Significance of Temperature on Conversion of Ethanol for Hydrogen Production by Steam Reforming -an Experimental Study

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Abstract

In the present paper the reaction steam reforming of ethanol for hydrogen production, over a commercial nickel- alumina catalyst was investigated. In particular, the dependence of the conversion on reaction temperature was experimentally studied. Kinetic study of ethanol steam reforming over a commercial nickel-alumina (Ni/Al_2O_3) catalyst was conducted in a fixed-bed reactor. The effect of the temperature on conversion of Ethanol to hydrogen by steam reforming was studied in the range of 623 – 798 K. The significance of temperature on conversion of ethanol for hydrogen production by steam reforming and optimum temperature based on efficiency of hydrogen generation calculated on experimental data and carbon deposition during steam reforming process. For ethanol, the minimum conversion obtained was around 53% at 623 K and the maximum conversion was around 89 % at 798 K. The acquired data was fitted to a power-law kinetic model and the kinetic parameters were evaluated. A considerable amount of coke formation was observed during the process; yet, the catalyst showed a negligible loss of activity, exhibiting the feasibility of using this catalyst for ethanol steam reforming.

Keywords: Hydrogen Production, Ethanol, Steam Reforming, Catalyst, Conversion

Introduction

Hydrogen has long been recognized as an ideal fuel for power generation systems with virtually zero emissions of air pollutants and carbon dioxide. Hydrogen-based fuel cell power plants are highly efficient and reliable, and generate virtually no undesirable air emissions. The use of hydrogen for fuel cell applications represents one of the most environmentally sound methods for the production of electrical energy and is expected to gain wide usage in the near future for both automotive and small-to-medium scale stationary applications. Until technical and economic issues related to hydrogen storage, transportation and distribution are solved, the generation of hydrogen for fuel cells is expected to be accomplished on-site with the use of fuel processors, i.e. devices able to convert liquid or gaseous fuels into hydrogen. We select ethanol as a feedstock among the various feedstock available and check the significance of temperature on conversion of ethanol for hydrogen production by steam reforming.

Steam Reforming Process

Catalytic steam reforming of hydrocarbon is a well-known, commercially available process for hydrogen production. Hydrogen production is accomplished in several steps: steam reforming, water gas shift reaction, and hydrogen purification. The steam reforming reaction is endothermic and requires external heat input. Economics favor reactor operation at pressures of 1 - 5 atmospheres and temperatures of the order of 500 to 850 ^{0}C. The external heat needed to drive the reaction is often provided by the combustion of a fraction (up to 25%) of the incoming natural gas feedstock or from burning waste gases (which contain CO), such as purge gas from the hydrogen purification system. Typically, the molar ratio of steam-to-carbon is about three or more to avoid "coking" or carbon build-up on the catalysts. (At lower steam to carbon ratios, solid carbon can be produced via side reactions).

Generalized Reactions

Steam reforming:

$$C_mH_n + mH_2O \rightarrow mCO + (m + (1/2)\,n)H_2 \quad (1)$$

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \quad (2)$$

Carbon formation

$$C_mH_n \rightarrow xC + C_{m-x}H_{n-2x} + xH_2 \quad (3)$$

$$2CO \rightarrow C + CO_2 \quad (4)$$

$$CO + H_2 \rightarrow C + H_2O \quad (5)$$

Water-gas-shift

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (6)$$

$$CO_2 + H_2 \rightarrow CO + H_2O \text{ (RWGS)} \quad (7)$$

CO oxidation

$$CO + 1/2\ O_2 \rightarrow CO_2 \quad (8)$$

$$H_2 + 1/2O_2 \rightarrow H_2O \quad (9)$$

Catalyst Characterization

Without the right catalyst, many reactions hardly proceed. Furthermore, the chemical nature of the catalyst can have a radical effect in selecting reaction pathways leading to different chemical products. The present work focuses on the study and characterization of the catalyst for steam reforming of hydrocarbons. M/s. Bharat Petroleum Corporation Limited, Mumbai, has supplied the catalyst. Attempts have been made to study the catalyst characterization using the techniques such as, Scanning Electron Microscope, X-Ray Diffraction. The BET surface area has been found out using Micromeritics surface area analyzer.

