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Consequence of Temperature on Conversion of Methanol for Hydrogen Production by Steam Reforming

BHANDE R.S. [1#], LANDGE Y. A.[1], GIRI P. A.[1]

[1]Department of Chemical Engineering,
Finolex Academy of Management and Technology, Ratnagiri-415639, M.S., India
[#] E-mail - hodchem@famt.ac.in bhande.ramesh@gmail.com

Abstract

The present work reports experimental results of concerning the influence of the temperatureon conversion of Methanol for hydrogen production by steam reforming in the range of 350–525 ^{0}C. The optimum temperature for steam reforming process of methanol fixed based taking into consideration on the conversion, efficiency of hydrogen production and intensity of carbon deposition. Kinetic study of Methanol steam reforming over a commercial nickel-alumina (Ni/Al_2O_3) catalyst was conducted in a fixed-bed reactor. The chemical reaction mechanism of steam reforming occurring on the catalyst, support makes its chemical nature an important factor affecting conversion and selectivity. We observed that, the minimum conversion obtained was around 40% at 350^0 C and the maximum conversion was around 59 % at 525 ^{0}C.The work also tested the feasibility of using methanol as feed for hydrogen production by considering the steam reforming data given in the literature and concludes that a more-elaborate scheme of reactions is necessary to describe the complex reactions that occur during the steam reforming process. 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 methanol steam reforming.

Keywords: Hydrogen fuel, Methanol, Steam Reforming, Conversion, Temperature

Introduction

Hydrogen has been termed as the “energy carrier of the future”.It burns cleanly, producing no polluting emissions suchas SOx, NOx, CO, volatile organic compounds (VOC), etc. This makes it necessary to process the primary fuel to obtain H_2 and then use it in energyproducing devices such as fuel cellsor use it as fertilizer feedstock.The catalytic steam reforming of alcohols involves the reaction of steam with alcohols (such as methanol, ethanol, and propanol) and methane, ethane over catalysts at high temperatures anddifferent pressures. The major concerns still are the endothermic nature of the reactions, which makes the process energy-intensive, and coke formation, which results in catalyst deactivation. In the present paper we studied the effect of temperature on conversion of methanol for hydrogen production by steam reforming and minimize coke formation, increasing catalyst life.

The fuels used in automotive vehicles today are mainly comprised of the petroleum derivatives diesel and gasoline. These hydrocarbon fuels, upon burning in an internal combustion engine, can emit compounds to the atmosphere such as carbon monoxide (CO), carbon dioxide (CO_2), nitrous oxides (NO_x), sulfur-oxides (SO_x), and particulate matter (PM). Hydrogen fuel cells, on the other hand, produce zero vehicle emissions except for steam and waste heat. One method of utilizing the benefits of the hydrogen fuel cell, while potentially lessening the impacts of the upstream fuel processing, is hydrogen delivery from a stored hydrocarbon fuel. This creation of hydrogen is commonly referred to as an "onboard reformation" process.[2,3]

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 H_2 yield (~ 75%). Steam reforming reaction generally shows high CO_2 selectivity. Being an endothermic reaction there is very low possibilityof 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:

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

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

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

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

$H_2 + 1/2O_2 \rightarrow H_2O$ ……………………………………………………… (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 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 ^{o}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.

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.

