Hydrogen production by steam reforming of biomass-derived glycerol over Ni-based catalysts

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A B S T R A C T

The steam reforming of bio-glycerol for the production of hydrogen has been investigated in a fixed-bed reactor containing spherical particle of Ni supported on γ-Al_2O_3 as catalyst. Several catalysts were prepared by the dry impregnation method at different calcination temperatures (750–950 °C) with/without the addition of various alkaline promoters (K, Ca, Sr). The physical and chemical properties of the prepared catalysts were characterized by nitrogen (N_2) physisorption, X-ray diffraction (XRD), temperature-programmed reduction, thermogravimetric analysis, scanning electron microscopy-energy dispersive X-ray spectroscopy and transmission electron microscopy techniques. The Ni/γ-Al_2O_3 catalysts showed a high glycerol conversion and hydrogen selectivity, however they gradually deactivated due to the formation of carbon over those catalysts.

Nevertheless, it was found that the catalysts calcined at high temperatures could inhibit the formation of carbon without affecting the glycerol conversion and hydrogen selectivity. The addition of alkaline promoters caused a slight decrease in the glycerol conversion, but also reduced the formation of carbon and thereby increased the long-term stability of the catalyst.

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1. Introduction

With an ever-increasing demand for energy and problems associated with global warming due to the use of fossil fuels, the quest for alternative and renewable fuels has become paramount [1]. In this respect, biodiesel is being gradually accepted as a replacement for mainstream diesel. Biodiesel is composed of fatty acid methyl esters (FAMEs), which are produced by an alkali-catalyzed transesterification reaction between biomass-derived triglycerides and methanol (Fig. 1). As can be seen in the reaction scheme, glycerol is produced as a by-product at about 10% of the amount of biodiesel, making it sufficiently significant.

Glycerol is an important feedstock in food, cosmetics, pharmaceuticals and other industries. Among the possible uses of glycerol, the production of hydrogen by steam reforming (SR) is considered attractive because it makes glycerol (and its raw materials) a potential source for a renewable zero-emission fuel [2].

The dominant reaction in the glycerol steam reforming process is as follows:

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

Eq. (1) is further constituted of the glycerol decomposition reaction (Eq. (2)) and the water–gas shift reaction (Eq. (3)).

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

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{3}$$

However, several side reactions also occur as shown in Eqs. (4)–(10)

$$C_3H_8O_3 + 5H_2 \rightarrow 3CH_4 + 3H_2O \tag{4}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{5}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{6}$$

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2 \tag{7}$$

$$CH_4 \rightarrow 2H_2 + C \tag{8}$$

$$2CO \rightarrow CO_2 + C \tag{9}$$
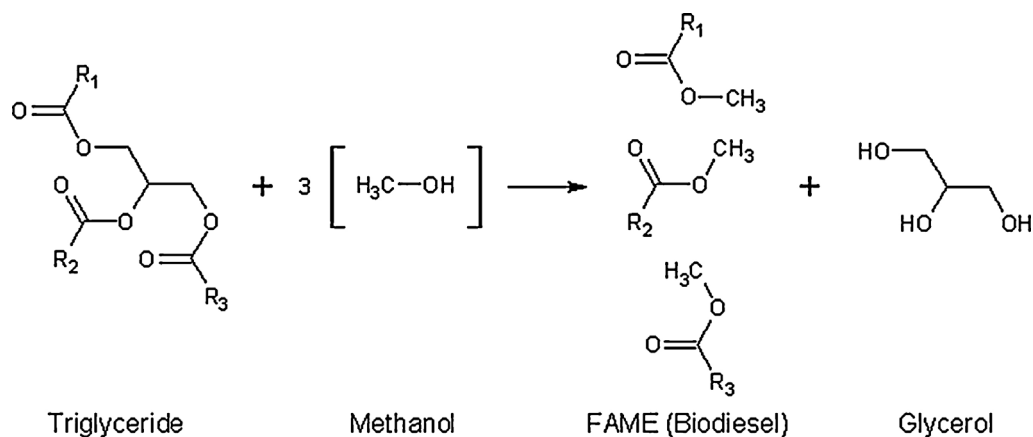
$$C + H_2O \rightarrow CO + H_2 \tag{10}$$

Fig. 1. Main scheme of biodiesel production from biomass.

Amongst the side reactions, Eqs. (8) and (9) show the two types of mechanisms for the formation of carbon. The former is the methane decomposition reaction and the latter is a carbon monoxide disproportionation reaction called the "Boudouard reaction." Despite the mechanism involved, the formation of carbon on the surface of the catalyst causes a loss of the effective surface area, decreases the mass and heat transfer rate in the catalyst bed, and reduces the lifetime of the catalyst.