Experimental Section

Feedstock

The infrastructure of INDIA is based on agriculture; hence raw materials, such as cassava, molasses, and corn, are available for fermentation to produce dilute ethanol solution. There are many ways to utilize concentrated ethanol especially as a fuel source e.g. gasoline blender. To obtain high concentration of ethanol, however, the dilute solution of ethanol from fermenter must be dehydrated to a very low moisture content product. Distillation and azeotropic separation contributed to the shortcomings of ethanol as a fuel. [1] The massive use of fuels derived from crude oil is a key factor in the environmental pollution problems and the world looks with increasing interests to enforce research activities on the development of alternative fuels. In this aim, one of the most interesting, ethanol that can be easy produced by fermentation of the starch contained product. [2] To identify the challenge in the development of electrical vehicles, literature was rapidly reviewed. Research on hydrogen production processes suitable for fuel cell applications is major challenge. Catalytic steam reforming hydrocarbons as well as alcohol is very promising route. [3] In the last few years, it has been paid much attention to ecological problems related to environment concerns. The efforts have led the research to orient toward alternative solutions as clean and renewable energies, particularly bioenergy. This bioenergy can be obtained from biomass or from other natural sources. Specific work on the hydrogen production has been investigated from mixtures of EtOH-H_2O for fuel cells. [4] A new promising way to utilize the dilute solution of ethanol is the reforming process of ethanol to produce hydrogen gas that can then be passed through a molten carbonate fuel cell (MCFC) to generate electricity.

Experimental Setup

The overall flow system consisted of the main parts such as Feeding system, Preheated cum mixer, Reactor, Condenser and cooling system, Sample collecting section, Gas analysis section as shown in figure 1.

Experimental Procedure

Ethanol solution was prepared by diluting 99 % Ethanol (Lab grade provided by Jiangsu Huaxi international trade Co.Ltd.) with demineralised water. The reforming catalyst, nickel supported on alumina, a commercial product of a catalyst used. It was crushed into small granules with 1 mm size. The experiment was carried out in a 1.27 x 32 cm (diameter x length) fixed bed reactor made of 316-stainless steel and assembled with fittings. The experimental setup to carry out the steam reforming of feedstock (Ethanol) is shown in Fig. 1. The reactor and the preheaters were first allowed to attain a steady temperature as per the required operating parameters. Then the prepared ethanol solution was fed by electromagnetic dosing pump, to a temperature controlled pre-heater unit. The pre-heater unit vapourised the methanol and ethanol solution prior to sending further to the temperature controlled reactor unit.

