

Catalytic Conversion of Synthesis gas to Dimethyl Ether over Cu-ZnO/meso-SiO₂-Al₂O₃ Bi-Functional Catalysts

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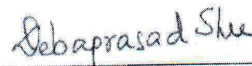
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Dedicated to

My Parents and Teachers

Abstract

Dimethyl ether (DME) is an industrially important intermediate, as well as a promising clean fuel, but the effective production through traditionally consecutive steps from syngas to methanol and then to DME has been hindered by the poorly organized structure of the conventional physical mixture catalyst. Here a Meso structured Silica Alumina support on which the catalyst Cu-ZnO has been impregnated was proposed to accomplish the DME direct synthesis from syngas. The catalysts has been characterized by techniques like BET surface area (N_2 adsorption studies), Temperature programmed Desorption (NH_3 - TPD), Temperature programmed Reduction (H_2 -TPR) and FTIR. Experimental set up and procedure for the synthesis has been discussed. The results obtained in these characterizations has been reported and analyzed.

Nomenclature

DME -Dimethyl Ether

FBR - Fixed Bed Reactor

FBMR - Fixed bed Micro Reactor

MR - Micro Reactor

RDC - Reactive Distillation Column

SR - Slurry Reactor

BR - Batch Reactor

PBR – Packed bed Reactor

$M_{(g)}$ - Methanol in gas phase

$M.S^*$ - Is active intermediate the unique zeolite surface species and adsorbed

$MeOH$, M_m (M.S) and W_n (M.S) - ‘Inactive’ intermediate species (m and n are integer number equal or larger than 1)

W - Water

$D_{(g)}$ - Dimethylether in gas phase

WS - Adsorbed water on free catalyst acidic sites.

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Chapter 1

INTRODUCTION

Fuel is the main source of energy for our daily needs. Burning of fuels gives energy in different forms such as heat and work. Fuels are of various types such as solid fuels like coal and biomass, liquids like petroleum, and gaseous fuels like natural gas, and also atomic energy fuels etc. and were used for generation of energy that can be used for various purposes.

Advances in technology has played a major role in our day to day lifestyle. Now we were able to perform various tasks in much lesser time than the previous times. Similarly the demand for energy was increased considerably .we have been relying on fossil fuel reserves which served as a major energy source since centuries. But the time has come that the fossil fuel reserves were being depleted and at the same time our energy demands kept increasing. Our energy needs are likely to double between 2000 and 2050. The usage of fossil fuels was creating various problems to the environment and was growing day by day. Enormous usage of these fossil fuels led to the release of greenhouse gasses and other harmful gasses. These situations has forced to lookout for alternative sources of energy which has potential to serve our daily energy requirements. Thus researches had lead us to focus on the biofuels which has potential to serve our needs and to preserve the environment. The CO₂ evolved during utilization of biofuels was consumed by the plants for photosynthesis and do not cause any environmental pollution and greenhouse effect. Limited energy reserves, economic crisis and environmental pressures on CO₂ emissions due to consumption of fossil fuel were the obstacles to realizing economic growth. Hydrocarbons and industrial chemicals can be derived from synthesis gas, which is obtained from coal, natural gas and biomass [Mbuyi et al., 2012]. The properties of biofuel is that it should be reliable, affordable and clean energy supplier. Biomass has the potential to be the replacement as a fuel in future. Biofuels, chemicals, hydrogen, and electricity etc. were produced in a reliable and attractive way from synthesis gas (syngas) that is obtained through biomass [Richardson et al., 2012].

Necessary properties of our biomass feed stock after processing as an energy source were, moisture content (intrinsic and extrinsic), calorific value, proportions of fixed carbon and volatiles, ash/residue content, alkali metal content, cellulose/lignin ratio. Synthesis gas obtained from biomass was used as a feed stock [McKendry et al., 2001]. There were number of process for synthesis of methanol, fuels, hydrocarbon products, and oxygenates from synthesis gas. Recently, the synthesis of dimethyl ether (DME) has been focused by the researchers due to its potential as a future fuel [Kang et al. 2008].

Dimethyl ether (DME) has certain properties like it is the simplest of ethers, it is not toxic, and is weakly narcotic, but a colorless gas and highly inflammable gas at standard conditions of temperature and pressure. It can be liquefied by a slight increase in pressure, and its properties were almost similar to those of liquefied petrol gas (LPG). The interest in DME has been increasing due to its wide ranges of applications. DME can be produced from various resources like coal, natural gas, or biomass(Stiefel et al. 2011)

Dimethyl ether (DME) is a useful chemical intermediate in the production of many important chemicals such as dimethyl sulfate, methyl acetate, and light olefins. DME corresponds to a substitute for LPG, refrigerants. DME can be used as an aerosol propellant because of its environment friendly properties unlike the chlorofluorocarbons (CFCs) that deteriorate the ozone layer. The newer R-134a (HFC-134a) has an added advantage over the traditional chlorofluorocarbon (CFCs, Freon), DME and fluoro-dimethyl ether were used as a green refrigerant and ecofriendly aerosol spray and because of their, zero Ozone Depletion Potential (ODP) and lower Globe Warming Potential (GWP). DME has recently been proven as a clean alternative fuel for diesel engines and has very low NO_x emission (contains oxygenated compounds), almost zero smoke production, and less noise in engines when compared to the conventional diesel fuels. (Khandan et al., 2008).

Main advantages of DME were, it has high cetane number, low boiling point and oxygen content. Similarly its disadvantage was its low combustion enthalpy and calorific value. Dimethyl ether was used in industries as an atomizing agent of spray cans, raw material in methyl acetate production and lower olefins. (Qingjie et al., 1998).

Some of the properties of DME and diesel fuel are listed below in Table 1 and 2.

Table 1: Properties of DME and diesel fuel [Park et al.,2013]

Fuel property	Unit	DME (dimethyl ether)	Diesel
Chemical structure		CH ₃ -O-CH ₃	-
Molar mass	g/mol	46	170
Carbon content	mass %	52.2	86
Hydrogen content	mass %	13	14
Oxygen content	mass %	34.8	0
Carbon-to-hydrogen ratio		0.337	0.516
Critical temperature	K	400	708
Critical pressure	MPa	5.37	3.00
Critical density	Kg/m ³	259	-

Liquid density	Kg/m ³	667	831
Cetane number		>55	40-50
Auto-ignition temperature	K	508	523
Stoichiometric air/fuelmass ratio		9	14.6
Boiling point at 1 atm	K	248.1	450-643
Lower heating value	MJ/kg	27.6	42.5
Modulus of elasticity	N/m ²	6.37E ⁰⁸	14.86E ⁰⁸
Kinematic viscosity of liquid	cSt	<0.1	3
Surface tension	N/m	0.012	0.027
Vapour pressure	kPa	530	<<10
Flammability range	(vol%)		
Lower limit		0.6	3.4
Upper limit		6.5	2.8

Table 2: Characteristics of DME and LPG (n-butane) fuels [Seokhwan et al., 2009].

Specifications	DME	LPG (n-Butane)
Chemical structure	(CH ₃) ₂ O	C ₄ H ₁₀
Liquid density (kg/m ³)	667	579
Molecular weight (g/mol)	46.07	58.12
Stoichiometric A/F	9.00	15.46
Vapor pressure (kPa)	539	210
Boiling point (°C)	- 25.0	0.5
Heat of vaporization (kJ/kg)	467	358
Cetane number	55–60	–
LHV (MJ/kg)	28.80	45.72

DME synthesis development is already at an advanced stage and production is feasible on industrial scale. There is still a large area to research and improve and to optimize STD technology [Stiefel et al., 2011].

Synthesis of DME from synthesis gas:

The major raw material for DME synthesis was synthesis gas which in turn was produced from biomass. There are several ways for the production of synthesis gas. Here we were concerned in producing synthesis gas from biomass through gasification. The composition of synthesis gas at the outlet of the gasifier is usually maintained ranging from (CO: H₂) 1:2 to 2:1. Studies mentioned the composition 1:1 has been proven optimum for DME production [Li et al., 2009].

The synthesis gas obtained from the gasifier is cleaned and refined according to the feed requirements in the synthesis of DME. The clean gas is fed to the fixed bed reactor where the catalyst was packed inside along with some inert material in a bed.

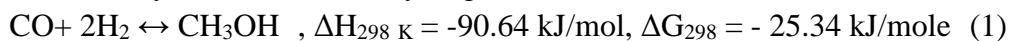
Particularly two major methods have been practiced in the synthesis of dimethyl ether from synthesis gas. They are Two-step method and single-step DME synthesis (STD). Presently, DME is synthesized commercially by the two step method of dehydration of methanol and methanol is produced from syngas. The two step method includes the synthesis of methanol and the dehydration of methanol in two separate reactors. This involves huge number of upstream and downstream processes which include to the overall cost. So in order to make the entire process economical researchers have developed the new single step DME synthesis method which carries out both the methanol synthesis and dehydration in the same reactor. This method reduces the overall cost of DME synthesis by reducing the installation and operation costs. Also DME synthesis when carried out in STD process have advantages over equilibrium effects. Methanol formation rate in STD process is greater than the methanol formation in a methanol synthesis reactor as the methanol formed is simultaneously consumed by the methanol dehydration reaction, which keeps the product concentration far from equilibrium and induces a strong driving force for the forward reaction towards formation of products like methanol and mainly DME. Mechanism of the overall process tells us the integration of CO hydrogenation sites and methanol dehydration sites, and the structure of the bi functional catalysts are of great importance for this process. [Nie et al. 2012]

The major issues in handling this process are preparation of suitable, resistant, and stable bi functional catalyst that can convert the incoming synthesis gas into DME with high conversions of CO and good selectivity to DME. Being cost effective is not the only criteria that needed to be focused, but the total conversions and the time taken for synthesis along with the safety to plant and people also must be taken into account.

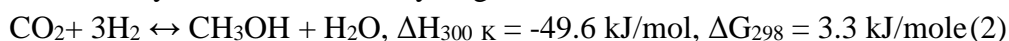
Dimethyl ether synthesis reactions: Kinetic Studies [Z. Chen et al. 2010].

The main reactions in DME synthesis process should be considered as follows:

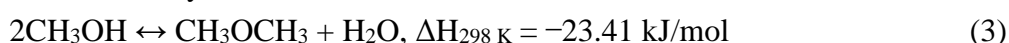
Methanol synthesis from CO hydrogenation:



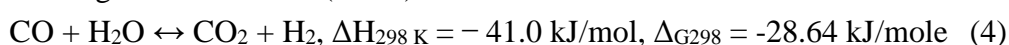
Methanol synthesis from CO₂ hydrogenation:



Methanol dehydration to DME:



Water gas shift reaction (WGS):



Direct synthesis of DME from CO hydrogenation:

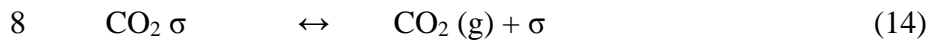
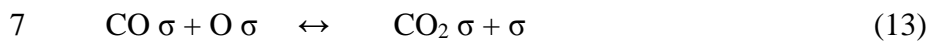
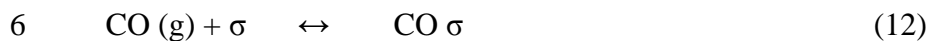
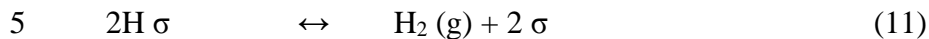
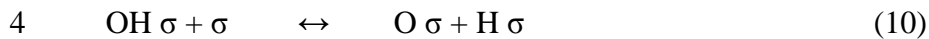
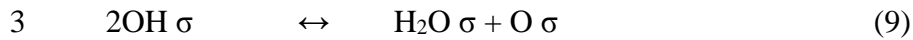
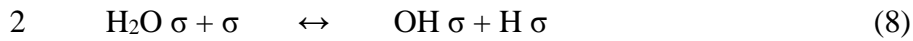
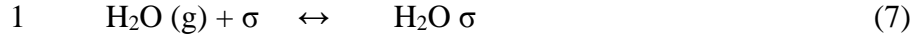


And direct synthesis of DME from CO₂ hydrogenation:



Methanol synthesis Mechanism

Elementary steps in methanol synthesis [M. Peter et al., 2012], [Askgard et al., 1995].



σ - Surface site, and adsorbed species x is symbolized by x σ , respectively.

Methanol Dehydration mechanism:



Where

$\text{M}_{(g)}$ - Methanol in gas phase

M.S^* - Is active intermediate the unique zeolite surface species and adsorbed

MeOH , $\text{M}_m \text{ (M.S)}$ and $\text{W}_n \text{ (M.S)}$ - 'Inactive' intermediate species (m and n are integer number equal or larger than 1),

W - Water,

$\text{D}_{(g)}$ - Dimethylether in gas phase

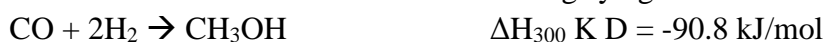
WS - Adsorbed water on free catalyst acidic sites.

1.1. Two step DME process

This two-step method of synthesizing DME is oldest way of production as it involves more investment and operational costs. This method as the name suggests have two processes one is methanol synthesis followed by methanol dehydration.

Methanol is currently produced on an industrial scale exclusively by catalytic conversion of the synthetic gas ($H_2 + CO$). Methanol synthesis is usually done by fisher-tropsch synthesis (FTS). Synthesis Processes are classified according to the operating pressure such as low pressure process operated between 5 to 10 MPa, the medium-pressure process operated between 10 to 25 MPa and the high pressure process operated between 25 to 30 MPa. Methanol production of 1 ton requires, $2.52 * 10^3 m^3$ of synthesis gas (70% H_2 , 21% CO , and 7% CO_2) [Demirbas et al., 2007].

Main reactions of Methanol formation using syn gas are:



The methanol synthesis catalysts Copper and zinc are the key components of the process. The low pressure process uses Copper-zinc catalysts and needs completely sulphur-free gas ($H_2S < 1 \text{ mL/m}^3$). Sulphide ion causes catalyst poison for this low pressure process. Medium- and high-pressure processes uses catalysts (ZnO and Cr_2O_3 activated with chromic acid) can accept 30 mL/m^3 of H_2S . Methanol Production by the high-pressure process with ZnO and Cr_2O_3 catalysts was less economical. Catalysts containing copper that have better activity and good selectivity were used [Demirbas et al., 2007]. Fisher-Tropsh Synthesis (FTS) process was carried out in ways such as high temperature and low temperature Fisher-Tropsh, depending on the products required. High temperature Fisher-Tropsh (HTFT) process operates at a temperature ranges of 573-623 K, and pressures ranging from 20-40 bar in a fluidized bed reactor in the presence of iron based catalyst and yields products like liquid hydrocarbons ranging (C1-C15), olefins and oxygenates. Low temperature Fisher-Tropsh (LTFT) operates at a temperature ranges of 473-513 K, and pressures ranging from 20-45 bar in a fluidized bed reactor in presence of catalysts based on iron and cobalt for paraffin's and linear long-chain hydrocarbon waxes synthesis. Hence methanol is produced by HTFT in a fluidized bed reactor [Andrei et al., 2007].

Once methanol is prepared then the next step was to dehydrate the methanol by using any acid catalysts by methanol to dimethyl ether (MTD) process. Typical acid catalysts that were used are $\gamma\text{-Al}_2\text{O}_3$, zeolites (mostly H-ZSM 5). Pure, and vaporized methanol is fed to a fixed-bed catalytic reactor, where the dehydration reaction takes place. The catalyst was loaded in the fixed bed reactor and methanol vapours are passed along the catalyst at a temperature ranging from 310-350 $^{\circ}C$ and atmospheric pressure. The outlet of this process contains DME, H_2O and unreacted methanol. DME was separated from Water and methanol by distillation and was purified [Royae et al., 2008].

1.2. Single step DME synthesis or synthesis gas to DME (STD) process

Because of the enormous uses and advantages of DME it is required to produce DME in an economical, reliable and better process than the two step synthesis. Many Researchers have explored different ways to synthesize DME. DME synthesis by single step STD process was more economical than the conventional two- step process, which was carried out in two different reactors. The STD process consists of a single fixed bed reactor in which catalyst was packed and feed gas (synthesis gas) was fed to the catalyst bed normally at a temperatures of 200- 260 °C and pressures ranging from 20- 40 bar. Various reactions take place in the reactor which includes the methanol synthesis, methanol dehydration, water gas shift reaction (WGSR). In order to run the STD process economically all these reactions should be provided with their respective catalysts and required reaction conditions. Catalyst is the major component that decides the rate of our reaction. Each of the reactions require a different catalysts to yield desired products. Methanol synthesis needs a metal catalyst whereas the methanol dehydration needs an acid catalyst. So we need to consider a bi functional catalyst that has the ability to catalyze both the reactions. Typically used bi- functional catalysts are CuO- ZnO/ γ -Al₂O₃, Cu- ZnO/ HZSM-5, Cu-ZnO/ Zr modified zeolites etc [[Kang et al., 2008](#)].

There are various bi functional catalysts that are used in the DME synthesis. They are classified into two categories, hybrid catalysts which are prepared by mechanical mixing of separately synthesized methanol synthesis and dehydration catalysts usually by grinding or milling methods and, composite catalysts where the methanol synthesis and dehydration catalysts coexist as single entity. These are generally prepared by co precipitation, wet impregnation or by mixing the precursors to make bi functional catalyst [[Naik et al., 2008](#)].

Chapter 2

LITERATURE REVIEW

Dimethyl ether (DME) has become the future hope as a promising fuel to our existing engines. Hence the researches continued to make the synthesis more economical and productive. Interesting things learnt in the research held till now are the major role in DME production is played by the catalyst and the type of reactor. Qi et al. [Qi et al., 2001] studied the activities of Cu deposited on γ -Al₂O₃ and found that the dispersion of Cu catalyst is low. Dispersion of CuO can be increased greatly by the addition of manganese oxide MnO₂ to CuO catalyst. Dispersion is increased because of the synergic interactions between Cu-O-Mn. [Kim et al., 2006] conducted several experiments and characterisation tests on both acetate and nitrate based precursors of Cu-ZnO catalysts on γ -Al₂O₃ and concluded that acetate based precursor have smaller particle sizes and larger surface areas. [Koizumi et al., 2004] studied the effects of deactivation of catalyst due to the presence of sulphur (as SO₂, H₂S etc.) in the synthesis gas feed. The Fe catalyst has good activity towards both methanol synthesis and also towards water gas shift reaction. But the drawback of the Fe catalyst is that it is highly deactivated by sulphur poisoning. So in order to overcome that effect MnO was added to the Fe catalyst which makes the size of Fe⁰ particles look bigger. As the sulphur is likely to react with small particles we have a fair chance of avoiding the sulphur deactivation.

