

Effect of Molar Ratio on Conversion of Methanol for Hydrogen Production by Steam Reforming for Fuel Cell Application

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Abstract

In the unsafe prospect of pollution, global warming and energy crises, all resulted owing to the fossil fuels, hydrogen production by steam reforming of methanol can be a consider clean energy carrier based on the renewable sources of energy. The paper reports experimental results concerning the effect of molar ratios on conversion of methanol for hydrogen production by steam reforming. The hydrogen produced can be utilized for application of fuel cell. The experimental study of steam reforming of ethanol was carried out using commercial nickel-alumina ($\text{Ni}/\text{Al}_2\text{O}_3$) catalyst in a fixed-bed reactor. For methanol, the minimum conversion obtained was around 40% at $W/F = 98$ gm-cat hr/mol and the maximum conversion was around 60 % at $W/F = 475$ gm-cat hr/mol at atmospheric pressure. It was found that hydrogen production proportional to the molar ratio. The experimental data obtained 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.

Keywords: Hydrogen Production, Methanol, Steam Reforming, Molar Ratio, Hydrogen

Introduction

Hydrogen has long been recognized as an ideal fuel for power generation systems with virtually zero emissions of air pollutants and carbon dioxide. It can be used in fuel cells to power automobiles or to provide electricity and thermal energy (cogeneration) in stationary distributed energy generation units. Hydrogen-based fuel cell power plants are highly efficient and reliable, and generate virtually no undesirable air emissions. Besides, fuel cell vehicles fueled by hydrogen derived from domestically produced alternative fuels such as ethanol, methanol, or natural gas with an efficient reformer would simultaneously reduce the global petroleum demand. A fuel cell is a device that uses hydrogen as a fuel to produce electrons, protons, heat, and water. Fuel Cells are addressed as "zero emission" technology. This is one of the reasons why fuel cells are attractive. They can be used in virtually any location, even there where normal power production is not possible due to emissions of pollutants and noise. Fuel cell

powered vehicles using hydrogen as a fuel are currently being developed in an effort to mitigate the emissions of green house gases such as CO₂, NO_x and hydrocarbons. The development of molten carbonate fuel cells for electrical power plants applications now approaches the size of sub-MW demonstrative facilities and this makes more important to have easily storable and processable fuels. In particular, the use of liquid fuels as alternative sources for hydrogen production for molten carbonate fuel cell is desired. 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 methanol 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

Steam Reforming is a chemical process where hydrogen-containing compounds react with steam, oxygen, or both into hydrogen-rich gas stream. Steam reforming is one of the most widely used technologies for hydrogen production, and achieved by reaction over a catalyst at elevated temperatures. Steam reforming reaction generally affords a substantial H₂ yield (~ 75%). Steam reforming reaction generally shows high CO₂ selectivity. Being an endothermic reaction there is very low possibility of hot spot formation, run away reaction, and sintering of catalyst particles, as compared to exothermic process like POX. From the generalised reaction it is clearly seen that hydrogen produced per mole of feed is maximum in case of steam reforming reaction (as compared to other processes e.g. POX, Auto thermal). The initial step in steam reforming are dissociative adsorption of oxygenates on the metal sites of the catalysts; the formed surface species subsequently reacts with water/hydroxyls that are, in most cases, activated on oxide supports.

Generalised Reactions:

Steam reforming:



Carbon formation



Water-gas-shift



CO oxidation



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 characterisation 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

There is growing interest in the use of H_2 as an alternative fuel mainly due to environmental aspects. Alcohols could constitute a good supply of hydrogen, as they are efficient H_2 -reservoirs and could avoid the difficulty of H_2 -distribution. In this context, many efforts have been applied to the production of hydrogen from steam reforming of methanol by using methanol synthesis-based catalysts. Catalytic production of hydrogen by steam reforming of methanol is an attractive option for use in decentralized production of clean electrical energy from fuel cells. Metal-supported catalyst systems that integrate the endothermic methanol steam reforming with exothermic combustion of methanol. [1]

Catalytic conversion of liquids with high hydrogen to carbon ratio, such as primary alcohols, is possible at relatively low temperatures (200–300 °C) and sought of by the automotive industry as one of the most promising solutions for generating the hydrogen on-board the automobile. Methanol is today the primary candidate, as hydrogen carrier, for the on-board production of hydrogen, due to its high hydrogen to carbon ratio (4:1), low boiling point, and availability. The absence of carbon–carbon bonds in methanol drastically reduces the risk of *coking*. Methanol can also be produced from renewable resources and thus lowering the production of greenhouse gases.[4]

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.

