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Steam reforming of Phenol-PET solution over Ni/Al₂O₃ catalyst for hydrogen production

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GRAPHICAL ABSTRACT
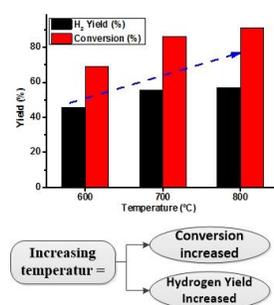
ABSTRACT

Hydrogen, a sustainable and clean energy carrier, has gained interest as a potential candidate in the global energy scenario in the past few years. In the present study, dissolved waste PET (polyethylene terephthalate) in phenol was proposed for catalytic steam reforming toward production of hydrogen. Phenol as an unwanted liquid product can be found in the pyrolysis oil and/or in many industrial wastewater streams. Moreover, PET is one of the major products of plastic waste which constitutes a major hindrance to the environmental conservation efforts and causes harm to living organism. The 10 wt.% Ni/γ-Al₂O₃ catalysts were prepared by impregnation method and characterized using BET-N₂, TPD-CO₂, TPR-H₂, and SEM-EDX, showed the presence of nickel on acid type catalyst support with high surface area of γ-Al₂O₃. The experiment were carried out in a fixed bed reactor operated at atmospheric pressure using 3 wt.% PET in the feed with the water:phenol:PET ratio of (1:0.107:0.003), 0.2 gram of the catalyst and in temperature range of 600 to 800 ºC. FTIR result shown no PET detected in the liquid product, indicated the PET achieved a complete conversion at the temperature range of this study. The maximum hydrogen yield was about 56.82 % at 800°C.

Keywords: H₂ Production, Steam reforming, Polyethylene Terephthalate, Phenol, Ni/Al₂O₃ catalyst

1. INTRODUCTION

Recently, concerns regarding carbon dioxide emissions from fossil fuel combustion and their impact on the Earth's climate are critical in many countries [1, 2]. Hydrogen has been identified as a suitable replacement to fossil fuel because of its abundant and regenerative feature [3-6]. The generation of hydrogen from bio sources, is increasing consideration as a CO₂ unbiased source of energy [7]. The basis of this method is in the thermochemical alteration of biomass and the emission of CO₂ into the atmosphere which counterbalances the capture of CO₂ by the viable biomass [8]. For hydrogen generation, biomass existing at ample concentrations can be measured by correlation means [9]. According to literatures, the economically feasible technique for production of hydrogen is biomass fast pyrolysis complexed with bio-oil steam reforming [10-12]. The aqueous solution of bio-oil specifically required for the methane steam reforming. Thus, the thermal variability of the oxygenated compounds and particularly heterogeneous composition of the bio-oil should be mentioned [13]. Apart from its easy storage properties and transportation, bio-oil can serve as a sustainable renewable fuel source exhibiting more energy density than biomass. Bio-oil can be classified into (i) a water-monomer-rich phase which is include typically carbohydrate-derived mixtures (which contains 80% water and 20% organics [14]) and (ii) a hydrophobic-oligomer-phase collected generally of lignin-derived oligomers by water adding process [15, 16]. In recent times, hydrogen is produced from sources such as water, coal gasification, acetic acid, natural gas, ethanol, butanol, methane, glycerol, naphtha catalytic steam reforming and bio-oil [17]. Not only has the development of hydrogen production as a renewable fuel being a keen area of research, attention has also been given to conversion of waste materials to energy [18, 19], including plastics. Studies in this field are of great importance because it resolves numerous problems brought about by plastic waste together with other forms of waste, especially after their consumption.

Among different types of plastic, polyethylene (PE) is widely used for numerous purposes, including packing and packaging materials with almost 63 wt.% of the total generated plastic waste [20]. Polyethylene terephthalate (PET) is one of the main sources of packing materials such as bottles for mineral water and soft drinks all around the world. Consequently, any novel implementation or artificial use of waste PET would be a momentous relief to the surroundings [21] and this is one of the main emphasis of the current study. Therefore, generation of hydrogen from plastics is indeed a promising technology environmentally and economically [22].

