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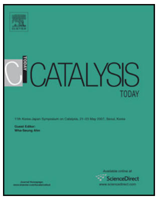

Production of hydrogen by steam reforming of ethanol over alumina supported nano-NiO/SiO_2 catalyst

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ABSTRACT

The production of hydrogen by catalytic steam reforming of ethanol was carried out over alumina supported nano NiO catalyst in silica synthesized using sol–gel method. The catalyst was characterized using SEM, TEM and BET surface area analyzer. The performance of the catalyst in ethanol reforming was investigated using three important operating parameters such as reaction temperature, feed steam to ethanol ratio and space-time. The activity tests were performed in the steam to ethanol molar ratio range of 2:1 to 9:1 and space-time from 2.78 to 9.25 kg catalyst h $kmol^{-1}$ of ethanol fed and in the temperature range of 550 to 700 °C. A maximum yield of 4.2 mol of hydrogen per mole of ethanol reacted were produced at 650 °C. A favorable operating condition was established at 650 °C using 8:1 steam to ethanol molar ratio and a space-time of 9.25 kg catalyst h $kmol^{-1}$ of ethanol fed. Under these operating conditions, ethanol conversion, product composition and H_2 yield were studied to see the contributions of water–gas shift reaction, ethanol cracking, methane steam reforming and also reverse water–gas shift reaction towards the yield of hydrogen. The kinetic study was performed over a wide range of space-time at different temperatures under negligible diffusional resistance. A power-law model rate equation was derived with acquired experimental data. The kinetic parameter and order of reaction were estimated by non-linear regression method. The activation energy was calculated to be 27 kJ mol^{-1}. A good agreement was obtained between experimental and model predicted results.

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1. Introduction

Continuous increase in emission of CO_2 in the environment from the use of conventional fuels has attracted researcher's attention to intensify the search for alternatives to fossil fuels for energy generation. Nowadays, most of the commercial hydrogen production is based on non-renewable fuels such as petroleum oil, naphtha, natural gas, etc. The development of alternative methods for hydrogen production, especially from renewable sources is of great interest [1–3]. Increasing concerns for the reduction of greenhouse gas emissions, atmospheric pollution and reduction of global dependency on fossil fuels have created interests in using fuel cells as a power source. Hydrogen has emerged as an energy carrier of the future with high energy content. It is also a clean fuel to produce electricity via fuel cells for use in automotive applications and portable power devices. Particularly, proton-exchange membrane (PEM) fuel cells have generated interest because they operate near room temperature with high power densities. Fuel-cells and hydrogen as a fuel can be a solution to the development of zero emission vehicles as its combustion produces only water [4–7]. An alternative and promising technology for the production of hydrogen is the use of ethanol as a renewable feedstock in the steam reforming process.

In comparison to fossil fuels and other liquid fuels, ethanol presents several advantages of being renewable and CO_2-neutral system; since it can be easily obtained by biomass fermentation and CO_2 produced from reforming reaction is consumed for biomass growth. It is significantly less toxic than methanol and safe to handle and store due to its high heat of vaporization.

Stoichiometrically, the overall ethanol steam reforming (ESR) reaction for hydrogen production can be represented as follows:

$$C_2H_5OH(l) + 3H_2O(l) \leftrightarrow 2CO_2(g) + 6H_2(g) \quad \Delta H^0 = 347.4\ \mathrm{kJ\ mol^{-1}} \qquad (1)$$

Ethanol steam reforming to syngas:

$$C_2H_5OH + H_2O \leftrightarrow 2CO + 4H_2, \qquad \Delta H^0 = 256\,\mathrm{kJ\,mol^{-1}} \qquad (2)$$

These reactions are highly endothermic and present significant differences to the steam reforming of methane due to the presence of a C–C bond and oxygen atom in ethanol. The reaction pathways occurring are very complex and several by-products may form

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Nomenclature

Y	conversion of ethanol (%)
W	weight of catalyst (kg)
F	molar flow rate of ethanol inlet (kmol h^{-1})
W/F	space-time ($\text{kg catalyst h kmol}^{-1}$)
r	rate of reaction (kmol kg^{-1} catalyst h^{-1})
k	rate constant (Unit based on the rate expression)
p_{EtOH}	partial Pressure of ethanol (atm)
$p_{\text{H}_2\text{O}}$	partial pressure of steam (atm)
α	order of reaction with respect to ethanol
β	order of reaction with respect to steam
F	objective function of error
N	number of experimental observations
r_{cal}	calculated rate from model equation
r_{exp}	experimental rate
A	pre-exponential factor or frequency factor
E_a	activation energy (kJ mol^{-1})
R	ideal gas constant ($\text{kJ mol}^{-1}\text{ K}^{-1}$)
T	temperature (K)

depending on the catalysts and reforming conditions used which affect the overall H_2 production reaction.

Ethanol steam reforming (ESR) for hydrogen production has been reported to be thermodynamically feasible [8] and several previous studies have been published over different catalysts, including metal oxides [9,10], mixed metal oxides [11,12]. It has been reported that transition-metal-supported catalysts, especially Ni, Cu, Co, Pt, Pd, Rh, and Ru are good candidates for steam reforming of ethanol [13–21].