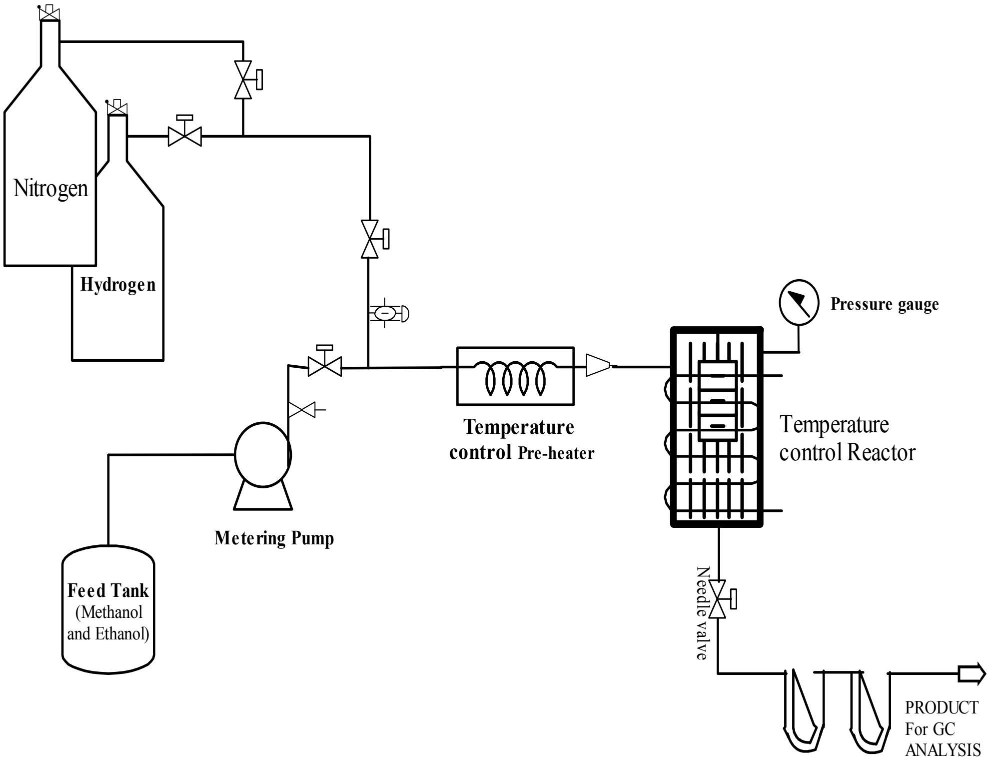

Figure 1 Schematic flow diagram of steam reforming unit.

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 for1 mm particle was found 12.4 m^2/g.From literature [6] 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-Miniflexdiffractometer using monochromatised Cu Kα radiation. The spectra were scanned from $2\theta = 10^0$ to 80^0at 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 structureparameter (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;

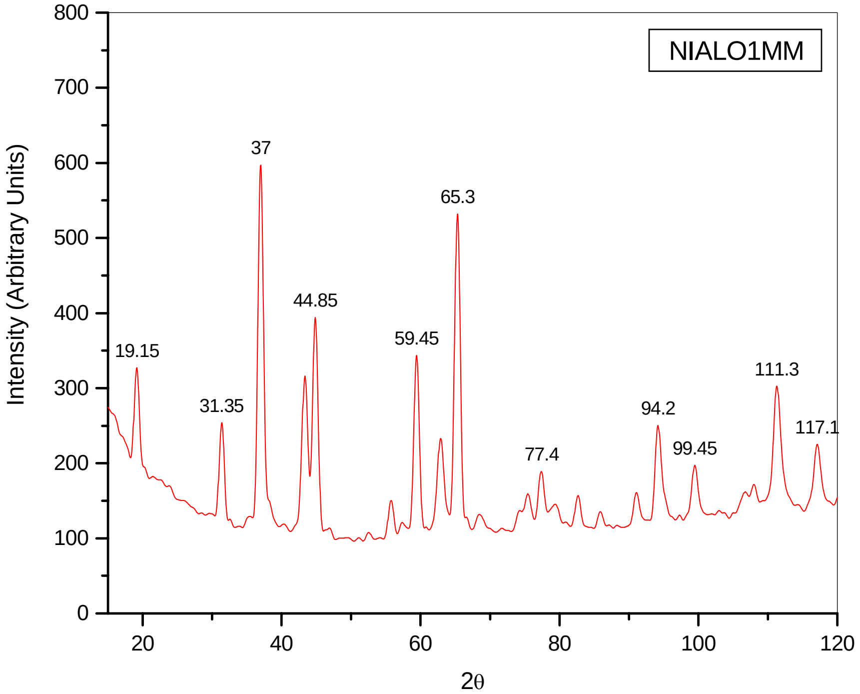

Figure 2 Intensity vs 2θ curve for catalyst of size 1 mm

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.

