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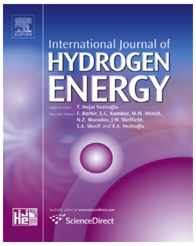

Preparation of Ni-based catalysts to produce hydrogen from glycerol by steam reforming process

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ABSTRACT

Nickel and Nickel–Palladium-catalysts supported on Al_2O_3–ZrO_2, Al_2O_3–ZrO_2–La_2O_3 and on Olivine were synthesized using a combination of sol–gel and wet impregnation methods. The influence of the formulation on their textural properties was examined by XRF, XRD and XPS. The influence of supports, promoters and temperatures of reactions was studied on glycerol steam reforming to produce hydrogen. $C_3H_8O_3$ and H_2O mixture was fed into a fixed bed reactor in a molar ratio of S/C = 5.0 (Steam/Carbon) and tested under atmospheric pressure at 800,700, 600 °C for 4 h. The most suitable catalyst was determined as Ni–Pd/Al_2O_3–ZrO_2specifically in the process carried out at 800 °C, since it reached the highest hydrogen yield around 74%.

Introduction

Hydrogen is known as one of the basic, clean and attractive alternative energy sources due to its compatibility with environment and its large, infinite potential source [1]. The steam reforming (SR) of glycerol by the low-cost catalysts synthesized would be advantageous from both the economic and environmental point of view [2]. Hydrogen is the lightest, simplest and most plentiful of all chemical elements in the universe. However, it occurs only in combination with other elements, primarily with oxygen in water and with carbon, nitrogen and oxygen in living materials and fossil fuels. Hydrogen is not a primary source of energy. But it becomes an attractive energy carrier when split from these other elements by using a source of energy. Some of the advantages of the hydrogen economy can be summarized as: (i) energy security by reducing oil imports, (ii) sustainability by taking advantage of the renewable energy sources, (iii) less pollution and better urban air quality by producing near-zero carbon, hydrocarbon and NOx emissions at the point of use, and (iv) economic viability by potentially shaping the future global energy markets [3].

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In future world, hydrogen would be produced from renewable sources by taking advantage of solar, wind, or geothermal energy to power an electrolyzer that produces hydrogen from water. Currently, this environmentally friendly energy cycle is not economically feasible. Renewable energy production systems and processes must continue to be improved in performance; their overall capacity must grow to support a robust infrastructure and their production must be cost effective. Electrolyzing water via thermal electricity is another alternative. However, since the most efficient water electrolyzing system is operating at roughly 30% efficiency and dominated by coal power, that option is neither efficient nor environmentally friendly [4].

The processing of hydrocarbons is the most popular production method nowadays in the industrial production of hydrogen. Collectively called oxyforming, the three most prominent technologies in hydrocarbon reforming are steam reforming, partial oxidation (POX), and auto thermal reforming (ATR), each of which has advantages and disadvantages. SR is the most common method in hydrogen production as it gives the highest hydrogen yields and uses the lowest processing temperature. However, the process is highly endothermic and requires an external heat source, and also has the highest air emissions [5]. So as per stoichiometric study, glycerol provides most number of moles of hydrogen and hence can be preferred over the fossil fuels. Though more amount of glycerol is required in terms of weight as compared to methane in order to get just double the amount of hydrogen, but in steam reforming of natural gas (methane), a fuel is burnt off to make another fuel while this is not the case in glycerol steam reforming and hence it would be advisable to use glycerol instead of methane [6].

Glycerol is a polyalcohol with several commercial applications in food and cosmetics that may be synthesized chemically from epichlorohydrin, derived from propylene, or biochemically by microbial fermentation. An increase of biodiesel production all over the world from 2000 year has caused to big increment of crude glycerol as a by-product [7]. Massive amounts of low-purity glycerol are being obtained as byproduct in the manufacture of fatty acids, and mostly in biodiesel production where glycerol represents around 10 wt% of the plant product. Due to its low-purity, crude glycerol from biodiesel cannot be used in cosmetics or food unless a costly refining process is undertaken, and that is why it is usually considered a refuse product. Still, its wide availability and cheap price offer new opportunities for chemistry and energy [8].

