

Synthesis of Dimethyl Ether from Synthesis Gas over Bi-functional Catalyst

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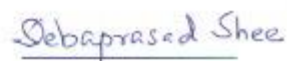
This Thesis entitled "*Synthesis of Dimethyl Ether from Synthesis Gas over Bi-functional Catalyst*" by Suhail Farokhi is approved for the degree of Master of Technology from IIT Hyderabad.



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Dedicated to my parents and all my teachers

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ABSTRACT

With the onset of the 21st century which has brought about giant leaps in science and technology, we see an increasing global population which brings about an increase in the energy and fuel requirement. The current fossil fuel is being utilized at an alarming rate and one of the most feasible alternatives we have is to turn to alternative sources of energy like Solar, Nuclear power etc. In addition to the above the current fossil fuels that are utilized create a lot of negative environmental impact releasing greenhouse gases such as CO₂, CO, Oxides of Nitrogen and Sulfur during their combustion thus contributing to global warming. The best alternative among the alternative sources of energy is to turn to biofuels which use biomass as the starting material and are hence neutral to the carbon cycle. Among the various biofuels DME is considered to be a very significant biofuel having the potential to replace existing fuels such as LPG. Usually manufactured by two step method industrially from synthesis gas, the methanol formation step followed by methanol dehydration step. In the present work the synthesis of Dimethyl ether from synthesis gas is studied by using a bifunctional catalyst in single step in a high pressure fixed bed reactor in the presence of nitrogen gas. A bifunctional catalyst was synthesized by the wetness impregnation method using Cu-Zn and γ -Al₂O₃ as the support of the catalyst. The Syn gas to Dimethyl ether which is a two-step process is studied systematically with the initial experiments focusing on the Methanol dehydration step using the Silica-Alumina catalyst molar ratio (9:1) and x Cu y Zn/Al catalysts of varying ratios (x:y= 1:1,1:2,5:4) to convert Methanol to Dimethyl ether. In the above reaction the conversion of Methanol and selectivity of Dimethyl ether was studied by varying the WHSV at varying reaction conditions. The second stage of the study was mainly concentrated on the conversion of Synthesis gas to Dimethyl ether in a single step using the bifunctional catalyst synthesized 40Cu10ZnAl₂O₃ and 50Cu10ZnAl Al₂O₃ catalysts which were similar to commercially available catalysts. The XRD results of the catalysts confirmed the presence of CuO, Cu₂O, ZnO over the bimetallic catalyst. In the initial studies the effect of WHSV was studied over the conversion of Methanol and the selectivity of Dimethyl ether. The

conversion of Methanol and the selectivity of Dimethyl Ether was found to be decreasing with increasing WHSV. The effect of temperature, pressure, gas composition and WHSV was studied using the $40\text{Cu}10\text{ZnAl}_2\text{O}_3$ catalyst. The results showed a decreasing conversion of Carbon monoxide with time for all the catalysts clearly indicating the catalyst deactivation happening over time. It was observed in most of the cases that the conversion was increasing with increasing pressure. With an increasing temperature the conversion showed no particular trend of increase or decrease, showing an increase in conversion with decreasing temperature at high pressure and a decline in the conversion at intermediate pressures. The best reaction conditions for the Syn Gas to DME conversion was found and the effect of varying space velocities and changing catalyst loading was also studied.

NOMENCLATURE

DME	Dimethyl ether
Syn Gas	Synthesis Gas
MeOH	Methanol
40Cu10ZnAl ₂ O ₃	40 wt% Cu 10 wt% / Al ₂ O ₃
50Cu10ZnAl ₂ O ₃	50 wt% Cu 10 wt% / Al ₂ O ₃
SiAl	Silica Alumina
STD	Synthesis Gas to Dimethyl ether
WHSV	Weight Hourly Space Velocity

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1. INTRODUCTION

The world is now facing a shortage of fuels. As the population worldwide continues to increase, which leads to dependence on fossil fuels which are predicted to get depleted about 80% in the coming decades. Taking the present scenario into consideration it is high time that we realize the need for alternative fuels, which are not only in abundance to meet the on growing global needs but also are environmentally friendly. Dimethyl Ether (DME) is one such recognized fuel among many other alternative fuels. It is the simplest Ether, having properties very much similar to LPG. As the fuel prices are rising it is considered as a very promising realistic alternative fuel. [\(Khandan, Kazemeini, & Aghaziarati, 2011\)](#)

The government of India has also recognized the importance of DME as an upcoming bio-fuel and has collaborated with other countries like Australia on production of Dimethyl ether in the recent times. Australia's CSIRO and its equivalent in India, the Council of Scientific and Industrial Research (CSIR), have launched a three-year, A\$6-million (US\$5.6-million) collaboration focused on improving processes involved in the production of dimethyl ether (DME).

DME can be derived from both fossil fuels (natural gas, coal etc) and biomass sources (biomass gasification). It can be produced from a variety of abundant sources like natural gas, coal, waste from pulp and paper mills, forest products, agricultural by-products, municipal waste and dedicated fuel crops such as switchgrass. [\(Semelsberger, Borup, & Greene, 2006\)](#) DME has a very good potential for power generation as a fuel for vehicles and also has remarkable applications in domestic heating. [\(Marchionna, Patrini, Sanfilippo, & Migliavacca, 2008\)](#)

DME has lower Ozone Depletion Potential (ODP) and lower Global Warming Potential (GWP compared with traditional chlorofluorocarbons (CFC's, Freons) [\(Semelsberger et al., 2006\)](#) It has replaced CFC gases (freons) as an environmentally friendly and safe aerosol propellant, which is one of its major current applications. It can be used as a refrigerant. It is a fuel with a high cetane number (indicator of the combustion speed of diesel) and has no particulates or smoke emission during combustion, the SO_x and NO_x are also significantly reduced. When used as an automotive fuel a soot free emission and reduced engine noise is noticed.

It is a volatile organic component (VOC) which is non carcinogenic (cancer causing) and non-teratogenic (causing defect in the fetus) unlike the other VOC's. In ambient conditions it is non corrosive colorless gas heavier than air. It has no threat of

polluting the ground water resources. It burns with a blue flame and has a sweet odor and doesn't require any odorant like methane does. (Chen, Lin, Lee, & Huang, 2012)

As the properties of DME are very much similar to LPG it is in gaseous state at ambient conditions but like LPG it can easily be liquefied when subjected to cooling or moderate pressures. The existing infrastructure can be used for the transport and storage of DME, hence not requiring any new infrastructure to be built, saving lot of capital cost. The transportation of DME can be done with the existing LPG tankers only with minor modifications in the pumps, gaskets and seals.

DME also has proven to be a versatile compound having potential uses in making hydrogen, for hydrogen fuel cells and production of Olefins. It is an intermediate in the production of dimethyl sulfate, methyl acetate, light olefins and high value oxygenated compounds (Chen et al., 2012).

The properties of DME are very much similar to that of propane and butane, the mixture of which is found in domestic LPG. The cetane number of DME is 55-60 which is near to Diesel which has a cetane number of 55 and much larger than propane. Because of similar Cetane number DME can be blended with Diesel and can be an attractive Diesel substitute. The Lower Heating Value (LHV) of DME is about 28.8 MJ/kg when compared to Diesel having 42.7 MJ/kg and Gasoline having 43.2 MJ/kg respectively. Figure 1.1 gives a comparison of the LHV of various fuels. The emissions of DME are soot free and contains no sulfur and emits less smoke and NO_x on combustion, and fewer hydrocarbons than LPG and conventional diesel fuel. However for using DME in conventional vehicles changes have to be made in the engines and valves to avoid leakage since DME has lower density. (Arcoumanis, Bae, Crookes, & Kinoshita, 2008) DME can also be used as a fuel for turbines and for power generation.

Table 1.1: Properties of Dimethyl Ether in comparison to other fuels (Arcoumanis et al., 2008) , (K. R. Patil, S. S. Thipse, Int. J. Emerg. Technol. Adv. Eng. 2 (2012) 35-41)

	Unit	DME	Diesel	Propane	Butane	CNG	Methanol	Ethanol	Gasoline
Boiling Point	°C	-25	180-360	-42.1	-0.5	-	64.7	78.37	37.78-204.44
Flammability limits in air	vol%	3.4-17	0.6-6.5	2.1-9.4	1.9-8.4	-	-	3-19	1.4-7.6
Lower Heating Value	MJ/kg	28.8	42.7	46.35	45.72	49	19.8	26.4	43.2
Density	kg/m ³	667	831	500.5	578.8	-	795	789	750
Auto ignition temperature	°C	350	200-300	470	365	650	450	420	-
Cetane Number	-	>55	40-55	5	-	-	-	40-50	-
Vapor Pressure 20°C	kPa	530	<<10	830	210	-	37	21	45/90

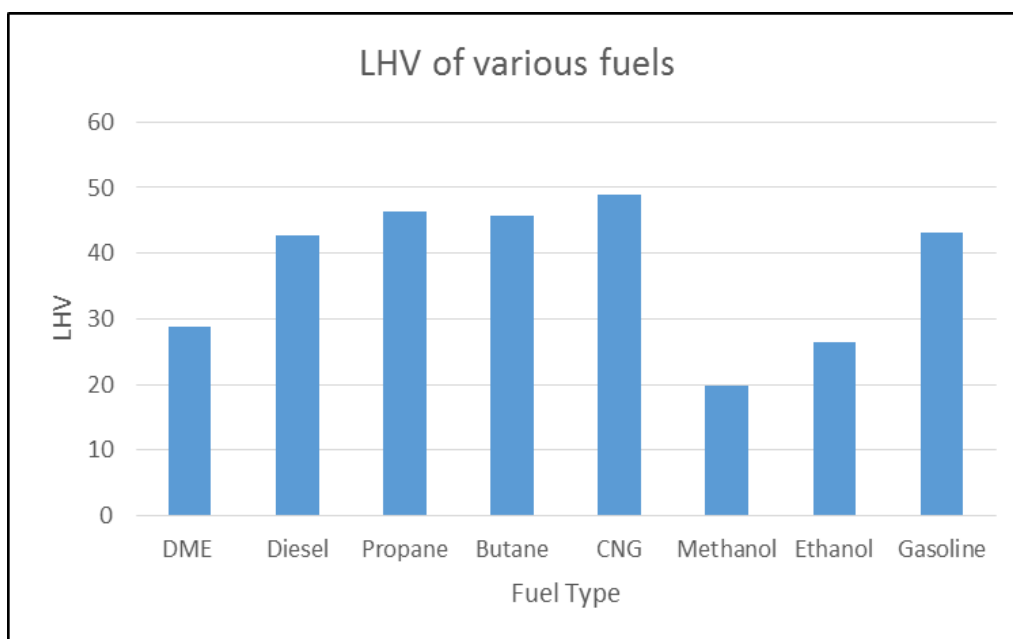


Figure 1.1: LHV of various fuels

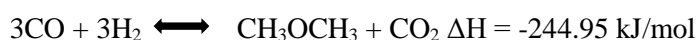
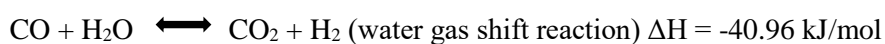
DME can be produced from a variety of abundant sources like natural gas, coal, waste from pulp and paper mills, forest products, agricultural by-products, municipal waste and dedicated fuel crops such as switch grass etc. World production today is primarily by means of methanol dehydration, but DME can also be manufactured directly from synthesis gas produced by the gasification of coal or biomass, or through natural gas reforming. Among the various processes for chemical conversion of natural gas, direct synthesis of DME is the most efficient.