In studies of catalytic steam reforming, phenol (C_6H_5OH) is often used as typical model compounds [23-25]. As an important constituent in the aqueous portion of bio-oil, phenol constitutes about 38% by weight [26]. Since PET is soluble in phenol, it has been selected in this study as a feedstock [27] which can make unique product that contains two main waste component. The phenols and phenolic compounds are not considered as fuels and they are corrosive to combustion engines.

Among the catalysts, alumina (Al_2O_3) is the most commonly employed support in various thermal processes because of chemical and mechanical stability, low cost and high surface area for metal dispersion [28, 29]. The chemical and hydrothermal stabilities of γ-Al_2O_3 are critical points for catalytic applications [30]. Although comparative studies [31] have shown better performance on basic supports, such as MgO and La_2O_3. The La_2O_3 and ZrO_2 as support materials have displayed a great vital catalyst-support interaction [32]. Bimetallic catalysts such as nickel and cobalt on Al_2O_3, ZrO_2 and La_2O_3 have been used for steam reforming [33] which are able to suppress the formation of coke. Ni is one of the most used metal in steam reforming processes due to its lower cost and excessive available in nature as compared to other noble metals [34]. Nickel-based catalyst has been commonly used for steam reforming of bio-oil due to its high selectivity and activity towards hydrogen production [35, 36]. Therefore, it is of great importance to apply Ni supported with Al_2O_3 composite for hydrogen production from PET plastic waste.

The present research aimed to explore catalytic PET conversion via steam reforming over Ni-Al_2O_3 catalysts for selective hydrogen production to provide a way to produce renewable and clean fuels from waste feed stock. Herein, we investigated the performance of Ni promoted Al_2O_3 catalyst for steam reforming of PET for hydrogen production in a fixed bed reactor. The catalysts were characterized with BET-N_2, SEM-EDX, TPD-CO_2 and TPR-H_2. The effects of different operating parameters such as feed flow rate, PET composition and reaction temperature on H_2 yield and conversion are critically discussed.

2. EXPERIMENTS

2.1 Catalyst preparation and characterization

Impregnation method was used for preparing Ni supported on Al_2O_3. In order to prepare the catalyst, 10 wt.% of active metal (10 wt.% Ni) with Al_2O_3 (wt.%) (all from Sigma - Aldrich) were the mixing percentages. In specific terms 9 g of Al_2O_3 was mixed with 250 ml of deionized water and the mixture was subsequently mixed with 4.94 g of Ni $(NO_3)_2.6H_2O$ catalyst. The resultant slurry was heated to 90 ºC while stirring at a constant temperature until all the water was evaporated. Next, the solid residue was dried at 110 ºC overnight in an oven and subsequently calcined at 750 ºC for 3 h. The final calcined samples were crushed and separated in two layers using 35 mesh (1.0 mm) and 34 mesh

(1.4 mm) sieves. Figure 1 shows the steps and procedure for the catalyst preparation.
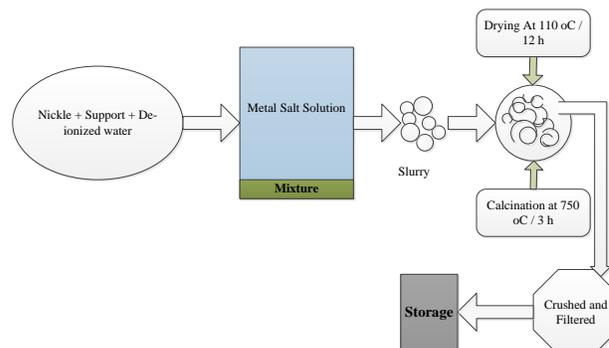
Fig. 1 Schematic presentation for the preparation of Ni co-impregnated Al_2O_3 catalyst.

