of La_2O_3 Modified Support and Ni and Pt Active Phases on Glycerol Steam Reforming to Produce Hydrogen. Catalysis Communications, 10(8), p. 1275–1278.

[6] Slinn M., Kendall K., Mallon C., Andrews J., (2008), Steam Reforming of Biodiesel by-Product to Make Renewable Hydrogen. Bioresource Technology, 99(13), p. 5851–5858.

[7] Luciene P.R. P., Edson A. T., Assaf E. M., (2009), Production of Hydrogen via Steam Reforming of Biofuels on $Ni/CeO_2–Al_2O_3$ Catalysts Promoted by Noble Metals. International Journal of Hydrogen Energy, 34(12), p. 5049–5060.

[8] Edward L. K., Ricardo R. S., Dante A. S., Dumesic J. A., (2009), An Integrated Catalytic Approach for the Production of Hydrogen by Glycerol Reforming Coupled with Water-Gas Shift. Applied Catalysis B: Environmental, 90(3-4), p. 693–698.

[9] Therdthianwong S., Siangchin C., Therdthianwong A., (2008). Improvement of coke resistance of Ni/Al2O3 catalyst in CH4/CO2 reforming by ZrO2 addition. Fuel Processing Technology. (89), p. 160-168.

[10] Iriondo A., Barrio V. L., Cambra J. F., Arias P. L., Gu¨emez M. B., Navarro R. M., Sa´nchez-Sa´nchez M. C., Fierro J. L. G., (2008), Hydrogen Production from Glycerol Over Nickel Catalysts Supported on Al2O3 Modified by Mg, Zr, Ce or La. Top Catal, 49(1-2), p. 46–58.

[11] Guodong W., Yunpeng X., Huaijun M., Zhusheng X., Zhijian T., (2008). Production of Hydrogen by Aqueous-Phase Reforming of Glycerol. International Journal of Hydrogen Energy. (33), P. 6657 – 6666.

[12] Adhikaria S., Fernandoa S., Steven R. G., Filip Toa S. D., Brickac R. M., Philip H. S., Haryantoa A., (2007), Athermodynamic Analysis of Hydrogen Production by Steam Reforming of Glycerol. International Journal of Hydrogen Energy, 32(14), p. 2875 – 2880.