In the two step production of DME the methanol formation reaction is followed by the methanol dehydration reaction. In this process two different catalysts are used one for each reaction. Commonly used catalysts for the methanol hydration reaction are CuO-ZnO-Al₂O₃ catalyst which is widely used. For methanol dehydration catalyst the widely used catalyst are γ -Al₂O₃, ZSM-5, HY- Zeolites and silica-alumina.

In the single step synthesis of DME direct conversion from Syn gas to DME is observed over a bi-functional catalyst, a catalyst which can efficiently perform two processes together i.e. the formation of methanol and the dehydration of methanol. Selectivity being more concentrated on DME and less on the by-products. Various catalysts have been used for the single step synthesis purpose like CuO-ZnO- γ -Al₂O₃/HZSM-5, CuO-ZnO- γ -Al₂O₃/ ferririte, CuO-ZnO-ZrO₂ / Al modified H-mordenite etc. The one step process of the conversion of DME from Syn Gas is thermodynamically more favorable and is considered to be more economical. (Shi et al., 2013)

The single step conversion seems to be more favorable because of the synergy in the process (Moradi, Ahmadpour, Nazari, & Yaripour, 2008) i.e. the product of one reaction becomes the reactant for the second reaction. Methanol which will be in its equilibrium concentration is consumed by the second reaction for the methanol dehydration process. The water gas shift reaction also generates Hydrogen which becomes the driving force for more methanol formation.

Synthesis Gas is produced from DME by the following set of reactions(Lee et al., 2014)



With the depleting global resources of fossil fuels the world is now facing a challenge to meet its ever growing fuel and energy requirements. The role of alternative fuels hence plays a large role in shaping the future. As exploration for environmentally friendly alternative fuel continues, Dimethyl Ether emerges as a major contender in the race, having properties similar to LPG (Liquefied Petroleum Gas), considered as a potential replacement for conventional diesel, and which can be made from various sources. The synthesis of Dimethyl Ether from Synthesis Gas is a two-step process having methanol formation and methanol dehydration reactions. Efforts have been made to synthesize Dimethyl Ether in a single step using a bi-functional catalyst CuO-ZnO- γ -Al₂O₃/HZSM-5, CuO-ZnO- γ -Al₂O₃/ferrite, CuO-ZnO-ZrO₂ / Al modified H-mordenite etc which is both economically and thermodynamically favorable.

2. LITERATURE SURVEY

2.1. Catalyst for one step conversion

As stated earlier the single step conversion of DME from Synthesis Gas requires a bi-functional catalyst. A catalyst which can affect both methanol formation and methanol dehydration reaction and form the product DME. The first reaction i.e. the formation of methanol is not thermodynamically favorable. Since in the direct conversion step methanol is not the product and whatever methanol formed is continuously converted to DME in subsequent reaction, this mitigates the thermodynamic limitation that is existing and hence a bi-functional catalyst actually helps us in achieving more yield of the product with good selectivity. The first reaction i.e. the methanol formation reaction (CO hydrogenation to methanol), the rate determining step, CuO-ZnO based catalyst are commonly used. However, due to the thermal sintering of Copper at temperature beyond 300°C other metals such as Palladium, Chromium, Manganese and Zirconium are used. (Zhu et al., 2010) For methanol dehydration the widely used solid acid catalyst are ZSM-5, Silica Alumina, γ – Al₂O₃ etc. The optimal mass ratio of the two catalyst is in the range of 1-2. The deactivation of the catalyst is observed during the 2nd step of dehydration of Methanol with high ratio of dehydration catalyst. (Zhu et al., 2010) The most common methods of preparation of catalyst are co-precipitation, incipient wet impregnation, sol-gel method, direct mixing method etc.

2.2. Catalyst preparation

There are a number of different type of catalyst that can be used for the reaction each made by different methods. CuO-ZnO- γ -Al₂O₃/ HZSM-5, CuO-ZnO- γ -Al₂O₃/ HSY made by co-precipitation method by Qing-jie Ge et al reported a conversion of 89% and DME selectivity of about 99% at a pressure of 4MPa. CuO-ZnO/ ZSM-5 mixed in the volume ratio of 2:1 is reported, where the pressure is maintained between 4-8 MPa and the temperature of 503-533 K i.e. 230-270 °C. (Zhiliang, 2001)

For CuO-ZnO- γ -Al₂O₃ catalyst most efficient method of preparation is the sol-gel impregnation method attributed to higher dispersion of metallic Copper. CuO-ZnO-Al₂O₃/ ferrite bi-functional catalysts were prepared by co-precipitation method using CuO-ZnO-Al₂O₃ component for CO hydrogenation on a solid-acid catalyst of Al₂O₃-modified H-ferrierite zeolite. (Lee et al., 2014)

Various methods of preparation of the catalyst have been compared according to the percentage conversion of CO, the DME selectivity, Methanol selectivity, CO₂ selectivity and hydrocarbon selectivity. We note that the CZA-Z- CS: co-precipitation sedimentation and CZA-Z-OX: oxalate co-precipitation methods are much more efficient than the CZA-Z-CF: co-precipitation impregnation or CZA-Z-IP: impregnation methods giving a better conversion of CO, the DME selectivity at almost the same amount of CO₂ selectivity. (Ahmad et al., 2014) The solid catalyst like Zeolite and Alumina have two kinds of catalytic activity sites. The strong acidic sites (Bronsted Sites) and the weak acidic sited (Lewis Sites) the weaker ones have the tendency to form DME and the strong sites will be forming by-products. (Sabour, Peyrovi, Hamoule, & Rashidzadeh, 2014)

Cu-ZnO-ZrO₂ / Al modified H-mordenite is used showing 99.8% conversion and 96.8% selectivity of DME, it was made by wet impregnation method. (Khandan et al., 2011) The wet impregnation of H mordenite with aqueous solution of aluminium nitrate. The first reaction CO hydration occurs on Copper surface and hence good dispersion of Copper is required having high surface area, the catalyst had good dispersion of copper and also modified the strong catalytic sites having high selectivity percentage.

According to studies the presence of Zirconium (CuO-ZnO-ZrO₂/ Na⁺ modified Zeolite) has a synergistic effect on the one step conversion of syn gas to DME. (Khandan et al., 2011) The Na⁺ modified Zeolite can be used, Zeolite which has strong acid sites promoting by-product formation are modified to weaker sites which are more selective to DME.

2.3. Support for Catalyst

The metal catalyst is dispersed on the surface of another material which acts as a platform for the reaction to take place and this material is called as the support. The most commonly employed support materials are Silicates, Aluminates, Ceramics, MgO, Zeolites TiO₂, ZrO₂ activated carbon etc.

The support not only gives physical strength to the catalyst enhancing the mechanical properties, enabling it to bear the thermal and pressure conditions of the reaction but also alters the physiochemical conditions (activity and selectivity), the product formed and the rate of product formation are dependent on the support. The support plays an important role in the delaying of the catalyst deactivation which usually happens due to sintering in the high temperatures of the reaction conditions. Sintering is avoided by interaction of the support and the catalyst which may involve Vander Walls forces, formation of metal reduced species on the metal surface.

The support loading and size are determined by the type of the process, pellet type of supports are used for liquid and gas continuous systems whereas powder supports are used for batch systems. If the catalyst is in liquid phase the support should be inert in the solvent so as to prevent the formation of any unwanted products.

Usually the reactor used is fixed bed reactor, slurry reactor or high pressure reactor for the reaction and the catalyst employed is a mixture of a metal catalyst on a support for the methanol hydration, with a solid acid catalyst for dehydration. (Naik et al., 2011) The metal will give high activity and it's dispersion on the support surface will give a large surface area which gives many acidic sites.

In general, the catalytic activity for DME synthesis by methanol dehydration is much higher on zeolite-type catalysts compared with γ -Al₂O₃, due to the presence of a larger number of acidic sites on zeolites. (Sun, Yang, Yoneyama, & Tsubaki, 2014)

2.4. Promoter for Catalyst

A promoter increases the activity of a catalyst and helps in speeding up the reaction process. In the direct synthesis of dimethyl ether bi-functional catalyst containing CuO-ZnO-Al₂O₃ is promoted by using Zirconium and Gallium showed higher catalytic performance and acidity. The methanol formation rate was enhanced due to the increased dispersion of Copper on the surface of the catalyst than that on the CZA catalyst because of the formation of smaller particles and superior performance is attributed to the geometric effect of the promoter by forming a strong ZrO₂-CuO interaction originating from oxygen vacancies of ZrO₂ hence increasing the DME yield. (Kang, Bae, Kim, Dhar, & Jun, 2010)

2.5. Effects of process parameters in DME Synthesis

In most of the researches the operating conditions are very much similar, moderate temperature of 200-300°C and pressures ranging from 2.5 MPa to high 8 MPa with varying degrees of conversion percentage and DME selectivity percentage obtained with various catalysts. Space Velocity, Temperature and Pressure are some of the parameters which will affect the final product which is formed.

2.5.1. Effect of Temperature

With the increase in the temperature as we already expect the selectivity of DME goes down (the reaction being exothermic in nature, i.e. the exothermic feature of methanol synthesis and dehydration reaction. (Perambuduri, 2014) The higher temperatures favor the methanol dehydration but a further temperature increase will result in the pyrolysis of DME and increases the selectivity of CO₂. The temperature is not favoring the reaction because the reaction is limited by Equilibrium kinetics. When γ - Al₂O₃ is used as the dehydration catalyst the conversion of CO increases with increase in temperature and reaches maximum at 270-280°C but decreases dramatically as 300°C. Higher temperatures beyond 300°C may also lead to catalyst deactivation (sintering). (Zhu et al., 2010)

2.5.2. Effect of Pressure

Pressure enhancement will actually lead to an increase in the conversion of H₂ and CO (Chen et al., 2012) (mole reducing CH₃OH formation reaction) methanol dehydration and water gas shift reaction are both indifferent to the pressure changes. The selectivity of DME goes down with constant temperature as the pressure increases.