In catalytic characterization to determine the surface area of the Ni/Al_2O_3 catalyst, single point BET-N_2 on a surface area analyzer (Micromeritics Gemini 2360) was employed. The device was set at 200 ºC for 2 h before outgassed samples. Morphology of the catalysts was studied by a scanning electron microscope (SEM, JEOL, JSM-6390) and EDX by energy-dispersive X-ray spectroscopy (Oxford Xmax 50 mm). The reducibility of the active metals on the support was investigated with the aid of a chemisorption analyzer (Micromeritics Chemisorb 2720) via temperature-programmed reduction of hydrogen (TPR-H_2). Similarly, the CO_2-TPD was obtained using the same apparatus (Micromeritics Chemisorb 2720 Chemisorption).

2.2. Catalytic activity testing

The setup consists of a furnace, preheater, ½ inch stainless steel fixed bed reactor, circular cooling unit, HPLC pump, Syringe pump, liquid-gas separator, a condenser and a gas chromatography (GC). The water was fed using a HPLC pump, and the phenol-PET was fed using a syringe pump at a total flow rate of 0.40 ml/min. The reaction product was cooled in a graham condenser with the aid of a circulating chiller model Polyscience 9106 at 5 ºC. The mixture of phenol and PET was fed into the reactor via syringe and the water was fed using a high pressure liquid chromatography (HPLC) pump (Bio-Rad^{TM}, Series 1350). Nitrogen was mixed with the liquid at a controlled rate of 30 ml/min with the aid of a mass flow controller (Tylan FC-260C), and then vaporized completely by crossing it through a pre-heater set at 200 °C. Typically, 0.2 g catalyst loading placed on the stainless steel mesh (particle size of 1.0 to 1.4 mm) and different temperature between 600 to 800 ºC was used in the course of the experiment. The effect of reactor and wire mesh made of stainless steel was assumed negligible effects on catalyst activity and selectivity. Prior to the experiment, the catalyst was reduced in-situ at 600 °C for an hour in purified hydrogen at 30 ml/min. The reaction product exiting the reactor was cooled to 10 °C in a graham glass condenser. The condensate and the gas products were

separated in a gas liquid separator. The gas was analyzed using an online GC-TCD (Agilent 6890N) equipped with a Carboxen Plot 1010 capillary column (Supelco, 30 m × 0.53 mm). The liquid was collected once the gas was injected into the GC, and analyzed using a GC-FID (HP5890 Series II) eluted in a CP-Wax 58 CB (Varian, 25 m × 0.32 mm) capillary column. The liquid products were also analyzed to determine the unconverted PET using FTIR, Shimadzu IRPrestige-21. Equations 1 and 2 were applied to compute the feed conversion and H_2 yield [23, 37, 38]. In equation 4, the total molar flow rate of the feed represented as $[feed]_{in}$, and the total molar flow rate at the exit of the reactor is defined as $[feed]_{out}$.

$$\text{Feed conversion (\%)} = \frac{[feed]_{in} - [feed]_{out}}{[feed]_{in}} \times 100 \quad (1)$$

$$H_2 \text{ yield (\%)} = \frac{\text{moles of } H_2 \text{ obtained}}{\text{moles of } H_2 \text{ stoichiometric potential}} \times 100 \quad (2)$$

3. RESULTS AND DISCUSSION

3.1. Surface area analyzer (BET-N_2)

Table 1 presents the result of BET-N_2 measurement for the fresh and used catalysts, analyzed with multi-point method. The total surface area of the prepared catalyst before the experiment was 34.31 m^2/g suggesting that Ni existed inside the pores and on the surface as well. In used catalysts, BET surface areas of Ni/Al_2O_3 catalyst was reduced to 30.42 m^2/g. The decreased in surface area might be attributed to blockage of pores with coke formation. This was also because of collapsing of the catalyst pores at elevated temperature [23].

Table 1 BET-N_2 surface area and reducibillity of the catalysts for fresh and used samples.