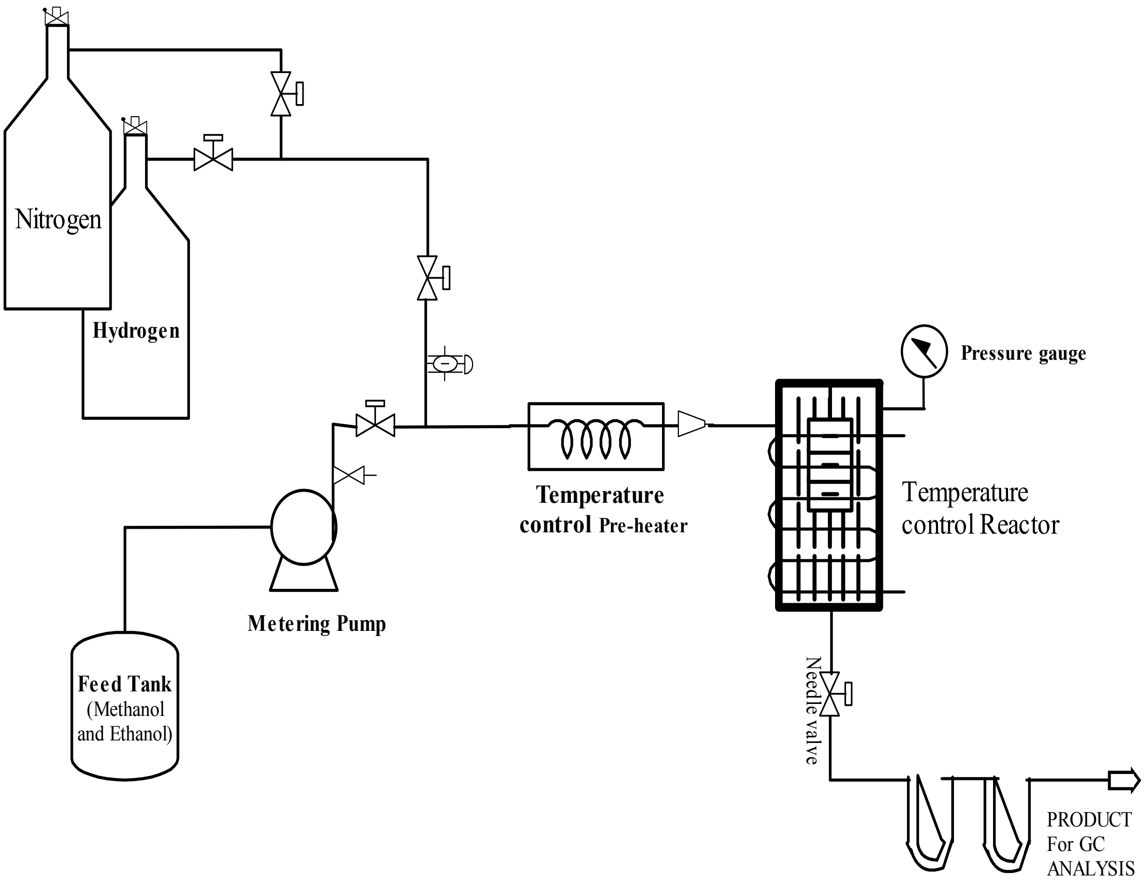

Figure 1 Schematic flow diagram of steam reforming unit.

A thermocouple was located in the catalyst bed. The reactor was heated by a high-resistance electric coil. The steam reforming reaction along with other side reactions takes place inside the reactor where a bed of catalyst is placed at the desired reaction temperature. The reaction product comes out from the bottom of the reactor through a needle valve. The product gases coming from the reactor are cooled and condensed; two U-shape gas sample tubes were used to gather the liquid. The gas was vented out. After condensation, a sample of gas is directly fed to the GC to get analysed. Gas samples were withdrawn every 5 min and then sent to the GC for analysis. Each run was stopped after 30 minutes of operation from the point of feeding the preheater.

Results And Discussion

Catalyst Characterization

Specific Surface Analysis Using BET (BET SSA)

The BET surface area has been found out using Micromeritics surface area analyzer. BET surface area for 1 mm particle was found 12.4 m^2/g. From literature [10] the value of SSA for Ni/Al_2O_3 has been reported as 14-42 m^2/g.

Elemental Analysis Using X-Ray Diffraction Method (XRD)

The XRD analysis was performed to determine the bulk crystalline phases of the nickel species in the catalysts. XRD patterns were collected with a Rigaku-Miniflex diffractometer using monochromatised Cu Kα radiation. The spectra were scanned from $2\theta = 10^0$ to 80^0 at a rate of 2^0/min (2θ). From the data obtained Crystalline or amorphous form was found having the cubic structure Dimension and unit cell structure parameter (a) = 8.048 $A^{0.}$ The diffraction profile is related to the size and perfection of the crystallizes and various instrumental parameter. The intensity versus 2θ curves are as follows;

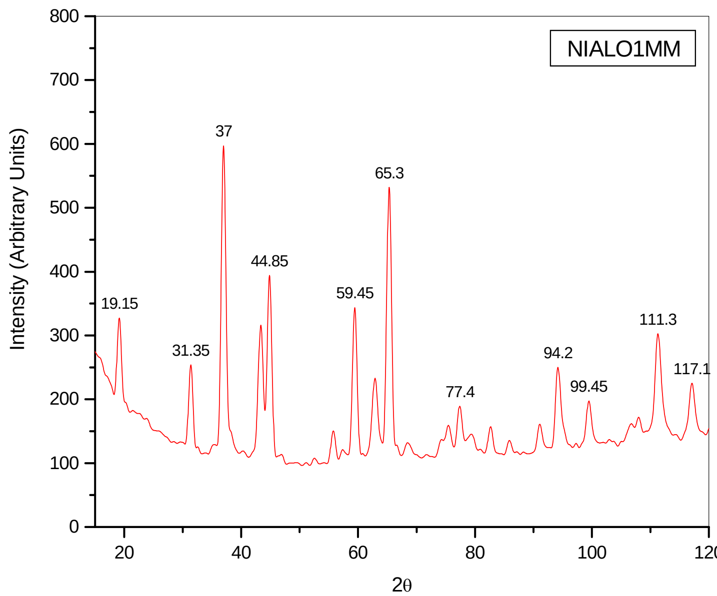

Figure 2 Intensity vs 2θ curve for catalyst of size 1 mm

Surface Study Using Scanning Electron Microscopy (SEM)

The following structures were observed using SEM photograph as shown in figure 3 for catalyst of 1mm sizes at magnification x 2500. From the photograph it is observed that there is no significance change in the micro structural appearance of the catalyst.