Along with the mole reducing reaction another thing that is helping is with the increased pressure the time of contact of the reactant with the catalyst is prolonged and the reaction progress is enhanced. But with rising pressure the selectivity of DME decreases and the yield of CH₄ (by-product) rises hence very high pressures are not favorable also reducing the compression costs. Optimum pressure is approximately 5 MPa.

2.5.3. Effect of Space Velocity

Increasing the SV will cause an increase in the gas velocity which promotes mass transfer but decreases the contact time of the reactant species. At a constant SV, CO conversion increases with increasing H₂/CO feed ratio. Increasing the proportion of H₂ in the reactant mixture favors the CO conversion.(Moradi et al., 2008)

Higher space velocity means that the contact will be less hence the reaction time will also decrease which will account for the lower conversion of Syn Gas. The carbon dioxide

coming from water gas shift reaction, higher space velocity will cause lesser yield of CO₂ and higher selectivity of DME.

2.6. Summary

Many catalytic active metals like Cu-Mn-Zn, CuO-ZnO, Cu-ZnO-ZrO₂, CuO-ZnO-Al₂O₃-ZrO₂/HZSM-5, Pd/ZnO/Al₂O₃ are used as catalysts. And many materials like HZSM-5, Alumina silicates, γ -Al₂O₃ are used as the supports giving mechanical strength to the catalyst, in addition to using metals like gallium and zirconium for acting as the promoters for the catalysts for the single step method, the single step method being economically and thermodynamically more favorable. The single step synthesis of DME from Syn Gas is affected by a few reaction parameters like temperature, pressure, the space velocity and the composition of the inlet gas being used.

3. OBJECTIVES

DME is to be synthesized in a single step method from Syn Gas by the use of bi-functional catalyst; the objectives of the investigation are given below.

1. Supported Cu-ZnO catalysts of different compositions were synthesized by wetness impregnation method. The solid acid catalysts such as γ -Al₂O₃, and silica-alumina were be used as methanol dehydration catalysts.
2. The effect of process parameters such as temperature, pressure, space velocity on the conversion of carbon monoxide, hydrogen was studied.
3. All the prepared catalyst were characterized.

4. EXPERIMENTAL

4.1. Material preparation

4.1.1. CZA Catalyst Synthesis

The copper nitrate [Cu(NO₃)₂ .2.5 H₂O] and zinc nitrate [Zn(NO₃)₂ .6 H₂O] was used as precursors for copper and zinc. The copper and zinc nitrate was made to dissolve in incipient volume of water which is equal to the pore volume of the support i.e. The solution was added to the support and mixed thoroughly. The wet material was dried first at room temperature overnight followed by 12 hours at 373 K in a hot air oven. The dried material was calcined in air at 823 K for 6 hours. The final catalyst was designated as xCu_yZnO/ γ -Al₂O₃ or SiO₂-Al₂O₃, where x and y represents the wt% of Cu and ZnO respectively.

4.2. Catalyst Characterization

4.2.1. Powder X-ray diffraction

Powder X-ray diffraction (XRD) measurement was performed on Philips P-analytical X-Pro diffractometer with Cu- $K\alpha$ radiation, with a scan speed of 15/min and a scan range of 4–70 at 40 kV and 40 mA/30mA. A continuous scan mode was used to collect 2θ data from 10° to 90°.

4.2.2. Temperature programmed reduction (TPR)

The test of H₂- temperature programmed reduction was carried out in Micromeritics AutoChem II 2920 chemisorption analyzer with a small quantity of about 0.1 gram used for each test. The sample is first introduced to a stream of inert gas, Argon and heated to 623K for 30 mins. to clean its surface and cooled down to room temperature. A mixture of Hydrogen 5% and Nitrogen 95% then act as the reducing gas at rate of 5K/min/10K/min, heating it to 673K/1073K and the signal was monitored using on-line GC with a thermal conductivity detector.

4.2.3. BET surface area measurement

The N₂ adsorption/desorption studies will be performed on the catalyst at 77K using Micromeritics ASAP 2020 physisorption analyzer. Initially the sample will be degassed under vacuum (5×10^{-6} mmHg) at 423 K for 6 hours. Then N₂ adsorption and desorption will be performed on the degassed sample to get adsorption/desorption isotherms. The surface area will be calculated from the adsorption isotherm data using BET equation in the relative pressure range of 0.05 to 0.3. The volume of adsorbed Nitrogen at relative pressure of 1.0 will be considered as the pore volume of catalyst.

4.2.4. Temperature programmed desorption (TPD)

Acidity measurements will be performed by temperature-programmed desorption of ammonia (NH₃-TPD) with a conventional flow apparatus equipped with a thermal conductivity detector (TCD). 0.1gram of the sample will be taken and pretreated in flowing helium at 773 K for 1 h, cooled to 423 K and then will be exposed to NH₃ (20 ml/min) for 30 min. Samples will be purged with helium at the same temperature for 1 h to remove the physisorbed NH₃. The TPD measurements will be conducted in flowing He (30 ml/min) from 373 to 973 K at a heating rate of 10°C/min.

4.3. Reaction Studies

4.3.1. Description of experimental set-up

The single step conversion of synthesis gas to DME was performed in an isothermally operated fixed bed reactor (Chemito Fixed Bed Micro Reactor). The measured of powder catalysts diluted with quartz beads was loaded in the SS tubular reactor (ID ½ inch). The tubular reactor was placed in tubular furnace. The temperature of catalyst bed was measured by a thermocouple at the top the bed and using a PID temperature controller. The reactant gases, carbon mono oxide and hydrogen was introduced in the reactor from the top their flowrates controlled by a mass flow controller (MFC, Bronkhorst).

The product gases coming out from the reactor was routed to the condenser. The low boiling compounds was condensed and separated out in the gas liquid separator from here the non-condensable gas mixture was sent to the online gas chromatograph (Agilent 490 Micro GC) equipped with TCD detector for analysis.

The gaseous product was analyzed online in gas chromatograph equipped with a thermal conductivity detector (TCD) and having two channels each for analysis of different products. The direct conversion of synthesis gas was performed at different process condition such as reaction temperature, reaction pressure, weight hourly space velocity (WHSV) using a particular synthesis gas composition. The condensed liquid product was collected and analyzed off line in gas chromatograph equipped with Flame Ionization Detector (FID).

4.3.2. Experimental Procedure

The measured amount of powder catalysts diluted with quartz beads was loaded in the SS tubular reactor (ID ½ inch).The valves are thoroughly checked for leakage the power is turned on for the reactor and the chiller. The Mass flow controllers, preheater, furnace heater and temperature controllers are turned on. The temperature of the chiller was maintained at about -5°C.The Mass flow controllers for Hydrogen and CO gas are turned on and increased by a factor 10 ml/min till 40ml/min flowrate is reached this flowrate is continued till the required pressure is reached. The preheater is turned on and the temperature of the preheater is increased by 25°C to the required inlet temperature level and maintained. The furnace heater is turned on and the temperature of the furnace heater is increased by 10°C to the required inlet temperature level and maintained. The flow rate of Hydrogen and CO are changed according to the H₂: CO ratio sent in the reactor. When doing the reaction with Methanol i.e. methanol dehydration reaction, the flowrate of methanol is controlled by using a syringe pump, which is sent in with Nitrogen as the carrier

gas. As the reaction proceeds the liquid product is condensed and is obtained at the bottom which is safely obtained in glass vials. Glass vials are weighed for quantity of liquid obtained and send for chromatographic analysis. The gas products are sent to GC which is connected in-line with the reactor for analysis of products. When the experiment is done the chiller is turned off, the flow rates and temperatures are brought down steadily and the reactor is turned off. The valves for hydrogen and CO are closed tightly to ensure no leakage. Figure 4.2 shows the schematic diagram of the experimental set-up.

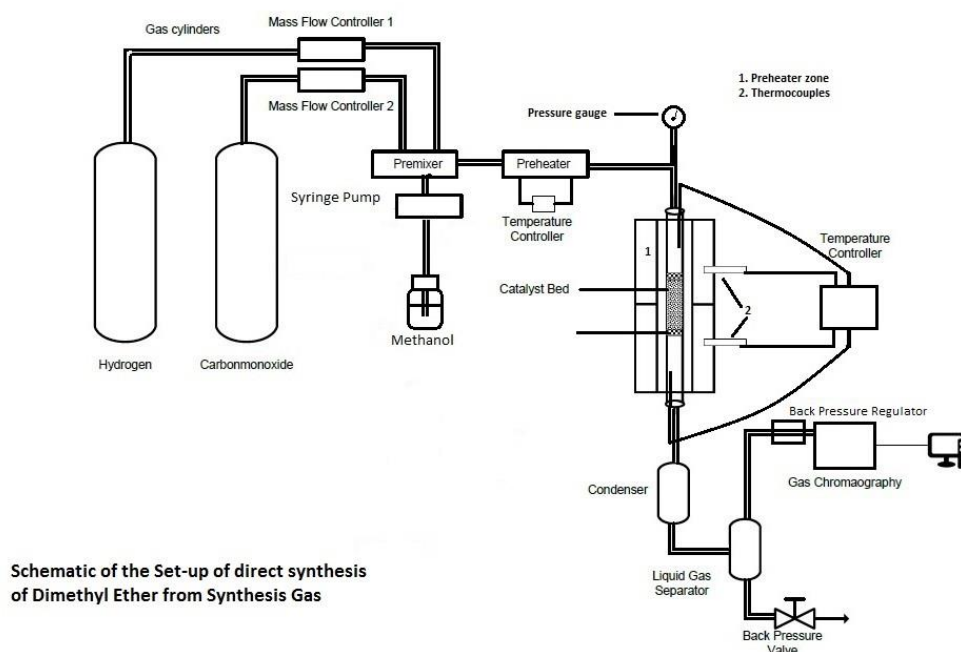


Figure 4.2: Schematic of the set-up

4.3.3. Analysis of Products

The products expected in this reaction are DME, methanol, water and small amounts of N_2 , CO_2 , CO , and hydrocarbons (light olefins). The organic products in the gas phase like DME, methane and other organic compounds like methanol are detected in Channel-1 of Agilent 490 Micro GC equipped with TCD (thermal conductivity detector) using pure Helium as carrier gas. Products like H_2 , N_2 , CO , CO_2 are detected in Channel-2 of Agilent 490 Micro GC equipped with TCD (thermal conductivity detector) using pure Argon as carrier gas. Generally the liquid products are identified by Gas Chromatography-Mass Spectroscopy. The organic products in both the liquid and gas phases like DME, methane

and other organic compounds are also detected in Agilent 7890 GC equipped with FID (flame ionization detector) using pure N₂ as carrier gas.

