Renewable Energy 128 (2018) 188–199

Contents lists available at ScienceDirect

Renewable Energy

journal homepage: www.elsevier.com/locate/renene

Renewable hydrogen production by ethylene glycol steam reforming over Al_2O_3 supported Ni-Pt bimetallic nano-catalysts

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ARTICLE INFO

Article history:
Received 3 January 2018
Accepted 19 May 2018
Available online 21 May 2018

Keywords:
Renewable hydrogen
Steam reforming
Ethylene glycol
Ni-Pt bimetallic nano-catalysts
Kinetic study

ABSTRACT

The steam reforming of ethylene glycol, a simple model compound for biomass-derived liquids, is considered to be an environmentally green process for producing renewable hydrogen. Both Pt and Ni species are known for their catalytic activity under steam reforming reaction conditions. In this investigation, alumina supported Ni-Pt bimetallic catalysts (X wt% Ni-Y wt% Pt/Al_2O_3 named XNi-YPt) were employed for steam reforming of ethylene glycol. The prepared catalysts were characterized by XRD, BET, H_2-TPR, H_2-Chemisorption, and TEM. It was observed that Ni/Pt ratio strongly affected the redox behavior, BET surface area, and particle size of the samples that in turn affected their catalytic performance. The optimum catalyst sample was 3.75Ni-1.25 Pt which resulted in the highest ethylene glycol conversion (60%), highest H_2 selectivity (45%) and yield (27%), and a minimum of 20 h of stability due to the lowest amount of coke formed the catalyst surface. The overall order of the catalytic performance of the samples was as follows: 3.75Ni-1.25 Pt > 2.5Ni-2.5 Pt > 1.25Ni-3.75 Pt > 0Ni-5Pt > 5Ni-0Pt. A kinetic model for the steam reforming of ethylene glycol in a packed bed reactor containing the 3.75Ni-1.25 Pt catalyst was employed indicating a good agreement between experimental and predicted H_2 selectivity and yield. Intrinsic reaction rate data in the absence of the heat and mass transfer limitations were obtained in parametric studies (Temperature range of 823–893 K, ethylene glycol mole fraction range of 0.056–0.116 and bed density of 18–26 kg m^{-3}). Higher temperature and bed density and lower ethylene glycol mole fraction enhanced the reactivity. The maximum ethylene glycol conversion (70%), H_2 yield (36.5%) and H_2 selectivity (52%) was observed for conditions of 893 K, bed density of 24 kg m^{-3} and ethylene glycol mole fraction of 0.056.

1. Introduction

In today's energy scene, an important concern is to reduce the dependence on fossil fuels since they are non-renewable and result in greenhouse gas emissions upon combustion. A promising alternative to fossil fuels is hydrogen since its combustion products are non-polluting. However, conventional hydrogen production methods, e.g. steam reforming of natural gas and water electrolysis, are neither sustainable nor economically feasible. Attention nowadays has therefore turned to hydrogen production from inexpensive renewable sources. Recent studies have shown that biomass-derived oxygenated compounds are economically feasible and environmentally friendly energy carriers [1]. The most abundant product of pyrolysis or catalytic hydrogenation of cellulose (which in turn is the major part of biomass) is ethylene glycol (EG) that can be considered as a model molecule of larger oxygenated compounds [2]. Relevant studies on hydrogen production from EG include both liquid-phase and gas-phase reactions. Although liquid-phase reactions take place under mild temperature conditions, reaction rates are low and EG concentration should be kept low in feed stream in order to decelerate catalyst deactivation [3,4]. Gas-phase reactions take place at higher temperatures but the higher concentrations of hydrogen in the product gas and in some cases relatively low costs of the employed catalysts can overcome the high cost associated with higher temperatures [5]. The main disadvantages of aqueous phase reforming (APR) in comparison with steam reforming (SR) are I) APR has lower hydrogen selectivity due to the lower temperatures that are employed enabling the alkane formation [6] and II) APR requires higher pressure in order

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https://doi.org/10.1016/j.renene.2018.05.070
0960-1481/

to keep the system in liquid phase, while SR is conducted under atmospheric pressure [7].

Group VIII metals, e.g. Ni [8–12], Pt [13–16], Pd [17], Rh [18] and Ru [19,20] are known as promising active phases for H_2 production from reforming reaction of oxygenated compounds [21]. Although availability and lower price are two major advantages of Ni compared with noble metals, Pt can provide higher selectivity towards hydrogen production. Only limited studies have reported the use of Ni-Pt bimetallic catalysts for steam reforming of oxygenated hydrocarbons. Almost all of these studies have concluded that bimetallic Ni-Pt samples have better catalytic performance compared with the monometallic catalysts. However, no attempt has been made to find the optimal Ni-Pt composition.

It was observed that the addition of Pt to Ni/SiO_2 catalyst did not affect the catalytic performance in steam reforming of glycerol [22]. Addition of Pt to Ni/(Al_2O_3+MgO) catalyst, however, enhanced both activity and H_2 selectivity in the aqueous phase reforming of ethylene glycol [23]. It was shown that addition of 3 wt% Pt to 10 wt %Ni/CeO_2 catalyst resulted in higher H_2 yield and also enhanced catalyst stability in steam reforming of ethanol [24]. When steam reforming of ethanol was carried out over Pt/(Ni-Al alloy) catalysts [25], it was observed that CO dissociation on the Ni surface was restrained and therefore the methanation reaction was suppressed by Pt addition thus enhancing H_2 production. Addition of Pt to Ni catalyst enhanced the reforming activity and also inhibited the deactivation of the catalyst [26]. This improvement in catalytic performance could be related to the structure of the catalyst, e.g. under the conditions of the aqueous phase reforming of glycerol, Ni segregates to the catalyst surface and forms Ni-terminated bimetallic surface which is more active than monometallic Pt [27]. The addition of Pt to the Ni/CeO_2 catalyst made it more stable in steam reforming of ethanol [28,29]. When Ni/CeO_2 catalyst was used, a nickel carbide phase was formed due to the amorphous carbon that was deposited on the catalyst surface further enhancing the catalyst deactivation. Pt addition to Ni/CeO_2 catalyst enhanced spillover of adsorbed H_2 spices on Ni surface which in turn suppressed the nickel carbide formation and enhanced catalyst stability.

