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MIXED METAL OXIDE CATALYSTS SUPPORTED ON H-BETA FOR
HYDROGENOLYSIS OF GLYCEROL INTO 1,3-PROPANEDIOL

by

AMIT KANT

A THESIS

Presented to the Faculty of the Graduate School of the
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In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE

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Approved by

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ABSTRACT

Bioglycerol is the by-product which is produced largely from the microbial fermentation, hydrogenolysis of glucose in the mixture of polyols, fatty ester, soap manufacturing process and fatty acid production. Hydrogenolysis of glycerol is one of the most promising ways to convert glycerol and many work has been done towards 1,3-propanediol, 1,2-propanediol and 1-propanol using various metals and mixed-metal oxides such as W, Ru, Rh, Pt, Pd, Cu, Ni and different zeolites have been extensively used as the active components.

It has been well documented that the presence of Bronsted acid sites leads to the formation of acrolein, while Lewis acid sites, and even basic catalysts, gives rise to hydroxyacetone as the main product. However, there is little research on the use of H-Beta zeolite as the catalyst and metals support for hydrogenolysis of glycerol.

The investigations conducted in this study consist of the development of active catalysts as well as optimize process conditions, in the dehydration of glycerol to value-added chemicals. The use of different H₂ pressures above 600-1200 psi, reaction temperatures 180-220 °C, reaction times (5-10 h), and the optimum catalyst/reactant ratios leads to significant impact of the liquid-phase reactions and the formation of products.

Various bi-metallic catalysts based on W, Cu, Ni, Sr, Zr and Zn are studied with regard to the dependence of activity and stability in hydrogenolysis of glycerol with H-Beta zeolite support. All prepared catalysts are characterized using various analysis techniques such as N₂ sorption, XRD, FTIR, and NH₃-TPD and the obtained organic products are then further analyzed with the help of GC-FID and GC-MS.

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1. INTRODUCTION

1.1. RENEWABLE ENERGY SCENARIO

The as usual concern of people regarding the energy demand is still persisting as the current development of the energy sources is not sufficient to meet the drastically growing demand of it. Still thanks to people who are putting their efforts continuously to bring out the solution in response of the growing industrial, commercial and residential demands. The overuse of the natural resources like fossil fuels has led to the depletion of the existing possibilities on which hopes of the people were relying [1]. Many countries, including both developed and undeveloped, even after the multifold production of energy sources, are not able to indemnify for the gap created between supply and demand [2]. Other problems include deterioration of the climate due to the excessive use of the fossil resources such as coal. These causes to release various gases in the atmosphere such as SO_2 , NO_x , C_xH_x , soot, ash, droplets of tar and other greenhouse gases like CO_2 [3]. As per the world energy consumption report by Shell, even if it were possible to maintain the share of fossil fuels with the growing demand, the CO_2 emission would remain the threaten to human well-being. The concentration of it in long term is expected to go beyond 550 ppm which started with 280 ppm in pre-industrial times [4]. If this is not controlled in the future then it will surely lead to some major natural issues like floods and acid rain [5, 6].

Also, the limited availability and excessive use of fossil resources has led to the drastic decrease in the production oil in last few decades. Again as shown in Figure 1.1, as per the report of world energy consumption by Shell, the demand of energy is going to be doubled by 2050 [4]. Since, it is now understood that the current situation is becoming

alarming so there is urgent need for everyone to rise and work towards the solution. This platform calls for all the scientists and researchers around the world to come together and work towards the development of clean and alternative sources of energy.

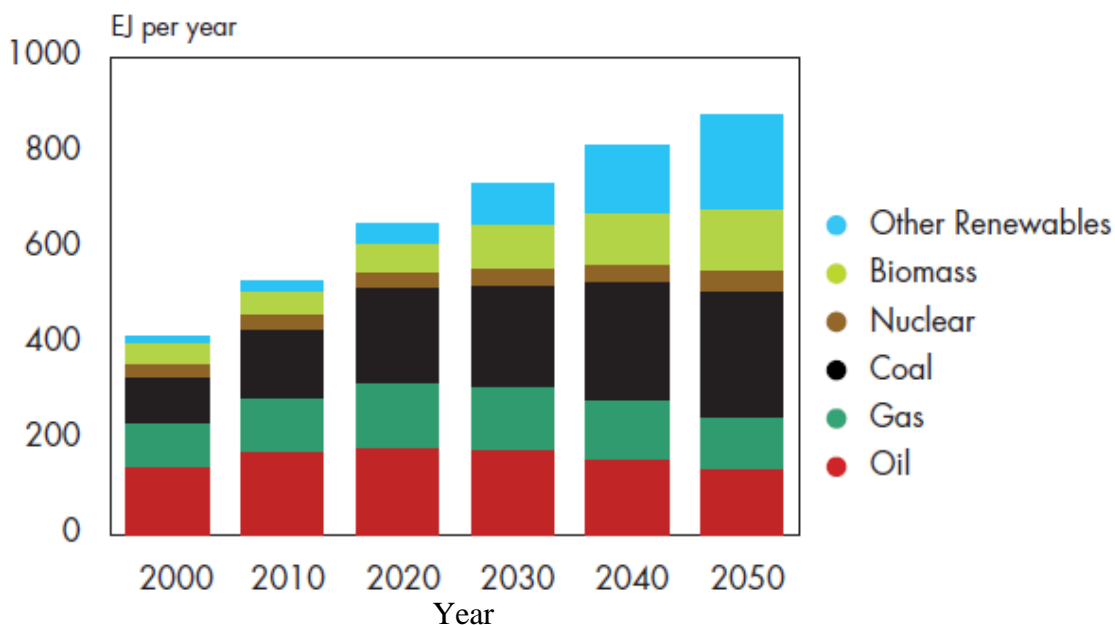


Figure 1.1 Energy consumption outlook to 2050 by Shell [4].