4.3.4. Calculations

The conversion of CO (X_{CO}) and H₂ (X_{H_2}) is given by the following formulae

$$X_{CO} = \frac{(n_{CO})_0 - n_{CO}}{(n_{CO})_0}$$

Where $(n_{CO})_0$ and n_{CO} will represent the flowrates of CO in the feed and the reactor outlet stream.

$$X_{H_2} = \frac{(n_{H_2})_0 - (n_{H_2})}{(n_{H_2})_0}$$

Where $(n_{H_2})_0$ and n_{H_2} will represent the flowrates of H₂ in the feed and the reactor outlet stream.

Selectivity of DME is determined as the ratio between the content of carbon in the product and sum of carbon content corresponding to all the products formed that are present in the reactor outlet stream

$$S_{DME} = \frac{2 n_{DME} \times 100}{\sum n_{C_i} n_i + 2 n_{DME} + n_M + (n_{CO})_F + (n_{CO_2})_F}$$

Here n_{DME} and n_M are the molar flowrate of DME and methanol in the outlet stream, n_{C_i} are the number of carbon atom for each hydrocarbon and n_i is the molar flowrate of the hydrocarbon.

Where

$$(n_{CO})_F = n_{CO} - (n_{CO})_0$$

$$(n_{CO_2})_F = n_{CO_2} - (n_{CO_2})_0$$

The above values are only considered when they are positive.

Yield of DME (Y_{DME}) is measured as a percentage of carbon atom fed in CO and CO₂ to that converts to DME

$$Y_{DME} = \frac{2n_{DME}}{(n_{CO} + n_{CO_2})_0} \times 100$$

Where $(n_{CO} + n_{CO_2})_0$ is the molar flowrate in the feed stream. (Aguayo, Ereña, Sierra, Olazar, & Bilbao, 2005)

15. RESULTS AND DISCUSSIONS

5.1. Characterization of support and metal catalyst

5.1.1. X-Ray Diffraction Analysis

The XRD patterns of the supported bimetallic catalyst are shown in the Fig. 5.1 and Fig. 5.2

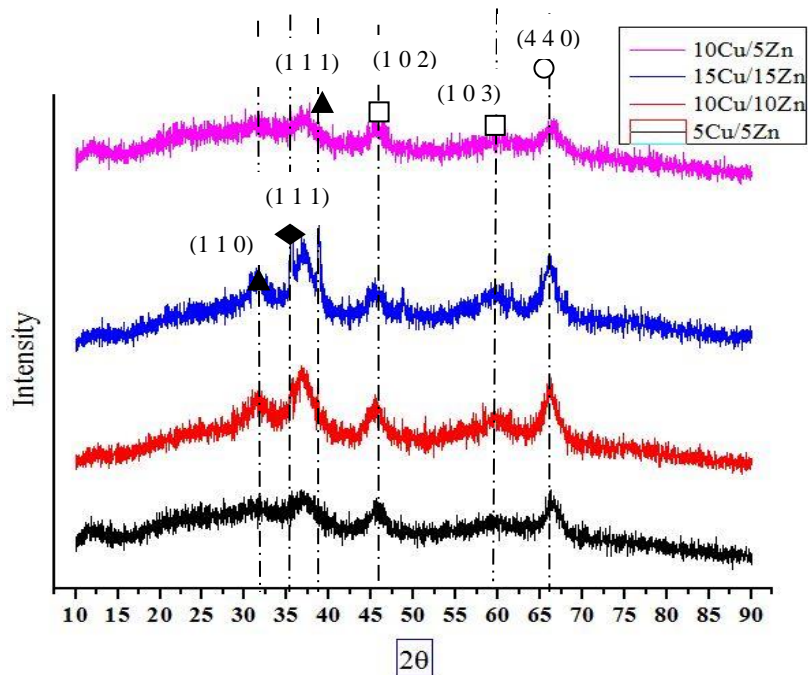


Figure 5.1: XRD patterns of CZA catalysts

▲ = CuO □ = ZnO ○ = γ -Al₂O₃ ◆ = Cu₂O

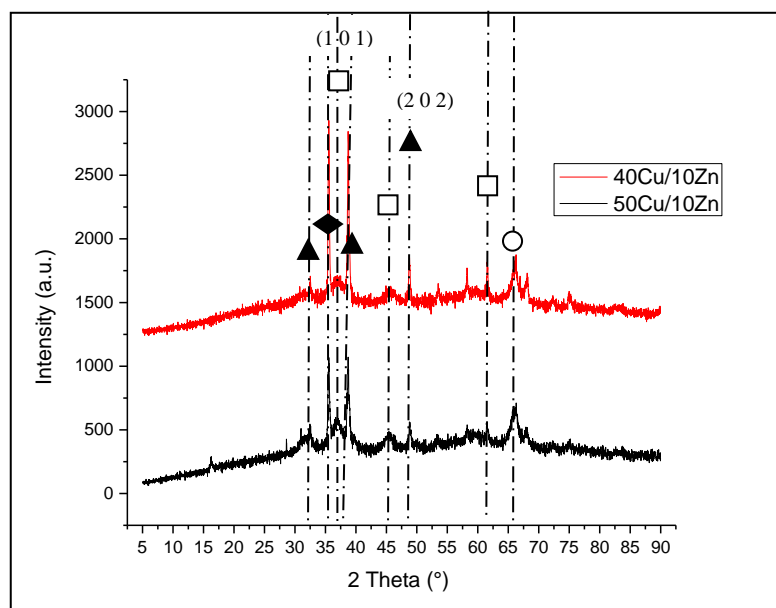


Figure 5.2: XRD patterns of CZA catalysts

The XRD patterns of the supported bimetallic catalyst reveals the peaks at different angles of 2θ . The patterns indicate peaks corresponding to CuO, ZnO as well as γ -Al₂O₃ which was used as the catalyst support. It is observed that the peaks corresponding to CuO and the peak corresponding to ZnO is increasing with the increasing loading of Cu and Zn on the catalyst surface. The peak corresponding to γ -Al₂O₃ is almost unchanged as the content of CuO and ZnO is increased on the surface of the supported bimetallic catalyst.

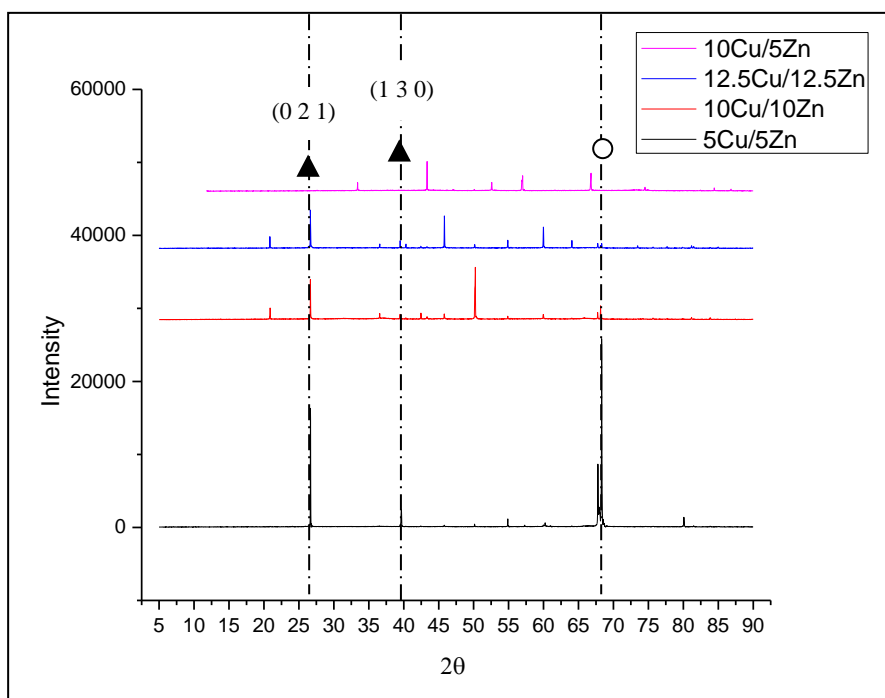


Figure 5.3: XRD patterns of CZA spent catalysts

○ = γ -Al₂O₃ ▲ = Cu (OH)₂

The figure 5.3 shows the spent, deactivated catalyst where no significant peaks are shown for γ -Al₂O₃

5.1.2. Temperature Programmed Reduction

The TPR profiles of the supported bimetallic catalyst is shown in the Fig. 5.3

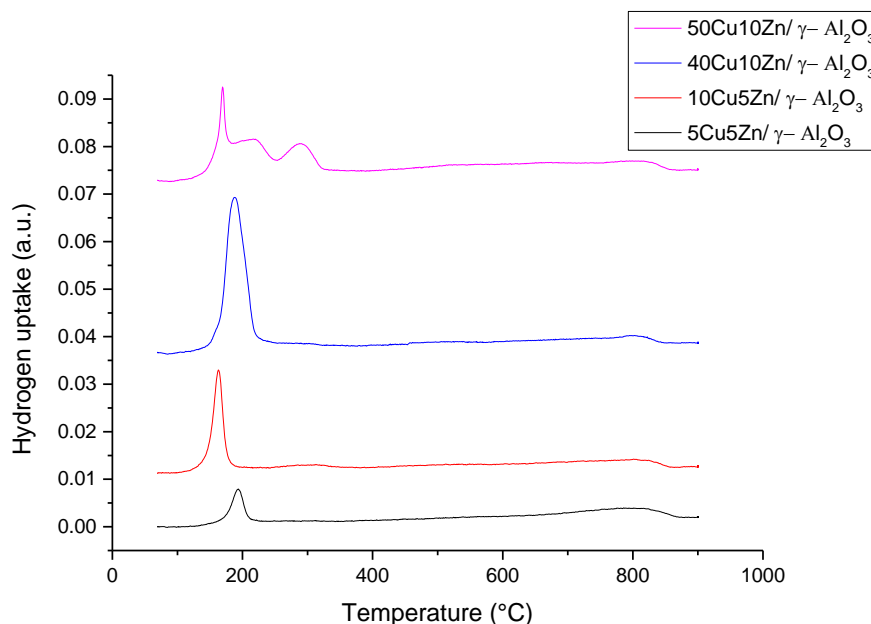


Figure 5.4: TPR profiles of CZA spent catalysts

The TPR patterns indicate the maximum temperature of Hydrogen gas uptake is observed in the range of 150°-200°C. For higher loading of Copper more peaks are observed, this may be due to the formation of CuAl_2O_4 complex which cannot be detected by XRD analysis.