Huber and his co-workers [30] suggested that alloying Ni with Pt lowers d-band center which in turn causes a decrement in the adsorption heats of CO and H_2. Thus, the fraction of the surface available for reaction with ethylene glycol increases which consequently improves the activity with respect to the H_2 production. Despite the fact that bimetallic catalysts are more active than monometallic ones for reforming of ethylene glycol, the optimization of the ratio of two metals has been less studied. In addition, kinetic studies on the reforming of polyols are very limited. With this background, a series of Ni-Pt bimetallic catalysts with different Ni/Pt ratios were prepared in order to investigate the effect of active phase composition on hydrogen production and catalyst stability in the steam reforming of ethylene glycol. Moreover, kinetic modeling was also performed.

2. Experimental

2.1. Catalyst preparation

All materials were purchased from Merck and were of analytical grade. The Ni-Pt/Al_2O_3 catalysts were prepared by the wet impregnation method. The support was γ-aluminum oxide (Alfa Aesar, 20 nm APS powder) and the precursor solutions were prepared using nickel nitrate [$Ni(NO_3)_2.6H_2O$] and hexachloro-platinic acid ($H_2PtCl_6 \cdot 6H_2O$) (Aldrich). All catalysts contained X wt% of nickel and Y wt% of platinum on the alumina support where $X + Y = 5$ ($Y = 0$, 1.25, 2.5, 3.75 and 5) and were named XNi-YPt catalysts. The mixture of appropriate amount of alumina and precursor salts was stirred in a rotary evaporator at 333 K. After 5 h the formed powder was collected and dried at 363 K overnight. The samples were then calcined in a muffle furnace at 873 K for 6 h and the resulting powder were crushed and sieved to a size of 50–75 mesh.

2.2. Catalyst characterization

X-ray powder diffraction (XRD) analysis was conducted in order to identify catalyst crystal phase (PW3040/60 X'Pert PROMPO PANalitycal diffractometer, Cu Kα radiation 40 kV, 40 mA and high-resolution scanning with step size of $2\theta^\circ = 0.02$ and count time of 10 s per step). N_2-physisorption analysis was performed to determine the specific surface area, average pore volume and pore size of the catalyst and to obtain adsorption/desorption isotherms (Belsorp mini II apparatus, all samples were degassed for 15 h at 373 K prior to each N_2-Physisorption experiment performed at 77 K). H_2-Chemisorption was carried out in order to evaluate the H_2 uptake and the active phase dispersion of the catalysts (BELCAT-B apparatus, 15 min of O_2 treatment at 573 K followed by 1 h H_2-treatment at 773 K, 1 h evacuating and cooling to room temperature was performed prior to the H_2-chemisorption analysis). Temperature programmed reduction (H_2-TPR) was performed in order to investigate the redox behavior of samples (Micrometric TPR/TPO 2900 apparatus equipped with a thermal conductivity detector, samples were degassed with He at 523 K for 2 h and subsequently cooled to the room temperature and reduced under the flow of the 5 vol% H_2/Ar). Transmission and scanning electron microscopy (TEM and SEM) images were obtained to examine the morphology of the fresh and spent catalyst samples (Zeiss EM900 Microscope). Temperature programmed oxidation (TPO) was performed to investigate the carbon deposition on the spent samples (Micrometrics chemisorb 2750 instrument, gas flow of 5 vol% O_2/He and 10 K/min heating rate were employed for TPO analysis).

2.3. Catalyst performance

Steam reforming of ethylene glycol was carried out in a continuous tubular fixed bed reactor as shown in Fig. 1. Details of the reactor set-up is presented in our previous work [31,32].

The reactor was a vertical stainless steel tube with an inner diameter of 5 mm. For each experiment, 250 mg of catalyst was loaded in the reactor and the catalyst bed was held in position by two plugs of quartz wool on each side. Afterwards, the reactor tube was placed inside a tube furnace equipped with type K thermocouple and a PID temperature controller. Prior to the reaction, the catalyst was reduced in situ for 1 h at 773 K under pure H_2 flow and subsequently purged by N_2 flow of 100 mL min^{-1} for 5 h. After cooling to the reaction temperature, the 10 wt% aqueous ethylene glycol solution (steam to carbon ratio of 15.52) was fed into the vaporizer using a Waters 510 HPLC digital pump (flow rate of 0.06 mL min^{-1} and W/F ratio of 1.33 g_{cat} mol^{-1} h^{-1}). The reactor was held at 873 K and atmospheric pressure. After removing the moisture from product gases, they were analyzed by gas chromatography (GC). The GC was equipped with both packed (Carbosphere) and capillary (PoraPLOT Q) columns in series-bypass configuration using thermal conductivity and flame ionization detectors. Liquid effluents collected from the gas-liquid separator were analyzed for elemental carbon by a Shimadzu HPLC instrument equipped with a Rezex RCM-Monosaccharide column using ultrapure deionized water as an eluent at 0.5 mL min^{-1}. In all experiments, carbon balance closure was approximately $100 \pm 5\%$. H_2, CO, CO_2 and CH_4 were the only components in the product gases that were analyzed by GC. The following definitions were used for evaluation of the catalyst performance: