Green Process Development for Production of 1,2 Propane-diol from Hydrogenation of Glycerol

By

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Green Process Development for Production of 1,2 Propane-diol from Hydrogenation of Glycerol

Major Project

Submitted in partial fulfillment of the requirements

For the Degree of
Master of Technology in Chemical Engineering

By

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Guided By

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MAY 2013

Undertaking for the Originality of the Work

Bharat Chatwani (11MCHE02), gives undertaking that the major project entitled "Green Process Development for Production of 1,2 Propane-diol from Hydrogenation of Glycerol" submitted by me, towards the partial fulfillment of the requirments for the degree of Master of Technology - Chemical Engineering (Environment Process Design) of Nirma University, Ahmedabad is the original work carried out by me and I give assurance that no attempts of plagiarism has been made.

I understand, that in the event of any similarity found subsequently with any published work or any dissertation work elsewhere, it will result in severe disciplinary action.

Endorsed by

Bharat Chatwani

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Date:
Place:

Certificate

This is to certify that the Project Part-I Report entitled "Green process development for production of 1,2 Propane-diol from hydrogenation of glycerol " submitted by Mr. Bharat Chatwani (11MCHE02), towards the partial fulfillment of the requirements for the award of Degree of Master of Technology in Environment Process Design of Nirma University is the record of work carried out by him under my supervision and guidance. The work submitted has reached a level required for being accepted for examination. The results embodied in this major project, to the best of my knowledge, haven't been submitted to any other university or institution for award of any degree or diploma.

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Abstract

In current scenario, in general researchers are looking for renewable resources for production of commercially important products. Biodiesel production, from various renewable resources, by conventional esterification /or trans-esterification reaction, produces glycerol as one of the major co-product. Thus glycerol from biodiesel is renewable resource. Due to presence of three –OH groups in glycerol its becomes higly functional molecule and various commercially important products can be produced like 1,2 Propane-diol. Production of 1,2 Propane-diol through glycerol is an attractive route to use renewable resources.

This work presents review of various routes for glycerol to 1,2 Propane-diol reaction using heterogeneous catalyst. Based on literature survey, copper alumina phosphate (CAP) shows highest possible conversion with very good selectivity for 1,2 Propane-diol. However such reactions were carried at very high temperature and pressure, i.e. more than 220°C and more than 52 bar(g) pressure.

CAP catalyst was synthesized with different synthesis method and different promoters to enhance conversion and selectivity. Liquid phase reactions were carried out in high pressure reactor in presence of synthesized heterogeneous catalysts. Reaction mixture was analyzed using gas chromatography techniques.

Objective to carry out this work was to reduce the severity of the operation with good conversion and selectivity. But results are not encouraging.

Copper alumina phosphate (with KOH as promoter) shows highest possible conversion, 5.5% at 30 bar(g) pressure, 180°C temperature and 5 hours reaction time. Under similar conditions NaOH promoted CAP shows 4.2% conversion compared to 51% in the literature at higher temperature and pressure conditions.

Two major reasons for poor performance can be contributed to improper preparation of catalyst and less severe conditions of operation can be considered.

Keywords**:** Glycerol, 1,2 Propane-diol, Hydrogenation, Conversion, Selectivity

Contents

List of Figures

List of Tables

Chapter 1

INTRODUCTION

Use of renewable feedstock and chemicals to valuable products is increasing day by day. Researchers are trying to convert renewable feedstock to petrochemicals that can provide the replacement of petroleum . Moreover it has been proposed that commodity chemicals that are derived from fossil resources are used to pharmaceuticals, agricultural adjuvant, plastics and transportation fuel [1].

Biodiesel has proved to be environmentally friendly diesel fuel. Its use is enlarged and has been used instead other [2]. The trans-esterification of triglycerides with various lower alcohols like methanol, ethanol or IPA, in the presence of acidic or basic catalyst results into biodiesel consisting of corresponding ester of fatty acids. The increase in production of biodiesel has lead to increase in production of glycerol. About 10 % (wt. basis) of glycerol is produced along with biodiesel production. So it is expected that with increase in biodiesel production, production of glycerol will also increase. Even economics of biodiesel largely depends on this important byproduct. It is considered as top 12 chemical building blocks that can be converted to more market value products [3].

Glycerol is having three hydroxyl groups in it structure. This provides immense possibilities to produce wide varieties of the products from glycerol starting from hydrogen to acrolein to 1,2 Propane-diol. Fig.1.1. describes production of commercially important products using glycerol as feed stock using various chemical processes [3-5]. It is expected that with better technology for production of such commercially important chemicals using glycerol as feed stock can improve the economics of biodiesel production and it can become more competitive to crude based diesel [6-8]. Viable alternates for chemical processes include oxidation, dehydration, halogenation, etherification, esterification, pyrolysis and hydrogenolysis of glycerol [7,9].

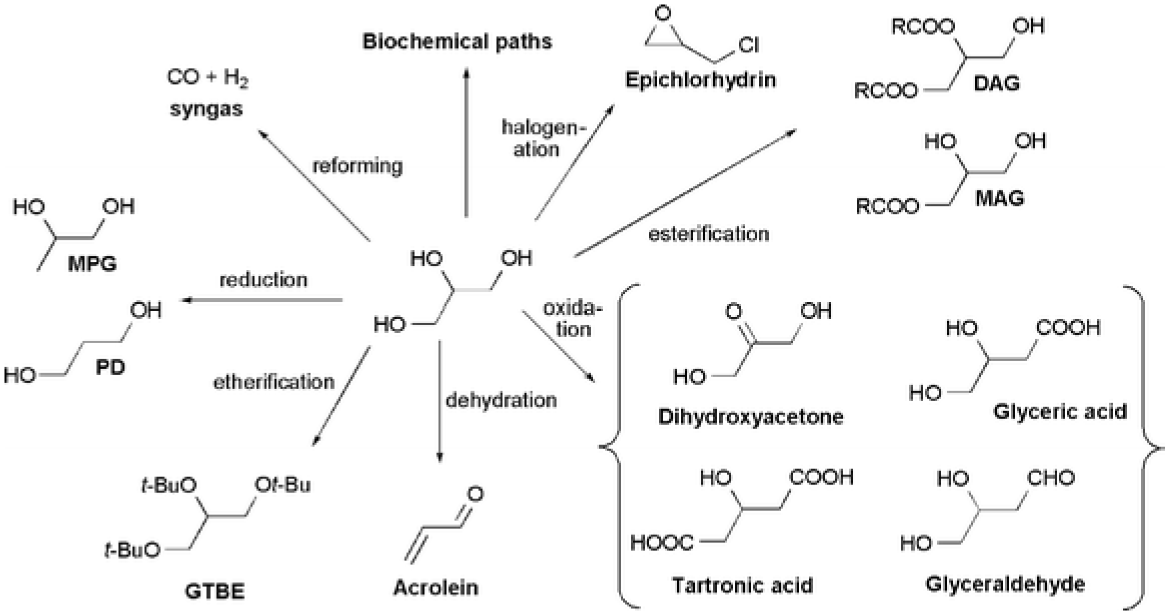


Figure 1.1: Various reaction pathway for Glycerol.

1,2 Propane-diol is an industrially interesting raw material. It is also used as a raw material for making other products. Viable alternates for chemical processes include oxidation, dehydration, halogenation, etherification, esterification, pyrolysis and hydrogenolysis of glycerol [7,9].

1.1 Application of 1,2 Propane-diol

1. Production of unsaturated polyester resins,
2. Functional fluids (Antifreeze,De-icing, and heat transfer),
3. Pharmaceutical products,
4. Cosmetic products,
5. Paints,
6. Humectant,
7. Polyesters,
8. Alkyd resins,
9. Additive in food,
10. Liquid detergents,
11. Flavours,
12. Fragrances,
13. Animal feed [3, 5, 17, 18].