Sample	BET Surface area (m^2/g)	H_2-Consumption (µmol/g)
Ni/γ-Al_2O_3 (fresh)	34.31	58.53
Ni/γ-Al_2O_3 (used)	30.42	41.26

3.2. Scanning Electron Microscopy (SEM) and EDX mapping

The SEM images in Figure 2 (a) display the overall morphology of the fresh catalyst. It could be seen that the micro particles were entangled in the outer surface of the Alumina. The distribution of Ni in the whole catalysts was studied with element analysis mapping at low magnification. From the Ni element map shown in Figure 2 (b), this metal is uniformly distributed in the catalyst which confirms the homogeneous distribution of Ni bimetallic particles on the surface of the support (c).
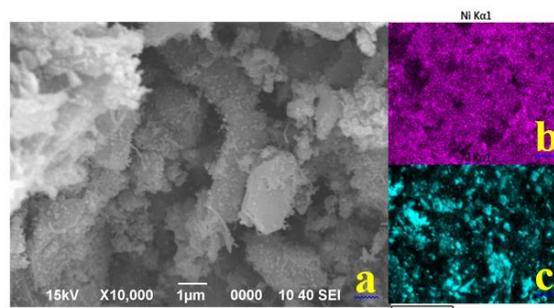
Fig. 2 SEM image of Ni/Al_2O_3 for (a) fresh catalyst and the corresponding element mapping of Ni (b) and Al (c).

3.3. Temperature Programmed Reduction (TPR-H_2)

TPR was carried out in order to determine the reducibility of the Ni-based catalysts as well as to investigate the metal-support interaction after calcination at 750 ºC as depicted on Figure 3. The total consumption of hydrogen for the catalyst has been tabulated in Table 1. It is known that nickel catalysts supported on alumina show different reduction patterns depending on the nature of interaction between the nickel oxide and alumina support [39-41]. The TPR-H_2 profile was noticed to have a peak centered at 292ºC for Ni/Al_2O_3 catalyst. The NiO species interacted weakly with the support as evident by the NiO reduction at lower temperature. However, no reduction was observed at temperatures above 600 ºC for Ni/Al_2O_3 catalyst. This shows high level of consistency to the observation of Cárdenas-Lizana et al. [42].
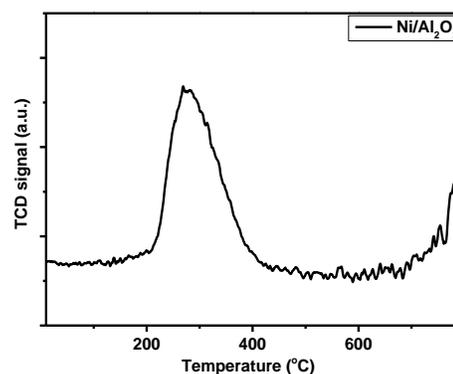
Fig.3 TPR-H_2 profiles of fresh Ni/Al_2O_3 catalyst.

3.4. Temperature Programmed Desorption (TPD-CO_2)

Temperature-programmed desorption of CO_2 (TPD-CO_2) was carried out in order to investigate the catalyst basicity after calcination at 750 ºC as depicted in Figure 4. As displayed in Figure 4, the peaks that appeared below 200 °C are considered as weak, 200-400 °C as medium, 400-600 °C as strong and above 600 ºC are considered as very strong basic sites [43]. The peak at about 100 to 200 ºC was assigned to the weak basicity related to CO_2 weakly

adsorbed on the support surface for the Ni/Al_2O_3 catalyst. This sample also shows a peak at around 300 °C.
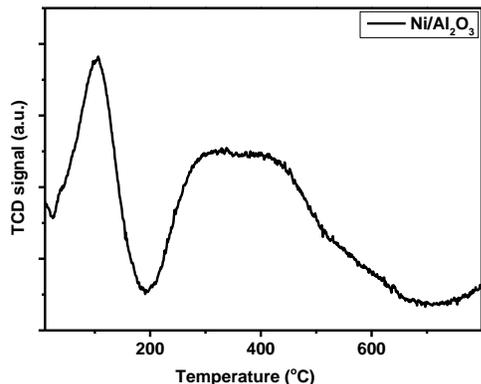
Fig. 4 TPD-CO_2 profiles of fresh Ni/Al_2O_3 catalyst.

