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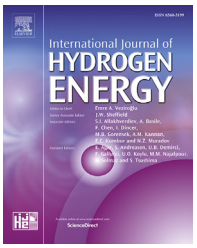

Production of renewable hydrogen through aqueous-phase reforming of glycerol over Ni/Al_2O_3–MgO nano-catalyst

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ABSTRACT

In this study, a series of Ni nano-catalysts supported on Al_2O_3 and MgO were prepared through the co-precipitation technique. Effects of the Al/Mg ratio on physicochemical characteristics of Ni/Al_2O_3–MgO catalysts were examined. Moreover, catalytic performance was investigated in order to determine the optimum catalyst for H_2 production in aqueous phase reforming (APR) of glycerol. It was revealed that, the APR activity of synthesized catalysts strongly depended on the aforementioned ratio. In addition, it was observed that, the catalytic activity of Ni/MgO and Ni/Al_2O_3 samples were both lower than that of the corresponding mixed oxide supports. Furthermore, it was shown that, amongst the compositionally different prepared mixed oxide materials, the respective catalytic activities increased through enhancing of the Al/Mg ratio. It was demonstrated that the Ni/Al_2Mg_1 catalyst possessed highest catalytic activity of 92% glycerol conversion and selectivity towards hydrogen production of 76%. Ultimately, it was concluded that, the APR activity lowered in the following order: $Ni/Al_2Mg_1 > Ni/Al_1Mg_1 > Ni/Al_1Mg_2 > Ni/Al > Ni/Mg$ for the understudied synthesized materials.

Introduction

The mean annual temperature of the Earth is considered increasing, known as the global warming led to a number of researches performed in order to lower emissions of greenhouse gases such as carbon dioxide (CO_2) and methane (CH_4) enhancing the aforementioned phenomenon [1–5]. This factor, as well as the reduction of reserves of fossil fuel [6,7] led to rising prices of petroleum in particular and world energy demand in general. This in turn encouraged utilization of renewable energies as well as developing different technologies in order to produce them from renewable sources [8–11]. In this venue, application of the pure hydrogen production technologies is considered by many experts as an alternative approach to replace fossil fuels due to their very low negative environmental impacts [12–20]. However, pure hydrogen availability is considered very uncommon through the Earth's atmosphere. This species naturally is found in compounds such as water and other organic matters. In order to produce

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hydrogen gas, such materials needed to be further processed [21].

The most common method which is utilized to produce hydrogen is known as the steam reforming of natural gas [22]. This is considered as an established method that has used since 1930s. This route indeed provided half of the world's hydrogen production. The main advantageous factor in this wide production range is known to be its low cost compared to gasification of coal and biomass as well as the electrolysis of water. However, large amounts of the CO_2 emissions which is resulted by steam reforming is a major disadvantage [23]. Nonetheless, hydrogen production from biomass, waste or byproducts is considered as one of the most efficient and environmentally interesting productions. The price of the glycerol that is used in various industries kept high and stable between 1998 and 2003. From 2004 however, there was an imbalance in the world market due to supply and demand of the glycerol [24]. This was due to new biodiesel plants mainly started in Europe [25–27]. Considering the large-scale production of biodiesel nonetheless, led to an excess of glycerol in the market. Destination of this glycerol as a byproduct of the biodiesel production, created a matter of concern. Major solutions were proposed included either burning or exporting it. Furthermore, this led biofuel companies to start considering that crude glycerol as a waste that might have not been ignored [28–32].

In this context, the current study focused on the development of a low cost and environmentally clean technology leading to production of hydrogen from glycerol, using heterogeneous nano-catalysts. Production of hydrogen by aqueous phase reforming of oxygenated compounds, like glycerol, provided several economic and technological advantages compared to that of the steam reforming [4]: (i) removal of the vaporization stages of water and raw material to be reformed (leading to significant reduction of the energy demand for the process), (ii) operation at lower temperatures (avoiding parallel reactions of decomposition of the oxygenated compounds and promoting the removal reaction of CO (through the water-gas shift reaction) making hydrogen production possible along with a low concentration of carbon monoxide in a single stage) and (iii) low pressure of operation (allowing hydrogen purification through adsorption or membrane technology) [5].

Catalysts for hydrocarbon reforming is mainly based on nickel as active component that supported on oxides with high thermal stabilities [33,34]. Nonetheless, noble metals (Ru, Rh, Pt) were considered to be more effective for the steam reforming of hydrocarbons than Ni and less susceptible to carbon formation [35]. However, such materials were not commonly used in industrial applications due to their high cost. Effective catalyst for production of hydrogen by aqueous phase reforming of oxygenated hydrocarbons ought to break C–C, O–H and C–H bonds in the oxygenated hydrocarbon reactants and facilitate the water–gas shift reaction removing adsorbed CO from the catalyst surface [36]. Studies on aqueous phase reforming of oxygenated hydrocarbons over various supported metals indicated that, Pt and Pd materials (especially in the case of Pt) were active and selective for the production of hydrogen [37]. Nevertheless, the high cost in general and limited availability in particular of noble metals (to produce H_2 on industrial scale) led to studies toward developing less expensive catalysts for aqueous phase reforming. Due to this background, in the present research nickel was selected as the active phase and modified by employing Al_2O_3–MgO support. Moreover, the structural characteristics and performance of supported nickel catalysts was considered to be strongly influenced by the nature of support where the metallic crystallites deposited. In addition,

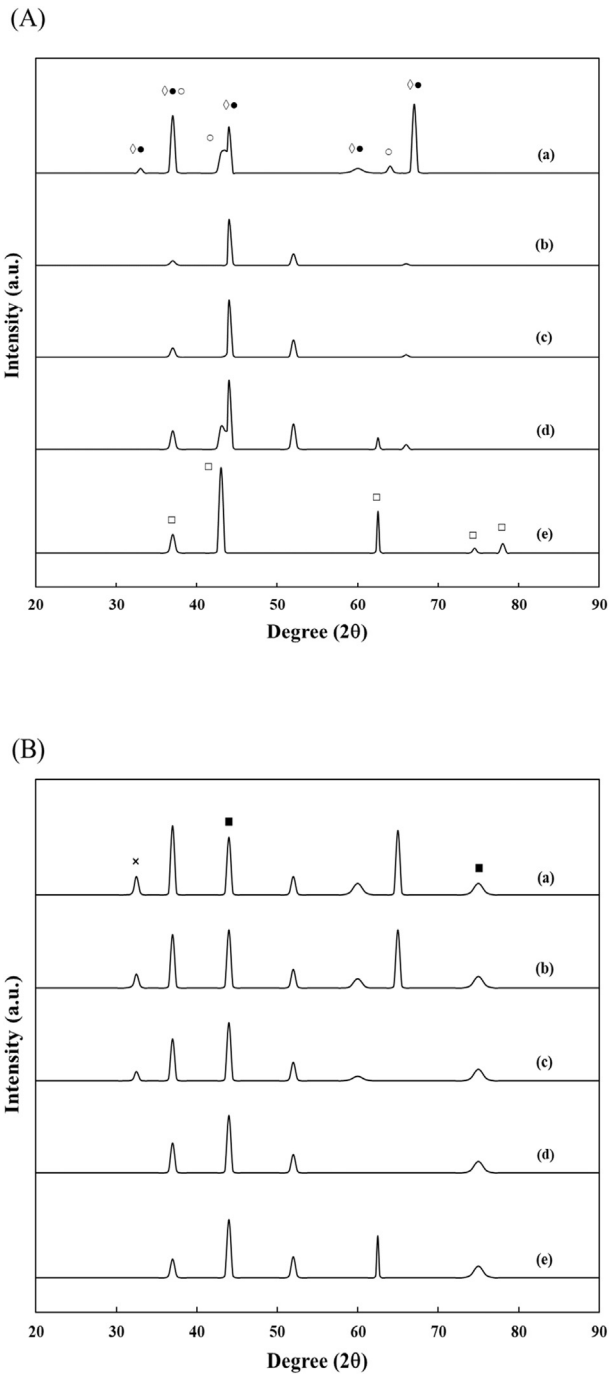

Fig. 1 – The X-ray spectra of (A) fresh and (B) reduced catalysts, (a): Ni/A, (b): Ni/A_2M_1, (c): Ni/A_1M_1, (d): Ni/A_1M_2 and (e): Ni/M (◊ = $NiAl_2O_4$, ● = Al_2O_3, ○ = NiO, □ = NiO–MgO, × = $NiAl_2O_4$ or $MgAl_2O_4$ and ∎ = Ni).

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