1.2 Thesis organization

1. The 2nd chapter deals with liquid phase and gas phase reaction, reaction conditions under which it is carried out and also alternate routes for glycerol hydrogenation to 1,2 Propane-diol.
2. The 3rd chapter describes catalyst preparation method, procedure and also the result obtained for particular catalyst reportedly in the literature.
3. The 4th chapter includes reaction carried out at specific conditions and analysis condition of the reaction sample for GC as well as some specification related to GC column used for analysis purpose.
4. The chapter 5th describes result of the reaction and major problem encountered during catalyst preparation and also the reaction conditions that were maintained during the reaction compared to reported.
5. The chapter 6th highlites various parameter that were varried.

Chapter 2

LITERATURE SURVEY

1,2 Propane-diol is a commercially very important molecule and its wide range of applications are listed in chapter 1.

Various routes for commercial production of 1,2 Propane-diol are briefly discussed as follows.

2.1 Alternate routes

The commercial route to produce propylene glycol is by the hydration of propylene oxide derived from propylene by either the chlorohydrins process or the hydroperoxide process.

It also include several routes to propylene glycol from renewable feedstocks, out of which the most common route of production is through hydrogenolysis of sugars or sugar alcohols at high temperatures and pressures in the presence of a metal catalyst producing propylene glycol and other lower polyols [10].

During hydrogenation of glycerol, along with the product 1,2 Propane-diol there is various byproduct formation that include, propanol, lactic acid, propanoic acid and ethylene glycol as major product that had a (4%) annual market growth. Selective hydrogenolysis of glycerol to 1,2 Propane-diol requires a cleavage of C-O bond by hydrogen addition without attacking C-C bond in the glycerol molecules [3,11].

Acrolein that is an intermediate in glycerol hydrogenation is an important chemical in industry as it serves as a raw material for production of acrylic acid ester, absorber polymers, and detergents [12].

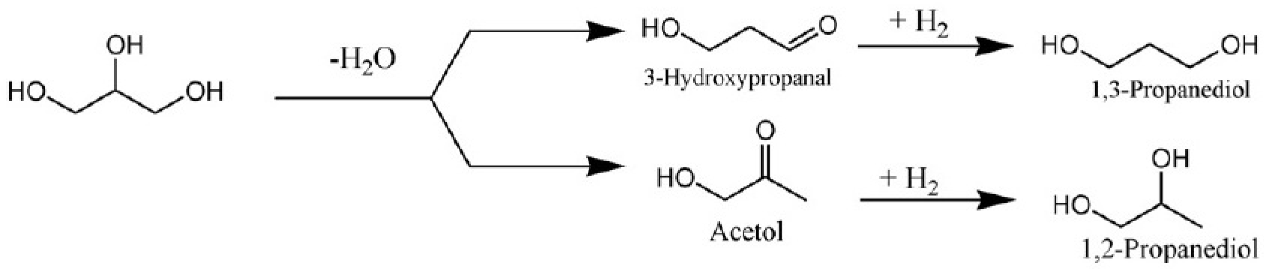
Ethylene glycol that is formed as a byproduct is used as antifreeze, and serves as a starting material for production of polyesters [13].

Several groups had reported hydrogenolysis of glycerol on different catalyst systems including supported transition metal catalyst such as Rh, Ni, Ru, Pt, Pt-Ru and Cu catalyst [3].

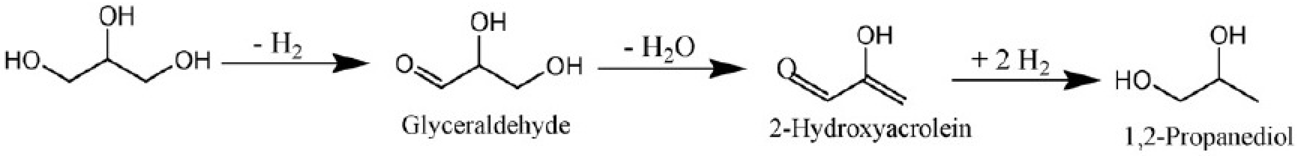
Usually glycerol hydrogenation to 1,2 Propane-diol is carried out by two step and three step processes:

2.1.1 Two Step Process

Under acidic conditions glycerol first dehydrated to acetol as an intermediate product prior to hydrogenolysis, furthermore hydrogenation to 1,2 Propane-diol. Thus, acid catalyst could play an important role in the glycerol dehydration stage as well as working under milder reaction conditions that might increase the conversion and selectivity as shown in scheme 1. [3].



Scheme 1. Glycerol hydrogenolysis pathways.



Scheme 2. Glycerol hydrogenolysis pathway to prepare 1,2-propanediol.

Figure 2.1: Glycerol hydrogenation to 1,2 Propane-diol using acid - base catalyst.

2.1.2 Three Step Process

Under basic conditions glycerol firstly dehydrogenate to glyceraldehydes and then further by dehydration to 2-Hydroxyacrolein followed by hydrogenation to 1,2 Propane-diol as shown above in scheme 2. [4, 14].

Generally due to high oxygen functionality and low thermal stability of polyol (glycerol), reaction typically occurs in aqueous phase at moderate temperature and pressures.

Besides going for hydrogen gas for glycerol hydrogenation there are other routes that acts as hydrogen source for glycerol hydrogenolysis that includes formic acid, 2-propanol, ethanol etc, as hydrogen donor molecule for inert atmosphere. Out of which in the literature formic acid is obtained with suitable conversion. during which hydrogen atom obtained from 2-propanol directly gets converted to 1,2 propane-diol. Other than that the literature also highlights in-situ hydrogen production and using it further for the reaction thereby suppressing the use of external hydrogen addition leading to improved operational safety but at mild pressure and inert gas that also improves economically. Moreover the use of molecular hydrogen over reactant is due to low solubility of hydrogen in aqueous solution and requires to be operated at elevated pressures. Besides this hydrogen has high diffusivity is easily ignited and presents considerable hazard.

Above all reported literature mentions the effect of additives (NaOH and CaO) being used for increasing the activity. Whereby use of residual sodium effects activity, selectivity, structure and stability of the catalyst are being effected reportedly.

2.2 Liquid phase reaction:

With higher hydrogen pressure and relatively lower temperature, glycerol hydrogenation in liquid phase reaction produces 1,2 Propane-diol with very good conversion and very high selectivity. Glycerol hydrogenation is carried out at pressure 2-10 MPa. During above reaction the various catalyst reported in the literature includes Ru, Cu, Pt, Pd, Rh, Ni etc, that also includes some promoters. And among those reported catalyst in the literature Ru, Cu is found to be mostly used catalyst so far.

Table 2.1: Catalysts for liquid phase reaction.

Sr. No	Journal Name,Vol & Page No	Title	Authors	Catalyst	Support	T (K)	P (bar)	Result (C,S)
LIQUID PHASE REACTION								
1	Applied Catalysis A: General 318 (2007) 244–251	Development Of A Ru/C Catalyst For Glycerol Hydrogenolysis In Combination With An Ion-Exchange Resin	Tomohisa Miyazawa, Shuichi Koso, Kimio Kunimori, Keiichi Tomishige	Ru	Carbon Support	393-493	80	(79.3,74.7)
2	J. Chem. Soc. Pak., Vol. 34, No.4, 2012	Effect Of Support On Hydrogenolysis Of Glycerol Over Cu Catalysts	Jie Zhou,Shunli Hao, Ning Zhao, Fukui Xiao, Wei Wei And Yuhan Sun	Cu	ZrO_2, SiO_2, HZSM-5, γ-Al_2O_3	513	60	(85.05, 85.71)
3	Applied Catalysis A: General 419– 420 (2012) 133– 141	Enhanced Activity Of Ru/TiO_2 Catalyst Using Bisupport, Bentonite-TiO_2 for Hydrogenolysis Of Glycerol In Aqueous Media	Noraini Hamzah, Norasikin Mohamad Nordin, Ainol Hayah Ahmad Nadzri, Yah Awg Nik, Mohamad B. Kassim, Mohd Ambar Yarmo	Ru	TiO_2, SiO_2, Al_2O_3, Bentonite, Bentonite-TiO_2, Bentonite + Ru/TiO_2,	423	20	Ru/ Bentonite Catalyst (C,S) = (61.2,80.1), Ru/TiO_2 Catalyst (C,S) = (38.8,84.4)