5.1.3. Brunauer-Emmett-Teller Surface Area Analysis

The table below shows the BET Surface Area Analysis of the bimetallic catalysts with different percentage of Copper loading, which also shows the decrease in the BET surface and the Langmuir Surface Area due to the increased metal crystal resulting in extensive pore coverage leading to decrease in both surface area and pore volume. The blockage of pores maybe also due to deposition of copper during wet impregnation method. With increasing copper load the average particle size increases due to particle agglomeration.

Table 5.1: BET Surface Area Analysis

	40Cu10Zn/ γ - Al_2O_3	50Cu10Zn/ γ - Al_2O_3
BET Surface Area (m^2/gm)	120.3024	80.4319
Langmuir Surface Area (m^2/gm)	182.6152	122.7984
Pore Volume (cm^3/gm)	0.464884	0.440853
Avg particle size (nm)	49.8736	74.5973

5.1.4. Temperature Programmed Desorption

The TPD profiles of the supported bimetallic catalyst is shown in the Fig. 5.5

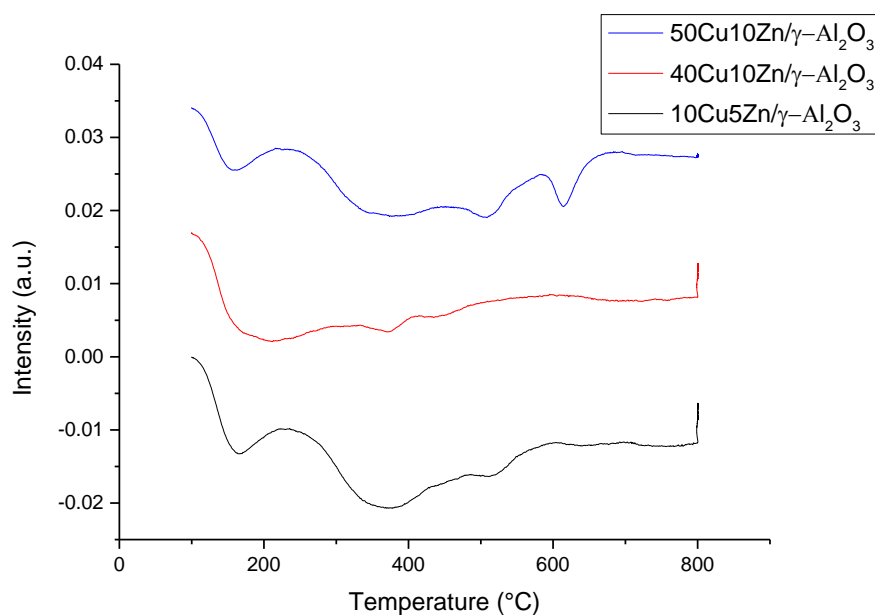


Figure 5.5: TPD profiles of CZA spent catalysts

TPD tells us the nature of acidic sites on the catalyst surface. Pure γ - Al_2O_3 shows a peak at temperature of 172°C indicating moderate acidic sites. With increasing Copper loading a decrease in peak intensity and again increase with higher loading is observed, telling us decrease and increase in acidic sites.

5.2. Effect of process parameters

The Syn Gas to DME single step conversion was studied in a fixed bed reactor over a bimetallic catalyst at a wide range of pressure and temperature conditions. Conversion of CO and Hydrogen was found according to the formulas given in the previous section.

5.2.1. Effect of Temperature

The conversion of Syn Gas to DME was performed at various temperatures with the pressure being constant to study the temperature effect on the reaction. The reaction was performed at temperatures of 200°C , 225°C , 250°C and 275°C respectively with the pressures changing from 25 bar being the lowest to 35 bar pressure which is the highest. In Figure 5.4 at low pressures the conversion showed an increasing conversion with increasing temperature.

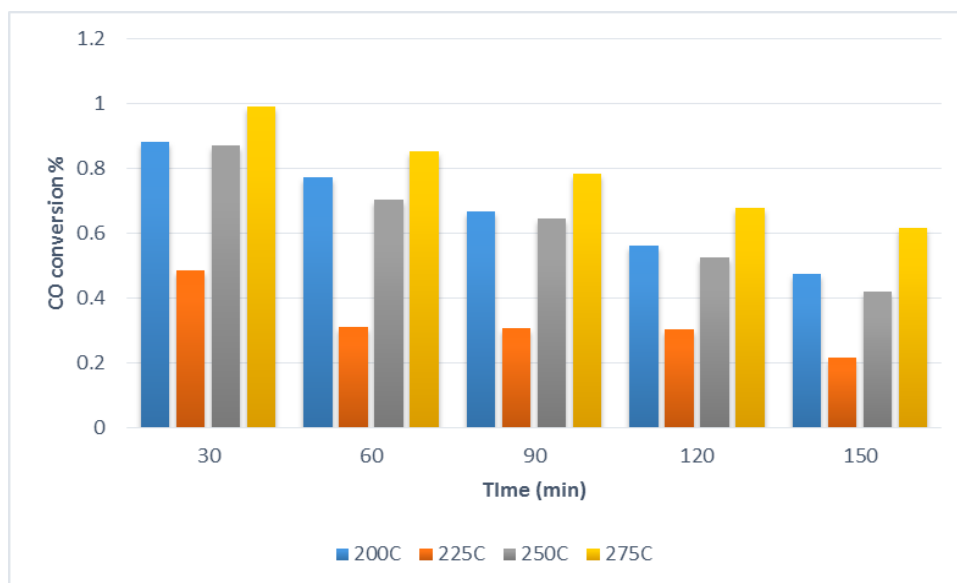


Figure 5.6: CO% conversion vs Time, Reaction conditions: Pressure = 25 bar, Metal loading = 2 gm

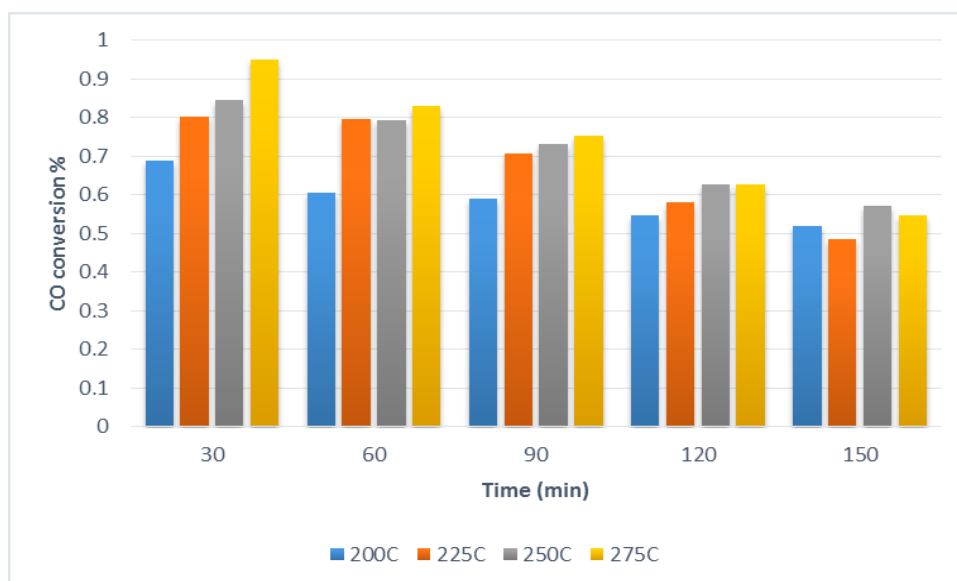


Figure 5.7: CO% conversion vs Time, Reaction conditions: Pressure = 30 bar, Metal loading = 2 gm

As predicted by the literature survey we can observe in Fig. 5.5 that the increase in temperature not favoring the kinetics we observe an decrease in the conversion of CO with an increasing temperature, which steadily decreases as the time progresses which is an accordance with the catalyst deactivation happening over as the time progresses.

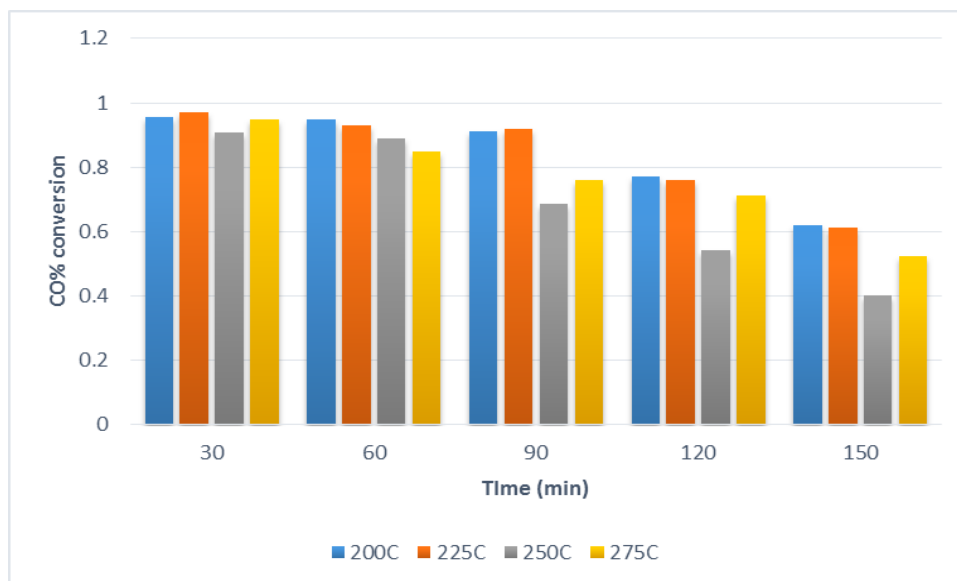


Figure 5.8: CO% conversion vs Time, Reaction conditions: Pressure = 35 bar, Metal loading = 2 gm

We observe in Fig. 5.6 that the increase in temperature accompanies a decrease in the conversion of CO with an increasing temperature.

5.2.2. Effect of Pressure

The conversion of Syn Gas to DME was performed at various pressures with the temperature held constant to study the effect of pressure parameter on the reaction. The reaction was performed at temperatures of 25, 30 and 35 bar respectively with the temperature ranging from 200°C to 275°C.

