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Activity of Ni–Cu–Al based catalyst for renewable hydrogen production from steam reforming of glycerol

Binlin Dou [a,*], Chao Wang [a], Yongchen Song [a], Haisheng Chen [b,*], Yujie Xu [b]

[a] School of Energy and Power Engineering, Key Laboratory of Ocean Energy Utilization and Energy Conservation of Ministry of Education, Dalian University of Technology, 116023 Dalian, China
[b] Institute of Engineering Thermophysics, Chinese Academy of Sciences, Beijing 100190, China

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ABSTRACT

In this study, the activity of Ni–Cu–Al based catalyst for renewable hydrogen production from glycerol steam reforming has been evaluated in a continuous flow fixed-bed reactor under atmospheric pressure at 500–600 °C. The catalyst synthesized by the co-precipitation method with rising pH technique was characterized by the elemental analysis, Brenauer–Emmett–Teller (N_2-BET) adsorption method, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscope (TEM) and thermogravimetric analysis (TGA). The thermodynamic analysis for glycerol steam reforming was conducted by using a non-stoichiometric methodology based on the minimization of Gibbs free energy. The obtained results revealed that the great quantity of hydrogen is produced at excess water and the formations of CH_4 and CO in the glycerol steam reforming were almost negligible. The deactivation of catalyst due to the formation of carbon residues was observed. The carbons removal was measured by TGA experiment during medium temperature oxidation conditions. The kinetics on glycerol steam reforming was described by means of the separability concept of reaction rate law and deactivation model, and the kinetic parameters were calculated.

1. Introduction

Biodiesel as a fuel component can be mixed in any ratio with standard diesel for use in the diesel engines, and biodiesel production has attracted considerable attention worldwide as an alternative energy source to replace traditional petroleum diesel product because of its environmental benefits and nearly neutral CO_2 emissions [1,2]. During the production of biodiesel, the transesterification converts approximately 10% of the total mass of triacylglycerol to glycerol using vegetable oils or animal fats with alcohols [3]. Recently, glycerol as a potential feedstock by catalytic steam reforming to produce hydrogen gas has received considerable research attention. A few studies have been carried out on glycerol steam reforming by the different metal catalysts including Ni, Ir, Rh, Ru, Co, Pt, Ce and Pd based catalysts [4–12]. For example, Nichele et al. studied Ni supported catalysts for hydrogen production by glycerol steam reforming, and the effects of the supports including TiO_2, SBA-15 and ZrO_2 on the performances of catalysts were evaluated [4]. Some studies showed that Co/Al_2O_3, Rh/Al_2O_3 and Ru/Y_2O_3 catalysts exhibited high H_2 selectivity and glycerol conversion, and the reaction process was negatively affected by coke formation [5–7].

Up until now, it is assumed that catalytic activity remains stable throughout the catalyst life in designing catalytic steam reforming reactors for hydrogen production. However, the formation of carbon residues in steam reforming reaction of glycerol is also inevitable. Carbons formed tend to deposit and cover the active sites of catalyst surface, which may lead the catalyst to lose its activity with the passage of time. Thus, a quantitative description and kinetic study of catalytic activity of catalyst, for the purpose of optimizing the design and operation of H_2 production process from glycerol steam reforming, are essential. These form the main motivation of carrying this study on the use of a synthesized Ni–Cu–Al catalyst with low-cost to investigate the feasibility of steam reforming of glycerol for hydrogen production. The Ni–Cu–Al catalyst was prepared by the co-precipitation method with rising pH technique. To obtain a better understanding of catalyst behaviors, the modeling of catalytic activity was carried out based on the catalyst deactivation model and reforming reaction rate law. A fixed-bed reactor in a temperature-controlled oven was employed under atmospheric pressure within a temperature range of 500–600 °C [13,14].

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* Corresponding authors. Tel.: +86 41184708460 (B. Dou), tel.: +86 1082543148 (H. Chen).
E-mail addresses: bldou@dlut.edu.cn (B. Dou), chen_hs@mail.etp.ac.cn (H. Chen).

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2. Experimental section

2.1. Preparation of catalysts

The Ni–Cu–Al catalyst was prepared by the co-precipitation with rising pH technique according to the method reported by Wu and Williams [15–17]. $Ni(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ and $Cu(NO_3)_2{\cdot}6H_2O$ with above 98% purity were used for the catalysts preparation and purchased from Sigma–Aldrich Shanghai Trading Co. Ltd. 1 M NH_4OH was added to an aqueous solution (300 mL) containing $Ni(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ with the addition of $Cu(NO_3)_2{\cdot}6H_2O$. The precipitation was carried out at 50 °C with moderate stirring until the final pH of 8.5 was achieved. The pH measurements were carried out by pH meter. The precipitate was filtered then washed by 50 °C deionized water, followed by being dried at 110 °C over 15 h. And finally, it was calcined under air atmosphere at a low heating rate of 5 °C min^{-1} until the final calcination temperature of 650 °C was achieved and maintained for over 3 h. The catalyst used in the experiments was crushed and sieved to granules with a size range between 0.20 and 0.45 mm.