1.2. BIODIESEL PRODUCTION (BIODIESEL MARKET)

Nowadays, significant work has been done and is still going on to use the renewable resources as a feedstock for the productions of chemicals, fuels and various other materials which are being used as an alternate for energy. For last many years, scientific community has turned preferentially towards the production of energy from the biomass by converting it into fuels and chemicals such as biodiesel. Biomass represents around 15% of the primary energy of the world by 2050 [4] and where biofuels particularly plays a major role in supply of fuels to meet energy demand of people as shown in Figure 1.2. The demand of biomass, which is considered as a desirable

candidate as an alternative and carbon neutral resource, is following the increasing trend [7, 8]. It is one of the carbon neutral source which can be used to convert into various kinds of fuels either in the form of solid, liquid or gases through various conversion process [9]. The consumption of biomass goes into production of biodiesel and some other biomass based products to mitigate the shortage of fossil fuels [1, 10]. Scientists claimed and proof that biodiesel is one of the renewable resources which is non-toxic, biodegradable and friendly to our environment [11, 12]. It is also termed as the “substitute or an additive to diesel fuel that is derived from the oils and fats of plants and animals” [13]. As per the report of US department of agriculture, the European market is having the largest market of biodiesel with the production of 12.5 million cubic meters in 2014 [14]. The US, who also plays a major role in the production of biodiesel, holds the contribution of 4.8 million cubic meters in 2014 [14]. Researchers also estimated that by 2016, the overall growth of biodiesel will increase to 37 billion gallons [15].

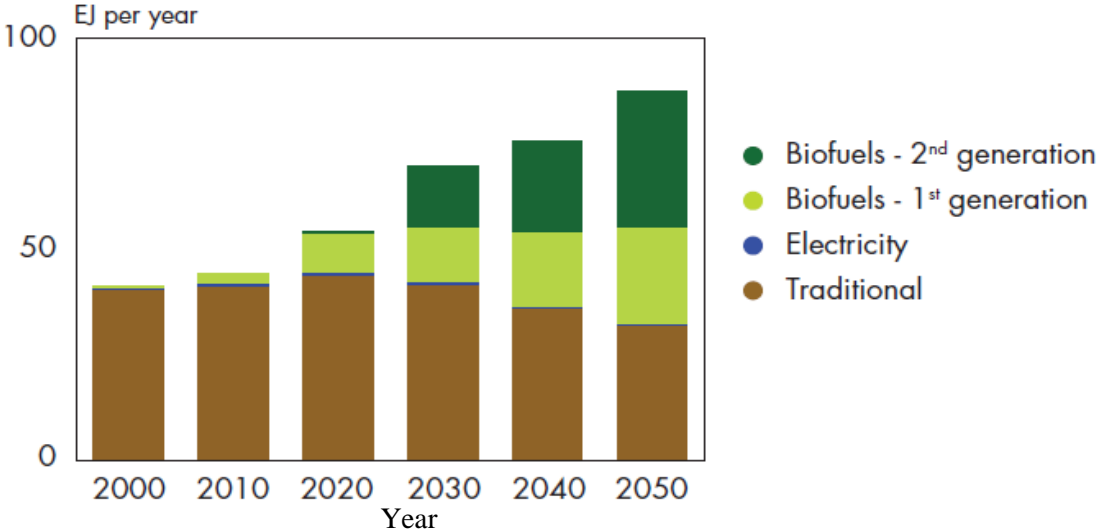
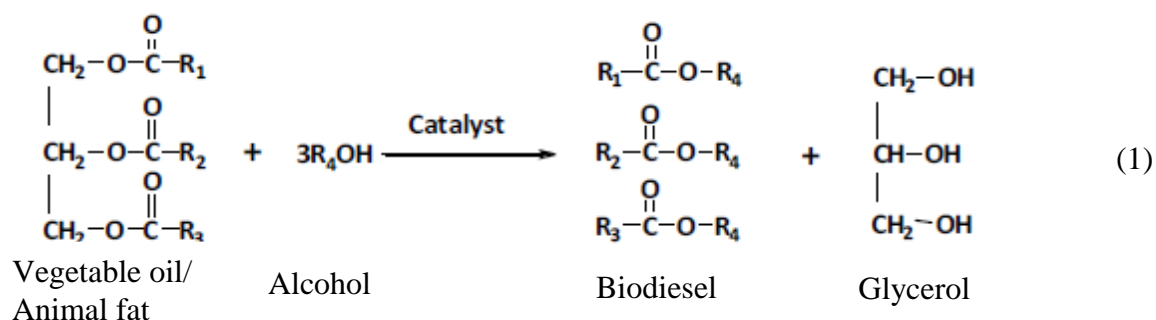


Figure 1.2 Biofuels consumption outlook to 2050 by Shell [4].

Biodiesel can be produced from lots of feedstock like soybean, mustard seed, rapeseed, canola, waste cooking oils, animal fats and also several chemicals has been used such as short chain alcohols (methanol or ethanol) [16, 17]. Basically, it is produced through the transesterification process in which fatty acids are reacted with alcohols as shown in the Equation 1 [18]. The process generally involves high cost due to the requirement of these feedstocks. But the processes can be made cost effective if the by-product of this reaction can be used to make other value added products.



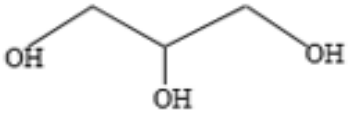
1.3. GLYCEROL AS A BY-PRODUCT AND ITS PROPERTIES

Glycerol (1,2,3-Propanetriol), as a renewable source is entering into the market in abundant amount as the side product of the biodiesel manufacturing [19]. Amongst all polyols present in biomass, glycerol is the smallest one and it is considered as the backbone of the triglycerides [20]. For every 100 kg production of biodiesel, 10.5 kg of glycerol is obtained as the by-product at very low price [21]. The US alone is responsible for the production of glycerol as the side product with around 340,000 tons of gallons entering into the market every year [22]. This boom in the market of glycerol has led to the declination of its price because of its incomplete use irrespective of its supply i.e.

excess supply and limited demand. Till now, several works has been reported about the conversion of glycerol into value added products and new process is still in developing stage which can make the biodiesel industry more economical.