4	Applied Catalysis A: General 403 (2011) 173– 182	Hydrogenolysis Of Glycerol On Bimetallic Pd-Cu/Solid-Base Catalysts Prepared Via Layered Double Hydroxides Precursors	Shuixin Xia, Zhenle Yuan, Lina Wang, Ping Chen, Zhaoyin Hou	Pd , Cu	Mg-Al	453	20	(76.9,97.2)
5	Catalysis Today 149 (2010) 148–156	Influence Of Catalyst Pretreatment On Catalytic Properties And Performances Of Ru–Re/SiO_2 In Glycerol Hydrogenolysis To Propanediols	Lan Ma, Dehua He	Ru–Re	SiO_2	433	80	(51.7,51.7)
6	Applied Catalysis A: General 396 (2011) 177–185	Investigating The Performance And Deactivation Behaviour Of Silica-Supported Copper Catalysts In Glycerol Hydrogenolysis	E.S. Vasiliadou, A.A. Lemonidou	Cu	HMS-Support, SiO_2-Support	513	80	5Ru/SiO_2 (21.7,60.5 5Cu/SiO_2 (4.1,90.1) :(10,83.6) 5(Ru–Cu)/ SiO_2 (39.2,85.9 HMS-Support 5Cu/HMS (28.5,93.2)

7	Chemical Engineering Journal 180 (2012) 277– 283	Liquid Phase Dehydration Of Glycerol To Acrolein Catalyzed by Silicotungstic, Phosphotungstic, and Phosphomolybdic acids	Lingqin Shen, Hengbo Yin, Aili Wang, Yonghai Feng, Yutang Shen, Zhanao Wu, Tingshun Jiang	Hpmo, HPW, Hsiw.	-	573	-	72% Yield
8	Catalysis Communications 11 (2010) 493–497	A Remarkable Enhancement Of Catalytic Activity For KBH_4 Treating The Carbothermal Reduced Ni/AC Catalyst In Glycerol Hydrogenolysis	Weiqiang Yu, Jie Xu, Hong Ma, Chen Chen , Jing Zhao , Hong Miao, Qi Song	Ni	AC	473	50	(63.2,77.4)
9	Chemical Engineering Journal 198–199 (2012) 457–467	Effect of niobia and alumina as support for Pt catalysts in the hydrogenolysis of glycerol	R. Rodrigues, N. Isoda, M. Gonçalves, F.C.A. Figueiredo, D. Mandelli, W.A. Carvalho	Pt	niobia and alumina as support	413	50	(>75,50)
10	Applied Catalysis A: General 281 (2005) 225–231	Low-Pressure Hydrogenolysis Of Glycerol To Propylene Glycol	Mohanprasad A. Dasari, Pim-Pahn Kiatsimkul, Willam R. Sutterlin, Galen J. Suppes	Cu chromite		473	14	Yield-73%

11	Journal Of Catalysis 249 (2007) 328–337	Hydrogenolysis Of Glycerol Over Carbon-Supported Ru And Pt Catalysts	Erin P. Maris, Robert J. Davis	Ru, Pt	C	473	40	(85,85)
12	Applied Catalysis B: Environmental 106 (2011) 83– 93	Glycerol Liquid Phase Conversion Over Monometallic And Bimetallic Catalysts:Effect Of Metal, Support Type And Reaction Temperatures	A. Iriondo, J.F. Cambra, V.L. Barrio, M.B. Guemez, P.L. Arias, M.C. Sanchez-Sanchez,R.M. Navarro, J.L.G. Fierro	Ptni	γ-Al_2O_3, La_2O_3-Modified, γ-Al_2O_3 Modified	513	40	Con: (53.1%)
13	Applied Catalysis A: General 371 (2009) 60–66	Dehydration–Hydrogenation Of Glycerol Into 1,2-Propanediol At Ambient Hydrogen Pressure	Masaki Akiyama, Satoshi Sato, Ryoji Takahashi, Kanichiro Inui, Masahiro Yokota	Cu	Al_2O_3 (N-242), Al_2O_3 (T317), ZnO (N211), Cr_2O_3 (N201), SiO_2 (N-111)	463-468	6.4-20	Cu/Al_2O_3 (N-242) = (100,78.2). Cu/Al_2O_3 (T-317) = (100, 75). Cu/ZnO (N-211) = (29.7, 21.9). Cu/Cr_2O_3 (N-201) = (100,77.3) Ni/SiO_2 (N-111) = (100, 4.4)
14	Bioresource Technology 101 (2010) 3242–3245	Treatment Of Glycerol Phase Formed By Biodiesel Production	Martin Hájek, František Skopal					

15	Applied Catalysis B: Environmental 101 (2011) 431–440	Hydrogenolysis Of Glycerol Over Homogenously Dispersed Copper On Solid Base Catalysts.	Zhenle Yuan, Lina Wang, Junhua Wang, Shuixin Xia, Ping Chen,Zhaoyin Hou, Xiaoming Zheng	Cu	MgO-Al_2O_3	453	30	(80.0,98.2)
16	Bioresource Technology 111 (2012) 282–293	Design And Analysis Of Biorefineries Based On Raw Glycerol: Addressing The Glycerol Problem	John A. Posada, Luis E. Rincón, Carlos A. Cardona					
17	Catalysis Today 156 (2010) 31–37	Aqueous Phase Hydrogenolysis Of Glycerol To 1,2-Propanediol Without External Hydrogen Addition	Debdut Roy, Bala Subramaniam, Raghunath V. Chaudhari	Ru, Pt	Al_2O_3	493	0-41	(50.2,48.7)
18	Catalysis Communications 12 (2010) 122–126	Glycerol Hydrogenolysis To 1, 2 Propanediol Over Ru/C Catalyst	Silvia Bolado, Ricardo E. Treviño, M. Teresa García-Cubero, Gerardo González-Benito	Ru	C	433	60	(60,31.72)

19	Journal of Catalysis 240 (2006) 213–221	Glycerol Conversion In The Aqueous Solution Under Hydrogen Over Ru/C + An Ion-Exchange Resin And Its Reaction Mechanism	Tomohisa Miyazawa, Yohei Kusunoki, Kimio Kunimori, Keiichi Tomishige	Ru, Rh, Pt, Pd	C	393	80	(38.8,28.8)
20	Applied Catalysis A: General 354 (2009) 82–87	Influence Of Solid Acids As Co-Catalysts On Glycerol Hydrogenolysis To Propylene Glycol Over Ru/C Catalysts	M. Balaraju, V. Rekha, P.S. Sai Prasad, B.L.A. Prabhavathi Devi, R.B.N. Prasad, N. Lingaiah	Ru	IER, Cstpa/ ZrO_2, Nb_2O_5, Cstpa, TPA/ZrO_2	453	60	(25, 40.9), (25, 67), (44.6,60.9) (21,60.2), (44, 64.3).
21	Applied Catalysis A: General 329 (2007) 30–35	Glycerol Hydrogenolysis To 1,2-Propanediol Catalyzed By A Heat-Resistant Ion-Exchange Resin Combined With Ru/C	Tomohisa Miyazawa, Shuichi Koso, Kimio Kunimori, Keiichi Tomishige	Ru	Carbon Support + amberlyst (15, 70)	453	80	(48.8,70.2)
22	Catalysis Communications 9 (2008) 2489–2495	Promoting Effect Of Rhenium On Catalytic Performance Of Ru Catalysts In Hydrogenolysis Of Glycerol To Propanediol	Lan Ma, Dehua He, Zhanping Li	Ru	C, Al_2O_3, ZrO_2	393-453	40-100	(64.1,59.5)

23	Catalysis Communications 6 (2005) 645–649	Highly Active Metal–Acid Bifunctional Catalyst System For Hydrogenolysis Of Glycerol Under Mild Reaction Conditions	Yohei Kusunoki, Tomohisa Miyazawa, Kimio Kunimori, Keiichi Tomishige	Ru	C, amberlyst, Zeolites, Sulfated Zirconia, H_2WO_4, and liquid H_2SO_4	393	40	(40.7,93.1)
24	Applied Catalysis A: General 366 (2009) 288–298	Characterization And Catalytic Properties Of The Cuo/SiO_2Catalysts Prepared By Precipitation-Gel Method In The Hydrogenolysis Of Glycerol To 1,2-Propanediol: Effect Of Residual Sodium	Zhiwei Huang, Fang Cui, Haixiao Kang, Jing Chen, Chungu Xia	Cu	SiO_2	453	64-90	(8.6-32.7, >94.3)
25	Applied Catalysis A: General 367 (2009) 93–98	Supported Cu Catalysts For The Selective Hydrogenolysis Of Glycerol To Propanediols	Liyuan Guo, Jinxia Zhou, Jingbo Mao, Xinwen Guo, Shuguang Zhang	Cu	HY, 13X, HZSM-5.Hb, γ-Al_2O_3	573	15-36	(34.6,93.9)
26	Applied Catalysis B: Environmental 94 (2010) 318–326	Modification Of Rh/ SiO_2 Catalyst For The Hydrogenolysis Of Glycerol In Water	Yasunori Shinmi,Shuichi Koso,Takeshi Kubot,Yoshinao Nakagawa,Keiichi Tomishige	Rh	SiO_2	393	10-80	(76,60)

27	Applied Catalysis A: General 371 (2009) 108–113	Co/MgO Catalysts For Hydrogenolysis Of Glycerol To 1, 2-Propanediol	Xiaohui Guo, Yong Li, Ruijuan Shi, Qiying Liu, Ensheng Zhan, Wenjie Shen	Co	MgO	453-523	10-30	Co/MgO: - 673 (5.3 ,45.3) Co/MgO: - 873 (44.8,42.2)
28	Applied Catalysis B: Environmental 111– 112 (2012) 27–37	Comparative Study Of Rh–Moox And Rh–Reox Supported On SiO_2 For The Hydrogenolysis Of Ethers And Polyols	Shuichi Koso,Hideo Watanabe,Kazu Okumura, Yoshinao Nakagawa,Keiichi Tomishige	Rh	SiO_2	393	80	(9.7,41)
29	Catalysis Today 164 (2011) 447–450	Role Of Promoters In Copper Chromite Catalysts For Hydrogenolysis Of Glycerol	R.B. Mane, A.A. Ghalwadkar, A.M. Hengne, Y.R. Suryawanshi, C.V. Rode	Cu-chromite	-	493	50	(65,85)
30	Applied Catalysis B: Environmental 92 (2009) 90–99	Ru-Based Catalysts For Glycerol Hydrogenolysis—Effect Of Support And Metal Precursor	E.S. Vasiliadou,E. Heracleous,I.A. Vasalos,A.A. Lemonidou	Ru	ZrO_2, SiO_2, γ-Al_2O_3	513	80	(69,60.5)
31	Applied Catalysis A: General 384 (2010) 107–114	Surface And Structural Properties Of Titania-Supported Ru Catalysts For Hydrogenolysis Of Glycerol	M. Balaraju, V. Rekha, B.L.A. Prabhavathi Devi, R.B.N. Prasad, P.S. Sai Prasad, N. Lingaiah	Ru	TiO_2	453	60	$5Ru/TiO_2$ (DP): (44 ,58) $5Ru/TiO_2$ (IM): (31,59)

32	Journal Of Catalysis 290 (2012) 79–89	Liquid-Phase Glycerol Hydrogenolysis By Formic Acid Over Ni–Cu/Al_2O_3 Catalysts	I. Gandarias,J. Requies,P.L. Arias, U. Armbruster,A. Martin	Ni-Cu	Al_2O_3	493	45	(90,82)
33	Catalysis Today Xxx (2012) Xxx– Xxx	Effect Of Preparation Parameters Of Cu Catalysts On Their Physico-Chemical Properties And Activities For Glycerol Hydrogenolysis	R.B. Mane, S.E. Kondawar, P.S. Niphadkar, P.N. Joshi, K.R. Patil, C.V. Rode	Cu	KOH, NaOH, Na_2CO_3	493	52	CAP Na_2CO_3R: (63,88)
34	Catalysis Today 174 (2011) 10–16	Studies On The Conversion Of Glycerol To 1,2-Propanediol Over Ru-Based Catalyst Under Mild Conditions	Seung-Hwan Lee, Dong Ju Moon,	Ru	Alumina, Ca-Zn	453	25-40	Ru–Mg/Al (47.3,61.1 Ru–CaMg/Al: (56.7,78.4) Ru–ZnMg/Al: (55.6,75.1) Ru–CaZn Mg/Al: (58.5,85.5 Ru/γ-Al_2O_3: (45.6,59.2)
35	Catalysis Today 187 (2012) 122– 128	Glycerol Hydrogenolysis To 1,2-Propanediol With Cu/γ-Al_2O_3: Effect Of The Activation Process	F. Vila, M. López Granados, M. Ojeda, J.L.G. Fierro, R. Mariscal	Cu	γ-Al_2O_3	493	24	Yield-10.2%

36	Catalysis Today Xxx (2012) Xxx– Xxx	Catalytic Transformation Of Glycerol On Several Metal Systems Supported On ZnO	Manuel Checa, Florian Auneau, Jesús Hidalgo-Carrillo, Alberto Marinas, José M. Marinas,Catherine Pinel, Francisco J. Urbano	Pt	ZnO	448	6	-
37	Applied Catalysis B: Environmental 117– 118 (2012) 253– 259	Hydrogenolysis Of Glycerol To Obtain 1,2-Propanediol On Ce-Promoted Ni/SBA-15 Catalysts	I.Jiménez-Morales,F. Vila,R. Mariscal,A. Jiménez-López	Ni	SBA-15	473	30	(56, 32.5)
38	Bioresource Technology 101 (2010) 7088–7092	Biodiesel Derived Glycerol Hydrogenolysis To 1,2-Propanediol On Cu/MgO Catalysts	Zhenle Yuan, Junhua Wang, Lina Wang, Weihui Xie, Ping Chen, Zhaoyin Hou, Xiaoming Zheng	Cu	MgO Support	453	30	(72, 97.6)
39	Bioresource Technology 104 (2012) 814–817	Catalytic Production Of 1,2-Propanediol From Glycerol In Bio-Ethanol Solvent	Shuixin Xia, ZhenleYuan,Lina Wang,Ping Chen, ZhaoyinHou	Rh, Cu	Al, Mg	453	20	(91,98.7)

40	Catalysis Communications 9 (2008) 1458–1464	Hydrogenolysis Of Glycerol To Glycols Over Ruthenium Catalysts: Effect Of Support And Catalyst Reduction Temperature	Jian Feng, Haiyan Fu, Jinbo Wang, Ruixiang Li, Hua Chen, Xianjun Li	Ru	TiO_2, SiO_2, Nay, γ-Al_2O_3 And Active Carbon	443	30	(66.3,47.7)
41	Applied Catalysis A: General 433–434 (2012) 128–134	Solid Acid Co-Catalyst For The Hydrogenolysis Of Glycerol To 1,3-Propanediol Over Ir-Reox/SiO_2	Yoshinao Nakagawa, Xuanhe Ning, Yasushi Amada, Keiichi Tomishige	Ir-Reox	SiO_2 Support	473	80	-
42	Catalysis Communications 24 (2012) 90–95	Preparation And Characterization Of Nanocrystalline $CuAl_2O_4$ Spinel Catalysts By Sol–Gel Method For The Hydrogenolysis Of Glycerol	Byoung Kyu Kwak, Dae Sung Park, Yang Sik Yun, Jongheop Yi	$CuAl_2O_4$ Spinel		493	50	(90,90)

43	Catalysis Today 183 (2012) 42–51	Cu/SiO_2 Catalysts Prepared By Hom- And Het Deposition–Precipitation Methods: Texture, Structure, And Catalytic Performance In The Hydrogenolysis Of Glycerol To 1,2-Propanediol	Zhiwei Huang, Fang Cui, Jingjing Xue, Jianliang Zuo, Jing Chen, Chungu Xia	Cu	SiO_2	553	64	Hom-DP:-(C,S):-(22.1,98),(11.7,97.8),(6.1,98.4). Het-DP:-(C,S):-(35,93.7),(30.1,95.2),(21.6,96).
44	Catalysis Today 190 (2012) 31–37	Copper Modified Waste Fly Ash As A Promising Catalyst For Glycerol Hydrogenolysis	C.V. Rode, R.B. Mane, A.S. Potdar, P.B. Patil, P.S. Niphadkar, P.N. Joshi	Cu	Waste Fly Ash	493	52	Sel:->85 % Conv:- 10-60%

2.3 Gas phase reaction:

It has been reported that propanediol is producible at gas phase conversion of glycerol with hydrogen pressure of 0.1– 5 MPa and reaction temperatures of 573 K have been applied [1].

Repotedly in gas phase reaction the yield of 1,2 Propane-diol is limited by equilibrium of the second step hydrogenation due to low hydrogen hydrogen pressure, so elevated pressure of hydrogen is preffered to shift equilibrium to produce 1,2 Propane-diol. Above all the selectivity of the intermediate, product is found to be affected with elevated temperature.

With ruthenium based carbon catalyst leads to excessive hydrogenation and results into cleavage of C-C bond and that results into formation of lower alcohol. Thus selectivity decreases in case of Ru supported carbon catalyst. However due to lower selectivity in gas phase reaction, it was proposed to carry out liquid phase reaction for further study for this report.

Table 2.3: Catalysts for gas phase reaction.

Sr. No	Journal Name,Vol & Page No	Title	Authors	Catalyst	Support	T (K)	P (bar)	Result (C,S)
GAS PHASE REACTION								
45	Catalysis Today 183 (2012) 3–9	Comparison Of Kinetics And Reaction Pathways For Hydrodeoxygenation of C_3 Alcohols On Pt/Al_2O_3	Baoxiang Peng, Chen Zhao, Isidro Mejía-Centeno, Gustavo A. Fuentes, Andreas Jentys,Johannes A. Lercher	Pt	Al_2O_3	473	40	Selectivity = 98.5%
46	Chemical Engineering Journal 168 (2011) 403–412	Gas Phase Hydrogenolysis Of Glycerol Catalyzed By Cu/ZnO/Mox(Mox =Al_2O_3, TiO_2, And ZrO_2) Catalysts	Yonghai Feng, Hengbo Yin, Aili Wang, Lingqin Shen, Longbao Yu, Tingshun Jiang	Cu/ZnO /Mox	Al_2O_3, TiO_2, And ZrO_2	513-573	1	(0,20)

47	Chinese Journal Of Chemical Engineering, 18(3) 384—390 (2010)	Kinetics Of Hydrogenolysis Of Glycerol To Propylene Glycol Over Cu-ZnO-Al_2O_3 Catalysts	Zhou Zhiming,Li Xun, Zeng Tianying, Hong Wenbin Cheng Zhenmin And Yuan Weikang,	Cu	ZnO, Al_2O_3	493-513	30-50	(81.5,93.9)
48	Journal Of Industrial And Engineering Chemistry 18 (2012) 818–821	Mediatory Role Of K, Cu And Mo Over Ru/SiO_2 Catalysts For Glycerol Hydrogenolysis	Xiaoyuan Liao, Kewen Li, Xiaomin Xiang, Sheng-Guang Wang, Xichun She,Yulei Zhu, Yongwang Li	Ru	SiO_2	<516	1	Conv: (K,Cu,Mo): (25,55,28) Selectivity : (6.3,26.2, 15.5)
49	Applied Catalysis A: General 391 (2011) 153–157	Selective Hydrogenolysis Of Glycerol Over Copper Catalysts Both In Liquid And Vapour Phase: Correlation Between The Copper Surface Area And The Catalyst's Activity	A. Bienholz, H. Hofmann, P. Claus	Cu	SiO_2	518	1-15	CuO, ZnO (52,98), Cu/ SiO_2 (19,78)

50	Chin. J. Catal., 2012, 33: 790–796	Comparison Of Ni_2P/SiO_2 And Ni/SiO_2 For Hydrogenolysis Of Glycerol: A Consideration Of Factors Influencing Catalyst Activity And Product Selectivity	Huang Jinhua, Chen Jixiang	Ni, Ni_2P	SiO_2	493	30	Ni/SiO_2:- (73.2, 49.9) Ni_2P/SiO_2:- (95.1, 85.9)
51	Bioresource Technology 111 (2012) 500–503	Aqueous Phase Hydrogenolysis Of Glycerol To Bio-Propylene Glycol Over Pt–Sn Catalysts	Maria L. Barbelli, Gerardo F. Santori, Nora N. Nichio	Ptsn	Support on SiO_2	473	40	Selectivity = 59% and 83%, Conv:- 54%

Chapter 3

CATALYST PREPARATION & CHARACTERISATION

3.1 CATALYST PREPARATION

3.1.1 CATALYST SELECTION

So far various catalysts are reported in the literature for hydrogenation of glycerol that includes Ru, Pt, Pd, Cu, Ni, Rh (Metals), Supports includes MgO, ZnO, SiO_2, Al_2O_3, γ-Al_2O_3,TiO_2 etc, and Promoters include K, Cu, Mo etc.

But among all Cu_Mg_Al Catalyst, Pd_Cu_Mg_Al and CAP (Na_2CO_3), CAP (NaOH), CAP (KOH) catalysts were reported with the best conversion, and selectivity, besides above all the major problem encountered among above catalysts is reaction time, Catalyst reduction temperature, etc.

Table 3.1: From various catalysts carried out the reaction condition for particular catalyst & result are:

Sr. No	Catalyst	Reaction Temperature (K)	Reaction Pressure (bar)	Reaction Time (hr)	Conversion (%)	Selectivity (%)
1	Cu_Mg_Al	453	30	20	80	98.2
2	Pd_Cu_Mg_Al	453	20	10	88	99.6
3	CAP(Na_2CO_3)	493	52	5	62	88
4	CAP(NaOH)	493	52	5	51	88
5	CAP(KOH)	493	52	5	58	88

With ref. to above mentioned catalyst it is planned to utilize these catalyst at less severe conditions and modifications was planned to enhance its activity and selectivity even at lower temperature and pressure conditions.

3.1.2 Catalyst preparation for Pd_Cu_Mg_Al & Cu_Mg_Al catalyst

1. Dripping Process:- The procedure follows as Solution A containing $Cu(NO_3)_2.3H_2O$, $Mg(NO_3)_3.9H_2O$, $Al(NO_3)_2.6H_2O$ with molar ratio of 0.4:5.6:2 are added in 400 ml distilled water. That is mixed with solution B containing Na_2CO_3, NaOH with concentration 0.25, 0.8 mol/L respectively. Solution A is mixed with B until pH of 9.5 is reached.

2. Reflux: Then the suspension is circumfluence in a 1L (RBF-Round Bottom Flask). The reflux is carried out for 12 hr at 110°C.

3. Washing & Filtration:- Then the resultant suspension is allowed to cool for some time and then washing and filtration is carried out until it reaches pH of 7 using distilled water.

4. Drying:- After which the slurry is dried in oven for 12 hr at 80°C until it is completely dried.

5. Calcination:- The dried contain is then powdered followed by calcinations at 300°C for 4 hr.

6. Reduction:- Before reaction the catalyst is reduced for 1 hr at 300°C.

Dripping Process :-
Mixing of solution A & B along with stirring for 2 hr.

↓

Reflux :-
Processing the suspension within for 12 hr.

↓

Filtration & Washing :-
Filtering & washing the slurry until pH of 7 is achieved.

↓

Drying & Calcination :-
The resulted suspension is dried for 12 hr followed by calcination for 4 hr

↓

Reduction:-
Reduction with H_2at 300°C for 1 hr.

↓

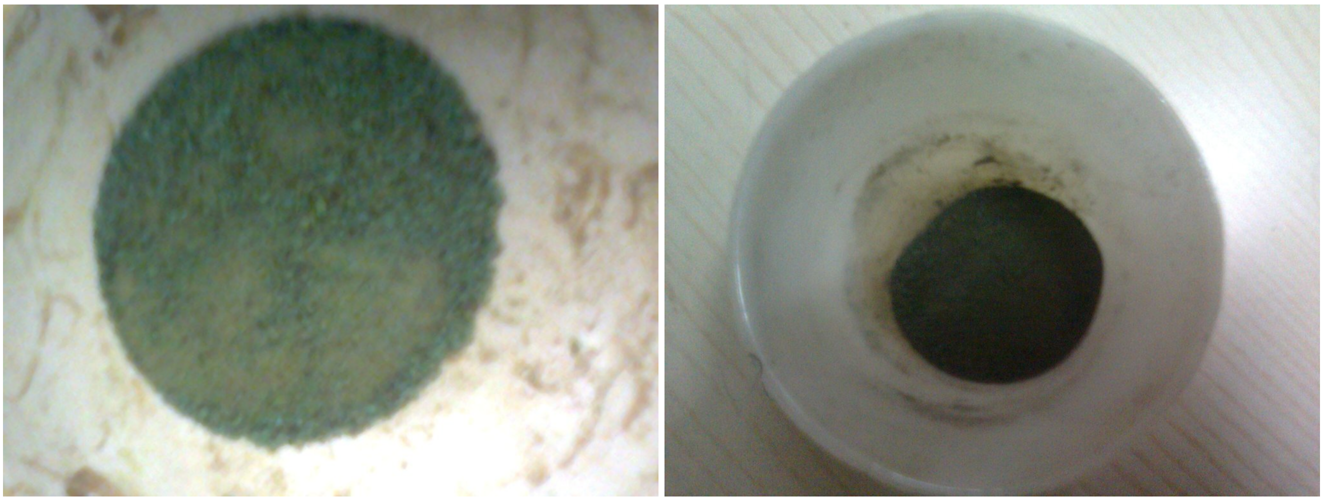


Figure 3.1: Final Form of catalyst Cu_Mg_Al & Pd_Cu_Mg_Al

3.1.3 Catalyst preparation for CAP(Na_2CO_3), CAP(KOH), CAP(NaOH)

1. In a typical procedure, simultaneous addition of equimolar (0.05 M) mixture of aqueous solutions of $Cu(NO_3)_2.3H_2O$, $Al(NO_3)_2.6H_2O$ and 0.2 M K_2CO_3 to 5–10 mL of water taken in a round bottom flask at room temperature gave the precipitate of the mixed precursor.

2. The final pH of the precipitate was maintained in a range of 8–9.

3. This was digested for 5–6 hr and then filtered and washed with deionized water to remove the traces of potassium.

4. Thus the obtained precipitate was dried in oven at 100°C for 5–8 hr.

5. By following the same procedure Cu–Al catalysts were prepared using different precipitating agent's i.e KOH, NaOH and Na_2CO_3.

6. The prepared catalysts were nominated as CAP (NaOH), CAP (Na_2CO_3), CAP (KOH).

7. All the prepared catalysts were calcined at 400°C for 3 hr.

8. The catalyst is activated under H_2 flow at 200°C for 12 hr.

Mixing of $Cu(NO_3)_2.3H_2O$ (6.66 gm), $Al(NO_3)_2.6H_2O$ (10.33 gm) and NaOH(4 gm)

↓

Mixing until pH of 8-9.

↓

Digested for 5-6 hr washed & filtered.

↓

Drying at 100°C for 5-8 hr.

↓

Calcined at 400°C for 3 hr.

↓

Activated at 200°C for 12 hr under H_2 flow.

↓

Figure 3.2: Final form of Catalyst CAP(NaOH), CAP(KOH), CAP(Na_2CO_3)

3.2 CATALYST CHARACTERIZATION

Heterogeneous catalyst is characterized by various components that includes (active species, physical and/or chemical promoters, and supports), shape, size, pore volume, pore distribution and surface area.

- Catalyst characterization is intended to correlate catalyst behaviour with their physical and chemical properties to predict catalytic result.
- Reasons for deactivation, and procedures for regeneration.
- Determining morphology/physical and chemical properties.

Catalyst characterization is carried out to determine effectivity, stability, activity etc.

3.2.1 Bulk

Though surface knowledge being essential, bulk properties finds its importance in being the nature of surface sites determined by those properties. the various techniques included are:-

1. Spectroscopic and diffraction techniques.
2. X-ray diffraction.
3. IR spectroscopy.
4. Raman spectroscopy.

3.2.2 Surface

The surface is place of catalytic activity where only its part is used for catalytic reaction. Catalyst based supported metal only occupies small portion of the total surface. whereas in case of acid catalyst that not only occupies surface but differ in acid strength and nature. To understand catalysts activity decaying with respect to time, performance, nature of active site is essential. The various techniques employed are:

1. Volumetric, gravimetric and dynamic adsorption methods,
2. Adsorption calorimetry,
3. IR spectroscopy,
4. Raman spectroscopy,
5. Temperature programmed desorption

3.2.3 Morphology

The importance of morpholgy lies in development of catalyst and provide necessary feedback required for obtaining suitable result. As a matter of fact to understand or study the catalytic behaviour requires the knowledge of the morphological characteristics.The morphological characteristics of interest are the specific surface area, the specific pore volume, and the distribution of the area and of the pore size.

1. micropores (+ < 2 nm),
2. mesopores (2 < 4 < 50 nm),
3. macropores (4 > 50 nm).

Most of the heterogeneous catalyst are porous solid, that arises from preparation method of solid.The porous structure provides the solid to have a total surface much higher than that corresponding to the external one. Most common catalysts have a specific surface area between 1 and 1000 m^2/g, while their external specific surface area is in the range 0.01-10 m^2/g. The various techniques used are

1. Vapour adsorption at low temperature (nitrogen adsorption),
2. Mercury porosimetry,
3. Incipient wetness method,
4. Permeametry and counterdifision,
5. Microscopy [scanning electron microscopy, transmisson electron microscopy].

So far copper alumina phosphate catalyst with NaOH and KOH provided some necessary result so CAP(NaOH) catalyst was carried out for characterization. Results of the characterization of NaOH catalyst for DLS is as follows:

DLS (Dynamic light scattering):

Dynamic light scattering test methods confirms size of catalyst particles. Dynamic Light Scattering is also known as Photon Correlation Spectroscopy. This technique is one of the most popular methods used to determine the size of particles. Shining a monochromatic light beam, such as a laser, onto a solution with spherical particles in Brownian motion causes a Doppler Shift when the light hits the moving particle, changing the wavelength of the incoming light. This change is related to the size of the particle. It is possible to compute the sphere size distribution and give a description of the particle's motion in the medium, measuring the diffusion coefficient of the particle and using the autocorrelation function.

The analysis of CAP(NaOH) has been carried out at Shah-schulman center for surface science and nanotechnology, D.D.University, Nadiad. which affirms that the average particle size of CAP(NaOH) id 291.1 dnm. DLS test had been carried out using water as an dispersant at 25°C for 150 second duration.

Following test conditions were maintained during test.

- Count Rate (kcps) : 201.8
- Measurement Position (mm) : 4.65
- Cell Discription : Disposable sizing cuvette.

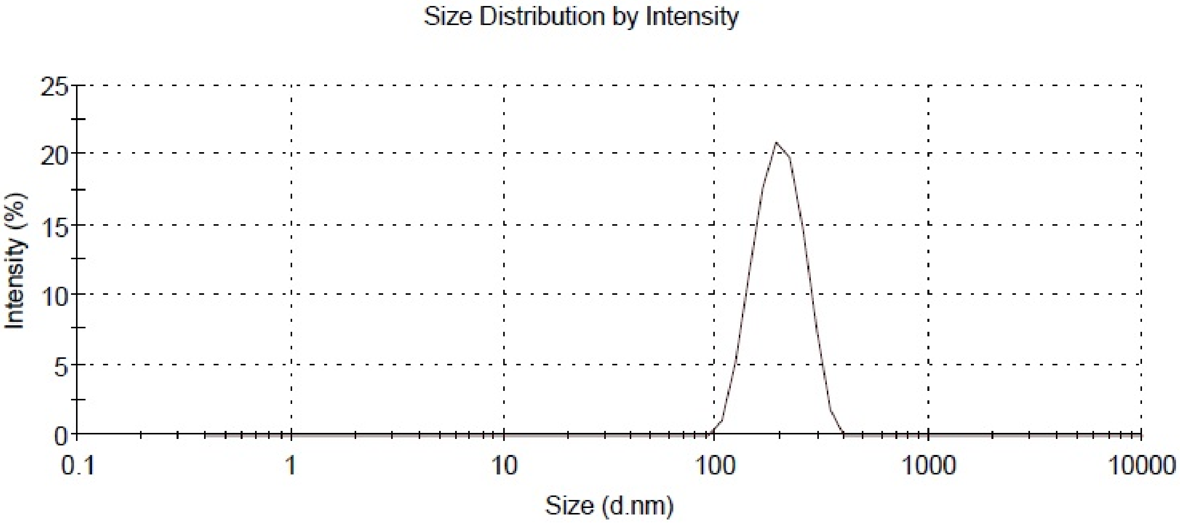


Figure 3.3: DLS(Dynamic light scattering) analysis of CAP(NaOH) catalyst

Based upon suitable conversion obtained from CAP (NaOH) and CAP(KOH). catalyst CAP(NaOH) was characterized with DLS (Dynamic light scattering) that confrims size of particle to be 291.1 d.nm

Chapter 4

EXPERIMENTAL SETUP

Before reaction is being carried out in the reactor, it is being cleaned with Water, 2-Propanol. Throughout all the catalyst the reaction temperature, reaction pressure and time were maintained the same i.e 180°C, 30 bar, 5 hr. Firstly the reactant is charged i.e Glycerol and 30 bar H_2 pressure. Secondly the temperature is increased from 35 to 180°C slowly. During the reaction each sample at every 1 hr is collected, the reaction is carried out for 5 hr. The obtained sample of the reaction is analyzed using GC (Gas Chromatography- 2010), Using RTX-Wax Capillary column. All the GC result are provided in Appendix B.

Figure 4.1: Image of the reactor.

Following GC analysis was carried out using RTX-Wax capillary column with a maximum temperature of 250°C, Inner diameter of 0.25 mm ID, with film thickness of 0.25µm at 30 m length. Following analysis was carried out with temperature of injection being 200°C, 90°C for column temperature and FID temperature at 230°C. The mode of injection was split, other than that in split injection mode the pressure was kept 14.5 psi with a total flow of 50 mL/min, and purge flow of 3 mL/min. In the FID section the flow of $H_2$was kept 40 mL/min and flow of air was kept 400 mL/min, the make up flow was kept 30 mL/min. And the total program time for the analysis was 28.57 min.

Chapter 5

RESULTS & DISCUSSIONS

After carrying out reactions with various catalysts. CAP(KOH), CAP(NaOH) catalyst came up with some possible outcome of 5.5 & 4.2%.

Table 5.1: Result of various catalyst carried out for reaction.

Sr.No	Type of catalyst	Conversion (%)	Selectivity (%)
1	CAP(KOH)	5.5	97.89
2	CAP(NaOH)	4.1	98.00
3	CAP(Na_2CO_3)	0.01	48.78
4	Cu_Mg_Al	2.5, 1.2	100
5	Pd_Cu_Mg_Al	0.15	91.25

Two major reasons can be contributed for poor performance of reaction. They are improper preparation of catalyst and less severe conditions of operation can be considered.

During catalyst synthesis following problems were faced

1. Catalyst reduction temperature.
2. pH.
3. Foreign contaiminants.
4. Reflux temperature.
5. Reduction time.

All reactions are carryout at 180°C and 30 bar (g) pressure. However these temperature and pressure values are much lower than the reported conditions. Apart from that reaction time is also very less, 5 hours compared to reported time ranging from 24 hours.

It is expected that due to these two major reasons, conversion of glycerol achieved over here are much less compared to reported conversion. Apart from these hydrogen pressure play a key role in increasing solubility of hydrogen in liquid mixture during reaction. Hydrogen pressure more than 50 bar (g) would be the minimum pressure required to have good solubility of hydrogen in reaction mixture. So such processes requires tremendous high pressure of hydrogen.

Chapter 6

FUTURE SCOPE

There were many catalyst carried out so far, the result obtained are stated below whereas during following carried out reaction various parameter were varied that include following:

1. Glycerol concentration.
2. Temperature.
3. Pressure.
4. Volume of the reactant.
5. Catalyst loading.
6. Reaction time.
7. Catalyst reduction time.

Chapter 7

CONCLUSIONS

Based on literature survey, high performance catalyst were selected and synthesized in laboratory. However results of these experiments are not encouraging.

Based on the experiments conducted, conversion was only about 4-6% with about 90-98% selectivity for 1,2 Propane-diol. However for the same catalyst, reported conversion in the literature is 58% with selectivity of 88% but at pressure of 52 bar,

Improper preparation of catalyst and less severe conditions of operation can be considered. Due to certain problems arise during catalyst synthesis, catalyst may not have gained its proper structure.

All reactions are carryout at 180°C and 30 bar (g) pressure. However these temperature and pressure values are much lower than the reported conditions. Apart from that reaction time is also very less, 5 hours compared to reported time ranging from 24 hours.

It is expected that due to these two major reasons, conversion of glycerol achieved over here are much less compared to reported conversion. Hydrogen pressure play a key role in increasing solubility of hydrogen in liquid mixture during reaction. Hydrogen pressure more than 50 bar (g) would be the minimum pressure required to have good solubility of hydrogen in reaction mixture. So such processes requires tremendous high pressure of hydrogen.

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APPENDIX A

Catalyst calculation for Cu_Mg_Al

Table 7.1: Molecular weight of various chemical component.

Sr.No	Chemical	Molecular weight (gm/mol)
1	$Cu(NO_3)_2.3H_2O$	241.60
2	$Mg(NO_3)_3.9H_2O$	256.4018
3	$Al(NO_3)_2.6H_2O$	375.13
4	$PdCl_2$	177.33
5	NaOH	40
6	Na_2CO_3	106
7	CuO	79.539
8	MgO	40.304
9	Al_2O_3	101.961
10	PdO	122.419

CuO + Al_2O_3+ MgO = 57.68 (acc to 0.4:5.6:2 molar ratios)

1 mole contains 57.68 gm

So,

5 gm = 0.08668516 total moles are required for preparing 5gm catalyst.

Table 7.2: Quantity of various chemical components required for preparation of 5 gm catalyst.

Sr.No	Chemical	Gm
1	CuO	0.344743
2	MgO	2.445631
3	Al_2O_3	2.209626
4	Catalyst	5

Table 7.3: Quantity of chemical required for preparation of 5 gm Cu_Mg_Al catalyst.

Sr.No	Chemical required	Gm
1	$Cu(NO_3)_2.3H_2O$	1.05
2	$Mg(NO_3)_3.9H_2O$	8.13
3	$Al(NO_3)_2.6H_2O$	15.56

Catalyst calculation for CAP(Na_2CO_3), CAP(KOH), CAP(NaOH)

$CuO + Al_2O_3$ = Cu_Al catalyst (181.5069774)

Table 7.4: Molecular weight of various components.

Sr.No	Components	Molecular weight (gm/mol)
1	Cu	63.5463
2	Al	26.98
3	O	15.9994
4	CuO	79.5457
5	Al_2O_3	101.96
6	$Cu(NO_3)_2.3H_2O$	241.60
7	$Al(NO_3)_2.6H_2O$	375.13

In the above reaction totally 2 moles are involved as they are equimolar and assuming 5 gm of catalyst.
So, 2 moles contains 181.5069774 gm of catalyst so for
Therefore 5gm catalyst contains = 5*2/181.5069774 = 0.0550943 moles
So each CuO and Al_2O_3contains 0.02754715 moles,
Now,
1 mole CuO contains 79.5457 grams ,
So, for 0.02754715 mole contains = 0.02754715*79.5457 = 2.19125736 grams,
1 mole Al_2O_3 contains 101.9612774 grams,
So, for 0.02754715 mole contains = 0.02754715*101.9612774 = 2.80874264 grams
That is total grams required for catalyst = 2.19125736 + 2.80874264 = 5 grams
Now, grams of$Cu(NO_3)_2.3H_2O$ required: - 241.60*0.02754715 = 6.65539153 gram
Similarly, grams of $Al(NO_3)_2.6H_2O$ required: - 375.13*0.02754715 = 10.3337625 gram.

APPENDIX B

- Standard sample:

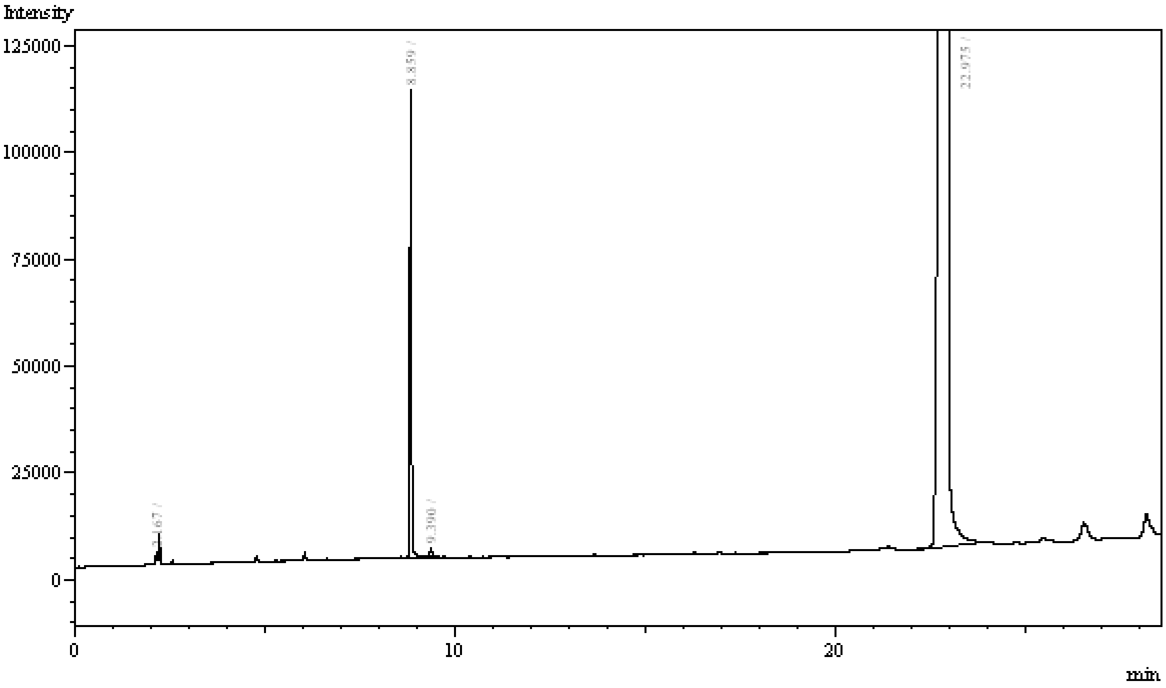

Figure 7.1: Standard sample

- Reaction sample of KOH:

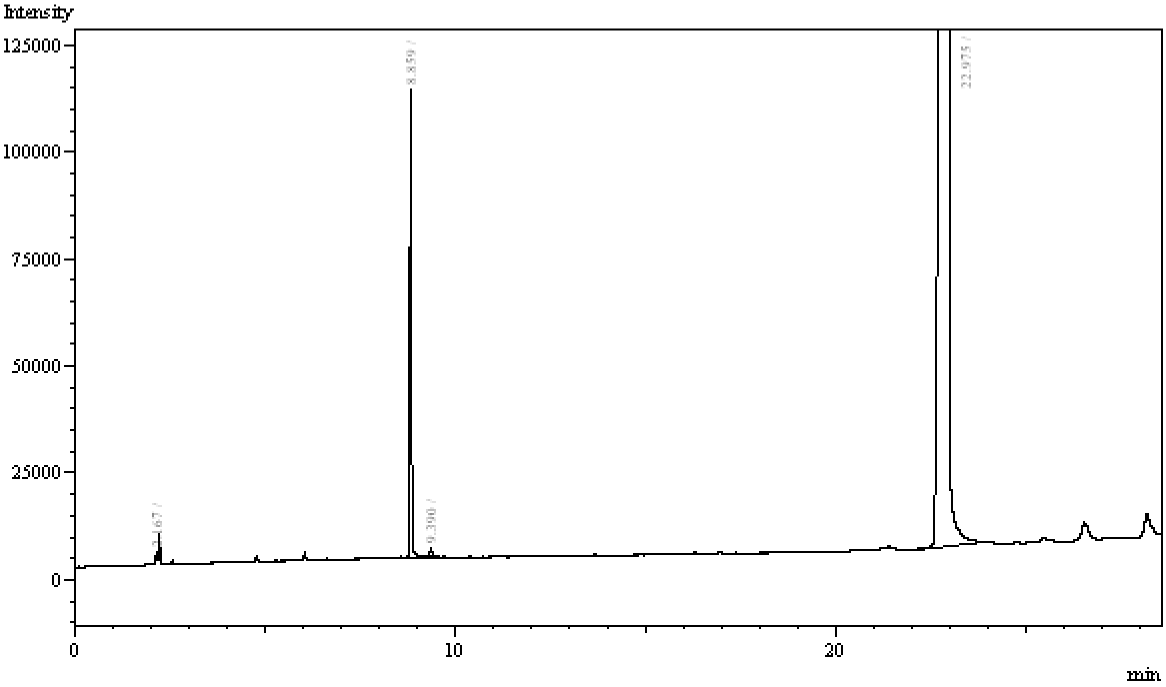

Figure 7.2: Reaction sample of KOH

- Reaction sample of NaOH

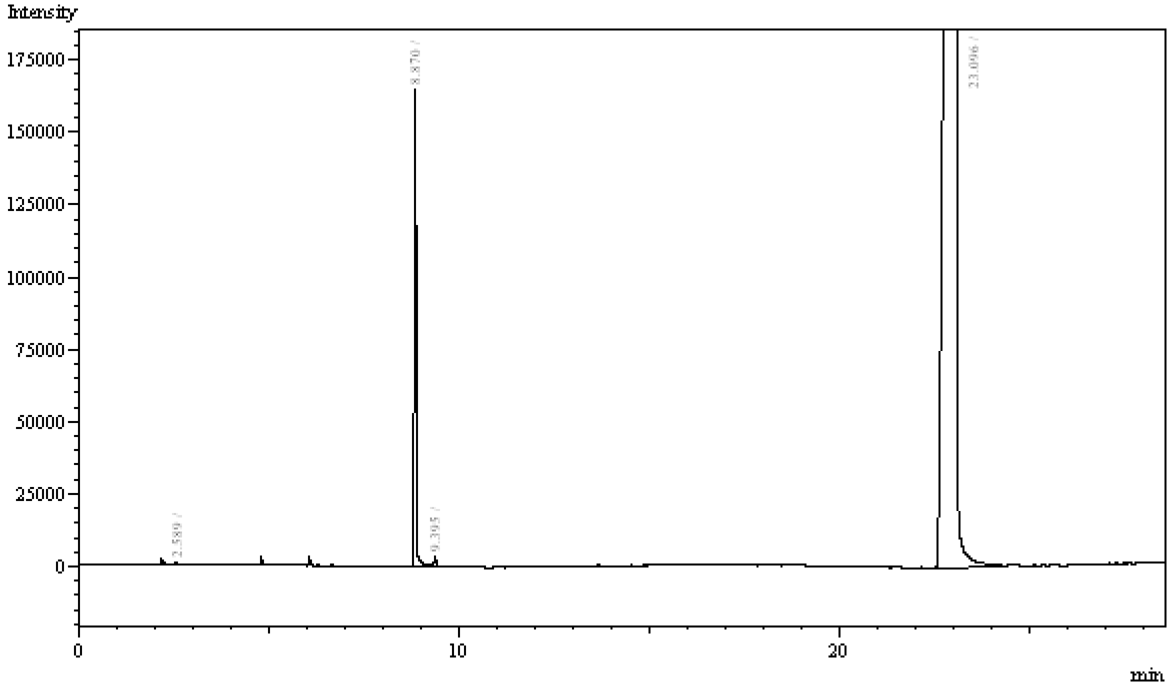

Figure 7.3: Reaction sample of NaOH