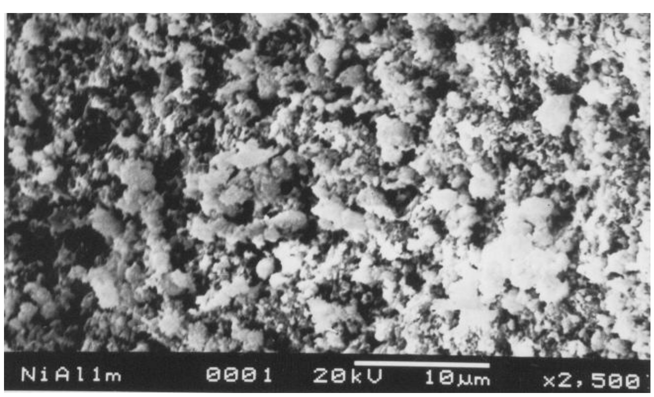

Figure 3 Photographs for catalyst 1mm sizes at magnification x 2500

Effect of Temperature on Conversion

For ethanol the minimum conversion obtained 53% (350^0 C, W/F =98 gm-cat hr/mol) and the maximum conversion was found 89 % (525 ^{0}C, W/F = 475 gm-cat hr/mol) with increase in both temperature and W/F.

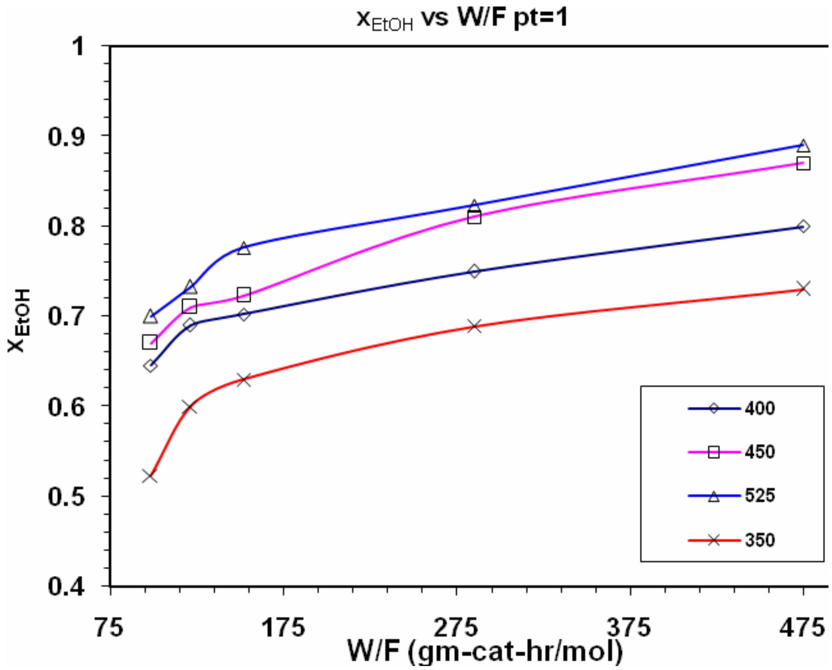

Figure 4 Variation of conversion of ethanol with W/F at different temperatures.

The reported conversions are higher compared to the current results. In addition, the temperature for reforming is reported to be lower than the present study. For steam reforming of ethanol, a limited number of data are available in the literature. The reported conversion [5, 6] for reforming on Ni/Al_2O_3 catalyst is in the range of 80-95 %. It may be noted that the values of conversion in this study are similar. However, the values of temperature and W/F are higher. Therefore it can be inferred that this Ni/Al_2O_3 catalyst is suitable for ethanol steam reforming. [7]

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