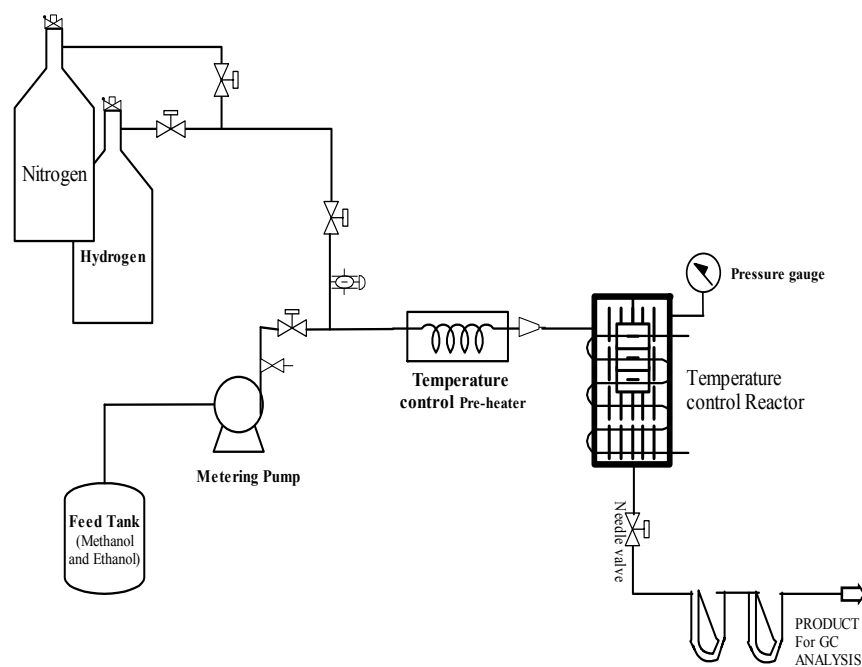


Figure 1 Schematic flow diagram of steam reforming unit.

Experimental Procedure:

Methanol solution was prepared by diluting 99 % methanol (Lab grade provided by Sisco research laboratories Pvt.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 feedstocks (Methanol/Ethanol) is shown in Fig. 1. For every five experimental runs (3 hrs), fresh catalyst was used. The fresh catalyst was reduced in situ by high-purity hydrogen gas (99.9%) for 2 hours. The reactor and the preheaters were first allowed to attain a steady temperature as per the required operating parameters. Then the prepared Methanol solution was fed by electromagnetic dosing pump, to a temperature controlled pre-heater unit. The pre-heater unit vapourised the methanol solution prior to sending further to the temperature controlled reactor 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 $12.4 \text{ m}^2/\text{g}$. From literature [6] the value of SSA for $\text{Ni}/\text{Al}_2\text{O}_3$ has been reported as $14\text{-}42 \text{ m}^2/\text{g}$.

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 $\text{Cu K}\alpha$ radiation. The spectra were scanned from $2\theta = 10^\circ$ to 80° at a rate of $2^\circ/\text{min}$ (2θ). From the data obtained Crystalline or amorphous form was found having the cubic structure Dimension and unit cell structure parameter (a) = 8.048 \AA . 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;

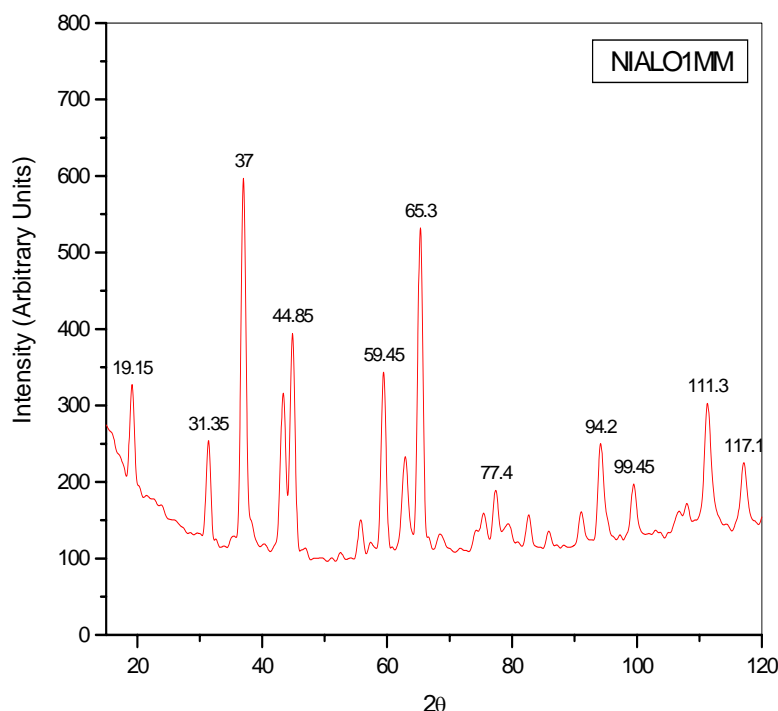


Figure 2 Intensity vs 2θ curve for catalyst of size 1 mm

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 1000. From the photograph it is observed that there is no significance change in the micro structural appearance of the catalyst