In these conditions, the possible reactions may be as follows:

$$Ni^{2+} + 2NH_4OH = Ni(OH)_2 \downarrow + 2NH_4^+ \tag{R1}$$

$$Al^{3+} + 3NH_4OH = Al(OH)_3 \downarrow + 3NH_4^+ \tag{R2}$$

$$Cu^{2+} + 2NH_4OH = Cu(OH)_2 \downarrow + 2NH_4^+ \tag{R3}$$

If the excess NH_4OH solution was added, $[Ni(NH_3)_6]^{2+}$ and $[Cu(NH_3)_4]^{2+}$ were produced:

$$Ni(OH)_2 + 6NH_4OH = [Ni(NH_3)_6]^{2+} + 2OH^- + 6H_2O \tag{R4}$$

$$Cu(OH)_2 + 4NH_4OH = [Cu(NH_3)_4]^{2+} + 2OH^- + 6H_2O \tag{R5}$$

Though the Ni and/or Cu deposits in the precipitates can be oxidized to NiO and CuO in the stage of air calcination, liquid ammonia was controlled carefully to add to the solutions by rising pH value (pH < 8.5).

2.2. Characterization of catalysts

The synthesized catalyst was characterized and tested using different techniques. The specific surface area was determined with the Brenauer–Emmett–Teller (N_2-BET) adsorption method using a Micrometric Acusorb 2100E apparatus. Crystal structure of catalyst was determined by X-ray powder diffraction spectra performed using a Shimadzu XRD-6000 powder diffractometer, where a Cu target Kα-ray (operating at 40 kV and 30 mA) was used as the X-ray source. A scanning electron microscopy (SEM) (LEO 1530) was used to study the surface morphology of the fresh and spent catalysts. The morphology of the prepared catalyst and consumed catalyst were investigated by transmission electron microscopy (TEM) (Tecnai G220 S-Twin). For the TEM analysis, the samples were ground and dispersed with ethanol, and deposited on a Cu grid covered with a perforated carbon membrane. The chemical composition in the catalyst was determined by the elemental analysis method. Thermogravimetric analysis (TGA) of the used catalyst using a Stanton–Redcroft thermogravimetric analyzer was carried out at a heating rate of 15 °C min^{-1} to 700 °C with a dwell time of 10 min under a flow of air with the flow rate of 100 ml min^{-1}.

2.3. Catalyst activity measurements

Details of the laboratory system used for the catalytic activity measurements in steam reforming of glycerol to hydrogen production were described in the previous papers [18,19]. The vaporizer in the reactor consists of electrically heated tube packed with quartz wool. Reagent-grade glycerol, with a purity of 99.5%, was purchased from Tianjin Fuyu Chemical Co., Ltd. The mixture of pure water and glycerol can be injected to the vaporizer housed in the reactor by an injector of ID of 1×10^{-3} m. A reactant mixture of glycerol and water, with a steam to carbon (S/C) ratio of 3 (molar ratio of glycerol/water = 1/9), was injected into a vaporizer (the temperature of the vaporizer is controlled over at 300 °C) using a syringe infusion pump with the feeding rate of 4 ml/hr. The reactant vapors were diluted with N_2 gas in the vaporizer, and then fed into the catalyst bed. The nitrogen served as a carrier gas was also aided in the elemental balance analysis. The nitrogen flow in a typical experiment was adjusted to 3×10^{-3} m^3 min^{-1}. A sample of 1.0 g catalyst supported by quartz wool was loaded into the center of reactor. K-type thermocouple was used to measure the catalyst bed temperature. Condensable compositions in a product gas were removed through a refrigerated coil. The product gas was collected in the sample bag and analyzed by a off-line gas chromatograph (GC) equipped with two columns connected in series (MS and Poraplot Q) with thermal conductivity and flame ionization detectors (TCD–FID), and the GC was properly calibrated for the detection of CH_4, CO, CO_2, and H_2 before the experiments. The experimental data were taken after the steady state reached which took approximately 0.5 h after the feed flow was started. The calculation of glycerol conversion ($x_{glycerol}$) for the experiments is based on carbon molar outflow of the gas products and the glycerol molar inflow of the reactor [13,14], n and y are the relevant molar flows (mol min^{-1}) and gas molar fractions respectively, and $n_{dry,out}$ is the dry total molar flow of gas products leaving the reactor, $y_{c,out}$ is the total carbon molar fraction for outlet:

$$X = \frac{c_0 - c}{c_0} = \frac{n_{dry,out} \sum y_{c,out}}{3n_{glycerol,in}} \tag{1}$$

The calculation of conversion of steam can be given [13,14]:

$$X_{H_2O} = \frac{n_{dry,out}(y_{H2} + 2y_{CH4}) - 4x_{glycerol}n_{glycerol,in}}{n_{H_2O,in}} \tag{2}$$

H_2 selectivity can be defined and calculated by [13,14]:

$$H_2, Sel = \frac{2n_{H2,out}}{2(n_{H_2O,in} - n_{H_2O,out}) + x_{glycerol} \times 8n_{glycerol,in}} \tag{3}$$

where c and c_0 shown as subscript are outlet and inlet glycerol concentrations, mol/m^3.

A non-stoichiometric thermodynamic code on the chemical equilibrium based on the minimization of Gibbs free energy was used to calculate the H_2 production from glycerol steam reforming. Four atoms, C, H, O, N, and seven compounds, $C_3H_8O_3$, H_2O, H_2, CO, CO_2, CH_4, N_2, are considered in the equilibrium system. The equations were solved by using an in-house Fortran Code based on the DNEQNF subroutine (DNEQNF solves nonlinear equations using a modified Powell hybrid algorithm and a finite difference approximation to the Jacobian (30)) of the IMSL® library. The details on thermodynamic analysis for glycerol steam reforming have been described in previous paper [20].