3.4. Effect of process parameters

The unconverted PET in the liquid products after reaction was measured using FTIR analysis as shown in Figure 5(a) for the whole spectrum (500-4000 cm^{-1}) and in Figure 5(b) for the specific range of 1675 to 1750 cm^{-1} that shows the presence of C=O peak of PET. It was observed that PET was not detected in the liquid product when 3 to 7 wt.% of PET into phenol was used. This observation indicated that a complete conversion of PET was achieved. Therefore, in this study only the conversion of phenol was considered. In other studies, similar result was also achieved on catalytic cracking on dissolved polymer [44].

The effect of different phenol concentration and different temperatures on the hydrogen yield and feed conversion was investigated as depicted in Figure 6. It can be observed that the highest yield of H_2 (56.82%) was established at a temperature of 800 °C as shown in Figure 6 (a). Nevertheless, H_2 yield decreased rapidly from 800 to 600 °C in comparison to the maximum CO_2 yield of 40.78% at 600 °C and reduced severely to 32.57% at 800 °C. Similarly, the conversion steadily increased at the 700 °C (from 68.94% to 86.3%) and increased to 91.32% within a temperature of 800 °C was employed. Thus, altering the heat duty of the reactor becomes the primary working factor of the steam reforming system. It was reported that water-gas shift reaction (WGSR) and steam reforming reactions were promoted when the reaction temperature was higher than 700 °C [45]. Generally, high temperature facilitates endothermic reactions; however, at too high reaction temperature, it is easy to form carbidic carbon, which is a precursor of graphitic carbon that results in the deactivation of catalyst [46]. Phenol concentration revealed an important relation to the product yield as well as feed conversion as shown in Figure 6 (b). By increasing phenol to water ratio results in a negative effect on the reaction, thereby decreasing the conversion from 86 to 53% as well as hydrogen yield from 55 to 52% at 30% phenol

concentration. In contrast, CO yield increased slightly (11.3 to 21.6%) by increasing the phenol ratio.
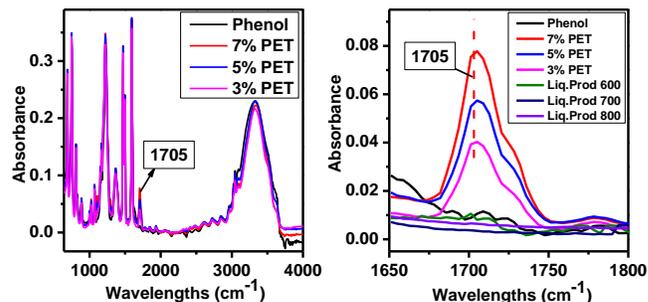
Fig. 5 FTIR result on PET-phenol solutions at different concentrations and at wide range of wavelengths IR scanning (a) wide range of 500 – 4000 cm^{-1} and (b) narrow range of 1675 to 1750 cm^{-1} with result of liquid product at 600, 700 and 800 °C.
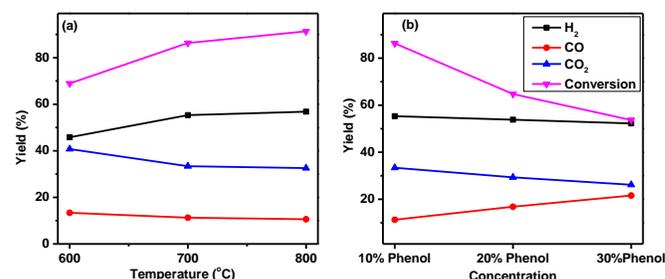
Fig. 6 Effect of temperature (a) and phenol-PET concentration (b) on product yield and feed conversion.

4. CONCLUSION

The present research work explored the production of hydrogen from polyethylene terephthalate as a plastic waste. The catalyst spent catalyst has reduced surface area after the reaction. In catalytic reducibility analysis of TPR-H_2, no peak was observed at temperatures above 500 °C, indicating the nickel metal deposited outer layer the catalyst support. SEM-EDX analysis shows that metal is uniformly distributed in the surface of the support. It was found that the PET was completely converted in the reaction condition. The maximum phenol conversion and hydrogen yield achieved 91% and 57% at 800 °C, respectively. This study shows a new promising clean technology to convert waste PET toward a valuable product such as hydrogen.

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