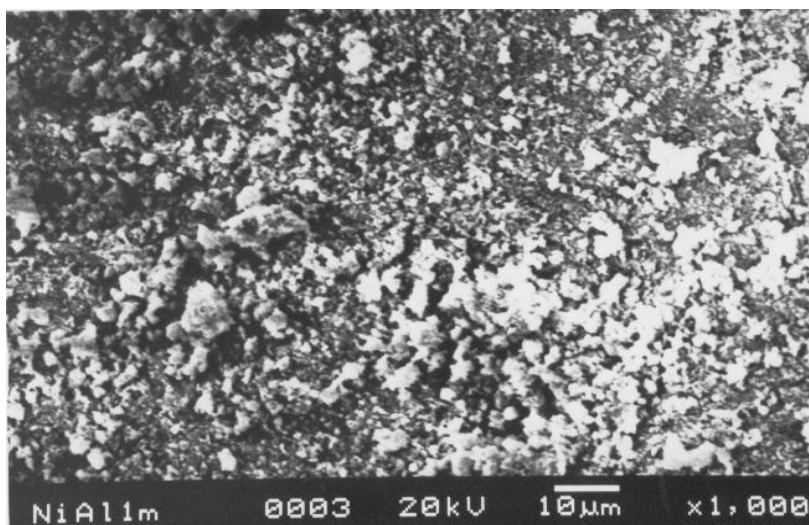


Figure 3 Photographs for catalyst 1mm sizes at magnification x 1000

Effect of Molar Ratio on Conversion

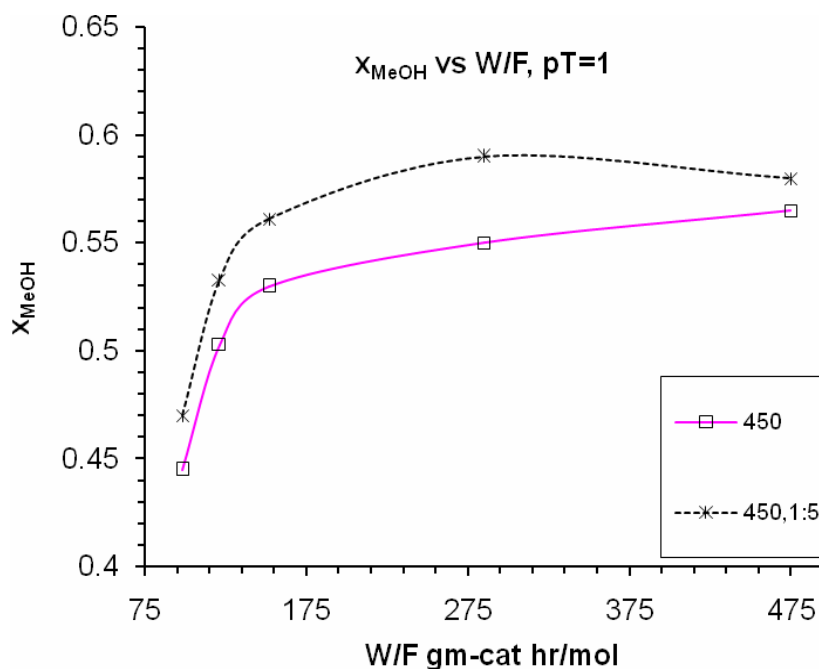


Figure 4 Variation of conversion of methanol with W/F at two different molar ratios.

From the obtained values of conversion of limiting component figure 4 have been plotted. For methanol the minimum conversion obtained 41% and the maximum conversion was found 59 % with increase in both temperature and W/F. However after a particular W/F the increase in conversion is relatively small (< 5%). The use of commercial alumina - supported nickel catalysts for steam reforming of methanol was reported for conversion of methanol using Ni/Al₂O₃ catalyst has been found in literature.[7] Runs were also performed at a higher molar ratio (1:5) at 450 °C. A marginal improvement in conversion of methanol was observed in comparison to molar ratio 1:3 at 450 °C at identical W/F ratios. However, data is available for steam reforming of methanol with Cu /ZnO catalyst. The reported conversion is higher compared to the current results [8].

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