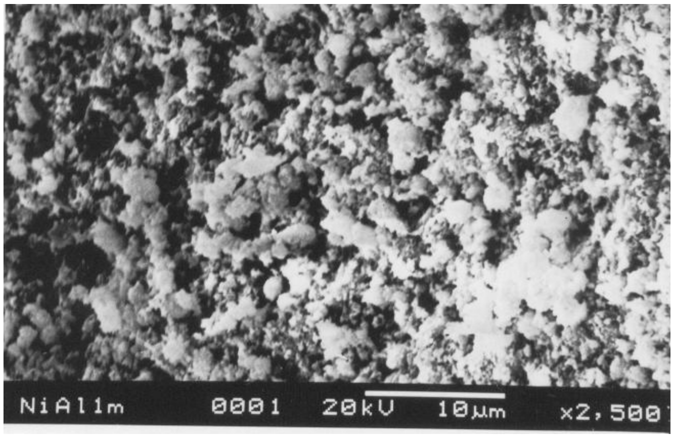

Figure 3 Photographs for catalyst 1mm sizes at magnification x 2500

Effect of Temperature on Conversion

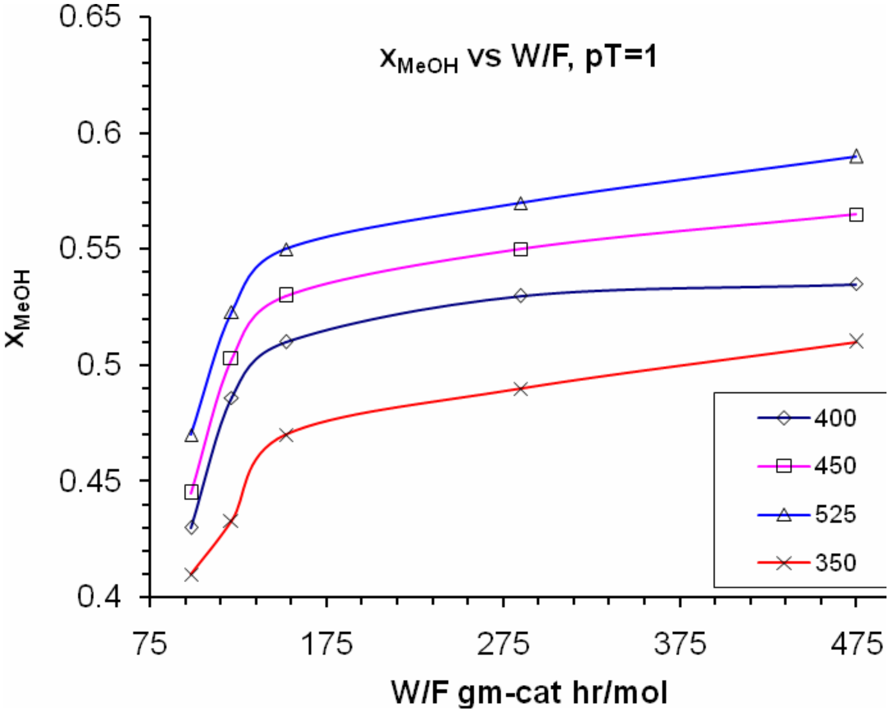

Figure4: Variation of conversion of methanol with W/F at different temperatures

From the obtained values of conversion of limiting component Figure 4 have been plotted. For methanol the minimum conversion obtained 41% (350^0C, W/F =98 gm-cat hr/mol) and the maximum conversion was found 59 % (525^0C, W/F = 475 gm-cat hr/mol) with increase in both temperature and W/F. However after a particular W/F the increase, the 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/Al_2O_3 catalyst has been found in literature.[7] However, data is available for steam reforming of methanol with Cu /ZnO catalyst. The reported conversion is higher compared to the current results [8]. In addition, the temperature for reforming is reported to be lower than the present study.

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