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Production of hydrogen by dry reforming of ethanol over alumina supported nano-NiO/SiO₂ catalyst

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ABSTRACT

Hydrogen was produced with very high yield by dry reforming of ethanol over alumina supported nano-NiO catalyst in silica synthesized using sol-gel method. The activity of the prepared nano-catalyst was assessed in terms of ethanol conversion, carbon dioxide conversion, carbon monoxide yield and hydrogen yield. The catalyst activity as well as distribution of products was observed to vary with Ni loading in the catalyst and the reaction conditions. Catalyst containing 10% Ni showed good activity among the screened catalyst for ethanol dry reforming. Detailed experimental investigations were carried out over a wide range of operating parameters such as reforming temperature from 500 °C–850 °C, feed carbon dioxide to ethanol molar ratio from 0.5 to 2 and space-time from 19.0 to 41.8 kg cat h/kmol of ethanol fed. The catalyst was found to be active within the range of parameters studied at atmospheric pressure. However, the most favorable reaction conditions were established at 750 °C with CO₂/EtOH molar ratio of 1.4 and space-time of 24.90 kg cat h/kmol of ethanol fed. Under the optimum condition, almost complete conversion of ethanol, 76.0% conversion of CO₂ and 100% yield of hydrogen were obtained. The space-time–conversion data in the temperature range of 500–600 °C were fitted into a power law model and the activation energy of the ethanol dry reforming reaction was determined to be 97.87 kJ/mol.

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1. Introduction

Hydrogen as a fuel is clean, non-polluting and renewable. Hence, it is considered as the “green” energy carrier of the future. Advances in fuel cell technology make hydrogen more important as a new energy source for both stationary and vehicular applications. It is also widely used in the production of pharmaceuticals, fine chemicals and bulk chemicals such as ammonia and methanol. As such, the demand for hydrogen in fuel cell application and also in chemical industry is continuously increasing [1]. However, the development of a feasible production method for hydrogen is necessary as most of the hydrogen is available in nature in bound form (as water or hydrocarbons). A number of catalytic reforming technologies, such as steam reforming, partial oxidation, and autothermal reforming, have been used for the production of hydrogen from various hydrocarbons [2–8]. Among these, catalytic steam reforming of natural gas, which contains mainly methane, is probably the most important and economic process for the production of hydrogen and synthesis gas in large scale. Recently, the production of hydrogen via carbon dioxide reforming (also called

dry reforming) has received considerable attention due to environmental concerns and the clear need to reduce green house gas (GHG) emissions. Presently, the study of CO₂ reforming for hydrogen production focuses utilization of natural gas. Nevertheless, natural gas is a fossil fuel and hence unsustainable. Therefore, the need for renewable alternatives has been felt globally.

Ethanol is a renewable hydrocarbon as it can be produced through the fermentation of biomass or renewable raw materials, including energy plants, waste materials from agro-industries or forestry residue materials, organic fraction of municipal solid waste, etc. Ethanol can be converted to hydrogen through steam reforming, partial oxidation, autothermal reforming (oxidative reforming) and dry reforming. Although ethanol steam reforming has been widely investigated [9–19], very insignificant study has been performed on dry reforming [20–24]. The present work involves dry reforming of ethanol to produce hydrogen.

Dry reforming of ethanol is strongly endothermic and produces only H₂ and CO if ethanol reacts in a most desirable way as follows:

Ethanol dry reforming:



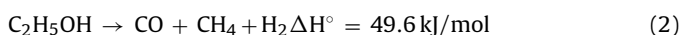
However, several other undesirable reactions take place at the condition of dry reforming giving rise to product composition different from that could be obtained from purely dry reforming. A list

* Corresponding author.

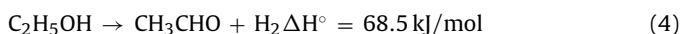
E-mail address: ncp@che.iitkgp.ernet.in (N.C. Pradhan).

of possible reactions that may take place during dry reforming of ethanol is presented below.

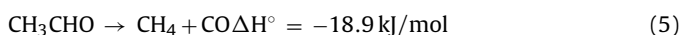
Ethanol decomposition:



Ethanol dehydrogenation:



Acetaldehyde decomposition:



Acetaldehyde CO₂ reforming:



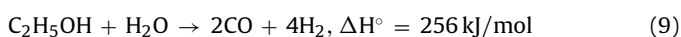
Ethanol dehydration:



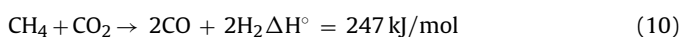
Polymerization of ethylene (Coke formation)



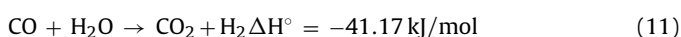
Ethanol steam reforming



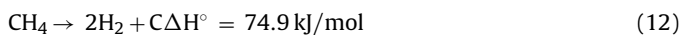
Methane dry reforming:



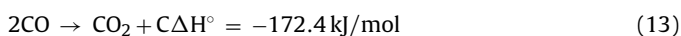
Water-gas shift reaction:



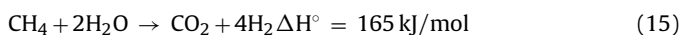
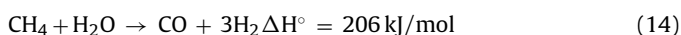
Methane decomposition:



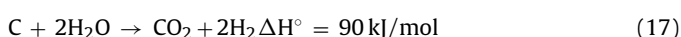
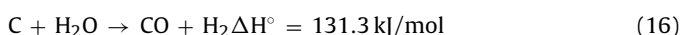
Boudouard reaction:



Methane steam reforming:



Carbon gasification:



Various catalysts based on transition metals [25–31] and noble metals [32–34] have been used for the production of hydrogen from ethanol by steam reforming. Among these, nickel-based catalysts are widely studied because of their high catalytic activity, comparable to expensive noble metal catalysts. However, nickel catalysts deactivate rapidly due to carbon deposition and metal sintering in severe operating conditions [35,36]. The Tamman temperature, above which nickel sintering can be expected (590 °C), is less than the normal operating temperatures (ca. 800–900 °C) for steam reforming [37]. The use of a support not only induces thermal stability but also offers an opportunity for assistance with coke control. High temperature sintering of nickel may be avoided by dispersing the metal in a support having very high metal-support interaction. It has been reported that dispersing Ni in silica gives a stable Ni catalyst in steam reforming of methane and ethanol [38,39]. In this study, nano-nickel highly dispersed into silica and supported on alumina was used for dry reforming of ethanol. The nickel loading in the catalyst was kept within 15 wt%. The activity of the prepared nano-catalyst was assessed in terms of ethanol

conversion, carbon dioxide conversion, carbon monoxide yield and hydrogen yield.

2. Experimental section

2.1. Chemicals used

The chemicals used in catalyst preparation and reforming reaction were of analytical grade. Nickel Nitrate hexahydrate (Merck), tetraethyl orthosilicate (TEOS) (Merck), ethanol (99%, Merck), aluminum oxide (active) (SISCO research laboratory), bentonite powder (Merck) were used in the present work.

2.2. Catalyst preparation and characterization

The catalyst was prepared by sol-gel method as described in our previous communications [38,39]. The fresh catalyst samples were characterized by X-Ray diffraction, Scanning electron microscopy with energy dispersive X-ray spectrometry, Transmission electron microscopy and BET surface area analysis as reported elsewhere [38]. The BET surface area, pore volume and average pore diameter of alumina supported NiO/SiO₂ catalyst were presented in Table 1 [38].

The CHNS analysis was performed with the used catalyst on an Elementer (Model- Vario Macro CUBE) instrument. The combustion and reduction chamber temperatures were maintained 1150 °C and 850 °C respectively. About 30 mg sample and 60–70 mg tungsten oxide (WO₃) were taken with tin foil and poured in a combustion chamber. The whole combustion process occurred in oxygen atmosphere.

2.3. Experimental procedure

Dry reforming reaction was carried out in a fixed bed vertical tubular reactor (10 mm inner diameter) placed inside a cylindrical furnace. The reactor was loaded with catalyst (2.0 g) in such a way that the centre of the catalyst bed corresponded to the central heating zone of the furnace. The catalyst particles were mixed with inert particles so that the bed height was maintained at 60 mm. The catalyst was reduced as well as activated while it was heated to 550 °C with the flow of hydrogen (40 cm³/min) 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 value, the hydrogen flow was stopped and preselected CO₂ and ethanol flows were started. The ethanol dry reforming reaction was performed isothermally at atmospheric pressure. The reactor outlet stream was passed through a condenser for separation of condensable components in the gas-liquid separator. A schematic diagram of the experimental set-up is given in Fig. 1.

The product gas stream flow rate was measured using a wet gas meter. The gas was periodically sent to a Gas Chromatograph (Model: Chemito GC 1000 DPR) for analysis. The gaseous products were analyzed using a thermal conductivity detector (TCD) with a Spherocarb column (3.175 mm diameter and 2.4 m length). Liquid samples were collected from the condenser and analyzed in Gas Chromatograph for its ethanol content.

A series of experiments were carried out at different temperatures, feed CO₂/EtOH mole ratios and space-times. The performance of the catalyst was evaluated by determining the conversion of ethanol, conversion of CO₂, yield of hydrogen and yield of carbon monoxide as defined below:

$$\text{Conversion of C}_2\text{H}_5\text{OH, } X_{\text{C}_2\text{H}_5\text{OH}}(\%) = \frac{F_{\text{C}_2\text{H}_5\text{OH, in}} - F_{\text{C}_2\text{H}_5\text{OH, out}}}{F_{\text{C}_2\text{H}_5\text{OH, in}}} \times 100,$$

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