Glycerol is a highly reactive molecule with 3 hydroxyl groups, two primaries and one secondary. Also, physically it is colorless, odorless, soluble and viscous with density of 1.261 g/ml [23, 24] as shown in Table 1.1. Chemically, glycerol is non-toxic, non-flammable and non-volatile and it reacts with most of the alcohol easily under most of the operating conditions. Due to all above mentioned properties, glycerol is having hundreds of uses and large volume of applications. It is also used in cosmetics, food products, antifreeze, solvent, sweetener and many more [23, 24]. Also, lots of work has been already done to utilize the glycerol into value added products through various chemical processes.

Table 1.1 General properties glycerol.

Molecular formula	$C_3H_8O_3$
IUPAC name	Propane-1,2,3-triol
Molecular weight	92.09 g/mol
Chemical Structure	
Density	1.262 g/ml
Boiling point	290 °C

1.4. APPLICATION OF GLYCEROL

In general, there is not much direct use of glycerol as such other than the cosmetic and food industry. Unfortunately, people burn large amount of glycerol directly and one of the renewable source is getting wasted [7]. In last few decades, scientists are able to utilize this compound in large number of industrial uses. As shown in Figure 1.3, large part of its share is involved in pharmaceutical which is 18%. Second largest share goes into polyols (14%) because through catalytic process it can be used in production of polyester, films and coatings. The remaining major share includes food and others as 11%, triacetin (10%) and various others [11].

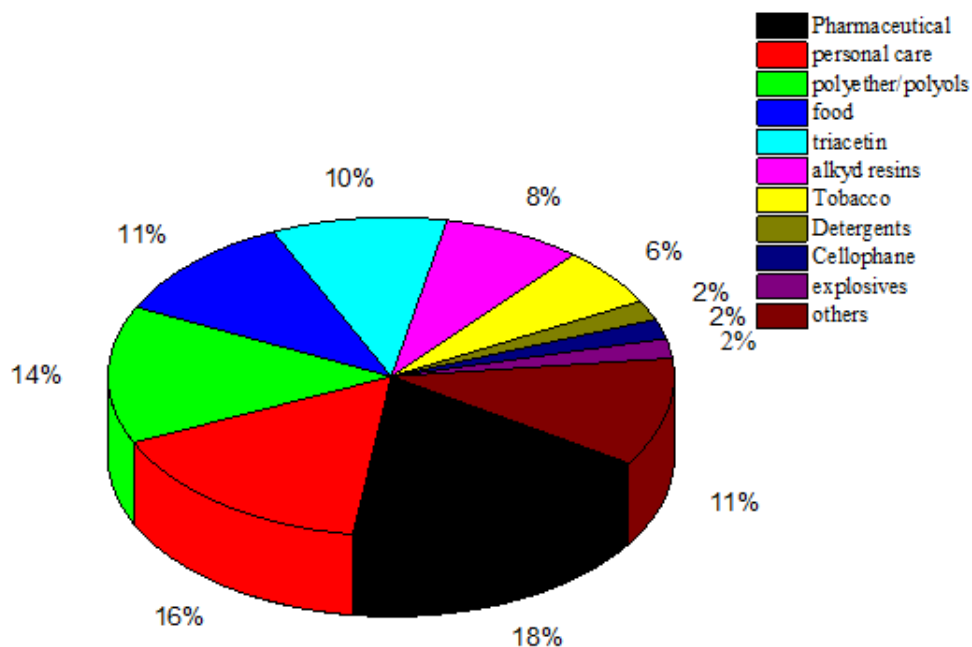


Figure 1.3 Glycerol market (general uses of glycerol).

In recent years, many researchers are mainly focusing on the hydrogenolysis of glycerol into 1,2-PDO and 1,3-PDO which is considered as the most promising and

highly effective process to utilize the surplus amount of glycerol into valuable chemicals [25]. 1,2-PDO can be used as an ingredient for manufacturing of variety of products like paints, antifreeze, pharmaceuticals, detergents, cosmetics, polyester raisins, flavors and many more [26]. The other chemical 1,3-PDO, which is considered as even more valuable and have much higher economic value than 1,2-PDO is used as an important monomer in the synthesis of polyester fibers, films and coatings [26, 27]. Further conversion of propanediols into lower alcohols also leads to the production of some useful chemicals such as propanol, methanol and ethanol which is also of great interest to the researchers from the industrial perspective [22]. The other important use of the glycerol is its conversion into one of the most important chemicals which is acrolein. It has again having the broad number of uses like feedstock for acrylic acid, used as an herbicide for growth of aquatic plants, pharmaceutical and other uses [28].

1.5. UTILIZATION OF GLYCEROL THROUGH VARIOUS PROCESSES

The obtained glycerol in the byproduct has too much impurities such as fatty acids, oils and other chemicals which cannot be used directly without undergoing any purification and filtration process [17]. This scenario calls for the urgent development of novel techniques to utilize the renewable glycerol for the sustainable development of biodiesel industry [29]. Through intensive research, scientists has developed various conversion processes of glycerol like oxidation [30], dehydration [31], hydrogenolysis [32], esterification, gasification, carboxylation and fermentation [4, 11-13]. These transformation processes gives various valuable products like 1,2-Propanediol (1,2-PDO), 1,3-Propanediol (1,3-PDO), 1-propanol (1-PO), isopropanol (2-PO), acrolein [33],

lactic acid [28], propylene glycol [34] and ethylene glycol (EG) [35]. Also, glycerol hydrogenolysis is one of the most attractive paths because glycerol contains high oxygen content and reduction of C-O bond is comparatively favorable. There are number of uses obtained from various conversion processes into valuable chemicals as illustrates in Figure 1.4.

There are also some works by the researchers which includes conversion of glycerol into hydrogen rich gas using catalytic process [36-38]. In one of the research by Thiruchitrambalam et al., the glycerol was converted into H₂ rich syn-gas by using the pyrolysis process at 800 °C in a fixed bed reactor [39]. In other work, Chaudhari and Bakhshi performed the steam gasification of glycerol to produce syn-gas and they reported that approximately 80 wt% of glycerol was converted and 92.3 mol% of syn-gas was produced. They proposed that the produced syn-gas can further be treated to produced hydrogen and also green fuels. But there has not been much work on this direction.