Supported Ni catalysts are most popular in industry as they are cheap compared to noble metal catalysts and generally provide good activity and high selectivity to H_2 in reforming reactions. Several researchers investigated the catalytic performance and kinetic study of ESR over various supported Ni catalysts such as Ni/Y_2O_3, Ni/La_2O_3, Ni/Al_2O_3, $Cu/Ni/K/\gamma\text{-}Al_2O_3$, Ni/MgO, Ni/ZnO [21–28].

The catalytic activity of nickel based catalyst is closely related to both nickel content and nickel dispersion, but the effects of these two factors on the catalytic activity are opposite [29]. For example, the catalytic activity of Ni/Al_2O_3 increases with nickel content due to increased number of active nickel sites, whereas the nickel dispersion decreases with increased nickel content due to the aggregation of nickel, thereby decreasing the catalytic activity. In general, nickel content of conventional Ni/Al_2O_3 catalysts used in steam reforming does not exceed 12 wt% to avoid severe aggregation or sintering of nickel particles during the reaction. Better dispersion could be obtained if the nickel particles were in the nanometer range with superior catalytic activity when used as catalysts. The objective of the present study was to prepare nano-nickel dispersed on silica and supported on alumina by a suitable technique for steam reforming of ethanol. The nickel loading in the catalyst was kept within 12 wt%. The activity of the prepared nano-catalyst was assessed in terms of ethanol conversion and hydrogen yield. A kinetic study was also carried out to propose a power law rate expression for ESR over nano-Ni catalyst.

2. Experimental

2.1. Catalyst preparation

NiO/SiO_2 nano-composite containing nickel oxide nano-particle in silica were obtained by sol–gel processing of nickel nitrate hexahydrate [$Ni(NO_3)_2\cdot 6H_2O$] precursor and the silica matrix was mainly formed from tetra ethyl ortho silicate (TEOS) in ethanol solution. A certain amount of tetraethyl ortho-silicate (TEOS) in ethanol solution was stirred using magnetic stirrer at room temperature. Nickel nitrate, with intended Ni loadings (7, 10, 12.5, 15 wt% in the catalyst), dissolved in the aqueous ethanol solution was added slowly to the silica sol with constant stirring. Since ethanol and water are completely miscible, a clear solution was obtained when they were mixed in appropriate quantities. The final solution was stirred at room temperature for about 5–6 h and allowed to age for a week. The obtained gel was then dried in hot air oven at 110 °C for 24 h to remove water and other volatile compounds. Then the dried gel was calcined at 400 °C.

To prepare Alumina supported NiO/SiO_2 catalyst, alumina, silica–nickel oxide and bentonite powder (clay type binder) were mixed in an appropriate proportion and then processed into extrudates. The extrudates are finally dried in hot air oven at 110 °C. The catalysts were prepared with different Ni loading as 7, 10, 12.5 and 15 wt%.

2.2. Catalyst characterization

The fresh catalyst sample was characterized by Scanning electron microscopy with energy dispersive X-ray spectrometry, Transmission electron microscopy and BET surface area analysis.

The microstructures, surface morphology and quantitative elemental analysis of the catalyst were obtained by scanning electron microscopy (SEM) coupled with an X-ray energy dispersive spectrometer (EDX).

SEM and EDX X-ray measurements were performed using EV060 ZEISS and Oxford instrument, respectively, to observe the microstructural surface morphology and elemental composition of the sample with an acceleration voltage of 20 kV. Before the scanning process, all the samples were coated with gold in a vacuum sputter coater.

The particle size was observed by transmission electron microscopic analysis. TEM image was taken on JEOL 2100 instrument operated at an accelerating voltage 200 kV. Specimen was prepared by ultrasonically dispersing the sample in acetone. A drop of the dispersion was then placed on clean carbon-coated copper grids and dried in air.

The surface area, average pore diameter and the pore volume were determined by the Brunauer–Emmett–Teller (BET) method in a Quantachrome AUTOSORB 1 instrument by adsorption of nitrogen at −196 °C on 200 mg of sample previously degassed at 200 °C for 2 h under high vacuum.

2.3. Experimental procedure

Ethanol steam reforming experiments were carried out in a fixed bed vertical tubular reactor placed inside a cylindrical electrical furnace. One gram of catalyst was loaded in the middle of the reactor of 10 mm inner diameter such that the centre of the catalyst bed corresponded to the central heating zone of the furnace. The catalysts were mixed with inert particles so that the bed height was maintained at 60 mm. The remainder of the reactor was filled with inert ceramic material. Prior to the reaction, catalyst was reduced as well as activated while it was heated to 550 °C with the flow of hydrogen ($40\text{ cm}^3\text{ min}^{-1}$) for 4 h. The thermocouple inserted into the thermowell of reactor recorded the catalyst bed temperature. After catalyst activation, the reaction temperature was fixed at a desired temperature and catalytic steam reforming reaction was performed isothermally at atmospheric pressure. The feed consisting of an appropriate ratio of ethanol–water mixture was pumped at the desired flow rate to vaporize at about 170 °C in the preheater before entering the reactor. After passing the outlet product stream through condenser, the liquid was separated in gas–liquid separator and gaseous product stream was analyzed online at different

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