Catalytic steam reforming of glycerol is a new method to renewable energy conversion. The studies of glycerol steam reforming indicated the parameters including temperature, ratio of steam to carbon (S/C), residence time, inlet gas composition and flow rate should be carefully controlled to maximize H_2 production with minimum coke formation. One of the problems for the production of hydrogen from glycerol steam reforming by catalysts is high CO_2, CO and CH_4 contents [7].

Glycerol can be converted into syn-gas by SR according to the following reaction:

$$C_3H_8O_3+3H_2O \rightarrow 3CO_2 + 7\ H_2 \tag{1}$$

This process can be formally written also as a combination of two separate reactions: glycerol decomposition into H_2 and CO (2) followed by the water gas shift (WGS) equilibrium (3):

$$C_3H_8O_3 \rightarrow 3CO + 4\ H_2 \tag{2}$$

$$CO + H2O \leftrightarrow CO2 + H2 \tag{3}$$

Typically, the glycerol SR is a catalytic process that occurs in vapor phase at atmospheric pressure and temperatures up to 900 °C. Due to its endothermicity, high temperatures, low pressures and a high steam-to-glycerol ratio are generally required to get high substrate conversions. Noble metal based catalysts are commonly used for the steam reforming reaction of hydrocarbons or alcohols since they are highly active while they are less susceptible to develop undesired carbon deposits. On the other hand, catalysts based on non-noble transition metals are far cheaper and present higher availability than the former [9]. Many metal catalysts have been scrutinized for the glycerol SR among which Ru, Rh, Ir, Pd, Pt, Co, and mainly Ni are the most representative ones. Pt is a good candidate for the glycerol SR allowing for efficient C–C, O–H and C–H bond cleavages with high activity and selectivity levels. On the contrary, other metals need the promoting effect of additional metals to ensure good activities and high H_2 selectivity values. A wide variety of supports for the metal active sites have also been tested in the glycerol SR reaction, from acidic supports to basic ones, in many cases without attention to the role of these materials on the paying performances of the catalytic system. An effective catalyst for the H_2 production from glycerol is expected to break-up the substrate via C–C, O–H and C–H bond cleavages promoting, at the same time, the elimination of the metal-passivating carbon monoxide via WGS reaction. Consequently, the suitable catalyst for hydrogen production should promote neither the C–O cleavage nor the CO or CO_2 hydrogenation to form either alkanes or more polar compounds [7].

Ni catalysts frequently suffer from deactivation caused by carbon deposition on catalyst surface, which blocks active sites and increases the concentrations of by-products, such as methane and ethylene. Modifying Al_2O_3 with La_2O_3, CeO_2, MgO and ZrO_2 can improve the catalytic activity and stability for steam reforming via preventing Ni from incorporation to Al_2O_3 phase, stabilizing Ni^0 particles and reducing support acidity. It is also known that the catalytic activity may be enhanced by modifying Ni catalysts with a small quantity of noble metal, such as Pt and Pd [10]. ZrO_2 as a modifier with excellent redox properties can be a feasible candidate for structural and chemical stabilizer of transition Al_2O_3. Besides it has been reported that addition of ZrO_2 into Al_2O_3 not only enhanced the coking resistance but also increased the active nickel surface area, resulting in high catalytic performance of supported nickel catalyst [11]. Wang et al. have studied on H_2 production from catalytic steam reforming of glycerol by Ni–Mg–Al based catalysts. Tests were evaluated experimentally in a fixed-bed reactor under atmospheric pressure within a temperature range of 450–650 °C. The Ni–Mg–Al based catalysts were synthesized by the co-precipitation method with rising pH technique. The results that they obtained showed that glycerol conversion and H_2 selectivity were