Another way of utilization of glycerol is through bioconversion process which provides broad range of methods. Being the carbon and energy source, fermentation is one of the bioconversion process of glycerol where microorganism attack takes place to convert it into value added products [40]. This conversion process may prove to use glycerol as a substitute of sucrose, glucose and starch [41-43]. In spite of having good feasibility and mild operating conditions, there are few restrictions in using this process at full capacity because of the longer pretreatment process due to impurities present in the crude glycerol which further leads to high cost factor [44-46].

Due to the above mentioned broad uses of these compounds, there has been an extensive study in the previous years in hydrogenolysis conversion of glycerol to these chemicals. Researchers have studied glycerol hydrogenolysis in both the phases, liquid and gas. Being a linear polymer with 3 hydroxyl groups, glycerol reaction into various chemicals seems to be very easy. But the selective reaction of glycerol is a tricky process which requires selective carbon-carbon or carbon-oxygen bond cleavage and addition of hydrogen atom takes place to form molecular fragment [25]. Researchers have experimented various mechanism using different heterogeneous and homogeneous catalysts like metallic and bi-metallic, zeolites and heteropolyacids. Various metals are included in the list like Cu [34, 47, 48], Ni [34, 49], Pd [34, 47], Pt [34, 50], Ru [51] and Rh [52] etc. of which Ruthenium has shown the comparatively high activity among these metals [19].

Also researchers concluded that generally glycerol conversion can follow two routes [22]. Out of which one is where oxidation or reduction of glycerol takes place into hydroxyacetone [53], propylene glycol [34], lactic acid [28] etc. And the other route is where reaction takes place between glycerol and the other compounds or molecules into some useful chemicals which can be further used as a precursor into some other new chemicals or polymer precursor [22]. Though there are too many process mentioned above for glycerol conversion but not all the process are feasible in terms of conversion, selectivity and yield. The process involves optimum operating parameters and conditions. Also, there is a need of right type of catalyst which is generally the driving factor to get the particular required products.

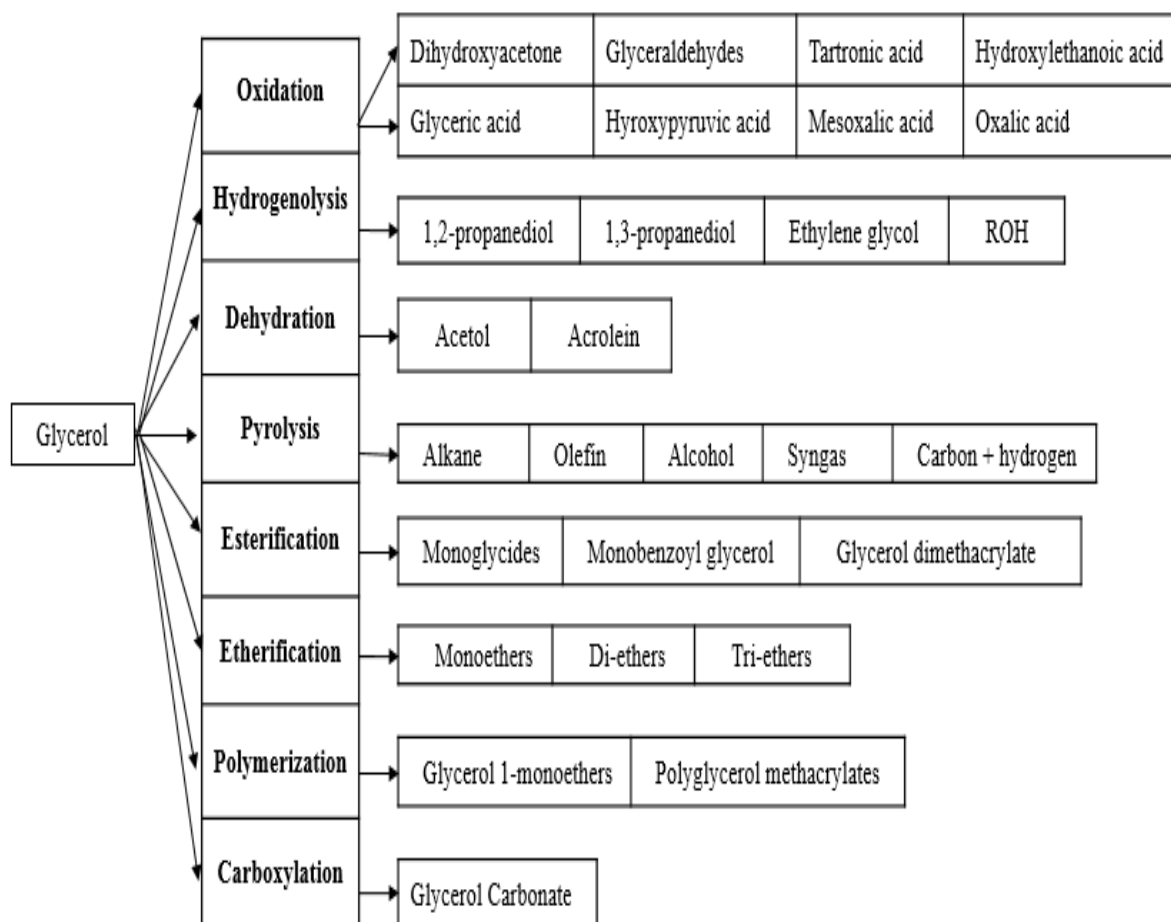


Figure 1.4 Glycerol conversion products from various mechanisms [26].