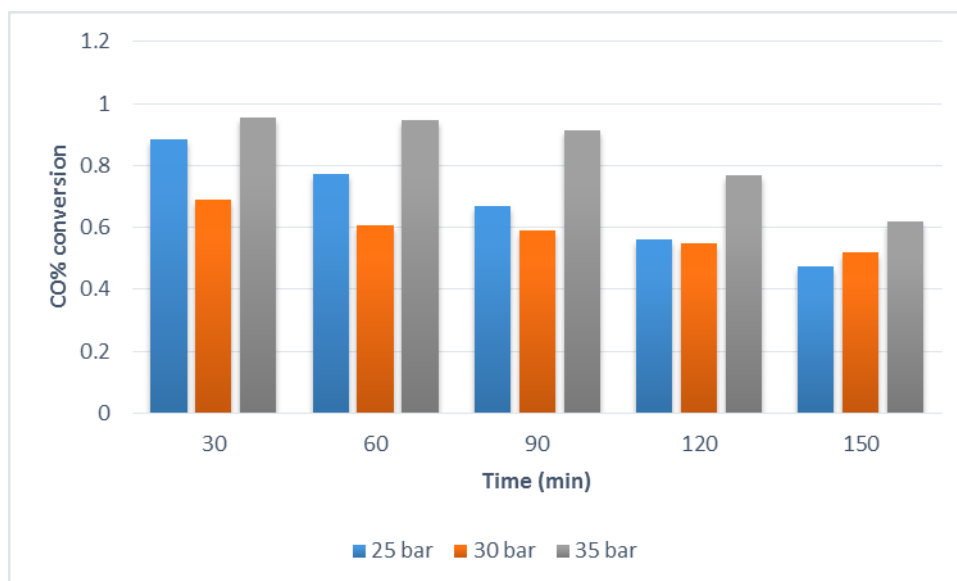


Figure 5.9: CO% conversion vs Time, Reaction conditions: Temperature = 200°C, Metal loading = 2 gm

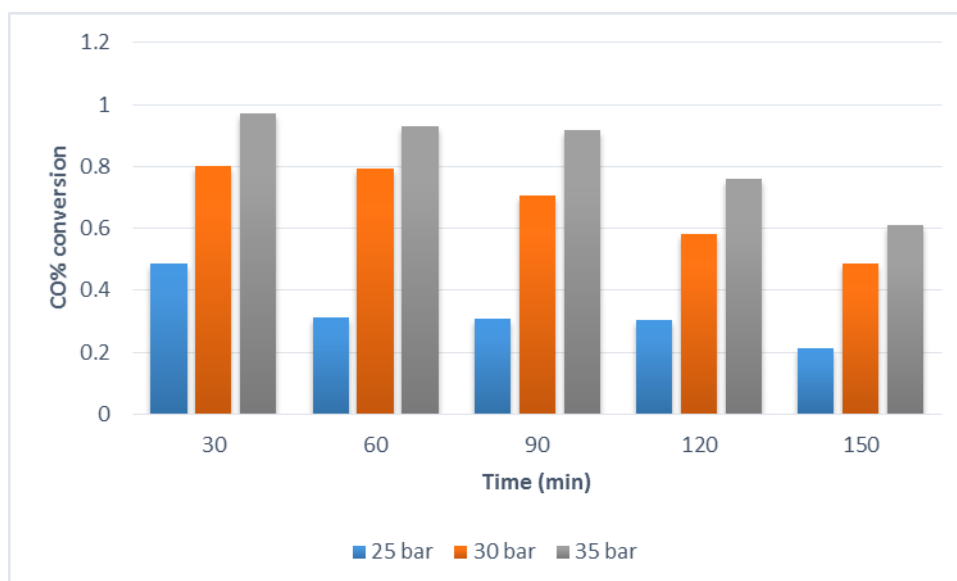


Figure 5.10: CO% conversion vs Time, Reaction conditions: Temperature = 225°C, Metal loading = 2 gm

According to Fig. 5.7 there is no particular trend in increasing pressure at 200°C showing an increase and a decrease respectively, and according to Fig. 5.8 the increasing pressure at 225°C showing a steady increase in the conversion levels of CO, which may be indicating a forward drive towards the methanol formation reaction.

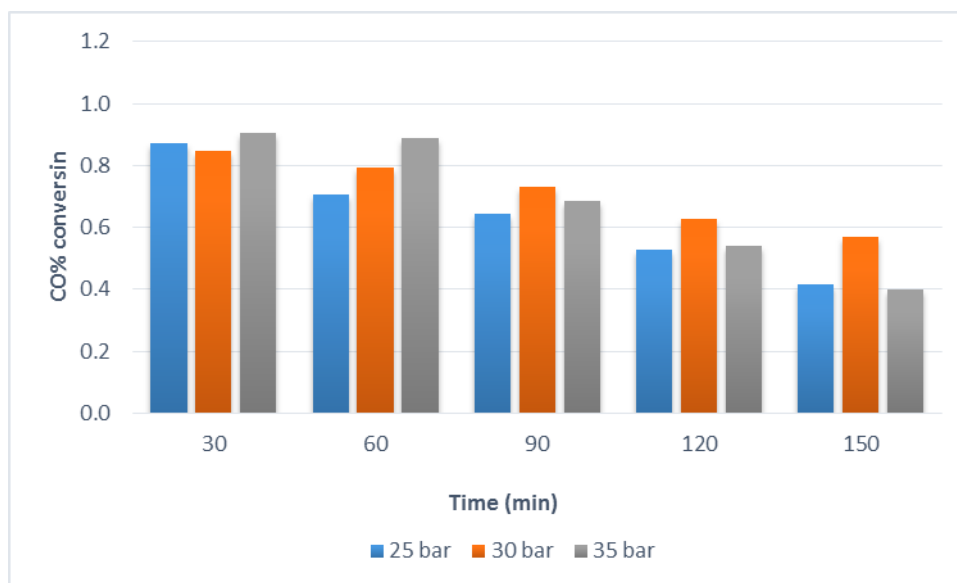


Figure 5.11: CO% conversion vs Time, Reaction conditions: Temperature = 250°C, Metal loading = 2 gm

We observe similar variations at temperatures of 250°C similar to figures 5.8 and 5.9

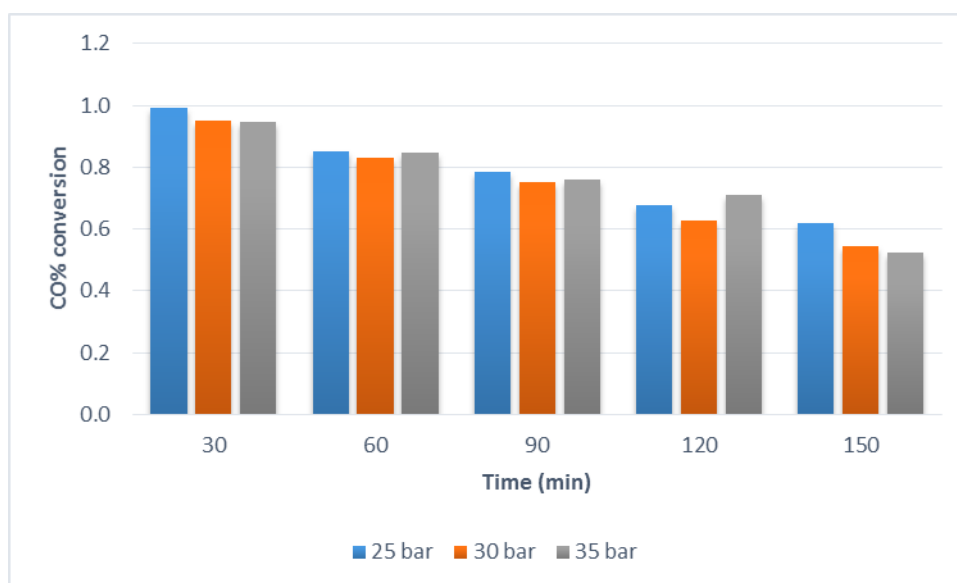


Figure 5.12: CO% conversion vs Time, Reaction conditions: Temperature = 275°C, Metal loading = 2 gm

According to Fig. 5.10 the increasing pressure at 275°C showing a steady decrease in the conversion levels of CO.

Using the above pressure and temperature conditions the reaction parameters were identified at which maximum CO% conversion was achieved and it was observed from the Table 5.1 that the maximum CO conversion was observed at pressure of 225°C and 35 bar pressure which was considered as the optimum conditions favorable for achieving maximum conversion.

Table 5.2: CO% conversion at various reaction conditions

Time	200C 25 bar	200C 30 bar	200C 35 bar	225C 25 bar	225C 30 bar	225C 35 bar	250C 25 bar	250C 30 bar	250C 35 bar	275C 25 bar	275C 30 bar	275C 35 bar
30	0.88	0.69	0.96	0.49	0.80	0.97	0.87	0.85	0.91	0.99	0.95	0.95
60	0.77	0.61	0.95	0.31	0.80	0.93	0.70	0.79	0.89	0.85	0.83	0.85
90	0.67	0.59	0.91	0.31	0.71	0.92	0.65	0.73	0.69	0.78	0.75	0.76
120	0.56	0.55	0.77	0.30	0.58	0.76	0.53	0.63	0.54	0.68	0.63	0.71
150	0.48	0.52	0.62	0.21	0.49	0.61	0.42	0.57	0.40	0.62	0.55	0.52

5.2.3. Effect of Space Velocity

A series of reactions were carried out at different Weight Hourly Space Velocities (WHSV) at 225°C and 35 bar pressure to study the effect of changing WHSV on conversion of CO. It was observed that with an increasing space velocity the conversion levels of CO fell down drastically from 4 hr⁻¹ to 6 hr⁻¹, also no significant changes were observed in the CO% conversion of 3 hr⁻¹ and 4 hr⁻¹. Best CO% conversion was seen at WHSV of 1 hr⁻¹ giving a steady high percentage conversion level above 90% with time.

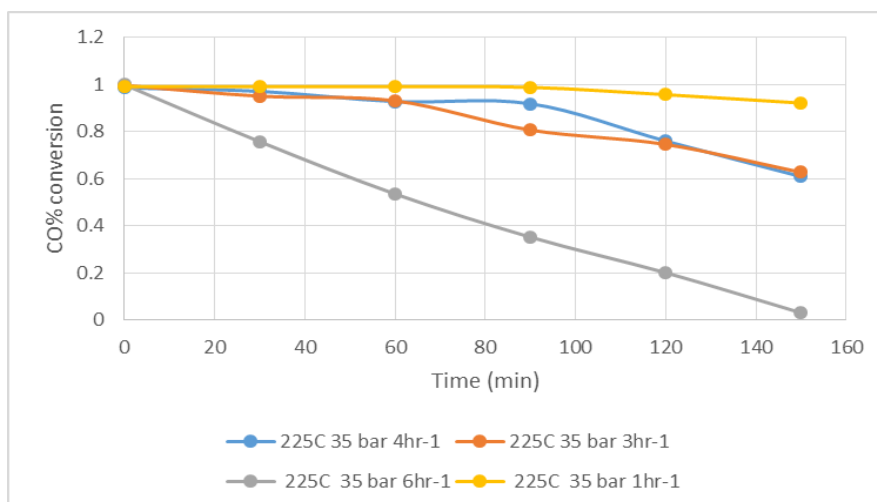


Figure 5.13: CO% conversion vs Time, Reaction conditions: Temperature = 225°C
Pressure = 35 bar, Metal loading = 2 gm

Table 5.3: Effect of WHSV on the CO% conversion

Time	225C 35 bar 4hr-1	225C 35 bar 3hr ⁻¹	225C 35 bar 6hr-1	225C 35 bar 1hr-1
0	0.986293	0.99762	1	0.992065
30	0.972023	0.951311	0.757962	0.992338
60	0.928384	0.931623	0.535987	0.992117
90	0.919472	0.807422	0.35254	0.9889
120	0.760841	0.746374	0.201292	0.957771
150	0.610033	0.62786	0.031095	0.92239

Reaction conditions: Temperature = 225°C Pressure = 35 bar, Metal loading = 2 gm

Also the effect of space velocities was studied during the initial stages studying the methanol dehydration reaction and the effect on conversion percentage of Methanol and selectivity of DME using Silica Alumina as the catalyst with the Si:Al ratio 9:1. Performing the reaction at two different process conditions at 250°C and 270°C, 1bar pressure and with a Nitrogen flow rate of 40 ml/min with varying Methanol flowrates, it was observed in both the cases that with an increase in the WHSV a decrease in conversion is seen from Methanol to DME and also a decrease in selectivity of DME is observed, indicating the lesser time the reactants spend on the catalyst surface and hence a decreasing conversion and selectivity.