Jianli et al. [Jianli et al., 2005] explored the ability of a micro channel reactor in the synthesis of DME. It has been observed that the reaction rates are consistent for a considerable time compared to the conventional fixed bed reactor, in which the catalyst deactivation rate is noticeable. Micro channel reactor has better DME selectivity due to improved mass and heat transfer and hot spots were eliminated which makes the catalyst unstable. Bulk diffusion length was reduced, back-mixing was minimized and accessibility was increased from the gas phase to the catalyst surface and resulted in better mass transfer and higher space time yield. Micro channel reactor usage leads to 3 times higher space time yield than commercially achieved space time yield, which shows strong process intensification potential for commercial application. Study of Khandan et al. [Khandan et al., 2009] tells us that the activity towards the dehydration is more rapid in case of zeolites, and among all H-Mordenite is highly active in dehydration of methanol. Al₂O₃ has been dispersed on H-Mordenite to increase the surface area of H-Mordenite and to decrease the acidity. Thus the optimum catalyst for DME synthesis was found to be Al-modified H-Mordenite zeolites containing 8 % wt of Al₂O₃ and was tested. Mbuyi et al. [Mbuyi et al., 2012] proposed a gold based catalyst Au/ZnO/ γ -Al₂O₃, that can be used at higher temperatures of about 340-460 °C and pressure of 50 bar, which improves the rates of

reactions without any deactivation of catalyst improving the life of the catalyst. The gold composite catalyst was mainly selective toward DME, Methanol and CH₄, and to C₂ - C₅ hydrocarbons. Kang et al. [Kang et al., 2008] tells us that the catalyst Cu–ZnO–Al₂O₃ on Zr- modified zeolites are prepared by the co precipitation of methanol synthesis catalysts on a good combination shows the presence of Cu sites that were easily reducible and has higher number of acid sites of required strength. Similar type of combination is present in CZA–FER catalyst showing well-dispersed Cu–ZnO–Al₂O₃ component and good acidity on Zr-modified zeolite.

Preparation of various catalyst and their effects and operating conditions of reactors have been studied and were listed in Table 6.

FBR - Fixed Bed Reactor
FBMR - Fixed bed Micro Reactor
MR - Micro Reactor
RDC - Reactive Distillation Column
SR - Slurry Reactor
BR - Batch Reactor
PBR - Packed bed Reactor

Table 3

Sno	Catalysts	Supports	Preparation Methods	Reactor	Conditions	Reference
1	CuMn _x / γ -Al ₂ O ₃	γ -Al ₂ O ₃	Wet impregnation	FBMR	T= 493-573 K, P=20 bars, GHSV= 1800 h ⁻¹	Qi et al., 2001
2	Cu-ZnO/ γ -Al ₂ O ₃	γ -Al ₂ O ₃	Co precipitation	FBR	T= 516-563 K, P=50.66 bars,	Kim et al., 2006
3	Cu/ZnO/ZrO ₂ / Al ₂ O ₃ - SiO ₂ Catalyst	Al ₂ O ₃ / SiO ₂	-	loop reactor	T= 493-573 K, P=70-80 bars, GHSV= 10500 h ⁻¹	Pontzen et al., 2011
4	1. Fe-MnO/SiO ₂ 2. Ca/Pd/SiO ₂	γ - Al ₂ O ₃ (γ - Al ₂ O ₃ modified with 1 wt% silica)	Co precipitation	-	1)T= 573 K, P=51 bars, WHSV= 0.6 h ⁻¹ 2)T= 746 K, P=20 bars, WHSV= 0.06 h ⁻¹	Koizumi et al., 2004
5	F518-PPT ,ZSM-5 (Si/Al ratio of 30) and(F- Al ₂ O ₃)	F- Al ₂ O ₃ Acidic Al ₂ O ₃ containing 4 wt % fluoride	-	Micro channel reactor	T= 493-593 K, P=20-50 bars, GHSV= 10600 h ⁻¹	Jianli et al., 2005
6	Cu-ZnO-Al ₂ O ₃ / Zr-modified zeolites	Zr-modified zeolites	conventional wet-impregnation and co-precipitation methods	Tubular FBR	T= 523 K, P=40 bars, SV= 5500ml gcat ⁻¹ h ⁻¹	Kang et al., 2008.

7	Cu-Zn-Al-M / γ - Al_2O_3 (M= Ga, La, Y, Zr)	γ - Al_2O_3	co-precipitation method	FBR	T= 523-553 K, P=41.36 bars, GHSV= 6000- 12,000 h ⁻¹	Venugopal et al., 2009.
8	CuZnAl / HZSM-5	HZSM-5 zeolite	Co-precipitation	FBR	T= 533K, P=40 bars, SV= 1700 ml gcat ⁻¹ h ⁻¹	Andres et al., 2012.
9	CuO/ZnO/ZrO ₂ /H ZSM-5 with different ZrO ₂	(γ -alumina or zeolites)	Co-precipitation sedimentation method	FBR	T= 573K, P=1.013 bar	Kunpeng et al., 2003
10	xCu-yMn / γ - Al_2O_3	γ - Al_2O_3	conventional impregnation method	High pressure MR	T= 493-573 K, P=40 bars, GHSV= 1800 h ⁻¹	Gong et al., 2001
11	CuO- ZnO/ Na-ZSM-5 and H-ZSM-5	Na-ZSM-5 and H-ZSM-5	-	High Pressure FBR	T= 523-553K, P=42 bars, SV= 6000 ml gcat ⁻¹ h ⁻¹	Kim et al., 2004
12	CuO-ZnO- Al_2O_3 / NaHZSM-5	NaHZSM-5	Co-precipitation	Three phase slurry reactor	T= 923K, P=100 bar	Javier et al., 2005
13	Cu-ZnO- Al_2O_3 /Zr-ferrierite	Zr-ferrierite	Co- precipitation-impregnation method	-	T=523 K, P=40 bars, GHSV= 5500 L gcat ⁻¹ h ⁻¹	Jong et al., 2001

14	Cu–Zn–Al slurry catalyst/ γ -Al ₂ O ₃	γ -Al ₂ O ₃	Modified sol–emulsion–gel method	SR	T=553 K, P=40 bars	Jinchuan et al., 2010
15	Cu-ZnO-Al ₂ O ₃ / γ -Al ₂ O ₃	γ -Al ₂ O ₃	Co-precipitation	SR	T=523 K, P=30.39 bars	Kim et al., 2001
16	(FT-K or FT-Ru),+ (Cu/ZnO/Al ₂ O ₃) / zeolite	zeolite	Co-precipitation	Tubular FBR	T=504 K, P=34.442 bars, GHSV= 900 h ⁻¹	Zonetti et al., 2010
17	Cu/ZnO/ Al ₂ O ₃ / SAPO catalysts	SAPO SAPO-5 and -11	Mechanical mixing	High Pressure FBR	T=533 K, P=42 bars, GHSV= 6000-24000 ml gcat ⁻¹ h ⁻¹	Yoo et al., 2007
18	Metal Oxalate salts + γ -Al ₂ O ₃	Glass Beads	Oxalate Ethanol Method	Temperature Gradient Reactor	T=498-550 K, P=10-50 bars	Omata et al., 2002
19	series of Pd-modified CuO–ZnO– Al ₂ O ₃ –ZrO ₂ / HZSM-5	HZSM-5	Co-precipitation sedimentation method	FBR	T=573 K, P=1.013 bars	Kunpeng et al. 2004
20	Cu- Zn- Al- Mn / γ -Al ₂ O ₃	γ -Al ₂ O ₃	impregnation method	SR	T=533 K, P=50 bars	Yisheng et al., 2005
21	(CuO/ZnO/ Al ₂ O ₃)	γ -Al ₂ O ₃	Co-precipitation	FBR	-	Song et al., 2008
22	Cu-Zn-Al(Scx) (x denotes the Si/Al ratio)	γ - Al ₂ O ₃	Liquid phase method	SR	T=553 K, P=40 bars	Z. Li et al., 2011
23	Cu –Zn-(Al/Cr/Zr)	γ - Al ₂ O ₃ (or)zeolite		FBR	T=523 K	L. Wang et al., 2006
24	Cu-Mn-Zn	(Fe-, Co-,	Co-precipitation	High pressure MR	T=518 K, P=20 bars,	Jinhua et al., 2006

		Ni-, Cr-, or Zr-modified) HY zeolite			GHSV= 1500 h ⁻¹	
25	Cu-Zno-ZrO ₂	γ - Al ₂ O ₃	Co-precipitation sedimentation method	FBR	T=483 K, P=30 bars, GHSV= 1500 h ⁻¹	Jia et al., 2002
26	Cr/ZnO with H-ZSM-5	Cr/ZnO Bi-metal	Dual-Layer Method	Stainless Steel FBR	-	Yang et al., 2011
27	CuO- ZnO- Al ₂ O ₃ / Al-MCM-41	Al-MCM-41	Evaporation-Induced Self-Assembly (EISA) Process	Tubular FBR	T=533 K, P=50.67 bars, GHSV= 2000 ml gcat ⁻¹ h ⁻¹	Naik et al., 2010
28	Cu- ZnO/ γ - Al ₂ O ₃ + HZSM-5/MnAPO-11	γ - Al ₂ O ₃ + HZSM-5/MnAPO-11	Sol-gel	FBR	T=553 K, P=20 bars, GHSV= 1000h-1	Jian Li et al. 2010
29	Cu/ZnO/ Al ₂ O ₃ / Phosphate γ - Al ₂ O ₃	Phosphate γ - Al ₂ O ₃	Co-precipitation	Tubular FBR	T=523 K, P=50 bars, GHSV= 8400h ⁻¹	Montesano et al., 2012
30	CuO-ZnO / H-ZSM-5(CZ/H(x)-M)	H-ZSM-5(CZ/H(x)-M)	Traditional Mixing	FBR	T=493-553 K, P=20 bars, GHSV= 7500 ml gcat ⁻¹ h ⁻¹	Nie et al., 2012
31	Cu- ZnO- Al ₂ O ₃ / γ - Al ₂ O ₃	γ - Al ₂ O ₃	Co-precipitation	FBR	T=723K, P=100 bars,	Stiefel et al., 2011
32	Cu-ZnO- Al ₂ O ₃ CZA/ ZrFER(X)	Zr-ferrierite catalyst(CZA/Zr FER(X)	Co-precipitation and deposition	Tubular FBR	T=523 K, P=50 bars,	(Jung et al., 2012)

					GHSV= 4000 ml gcat ⁻¹ h ⁻¹	
34	La ₂ O ₃ modified Cu-ZrO ₂	γ- Al ₂ O ₃ (x-CLZ-A)	Co-precipitation	FBR	-	(Z. Li et al., 2012)
35	CuO-ZnO-Al ₂ O ₃ /γ- Al ₂ O ₃ -HZSM-5	γ- Al ₂ O ₃ -HZSM-5	Co- precipitation sedimentation method	FBR	-	(Zhu et al., 2010)
36	Cu- Zn- Al / γ- Al ₂ O ₃	γ-Al ₂ O ₃	-	RDC	P=10.13 bars	(Suszwalak et al., 2012)
37	CuZnAl slurry catalyst/ γ-Al ₂ O ₃	γ-Al ₂ O ₃	Liquid-phase technology	SR	T=563K, P=40 bars, GHSV= 250 ml gcat ⁻¹ h ⁻¹	(Zhihua et al., 2009)
38	CNTs intercrossed Cu/Zn/Al/Zr catalyst / γ- Al ₂ O ₃	γ- Al ₂ O ₃	Co-precipitation	FBR	T=513K, P=40 bars, GHSV= 6000 ml gcat ⁻¹ h ⁻¹	(Q. Zhang et al., 2010)
39	(x% Ni/CNTs) promoted Ni-Mo-K / γ- Al ₂ O ₃	γ- Al ₂ O ₃	Combined co precipitation impregnation method	Continuous Flow FBR	T=761-841 K, P=20-80 bars,	(Ma et al., 2010)
40	Nb ₂ O ₅ - Al ₂ O ₃ / γ- Al ₂ O ₃	γ- Al ₂ O ₃	Incipient wetness impregnation	BR	T=523K, P=1.01 bars	(Rocha et al., 2012)
41	Cu / γ- Al ₂ O ₃	γ- Al ₂ O ₃	Evaporation induced self-assembly procedure	FBR	T=553-598 K, P=50 bars,	(Jiang et al., 2012)
42	Cu-ZnO- Al ₂ O ₃ / ZSM5	ZSM5	Co-precipitation	FBR	T=473-553 K, GHSV= 15000 ml gcat ⁻¹ h ⁻¹	(W.H. Chen et al., 2012)
43	CuO/ZnO/ Al ₂ O ₃	γ - Al ₂ O ₃	Co-precipitation	dual-type reactor	-	(Vakili et al., 2012)

44	CuO–ZnO/ Mesoporous boria–alumina composite	Mesoporous boria–alumina composite	Evaporation- Induced Self- Assembly (EISA) Process	Vertical FBR	T=623K,	(Xiu et al., 2011)
45	CuZnAl slurry catalyst / AlOOH	AlOOH	liquid-phase technology	continuou s SR	T=523-563 K, P=1.013 bar.	(L. Liu et al., 2012)
46	CuO–ZnO– Al ₂ O ₃ + γ -Al ₂ O ₃	γ -Al ₂ O ₃	-	micro PBR	T=513K, GHSV= 9000 ml gcat ⁻¹ h ⁻¹	(Hayer et al., 2011)
47	Cu–Zn–Al/ ZSM- 5	ZSM-5	-	FBR	T=523-553 K,	(X. Ma et al., 2013)
48	6CuO–3ZnO– Al ₂ O ₃ / γ -Al ₂ O ₃	γ -Al ₂ O ₃	conventional precipitation method	FBR & SR	T=533K, P=50 bars, GHSV= 3000 ml gcat ⁻¹ h ⁻¹	(Naik et al. 2011)
49	Cu-ZnO- Al ₂ O ₃ / Zr-ferrierite	Zr-ferrierite	Co-precipitation impregnation method	FBR	T=523K, P=40 bars, GHSV= 5500 ml gcat ⁻¹ h ⁻¹	(Bae et al. 2009)
50	Cu/Zn/Al/ HZSM- 5	HZSM-5	-	FBR	T=533K, P=43 bars, GHSV= 650- 2200 ml gcat ⁻¹ h ⁻¹	(Y. Li et al. 2009)
51	Au- ZnO/ γ -Al ₂ O ₃	γ -Al ₂ O ₃	Physical mixing	-	T=653-673 K, P=35 bars,	(Mbuyi et al. 2012)

2.1. Summary of Literature Review:

DME synthesis is monitored by factors like catalyst, reactor and the conditions of the reaction. Various synthesis catalysts of dimethyl ether were prepared and were effective in DME synthesis. Methanol synthesis catalyst that were used are Cu, CuO, Cu- Zn, CuO- ZnO [Pontzen et al., 2011, Koizumi et al., 2004, Jianli et al., 2005, Kan et al., 2008], Cu- ZnO- ZrO₂, Fe- MnO, Ca- Pd, Cu-Zn-Al-M (Ga, La, Y, Zr)[Jinchuan et al., 2010, Kungpeng et al., 2004], Cu- Mn, Pd- modified CuO- ZnO- Al₂O₃, CuO- ZnO- Al₂O₃- ZrO₂[Zhihong Li et al., 2011], Cu- Zn- Al- Mn, Cr-ZnO, zirconium-ferrite, Ni-Mo-K [Yang et al., 2011, Jung et al., 2012] etc. Various dehydration catalysts used are γ -Al₂O₃, SiO₂- Al₂O₃ [Bae et al. 2009], F- Al₂O₃, Zolites like ZSM 5, H-ZSM 5 [Yang et al., 2011], Na- H- ZSM 5, Zr modified zeolites, SAPO catalysts (silica allumino phosphate).

2.2. Synthesis of catalyst Materials

Various methods used in preparation of catalyst are incipient wet impregnation, co-precipitation, co- precipitation-sedimentation, co- precipitation- impregnation [Kungpeng et al., 2004], sol- gel method, modified sol- gel method [Jinchuan et al., 2010], modified sol- emulsion- gel method, oxalate ethanol method, liquid phase method, dual layer method [Koizumi et al., 2004], direct mixing method, mixing of precursors method, co- precipitation- deposition, , EISA(evaporation induced self-assembly) etc[Koizumi et al., 2004, Kan et al., 2008, Kungpeng et al., 2004, Pontzen et al., 2011, Zhihong Li et al., 2011, Jianli et al., 2005, Yang et al., 2011, Jung et al., 2012 Jinchuan et al., 2010,].

2.3. Types of catalyst

Certain types of catalysts are available and can be synthesized by the above mentioned methods. These are some of the various catalysts types

Metal – Metal catalyst: Cu – Zn, Ca – Pd, Cu – Mn,

Metal – Metal oxide catalyst: Cr-ZnO

Metal oxide – Metal oxide catalyst: CuO- ZnO

Composite catalysts:

CuO- ZnO- Al₂O₃;

Cu- Zn- Al- Mn;

CuO- ZnO- Al₂O₃- ZrO₂;

Cu-Zn-Al-M (Ga, La, Y, Zr)

Various reactors used in this process studied in are fixed bed reactor, loop reactor, micro channel reactor, fixed bed micro reactor, three phase slurry reactor, temperature gradient reactor, slurry reactor, batch reactor, dual type reactor, micro packed bed

reactor etc. The reaction is usually operated in a temperature ranges of 200-350 °c, and at a pressure ranges of 20- 40 bar.

2.4. Effect of catalyst

Main factors that influence the methanol synthesis catalyst activity are particle size, composition of catalyst, support surface area, and metallic surface area. Active sites correspond to the copper atoms in contact with the crystallites [Y.Zhang et al., 1997]. The active center in copper/zinc oxide combination was the Cu⁺ species in the zinc oxide lattice. Zinc oxide creates active sites such as Cu⁺-O-Zn in these Cu/ZnO-based catalysts.

The main factors that suppress catalyst activity are large Cu Particle size, weak interaction between the Cu-ZnO, viscosity of the precursor solution, surface tension of the solvent used for making precursor solution.

2.5. Effect of support

1. More number of lewis acid sites leads to improvement in the selectivity and conversion to DME. Bronsted acid sites leads to the formation of higher alcohols and aldehydes.
2. γ -Al₂O₃ is less acidic compared to zeolites and has a low activity at lower temperatures. Another major drawback of the support is it absorbs and retains water formed in the reaction which ultimately leads to deactivation of catalyst.
3. More Si/Al ratio for zeolites indicates more acidic nature for the zeolite. Strength of acid sites increases and at very high Si/Al ratio ratios the sites become very strong and further dehydrate the products to other unwanted higher alkenes. Hence conversion and selectivity are reduced.
4. Zeolites with H and NH₄ cations are much more active than those with Na-form without causing any decrease in the DME selectivity. This is attributed to the acidic properties of hydrogen and ammonium cations. As the acidity increases the dehydration rate also increases. The order of acidity is as follows NH₄⁺ > H⁺ > Na⁺

Table 4

Properties of the studied Supports [N.Khandan et al., 2008]

Zeolite /code	Si/Al ratio (%)	Cation form	Surface area (m ² /g)	Conversion (%)	Selectivity		
					DME	HCs	
ZSM-5	Z1	23	NH ₄	425	94.7	54.	43.8
	Z2	30	H	400	92.5	51.3	46.5
	Z3	50	NH ₄	425	93.8	46.3	51.2
	Z4	280	NH ₄	400	92.4	20.8	76.7
Y	Y1	5.1	Na	900	81.9	9.8	87.2
	Y2	5.1	H	730	93.3	48.1	49.8
	Y3	80	H	700	91.2	30.2	67.6
Mordenite	NaM	13	Na	425	85.6	61.7	36.2
	HM	90	H	500	96.4	68.2	29.8
Ferrierite	F1	20	NH ₄	400	92.8	26.2	71.5
	F2	55	NH ₄	400	91.3	21.1	76.6
Beta	B1	25	NH ₄	880	94.5	31.5	66.1
	B2	150	H	850	89.8	20.5	77.0
SiO ₂	–	–	–	250	82.3	21.3	77.3
γ -Al ₂ O ₃	–	–	–	290	87.5	25.6	72.1

2.6. Kinetic studies:

2.6.1. Kinetic modelling [Zheng Li et al., 2011]

a) Methanol synthesis

basic methanol synthesis reactions were



Here are simple kinetic models that represent the methanol synthesis models.

$$r_{\text{CO}} = \frac{k_1 f_{\text{CO}} f_{\text{H}_2}^2 (1 - \beta_1)}{(1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{CO}_2} f_{\text{CO}_2} + K_{\text{H}_2} f_{\text{H}_2})^3}$$

$$r_{CO_2} = \frac{k_2 f_{CO} f_{H_2}^3 (1 - \beta_2)}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2} + K_{H_2} f_{H_2})^4}$$

Where

$$\beta_1 = \frac{f_M}{K_{f_1} f_{CO} f_{H_2}^2}$$

$$\beta_2 = \frac{f_M f_{H_2O}}{K_{f_2} f_{CO} f_{H_2}^3}$$

Where r denotes reaction rates, f denotes fugacities of respective compounds, T denotes absolute temperature, and R denotes the ideal gas constant.

b) DME synthesis

Synthesis of DME from syngas was represented by these 3 reactions:



Reaction rates of these reactions are obtained from Brown and Fenduto (1992), as follows:

Methanol synthesis reaction

$$r_{CH_3OH} = k_1 f_{CO}^{\frac{1}{3}} f_{H_2}^{\frac{2}{3}} \left(1 - \frac{f_{CH_3OH}}{K_{eq1} f_{CO} f_{H_2}^2}\right)$$

Methanol dehydration reaction

$$r_{DME} = k_2 f_{CH_3OH}^n \left(1 - \frac{f_{DME} f_{H_2O}}{K_{eq2} f_{CH_3OH}^2}\right)$$

Water-gas shift reaction, i.e., reaction

$$r_{wg} = k_3 f_{CO} f_{H_2O} \left(1 - \frac{f_{CO_2} f_{H_2}}{K_{eq3} f_{CO} f_{H_2O}}\right)$$

K₁: rate constant of reaction 28

K₂: rate constant of reaction 29

K₃: rate constant of reaction 30

K_{eq1} , K_{eq2} , K_{eq3} were equilibrium constants of the respective reactions.

Where r denotes reaction rates, f denotes fugacities of respective compounds, T denotes absolute temperature, and R denotes the ideal gas constant.

2.7. Thermodynamic studies:

DME synthesis from syngas is a highly exothermic process from thermodynamic point of view. The reactions cause temperature rise in the traditional tubular fixed-bed reactor. The catalyst is deactivated due to the runaway of temperature inside the reactor and due to the water present in the products stream. Looking into thermodynamic aspects of the process it is seen that the methanol synthesis reaction is an endothermic reaction and methanol dehydration reaction is an exothermic reaction. Direct synthesis of DME from syngas is a highly exothermic process. Increase of temperature leads to the decline of equilibrium conversion of CO. According to reaction thermodynamics increase in temperature favours the methanol formation but not dimethyl ether. But as the temperatures increases the kinetic rate constants increases and hence reaction kinetically controlled. When the reaction temperature was further increased, the thermodynamic influence was greater than the kinetic influence [Z. Chen et al. 2010]. So in order to overcome the thermodynamic effects the reaction should be held at moderate temperatures 200-260 °C. That is done with the help of proper catalysts that reduce the activation barrier for the reaction to occur at low temperatures. Energy can be saved significantly in thermodynamically controlled equilibrium reactions either by improving the activity of catalysts and by modifying the process for better conversions in the reactor [Sofianos et al., 1991].

Chapter 3

OBJECTIVE

DME production has become a major challenge accounting to its economic concerns. So there is always a fair chance of research for various catalysts that can be prepared to increase the productivity of DME, along with selectivity of DME and methanol. Currently DME is produced by two step method which has many drawbacks, and single step method using several catalysts which has certain pros and cons. This thesis was targeted on the single step dimethyl ether synthesis by using a catalyst copper zinc alumina supported by silica alumina, in a fixed bed reactor. The catalyst was characterized and is checked for desired properties. The products obtained are analyzed for confirmation.

Objectives are:

1. Synthesis of mesoporous $\text{SiO}_2\text{-Al}_2\text{O}_3$ by EISA method.
2. Synthesis of $\text{Cu-ZnO/meso-SiO}_2\text{-Al}_2\text{O}_3$ by co impregnation method.
3. Characterization of synthesized catalyst by BET, TPR, TPD, FTIR.
4. Comparison of catalyst activity for $\text{Cu-ZnO/ } \gamma\text{-Al}_2\text{O}_3$ and $\text{Cu-ZnO/meso-SiO}_2\text{-Al}_2\text{O}_3$.
5. Synthesis of DME from synthesis gas in a fixed bed reactor, and to study the effect of various parameters on selectivity of methanol and DME

Chapter 4

Experimental

4.1 Chemicals

- Alip - Aluminum Isopropoxide
- TEOS – Tetra Ethyl Ortho Silicate
- HNO₃ – Nitric acid (67-70 wt %)
- Ethanol (98 % wt)
- Copper Nitrate Tri Hydrate (Cu (NO₃)₂·3H₂O)
- Zinc Nitrate Hexa Hydrate (Zn (NO₃)₂·6H₂O)

All chemicals purchased from Sigma Aldrich.

4.2 Bi functional catalyst Preparation

4.2.1. Synthesis of Silica-Alumina. [Morris et al., 2008]

2.0 g of (EO)₂₀(PO)₇₀(EO)₂₀ triblock copolymer (Pluronic P123) was dissolved in 20.0 mL of 99.5+% anhydrous ethanol, and was agitated for 4 h. 20 mmol of aluminum isopropoxide (Alip) (98+%) was dissolved in 3.2 mL of nitric acid (68-70 wt %) and 10.0 mL of anhydrous ethanol and was stirred for 5 hours to hydrolyze the aluminum isopropoxide. Calculated amount of tetraethyl orthosilicate (TEOS) (98+%) was dissolved in sufficient amount of nitric acid (68-70 wt %) and 10.0 mL of anhydrous ethanol and was stirred for 8 hours to hydrolyze the tetraethyl orthosilicate. After the salts are dissolved, the two solutions were mixed together and 10.0 mL of anhydrous ethanol was used to cleanly transfer the aluminum isopropoxide and tetraethyl orthosilicate solution. The combined solution was stirred for 5 h. Solvent was evaporated in an oven evaporation will be performed at 60 °C for 48 h in air in a petri dish. The resulting samples were calcined at 550 °C in a furnace with a heating rate of 1 °C/min and was held at the final temperature of 550 °C for 6 h. All calcinations will be performed in flowing air.

Calculations:

a) $\text{SiO}_2:\text{Al}_2\text{O}_3 = 2:1$

Solution 1: (4g P₁₂₃ + 40 ml Ethanol)

Solution 2: (4.085g Alip + 3.2 ml HNO₃ + 10 ml Ethanol)

Solution 3: (4.17g TEOS + 4.21 ml HNO₃ + 10 ml Ethanol)

b) $\text{SiO}_2:\text{Al}_2\text{O}_3 = 1:1$

Solution 1: (3g P₁₂₃ + 30 ml Ethanol)

Solution 2: (4.085g Alip + 3.2 ml HNO₃ + 10ml Ethanol)

Solution 3: (2.085g TEOS + 2.105 ml HNO₃ + 5 ml Ethanol)

c) $\text{SiO}_2:\text{Al}_2\text{O}_3 = 1:2$

Solution 1: (2.5g P_{123} + 25 ml Ethanol)

Solution 2: (4.085g Alip + 3.2 ml HNO_3 + 12.5 ml Ethanol)

Solution 3: (1.042g TEOS + 1.052 ml HNO_3 + 2.5 ml Ethanol)

4.2.2 Bi functional catalyst preparation: Co impregnation method

The precursor solution of copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and supports silica alumina ($\text{SiO}_2\text{-Al}_2\text{O}_3$) are mixed simultaneously by taking volume of solution equal to the pore volume of the support. The mixture is well mixed and is dried at room temperature for whole night. Then the sample is dried in an oven at a temperature of 110°C for 6 hours and 200°C for another 6 hours. Finally the dried sample is calcined at 550°C for 6 hours before use.

Calculations:

Basis: 1 gram of support ($\gamma\text{-Al}_2\text{O}_3$, ($\text{SiO}_2/\text{Al}_2\text{O}_3$) = 1:1, 1:2, 2:1)

For Catalysts we use Metal Nitrates of Copper ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and Zinc ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)

- ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) = 2 grams
- ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) = 2.466 grams

Volume of Water taken is equal to the pore volume of the support.

4.3 Catalyst characterization

Characterization is done for a catalyst to determine the various physical and chemical properties and Changes during the catalysis process like deactivation of catalyst.

- Physical properties: pore size, surface area, and morphology of the support and the geometry and strength of the support.
- Chemical properties: composition, structure, and nature of the support and the active catalytic components.

4.3.1 N₂ adsorption studies and pore size distribution (PSD) measurement by Brunauer Emmett Teller Method (BET)

The N₂ adsorption/desorption studies was performed for all the support and supported Cu-ZnO catalyst using a Micromeritics ASAP 2020 physisorption analyzer. Before the N₂ adsorption studies, all the samples were degassed under vacuum (5×10^{-6} mmHg) at 473 K for 6 hrs. The surface area was calculated from the adsorption isotherm data using multi point BET (Brunauer Emmett Teller) equation in the relative pressure range of 0.05 to 0.3. The pore size distribution was calculated from desorption isotherm data using Barrett-Joyner-Halenda (BJH) method and the maximum of PSD was considered as the average pore size. The pore volume was considered as the average pore size volume of adsorbed nitrogen $P/P_0 = 1$.

4.3.2 Temperature programmed desorption (NH₃ –TPD)

Total number of acidic sites available on a catalyst is found using NH₃ –TPD. The experiment was conducted in Micromeritics Auto Chem II 2920 equipped with Thermal Conductivity detector (TCD). The sample was loaded inside a quartz u – tube between quartz wool. The quartz u tube was fixed inside a furnace. Initially the sample will be outgassed at 473 K or 523 K in inert atmosphere for 60 minutes. Then the furnace was allowed to cool to a temperature of 373 K and saturated / equilibrated for 30 minutes with 10% NH₃ – He mixture. Helium gas was sent for 60 minutes at 373 K to remove physically adsorbed ammonia on the sample. Afterwards the sample will be heated to 1073 K at a ramp of 10 K/min in a controlled manner and the ammonia desorption was observed with a TCD detector.

4.3.3 Temperature Programmed Reduction (H₂-TPR)

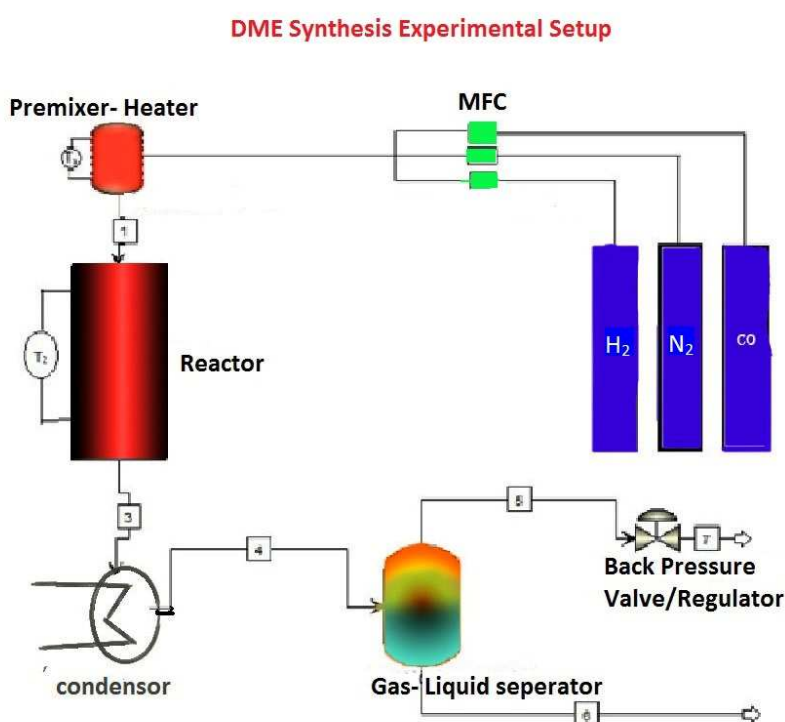
The ability of TPR to identify different species of the same element. This tells us the temperature at which the oxide form reduces to the metallic form. The experiment will be conducted in Micromeritics Auto Chem II 2920 equipped with Thermal Conductivity detector (TCD). The sample was loaded inside a quartz u – tube between quartz wool. The quartz u tube was fixed inside a furnace. Initially the sample will be outgassed at 473 K or 523 K in inert atmosphere for 60 minutes. Then the furnace will be allowed to cool to a temperature of 323 K and the gas is switched to 10% H₂ – Ar and the flow is maintained. Afterwards the sample will be heated to 1073 K at a ramp of 10 K/min in a controlled manner and the metal reduction was observed with a TCD detector.

4.3.4 FTIR Spectroscopy analysis

Fourier transform infrared (FTIR) spectra of adsorbed CO was recorded on a Bruker Tensor FTIR Spectrometer equipped with Harrick accessories. Sample powder was mixed with potassium bromide and is pressed into a pellet. The base line spectra was taken without the sample. Spectra were obtained after subtracting the base line. The spectra was recorded at ambient pressure 1 atm and temperature of 273 K in the range of 350- 4000 nm in a closed chamber.

4.4 Experimental Setup and Procedure

Fig 1



Description

The setup was a fixed bed Micro reactor which consists of three cylinders each containing N₂, H₂, and CO equipped with pressure gauges. All the three cylinders were connected to their respective mass flow controllers (MFCs) that regulates the mass flow of the respective gasses to have a desired composition. Then the synthesis gas that was obtained by mixing the three gasses was sent into a pre heater and mixer where the gasses were heated to a certain temperature and the heated gasses were sent to the reactor. The reactor was packed with the catalyst along with some inerts. The temperature of the reactor was controlled by the thermocouple and was maintained at

a desired set point. The reactor and preheater were provided with a heating coil to supply required heat. The pressures and flow rates were maintained by the respective valves and gauges. After conversion of the reactants into products, the products were collected by the condenser which cools down the product stream and sends the cooled product to the Gas- Liquid separator that separates the gas and liquid products in the product stream. A back pressure regulator is fixed at the product stream of liquid- gas separator as to maintain desired pressure and to control the flow. The products were sent to a gas chromatograph for analysis.

Chapter 5

Results and Discussion

Various catalysts that has been prepared were analyzed and their properties were discussed here. The catalysts prepared by wet impregnation method have shown slight difference in colour and texture.

5.1 N₂ adsorption studies and pore size distribution (PSD) measurement by Brunauer Emmett Teller Method (BET):

Table 5

S.No	Catalyst/ Supprot	Surface Area(m ² /g)	Pore Volume (cm ³ /g)	Avg. Pore Width (nm)
1	SiO ₂ :Al ₂ O ₃ = 2:1	498.37	0.876	6.896
2	SiO ₂ :Al ₂ O ₃ = 1:1	469.95	0.71	6.64
3	SiO ₂ :Al ₂ O ₃ = 1:2	419.76	0.64	6.11
4	Cu-ZnO/SiO ₂ :Al ₂ O ₃ = 2:1	389.02	0.69	6.46
5	Cu-ZnO/SiO ₂ :Al ₂ O ₃ = 1:1	367.89	0.65	6.02
6	Cu-ZnO/SiO ₂ :Al ₂ O ₃ = 1:2	339.02	0.59	5.42

Fig 2: Support (Volume adsorbed Vs Relative Pressure)

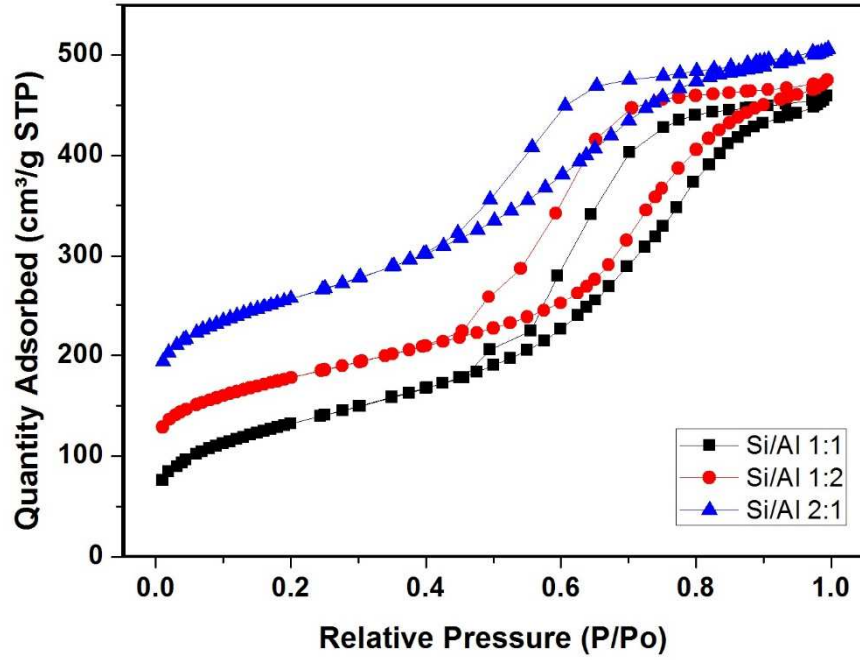


Fig 3: Support (Pore Volume Vs Pore Diameter)

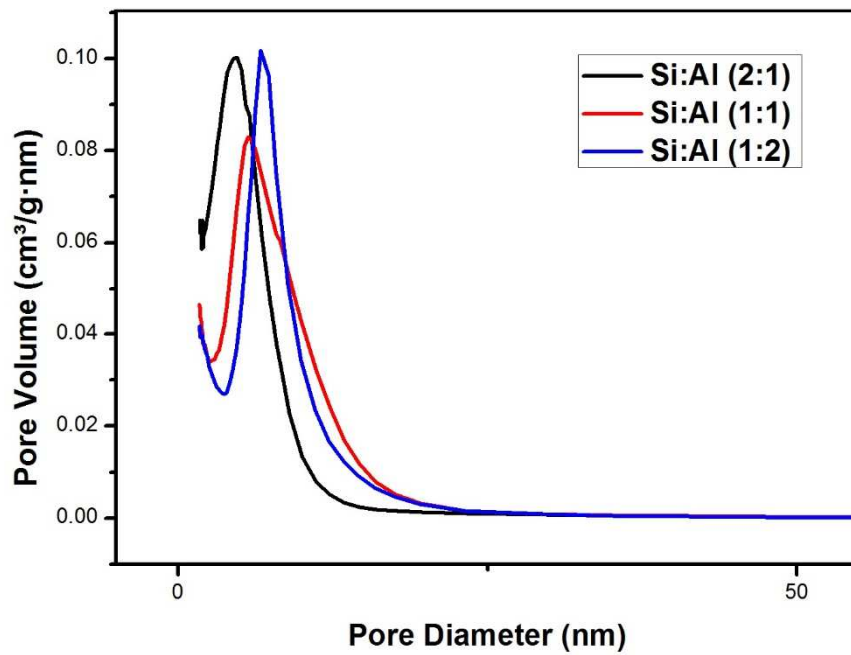


Fig 4: Catalyst (Volume adsorbed Vs Relative Pressure)

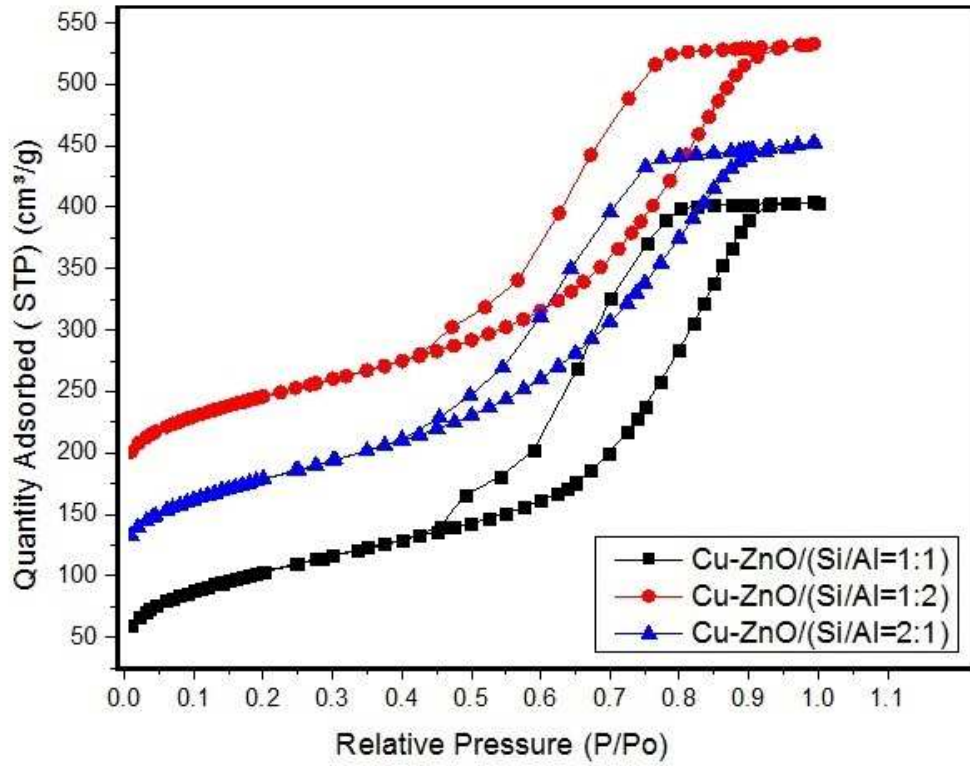
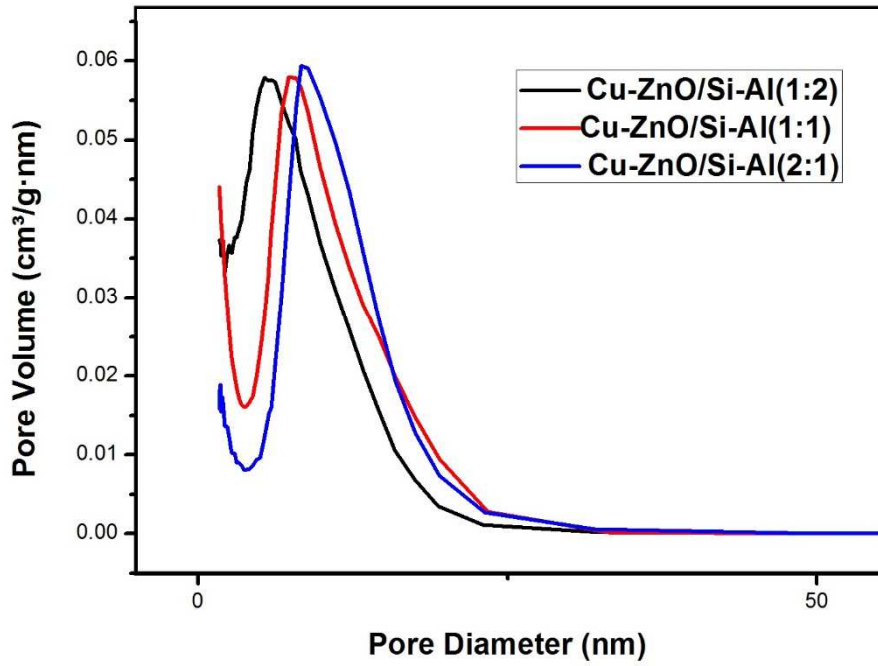


Fig 5: (Pore Volume Vs Pore Diameter):



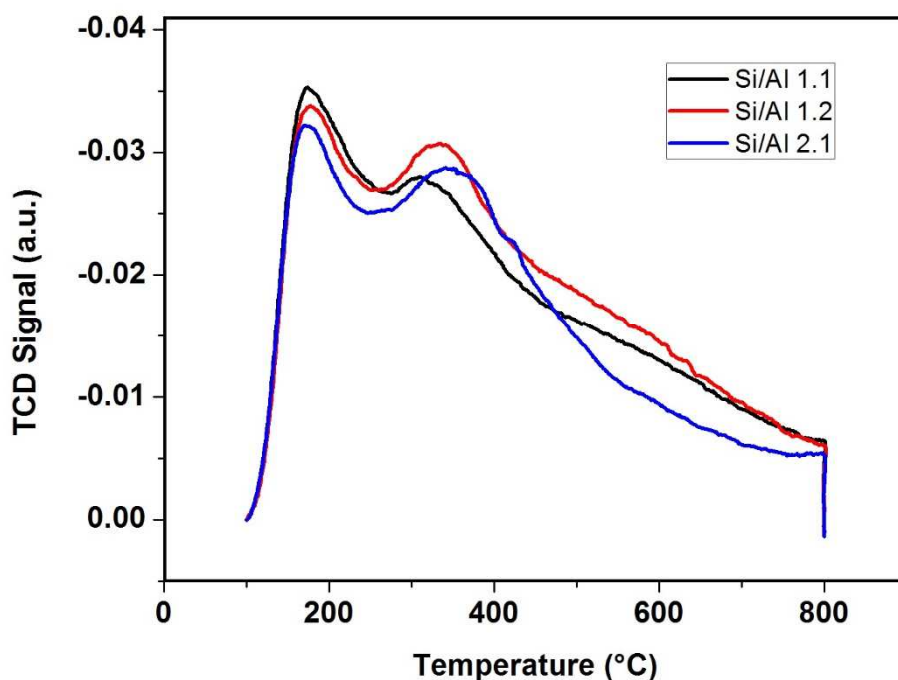
The BET surface area, pore volume and average diameter data of the supported catalysts are shown in Table 1. It can be observed that the surface area of the catalysts increases with increase of silica content in the catalyst. The prepared catalysts ranges from silica content of 33-66 mol %. It is also observed that the pore volume of catalyst containing more silica is greatest among them. It is observed that the surface area and pore volume of the support got reduced after the impregnation of metal oxide. This is due to the dispersion of the metal oxide on the surface of silica alumina which reduces the available area for N₂ Adsorption. The catalysts being meso structured have pores in the range of 2-50 nm. The pores are usually cylindrical in shape but can be partially distorted. By looking at the above figures 1-4, it is clearly shown there are two curves, lower one for adsorption of N₂ gas and upper for desorption. Both the curves do not take the same path because of which the hysteresis is observed. This is mainly because of capillary condensation occurring at the inner pores at higher relative pressures, and also to the uneven shapes of pores.