2. OBJECTIVE

The overall objective of this thesis is to convert the glycerol into valuable chemicals which are 1,3-propanediol, 1,2-propanediol, and 1-propanol with good conversion and selectivity. Also in order to achieve these goals, following steps are followed:

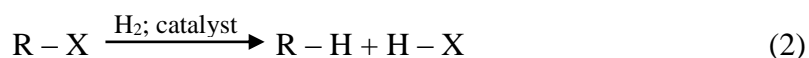
1. Preparation of the heterogeneous catalysts using zeolite beta and mixed metal oxides.
2. Characterization of the developed catalysts with the various techniques such as X-ray diffraction (XRD), N₂ sorption, Fourier Transformed-Infrared spectroscopy (FT-IR) and Ammonia-Temperature Programmed Desorption (NH₃-TPD).
3. Evaluation of all the catalysts by using batch continuous stirred tank (CSTR) reactor at high pressure and temperature.
4. Analysis of the obtained products by using Gas Chromatography- Flame Ionization Detector (GC-FID) and Gas Chromatography Mass Spectrometry (GC-MS).

For all the tasks, proper methodology and process development was done and applied in the experiment.

3. LITERATURE REVIEW

3.1. HYDROGENOLYSIS OF GLYCEROL

Hydrogenolysis reaction is basically involves the cleavage of C-O bonds and C-C bonds in order to produce variety of bulk organic chemicals as shown in the Equation 2. The reaction generally occurs in the presence of H₂ source and catalysts. Hydrogenolysis is one of the most important reactions in the biomass industry to upgrade it into hydrocarbons, polyols and other alcohols [47]. Many catalytic hydrogenolysis systems under basic operating conditions has been developed by researchers which includes metal catalysts like Ru, Pd, Pt, Ni, Cu etc [34, 47, 51, 54, 55].



Hydrogenolysis of glycerol has been studied by many people in the past few years. The presence of the highly functionalization group in the molecule, which is 1,2,3-propanetriol, opens the door to many valuable and useful chemicals [11, 56]. The cleavage of the C-O bond of the glycerol molecule becomes an alternative path for hydrogenolysis of glycerol into polyols (1,2-PDO, 1,3-PDO, ethylene glycol), alcohols (1-propanol) and hydrocarbons (propane, propene) [57].

Montassier et al. proposed the reaction mechanism which involves the base and the metal catalyst to convert the glycerol into diols as shown in Figure 3.1 (a). This reaction involves glyceraldehyde as the intermediate [58]. Dasari et al. on the other hand proposed the mechanism which involves the formation of acetol in the presence of acid and metal catalysts [34] as shown in Figure 3.1 (b). These mechanisms were also

followed by many other researchers and to obtain the high selectivity many different kinds of metal and different operating conditions were implied.

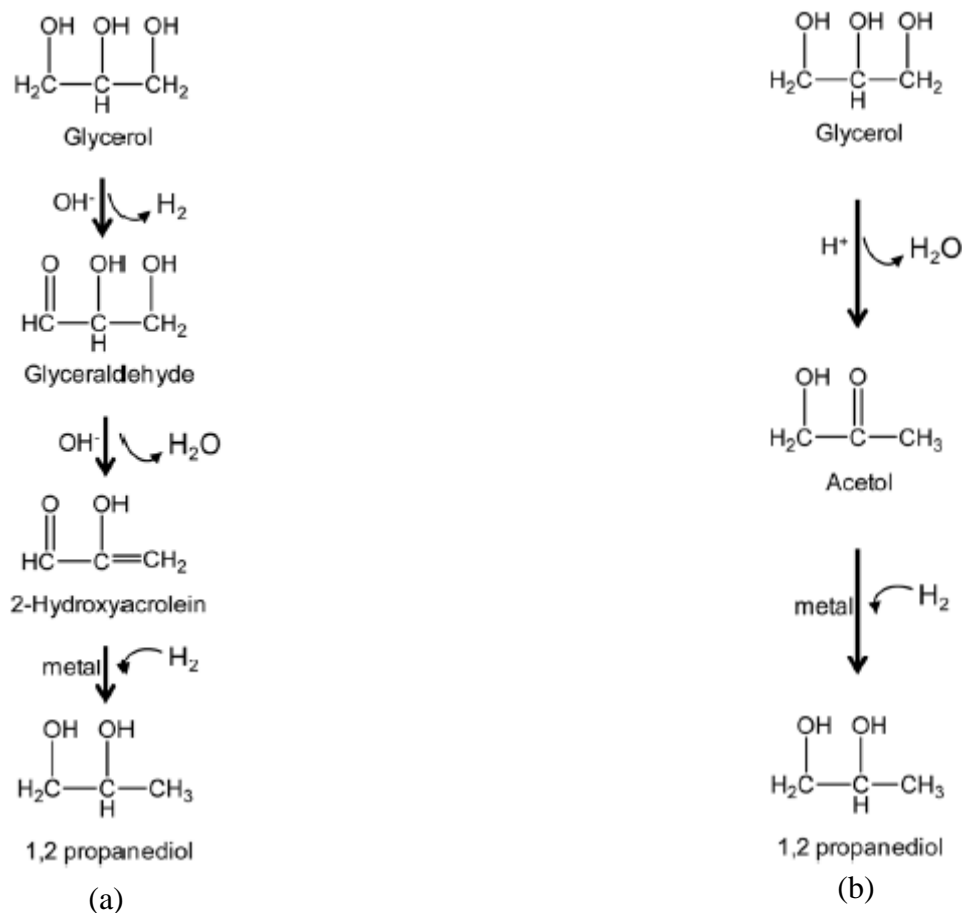


Figure 3.1 Glycerol hydrogenolysis into 1,2-PDO (a) Montassier mechanism (b) Dasari mechanism [34].

3.2. GLYCEROL CONVERSION TO 1-PROPANOL

There have been a lots of studies on glycerol hydrogenolysis to 1,2-PDO and 1,3-PDO but few reports on conversion of glycerol to lower alcohols has also been reported. Rabello et al. obtained the high percentage of conversion for glycerol around 89% into n-propanol and selectivity of around 79.4%. The reaction was done in the presence of noble

metals catalysts such as Pd or Pt supported on alumina. The reaction conditions used was 35 Bar H₂ pressure and 240 °C of temperature in the reactor. The reaction was allowed to run for 12 h in the batch mode [18].