Table 5.4: Effect of WHSV on Methanol % conversion and % Selectivity of DME

Methanol flow rate (ml/min)	WHSV (hr ⁻¹)	250°C , 1 bar		270°C , 1 bar	
		Average % conversion of Methanol	% Selectivity of DME	Average % conversion of Methanol	% Selectivity of DME
0.2	3.054	81.29	95.15	84.13	95.89
0.15	2.46	88.75	95.89	92.49	97.29
0.1	1.866	93.88	96.18	96.41	97.40

The figures 5.12 and 5.13 show the % conversion of Methanol with varying WHSV and the % selectivity of DME with varying WHSV

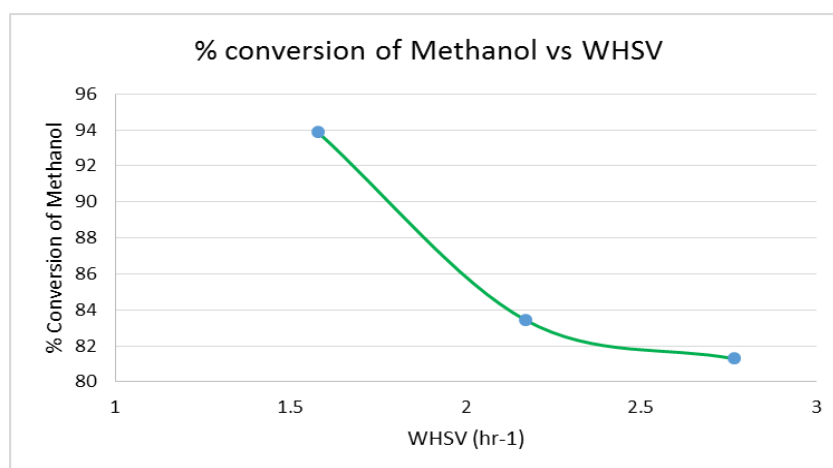


Figure 5.14: Methanol% conversion vs WHSV, Reaction conditions: Temperature = 250°C
Pressure = 1 bar, N₂ flowrate = 40 ml/min

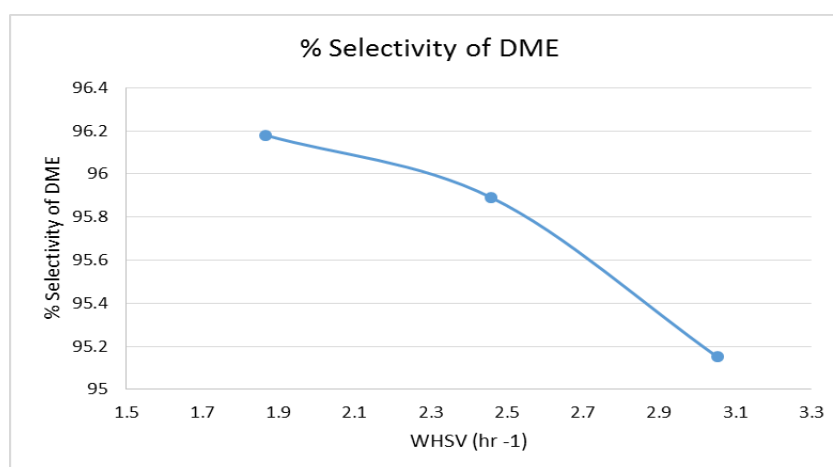


Figure 5.15: DME% selectivity vs WHSV, Reaction conditions: Temperature = 250°C
Pressure = 1 bar, N₂ flowrate = 40 ml/min

With increasing weight hourly space velocity the selectivity of DME and the conversion of Methanol is decreased in both the cases.

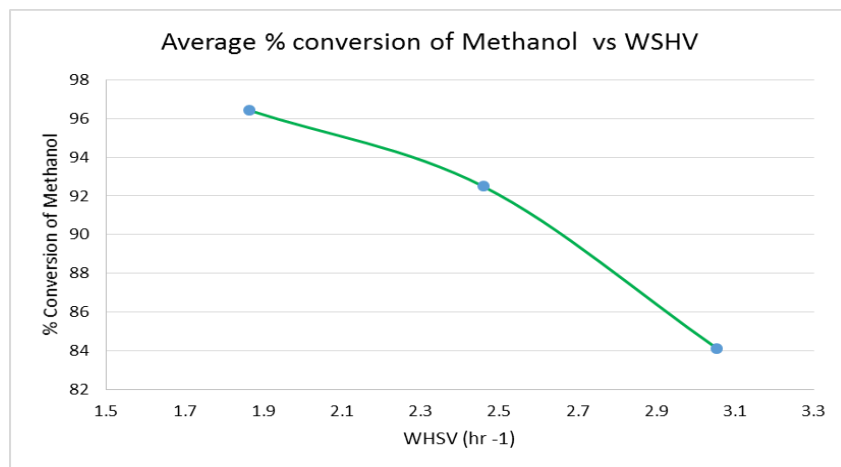


Figure 5.16: Methanol% conversion vs WSHV, Reaction conditions: Temperature = 270°C
Pressure = 1 bar, N₂ flowrate = 40 ml/min

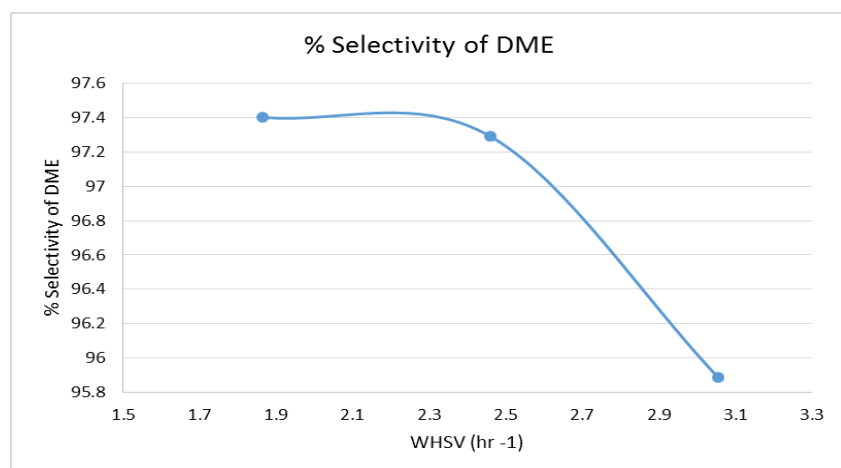


Figure 5.17: DME% selectivity vs WSHV, Reaction conditions: Temperature = 250°C
Pressure = 1 bar, N₂ flowrate = 40 ml/min

5.2.4. Effect of H₂: CO ratio

The effects of changing H₂: CO mole ratio was studied after the identification of ideal process parameters. The 2:1 H₂: CO mole ratio is found in the methanol formation reaction which is the first step for the one step Syn gas to DME synthesis. All the previous reactions were carried out with the same mole ratio and was only changed to 3:1 and 1:1 in two cases to study the CO% conversion with increasing H₂ moles compared to CO as well as equal number of moles as CO. Interestingly it was found that 2:1 H₂: CO mole ratio gave the best results compared to its counterparts.

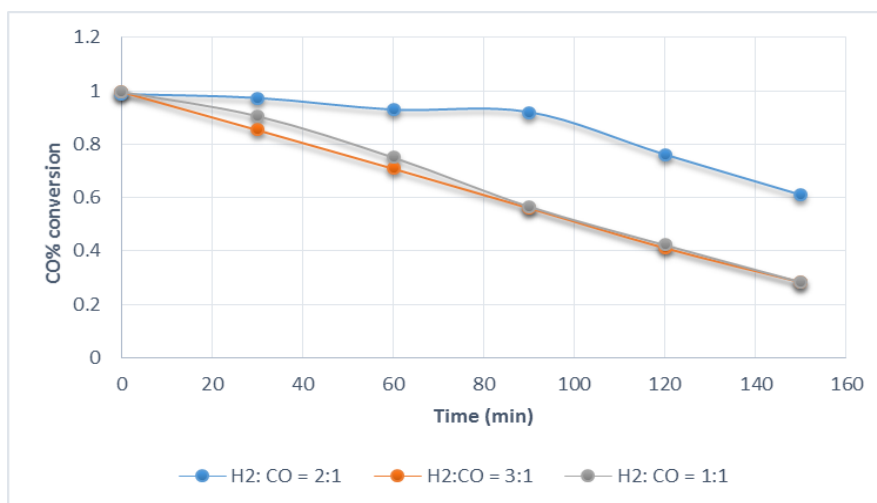


Figure 5.18: CO% conversion vs Time, Reaction conditions: Temperature = 225°C
Pressure = 35 bar, Metal loading = 2 gm

Table 5.5: Effect of H₂: CO ratio on the CO% conversion

Time	H ₂ : CO = 2:1	H ₂ :CO = 3:1	H ₂ : CO = 1:1
0	0.986293	0.997249	0.996135
30	0.972023	0.85433	0.905467
60	0.928384	0.709611	0.750731
90	0.919472	0.562074	0.566664
120	0.760841	0.412257	0.422479
150	0.610033	0.28442	0.283846

Reaction conditions: Temperature = 225°C Pressure = 35 bar, Metal loading = 2 gm

5.2.5. Effect of Metal loading

The figure 5.13 and table 5.3 shows the effect of metal loading of Copper and Zinc on the catalyst surface. It represents that an increase in the metal loading from Cu: Zn from 2:1 to 5:1 will bring an increase followed by a decrease in the conversion of CO. It indicates the excess loading of copper and zinc on the surface of the support which is acting as the methanol dehydration catalyst and hence bringing about a backward reaction where methanol forms carbon monoxide and hydrogen, and hence the conversion levels decrease. The 40Cu10Zn/ γ -Al₂O₃ is identified as the ideal bifunctional catalyst for the STD reaction.