5.2 Temperature programmed desorption (NH₃ –TPD)

Table 6

S.No	Support	Peak No	Peak Temperature (°C)	Quantity Adsorbed (mmol/gram)	Peak concentration
1	SiO ₂ :Al ₂ O ₃ = 2:1	1	171.2	0.83	0.37
		2	341.7	1.38	0.32
2	SiO ₂ :Al ₂ O ₃ = 1:1	1	173.3	0.92	0.39
		2	309.8	1.33	0.29
3	SiO ₂ :Al ₂ O ₃ = 1:2	1	176.4	0.86	0.38
		2	320.8	1.7	0.33

Fig 6: Intensity Vs Temperature



NH₃-TPD was used to estimate the amount and the strength of acid sites formed on the surface of the catalyst. Figure 5 shows similar desorption patterns, with two distinct regions, from 150 °c to 300°c and 300°c to 450°c, respectively, indicating that the samples have two kinds of acid sites, weak acid sites and the strong acid sites. The peaks represent the temperature at which NH₃ is desorbed from the surface of the catalyst. It is observed that with increase in the alumina content in the catalyst the peaks shift towards the right showing more acidic nature. The corresponding low temperature peaks of 33, 50 and 66 mol % of alumina in samples are 171,173 and 176. And high temperature peaks are at 341, 309 and 320. 33wt% alumina sample should exhibit a low temperature peak but the odd behavior is attributed to the synergetic effect of silica alumina complex formations.

5.3 FTIR analysis:

Fig 7: Absorbance Vs Wave Number in the range of 400 – 1000 cm^{-1} .

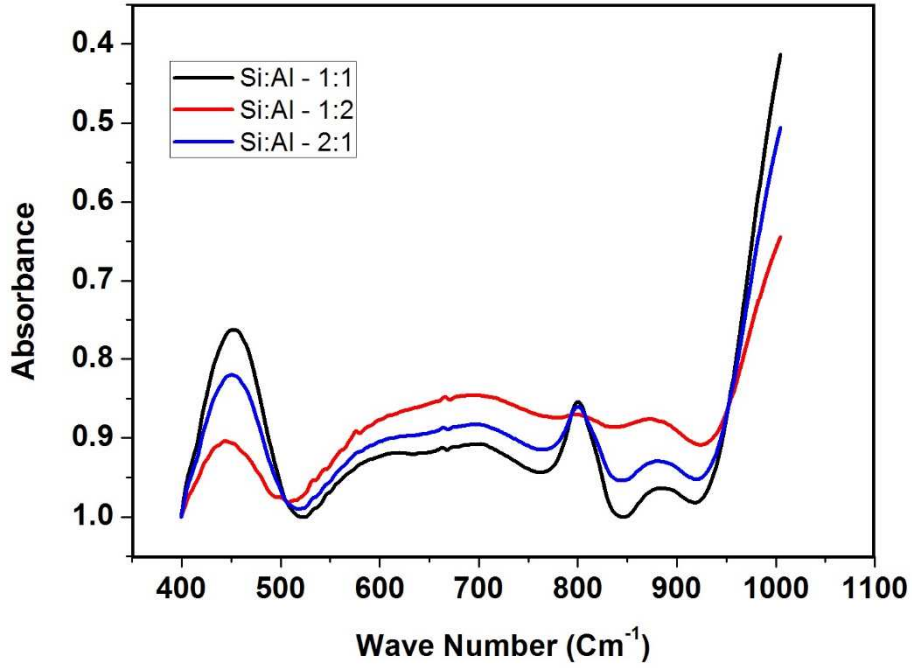
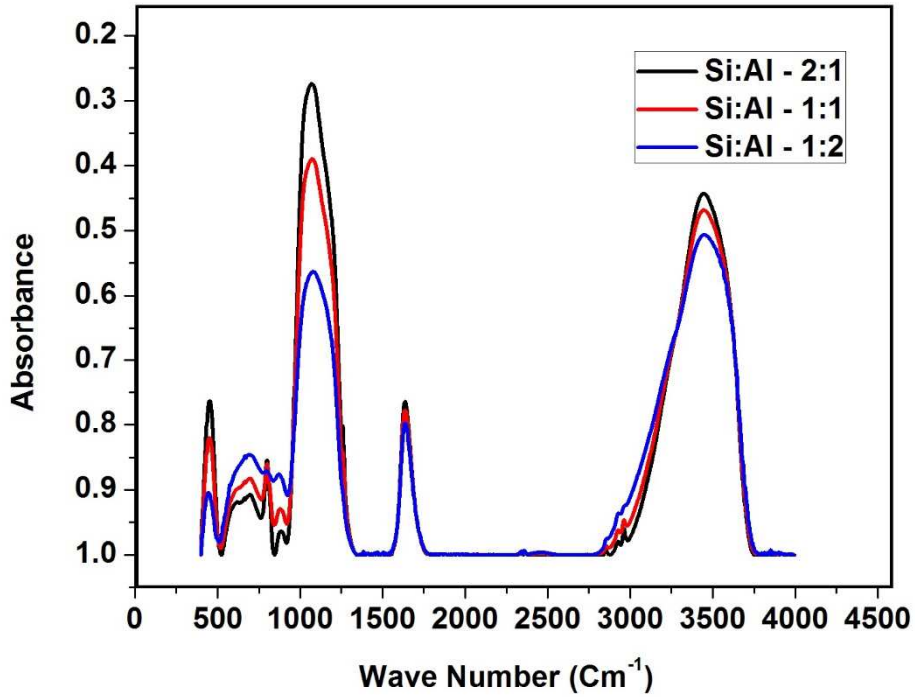


Fig 8: Absorbance Vs Wave Number.



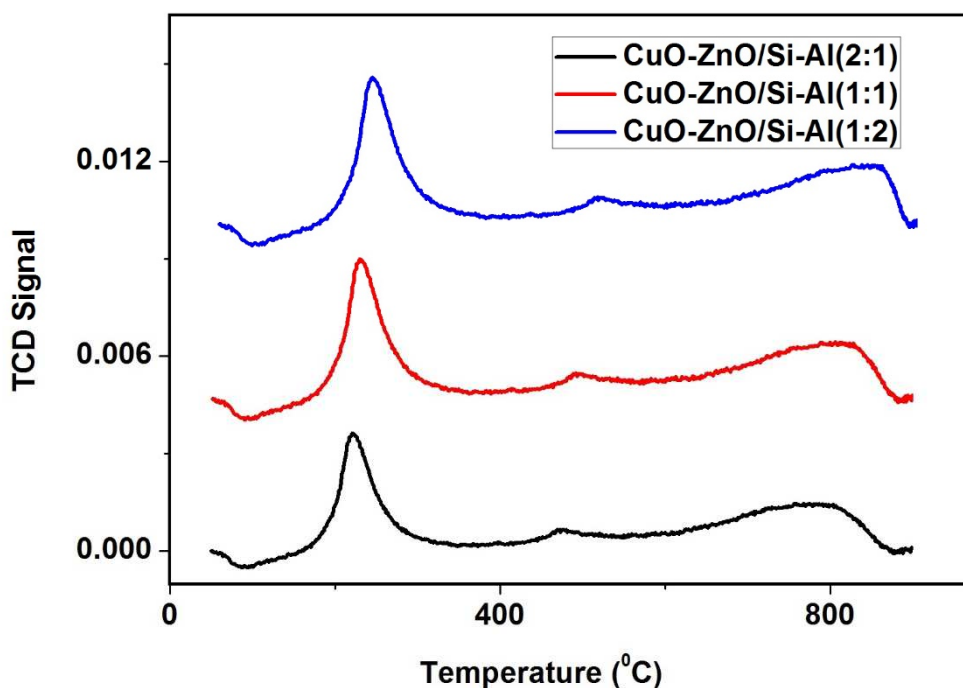
FTIR spectroscopy tells us about the interactions of various molecules in the catalyst material. Various Functional groups and different types of bonds can be detected by the amount of radiation absorbed.

- 3459 O-H stretching
- 1637 C=O stretching
- 801 O-H Bend out of plane
- 450 Si-O-Al Bending
- 1079 Si-O-Al Stretching

The bands at wave numbers less than 600 cm^{-1} i.e. 450 cm^{-1} corresponds to the Si-O bending which can be both Si-O-Al and Si-O-Si. After that the OH bending wavenumber is observed at 801 cm^{-1} . Si-O-Al and Si-O-Si stretching is observed at wavenumber 1079. Here because of the difference in amount of silica and alumina present in the there is an attenuation of the peaks. The catalyst with more of silica content has more Si-O-Si stretching and with less silica has more of Si-O-Al stretching. Next peak at 1637 cm^{-1} corresponds to the stretching of C=O bond. Finally the O-H stretching is observed at 3459 cm^{-1} .

5.3 Temperature Programmed Reduction (H_2 -TPR)

Fig 9



TPR tells us about the temperature of reduction of the catalyst which is in oxide form to its metallic state. The catalyst discussed here is the CuO-ZnO impregnated on silica alumina. For reduction of the metallic species there are 3 possible transitions. $\text{Cu}^{2+} - \text{Cu}^0$ (CuO to Cu), $\text{Cu}^{1+} - \text{Cu}^0$ (Cu_2O to Cu), and $\text{Zn}^{2+} - \text{Zn}^0$ (ZnO - Zn). It is observed that the presence of Aluminum has a strong effect on the reducibility of copper oxide. Samples with lesser alumina content (Si/Al -2:1) has lesser Reduction temperatures and samples with more alumina content (Si/Al -1:2) has their peaks shifted to right. This increment in reduction temperature is because of the formation of Cu-Al Compunds, and Zn-Al compounds.

Conclusion:

Various attempts of comparing the synthesized mesoporous CuO-ZnO/Silica-Alumina among different ratios of Si/Al gives us the idea of choosing the better catalyst among them. However all the synthesized catalysts were proven to be better than the commercially available γ - Al_2O_3 , the choice of the catalyst depends on the maximizing the desired product in the reaction. Catalyst with 66% silica has more surface area and lower reduction temperatures and are more stable. Whereas the catalyst with 66% alumina has more acidity but it is less resistant to deterioration from water and also has less surface areas and high reduction temperatures.

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