During the hydrogenolysis of glycerol in aqueous phase, a good selectivity of 42% to 1-propanol and 13% to 2-propanol was reported using various kinds of metal catalysts with different supports (Ru, Rh, Pt, Pd on active carbon, SiO₂, Al₂O₃). Glycerol conversion of 14.3% and selectivity of 26% towards 1,2-PDO were also obtained under the optimized operating conditions [52].

In one of the paper by Tomishige and co-workers, they reported the hydrogenolysis of 1,2-PDO to propanols during the reaction done in the batch mode using the heterogeneous catalysts. They used the Rh-ReO_x/SiO₂ which gives the conversion of 87% and the selectivity towards 1-propanol and 2-propanol were 74 and 19% respectively after the reaction of 24 h at 120 °C. They also observed the degradation products (ethanol, ethane and methane) which were seen in very less quantity of around 1%.

3.3. GLYCEROL CONVERSION TO 1,2-PROPANEDIOL

1,2-propanediol, also named as propylene glycol (CH₃CHOHCH₂OH) is a three carbon diol with a stereogenic center located at the middle carbon atom [28]. Due to its number of uses and its wide applications in daily life such as pharmaceutical, cosmetics, raw material for polyester resins, paints, antifreeze, flavors etc., its annual production in the United States is over 1 billion pounds [28, 33, 59].

Till now much study has been done on the production of 1,2-PDO. Previous results indicate that scientists have been able to get the high yield and selectivity of it by using different types of catalysts. Many processes were developed and first commercialized plant has been opened with capacity of 0.1 million tons [40]. Hydrogenolysis of glycerol into 1,2-PDO has been reported over several catalysts which includes Cu, Rh, Rh, Ni, Pt and Ag [22, 25, 45, 49-51, 60]. In one of the paper by Sun et al., they reported the yield of 98.3% for 1,2-PDO over Ag-modified Cu/Al₂O₃ catalyst in vapor phase [46]. Fend et al. did the study of Ru on various support and reported that Ru supported on TiO₂ showed the highest activity and selectivity of 50% for 1,2-PDO [44].

The disadvantage of this reaction is that the hydrogenolysis reaction is done under high pressure of H₂ (5-8MPa), which increases the concern for safety, high reactor maintenance demand and also because of the use of H₂ it increases the production cost [22]. But some researchers claimed to achieve hydrogenolysis 10 1,2-PDO without adding H₂ through APR technique which gave them the selectivity of 87.5% for 1,2-PDO [61].

3.4. GLYCEROL CONVERSION TO 1,3-PROPANEDIOL

1,3-propanediol, normally referred as tri-methylene glycol, is a colorless liquid with chemical formula (CH₂OHCH₂CH₂OH), molar mass 76.09 g/mol and density of 1.0597 g/cm³[23]. 1,3-PDO has many valuable properties because of which it is used as a monomer in the synthesis of biodegradable polyesters, polyurethanes and polyethers in the chemical industry, providing them greater strength. Also as mentioned before, it is used in cosmetics, textile and pharmaceutical industries [33]. It is also used to produce

the polymer which are used in making of the bullet proof jacket and also used to make biocide for example 2-nitro-1,3-PDO [44].

The demand for this compound was increased drastically and worldwide production of it reached to around 100 million kg [22]. Generally, the conversion of glycerol into 1,3-PDO mainly involves two steps: i) dehydration of glycerol to 3-hydroxypropaldehyde over acidic sites and ii) hydrogenation of 3-hydroxypropaldehyde on metal center [47, 62] as shown in Figure 3.2 [25]. It is very vital to have the proper combination of the metal catalyst, acidic species and reaction conditions to control the proper ratio of 1,2-PDO/1,3-PDO which requires selective cleavage of the C-O bonds [21, 63]. Researchers carried out some of the hydrogenolysis reaction successfully and figured out some effective catalysts that has shown some selectivity towards 1,3-PDO, which includes platinum based catalysts combined with tungstun (Pt/WO₃/ZrO₂) [64, 65], Pt-H₄SiW₁₂O₄₀/SiO₂ [25, 66], Rh-ReO_x/SiO₂ [47], Ir-ReO_x/SiO₂ [67, 68], Cu-H₄SiW₁₂O₄₀/SiO₂ [62], Pd-complex, Ru/C-Amberlyst, Pd and Ru complex catalyst [63].

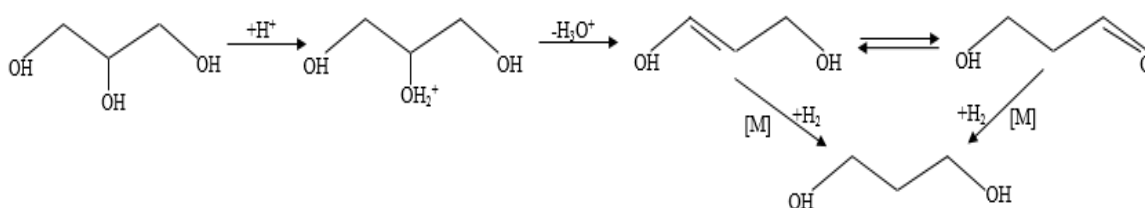


Figure 3.2 Reaction mechanism for glycerol hydrogenolysis to 1,3-Propanediol [25].

Kusunoki et al. [69] showed in his paper the activity towards glycerol conversion improved to 33.1% by using Ru/C-Amberlyst as the catalyst at 120 °C, 4 MPa H₂ as compared to the Chaminand et al. [47] who reported the conversion to be 32% using

Rh/C and H₂WO₄ as catalyst. Also author explained in his paper that the conversion of glycerol is better if we use catalyst with higher acid strength. Kurosaka et al. obtained the glycerol conversion to 1,3-PDO using Pt/WO₃/ZrO₂ with the yield of 24.2%. Nagawaka and his co-workers [35] improved the yield of 1,3-PDO to 38% with selectivity of 68% over Ir and ReO_x modified catalyst using SiO₂ as a support. He carried out the reaction at 125 °C, 8MPa and for 36 hrs and was able to reach the yield of 38% and selectivity 68%.