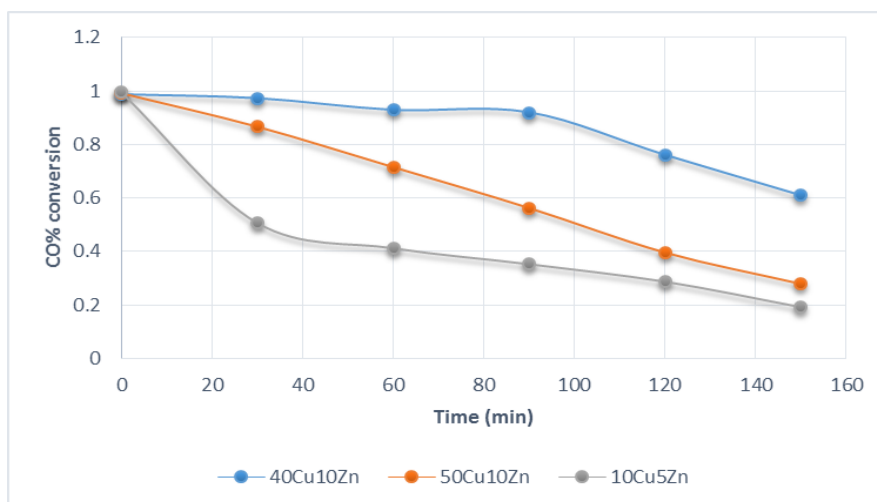


Figure 5.19: CO% conversion vs Time, Reaction conditions: Temperature = 225°C
Pressure = 35 bar

Table 5.6: Effect of Metal loading on the CO% conversion

Time	40Cu10Zn	50Cu10Zn	10Cu5Zn
0	0.986293	0.992608	0.9979
30	0.972023	0.8672	0.508184
60	0.928384	0.715757	0.412919
90	0.919472	0.56268	0.353244
120	0.760841	0.39578	0.288073
150	0.610033	0.278356	0.192663

Reaction conditions: Temperature = 225°C Pressure = 35 bar, Metal loading = 2 gm

6. CONCLUSIONS

The direct synthesis of Dimethyl ether in a single step is very important as we know the innumerable uses and the potential of dimethyl ether as a fuel, a source for other valuable chemicals and its existing use as a propellant. All the above characters of DME enhance its significance when we come to know that DME is environmentally friendly. In the present work the single step synthesis from Synthesis Gas to Dimethyl ether (STD) was carried out employing a bifunctional catalyst in a high pressure fixed bed reactor in the presence of Nitrogen. Copper Zinc Alumina catalyst of different Cu/Zn weight percentage (2:1, 4:1 and 5:1) were synthesized by using γ - Al_2O_3 as the support. The catalyst supported by γ - Al_2O_3

was prepared by using the wetness impregnation method. The STD reactions were carried out under various combinations of temperature and pressure conditions to identify and study the interaction of pressure and temperature in the STD reactions and also to identify the best reaction conditions for carrying out the reaction. The XRD of the catalyst showed the presence of metals Copper and Zinc on the surface of the catalyst. The XRD of the spent catalyst in contrast to the new catalyst showed no peaks of CuO, Cu₂O or ZnO showing the deactivation of catalyst happening over time. The effect of process parameters was studied on the percentage conversion of CO and it was revealed that higher pressures showed higher conversion rates at constant temperatures, with 35 bar pressure showing the best conversion percentage. At low temperatures we noticed that conversion of CO shows an increase with increasing pressure followed by a fall as the pressure rises further. At lower pressure conditions an increase in temperature showed increasing percentage conversion. As the reaction progressed with time a steady decline in the conversion was observed pointing to a deactivation in catalyst happening as the time progresses. The temperature of 225°C and pressure of 35 bar were identified as the best conditions for the STD reaction showing a steady conversion of more than 90% happening over time. The effect of WHSV, Syn Gas composition and metal loading were studied using these reaction conditions as our reference. It was observed that with increasing WHSV the conversion of CO went down since the higher velocity gives lesser time for the H₂ and the CO molecules to react and for the products and in a similar way the results of the initial studies of Methanol to Dimethyl Ether conversion showed that with an increase in the WHSV, we observe a decrease in the conversion of Methanol and the selectivity of DME at different conditions. The 2:1 H₂: CO mole ratio found in the methanol formation reaction which is the first step for the one step STD reaction, gave the best CO percentage conversion. The 40Cu10Zn/ γ -Al₂O₃ is identified as the ideal bifunctional catalyst for the STD reaction.

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8. APPENDIX

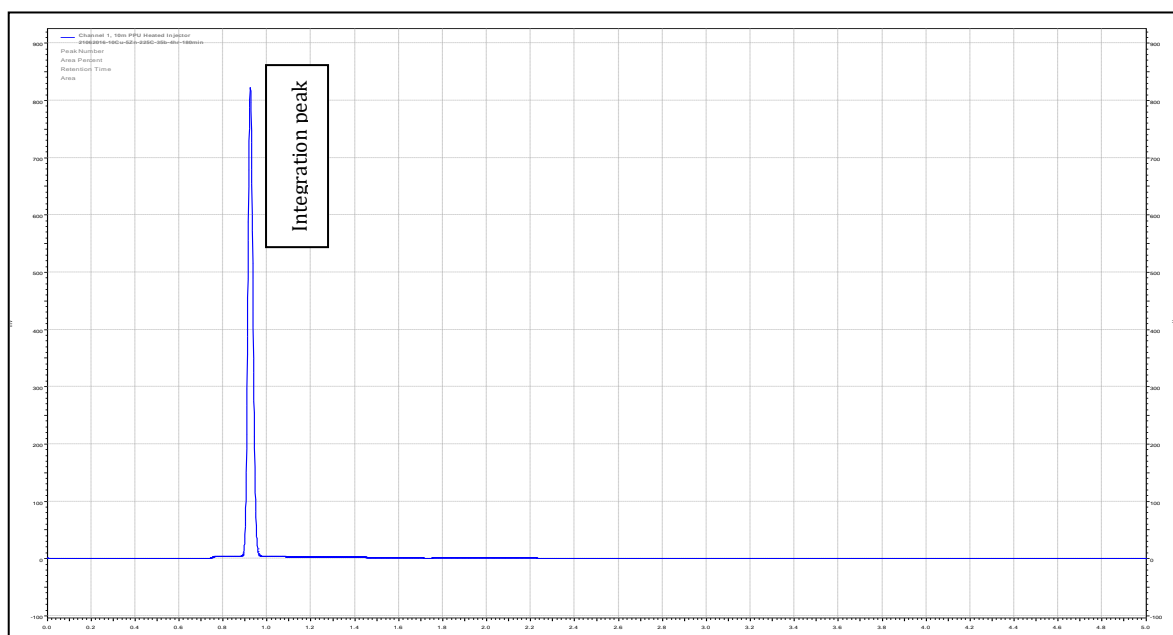


Figure 8.1: Chromatogram observed in Channel-1 of Micro-GC analysis of gas products $40\text{Cu}10\text{Zn}/\gamma\text{-Al}_2\text{O}_3$ catalysts for STD reaction in single step, Reaction Conditions: Pressure = 35 bar, Catalyst = $40\text{Cu}10\text{Zn}/\gamma\text{-Al}_2\text{O}_3$, Metal Loading = 2 gm., Batch Time = 180 min

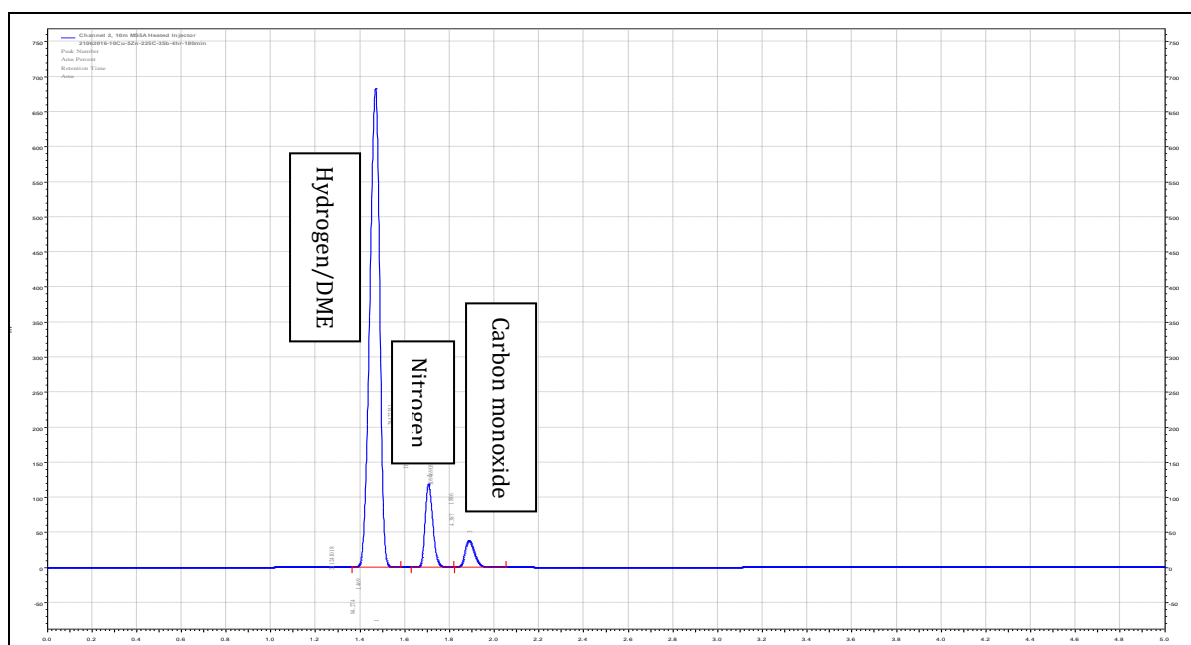


Figure 8.2: Chromatogram observed in Channel-2 of Micro-GC analysis of gas products $40\text{Cu}10\text{Zn}/\gamma\text{-Al}_2\text{O}_3$ catalysts for STD reaction in single step, Reaction Conditions: Pressure = 35 bar, Catalyst = $40\text{Cu}10\text{Zn}/\gamma\text{-Al}_2\text{O}_3$, Metal Loading = 2 gm., Batch Time = 180 min