Many studies have been conducted to limit the formation of carbon during the steam reforming process. Urasaki et al. [3] suggested the use of perovskite-type oxides as a catalytic support because they reduced the formation of carbon with their lattice oxygen. Sánchez-Sánchez et al. [4] reported that the presence of basic additives or promoters on an alumina (Al_2O_3) support lowered the rate of carbon deposition on the catalyst surface because they favored the adsorption of water and the surface mobility of hydroxyl ions during the steam reforming of ethanol. Sahli et al. [5] found that the nickel aluminate ($NiAl_2O_4$) spinel having an optimized Ni/Al ratio exhibits a good performance in the reforming of methane into synthetic gas with limited formation of carbon.

Many researchers reported that, the effect of the addition of alkaline earth promoter to a nickel based catalyst will enhances the resistivity toward carbon formation.

Sekine et al. [6] showed that the addition of strontium enhance the active oxygen species under steam reforming of tolune. Hadden et al. [7] proved that the potassium promoted the adsorption ability of water under steam reforming reaction. Elias et al. [8] showed that calcium oxide having less acidic sites showed the less carbon deposition under steam reforming reaction of ethanol.

In this study, we have investigated the reduction of carbon formation by changing the calcination temperatures and studied the effect of alkali earth metal as promoters to Ni/γ-Al_2O_3 catalysts for the steam reforming of glycerol.

2. Experimental

2.1. Catalysts preparation

The Ni/γ-Al_2O_3 catalysts were prepared by the dry impregnation method. In a typical experiment, aqueous solution of nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$ 98.0% Samchun Chemical] was impregnated (15 wt.%) on the calcined alumina support (Alumina spheres Φ1.0 SASOL). After impregnation, the catalyst was calcined at different temperatures (750, 850 and 950 °C) for 5 h. The catalysts are denoted as A, B and C, respectively. For the comparison, $NiAl_2O_4$ spinel phase catalyst was also prepared by sol–gel method [9].

The alkali promoter modified M–Ni/γ-Al_2O_3 catalysts (M: K, Ca, Sr) were prepared by the same method used for the Ni/γ-Al_2O_3 catalysts. Aqueous solutions of the respective alkali and alkaline-earth metal nitrate, which include potassium nitrate (KNO_3, 98.0%, Samchun Chemical), calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$, 98.5%, Samchun Chemical), and strontium nitrate ($SrNO_3$, 98.0%, Samchun Chemical) were impregnated (1 wt.%) on the Ni/γ-Al_2O_3 catalyst. After impregnation of promoters, catalysts were calcined at 950 °C for 5 h.

2.2. Catalysts characterization

The specific surface area, pore sizes and pore volumes of the catalysts were calculated by applying the Brunauer–Emmett–Teller (BET) method to the nitrogen adsorption/desorption isotherms, measured at 77 K (liquid nitrogen temperature) on a Moonsorp-II apparatus (BEL Japan). The catalyst samples were pretreated with nitrogen gas at 200 °C for 2 h.

The temperature-programmed reduction (TPR) experiments were carried out with an Autochem II apparatus (Micromeritics) equipped with a thermal conductivity detector (TCD). Prior to the TPR experiments, about 0.1 mg of the samples was washed under a helium stream (50 mL/min) at room temperature for 2 h to remove water and other contaminants. TPR profiles were obtained by heating the samples under a 5% H_2/Ar flow (50 mL/min) from 50 to 980 °C at a linearly programmed rate of 10 °C/min.

X-ray diffraction (XRD) patterns of the calcined and used (after SR) catalysts were recorded using an XRD-6000 apparatus (Shimadsu Co.) with a monochromatized CuKα radiation ($λ = 1.5404$ Å) as the source over the diffraction angle, $2θ$ scan range of 20–80° with a scan rate of 4°/min.

Temperature-programmed oxidation analysis of the used catalysts was carried out on a thermogravimetric analyzer (TGA) SDT-Q600 apparatus (TA Instruments) to determine the amount of carbon deposited on the catalysts. In the procedure, 20 mg of the used catalysts were subjected to a flow (100 mL/min) of dry air from room temperature to 1000 °C at a heating rate of 5 °C/min.

The composition and morphology of the calcined and used catalysts were examined by field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDX) using an S-4200 apparatus (Hitachi). The catalyst samples were ground and mechanically dispersed on an electrically conductive carbon tape placed on an aluminum stub.

The morphology of the catalysts before and after the reaction was also investigated by transmission electron microscopy (TEM) using a Tecnai F20 G2 microscope (FEI Company). For samp-