Hydrogenolysis of glycerol involving removal of hydroxyl group from the primary carbon atom leads the reaction towards 1,2-PDO. One of the recent studies by Zhu et al., towards the selectivity of 1,2-PDO proved to be in high number which is 98% by using the Cu/SiO₂ catalyst [70]. Friedrich et al. [71] reported in his study that Ni supported Al₂O₃ and SiO₂ can be used for the production of 1-PO from glycerol. The selectivity towards 1-PO with these catalysts was 35.3% and 42.8% respectively. It is believed that acidic sites are responsible for dehydration step and the metallic sites are responsible for hydrogenation/dehydrogenation step. But detailed study of such kind of catalysts is still not clear [70].

3.5. GLYCEROL HYDROGENOLYSIS USING ZEOLITES

Among the various catalysts used for glycerol dehydration, most of them are solid acid catalyst and some of the reactions are done in the vapor phase and some are done in liquid phase. However, because of the acidic nature of the catalysts and the reaction harsh conditions together it will result into very critical process to work with as it demands high equipment investments and maintenance costs. Despite lots of studies done before, there

is still a need to develop an eco-friendly catalyst which can be proved to be efficient under mild and cheap conditions.

Zeolites nowadays are the most feasible and promising catalyst used in industries like petrochemical and biomass conversions. Zeolites are environmentally harmless, non-corrosive and it easily gets separate from the reaction solution [72]. Moreover, zeolites are microporous structure with large surface area, good strength, good thermal stability and right acid sites density [73]. Researchers have used various zeolites like ZSM-5, Y-zeolite and zeolites-beta for the glycerol hydrogenolysis but all those reactions results into production of either 1-PO, EG or acrolein. In the previous studies, scientists have been successfully able to increase the selectivity and activity towards the production of acrolein but there is still a large gap present in improving the process to a large scope towards the more valuable production of 1,3-PDO. Technically, the activity of the catalyst depends on the acidic properties and also on the pore size of the material. Small pore size catalyst shows lower activity than the mesoporous size catalysts which are ranged between 6 and 10 nm [74]. Also the catalyst with good number of Bronsted acidic sites and moderate acidic strength results into removal of secondary hydroxyl group of glycerol to generate 1,3-PDO.

One of the main reason for which zeolites are in use as the catalyst is their inherent acidity. This can be explained on the basis of the presence of exchangeable protons attached to the zeolite framework. In other words, the reason can be explained as (i) they are cation exchangers (refers to acidity), (ii) have pore sizes as the same order of the dimension of our reactants and products, (iii) their large surface areas. The presence of the Al^{3+} tetrahedral which actually creates the acidic sites gives the zeolites ability for

the catalytic function. The increase in negative charge on the coordinating oxygen ions is the result of the extra electron present which is because the aluminum ion carries an effective negative charge [18].

Zeolite beta which comes under the category of large pore size zeolites consists of 3-dimensional channel structure consisting of 12 oxygen atoms in its ring. In two directions the channels are mainly straight having the cages at their interconnections. Also, in the third direction, the channels are twisted and they are not blocked. It's typical unit-cell formula is $H_7[Al_7Si_{57}O_{128}]$. It has the pore size of 6.6 x 7.7 in the $\langle 100 \rangle$ direction and 5.6 in the $\langle 001 \rangle$ direction [18, 74].

3.6. GLYCEROL CONVERSION USING MIXED METAL OXIDES

Much work has been done to convert glycerol using the mixed metal oxide catalysts also. Chen et al. studied the deoxygenation of the glycerol into 1,3-PDO and 1-propanol using the Pt/WO₃/ZrO₂ catalysts. Their team used the fixed bed reactor under the hydrogen pressure of 20-50 Bar and temperature of 110-140 °C. At these conditions, the conversion they were able to obtain was 61% and 36% selectivity to 1,3-PDO and 52% selectivity to 1-propanol [75]. The purpose of using WO_x is to regulate the acidity of the catalyst by introducing the Bronsted acid sites which plays the key role during production of 1,3-propanediol [76].

Some workers also investigated the CuO/ZnO catalysts prepared by oxalate gel method and reported a very high conversion of 46% than the catalysts prepared by co-precipitation method which was 17%. The selectivity was observed similar which was

around 90%. The reaction was done at the temperature of 180-240 °C and the hydrogen pressure was around 20-100 Bar in autoclave [16].

In one of the paper by Huang et al., vapour phase hydrogenolysis of glycerol in a fixed bed reactor was reported using the catalysts Ni/Al₂O₃ and Cu/ZnO/Al₂O₃. They observed the Ni/Al₂O₃ is not an effective catalyst for 1,2-PDO production as its selectivity is more towards the CH₄ and CO. However, Cu/ZnO/Al₂O₃ showed much impressive conversion of glycerol, which is 93% and 96.2%, into value added products. It also showed high selectivity of 92.2% towards 1,2-propanediol at H₂ pressure of 6.4 bar. The various conversions and selectivity using mixed metal catalyst system is shown in the Table 3.1 below.

Table 3.1 Vapor Phase hydrogenolysis of glycerol over mixed metals catalysts [45].

Catalysts	Conversion (%)	Selectivity to products (%)					
		1,2-PDO	EG	Acetol	1-PO	2-PO	Others
Ni/Al ₂ O ₃ ^a	92.3	43.6	18.6	13.4	3.2	1.5	19.7
Cu/ZnO/Al ₂ O ₃ ^a	93	65.3	2.5	23.5	1.4	0.6	6.7
Cu/ZnO/Al ₂ O ₃ ^b	96.2	92.2	0.7	0.8	2.4	0.7	3.3

a) Reaction conditions: WHSV=0.18h⁻¹, 60wt% glycerol, 190 °C, 1 Bar H₂

b) 6.4 Bar H₂

*Others=C₁ gases(CO and CH₄), ethanol, methanol and unknown products

4. EXPERIMENTAL SET-UP

4.1. CHEMICALS

A commercially available Ammonia zeolite-beta (from Zeolyst international, CP814E) with the silica/alumina ratio of 25 is used for the preparation of the catalysts. Before proceeding further, the zeolite had been calcine in furnace for 5 hours at 550 °C at the rate of 5°C/min and then was cooled down naturally. Various metals, viz. Zirconium chloride (Aldrich, $\geq 99.5\%$), Nickel (II) acetate tetrahydrate (Aldrich, $\geq 99.0\%$), Zinc nitrate hexahydrate (Sigma-Aldrich, 98%), Copper (II) nitrate trihydrate (Sigma-Aldrich, 98.0-103%), Strontium nitrate (Sigma-Aldrich, $\geq 98\%$) were purchased and utilized in catalysts synthesizes.

Hydrogen gas cylinder (UHP, 99.9999%) is purchased from the Airgas company for the reduction of the catalysts and also in the reaction and Helium gas cylinder (UHP, 99.9999%) for the GC is also purchased from the Airgas. For catalysts characterization like BET, helium gas cylinder (UHP, 99.9999%), Nitrogen gas cylinder (UHP, 99.9999%) and liquid nitrogen are also purchased from the Airgas.

4.2. CATALYSTS PREPARATION

Cu-Zr/Zeolite-beta catalyst is prepared by sequential wetness impregnation method. The loading amount used is 5 wt% for all the metals involved. The starting materials which are copper nitrate trihydrate and Zirconium chloride ($ZrCl_3$) are dissolved in deionized water (10 mL) separately in different flasks and then stirred for 3 hours at room temperature at 500 rpm. After stirring, the solution is then mixed with zeolite beta (1g) and then again stirring is continued for 6 h at room temperature to make

it a homogeneous solution. The rpm for the stirring is maintained at 500 throughout the process. The homogeneous solution is then separated by centrifugation, dried in oven at 110 °C overnight and then calcined at 500 °C in furnace for 5 hours at the rate of 5°C/min. The temperature profile of drying and calcination is shown in Figure 4.1 below.

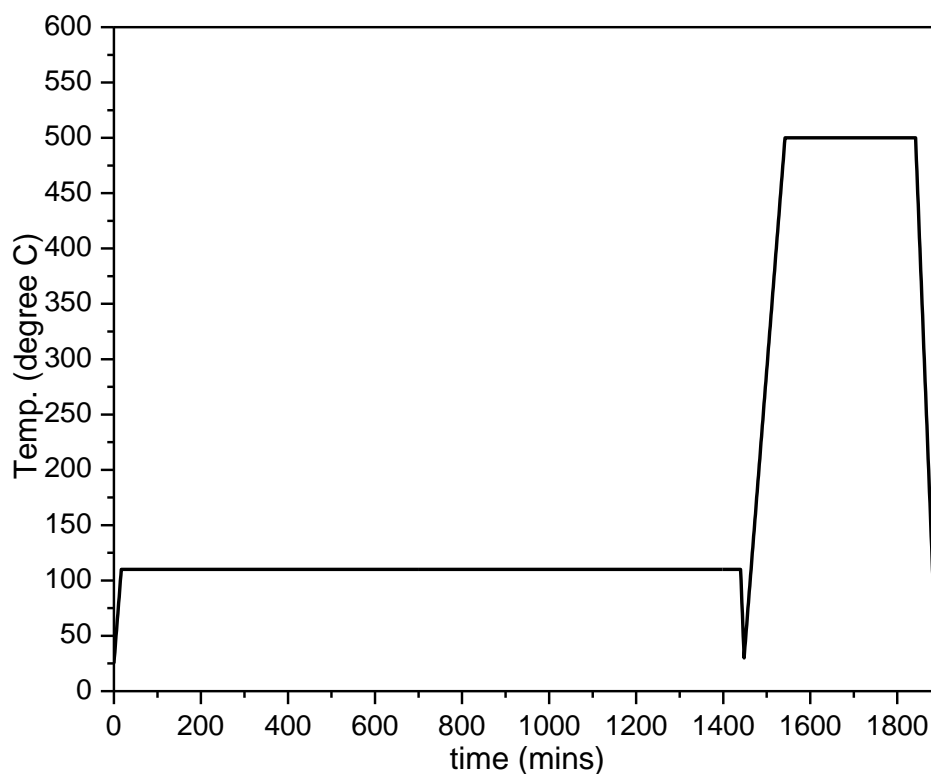


Figure 4.1 Temperature profile for catalyst drying and calcination.

The same procedure is followed to prepare the other set of catalysts which are Zn-Zr/Zeolite-beta, Ni-Zr/Zeolite-beta, and Sr-Zr/Zeolite-beta. The metal loading is kept 5 wt% for all the catalysts synthesized here.

Also to know the effect of metal loading, a different set of catalysts were prepared using zirconium and zeolite-beta only. The loading of Zr used were 5, 10, 15, 20 wt% and

the amount of zeolite-beta used was 1 gm. The procedure for synthesise followed is same as the above preparation.

4.3. REACTOR SET-UP AND CATALYST EXPERIMENT

The process flow diagram of the experimental set-up is shown in Figure 4.2 below. The reaction of glycerol hydrogenolysis is carried out in a 100 ml stainless steel autoclave which is equipped with a magnetic stirrer and thermocouple connected to the 4848 reactor controller. The rpm and temperature is controlled by the set point of the controller. The reactor set-up has two input valves for liquid and gas injection connected to the reactor and one output valve for gas releasing. The glycerol reaction is done in the two steps. In first step of reaction, catalysts were reduced by H₂ at 200 °C for 2 h while the second step includes the glycerol feed into the reactor followed by hydrogen gas input.

About 40 ml of glycerol aqueous solution (20 wt% glycerol) were rapidly introduced into the autoclave to prevent the reduced catalyst from contacting with air for too long. After that, autoclave is sealed and purged with hydrogen to eliminate air, then pressurized to the desired hydrogen pressure which is 600 psi. The temperature and rpm is set on the controller at 200 °C and 550 respectively. The reaction is then allowed to continue for next 10 h at same temperature and rpm. After the reaction the autoclave was allowed to cool down to room temperature and the pressure is brought down to ambient pressure. The liquid samples were then collected and analyzed using the GC-FID. The experimental set-up has been shown in Figure 4.3.

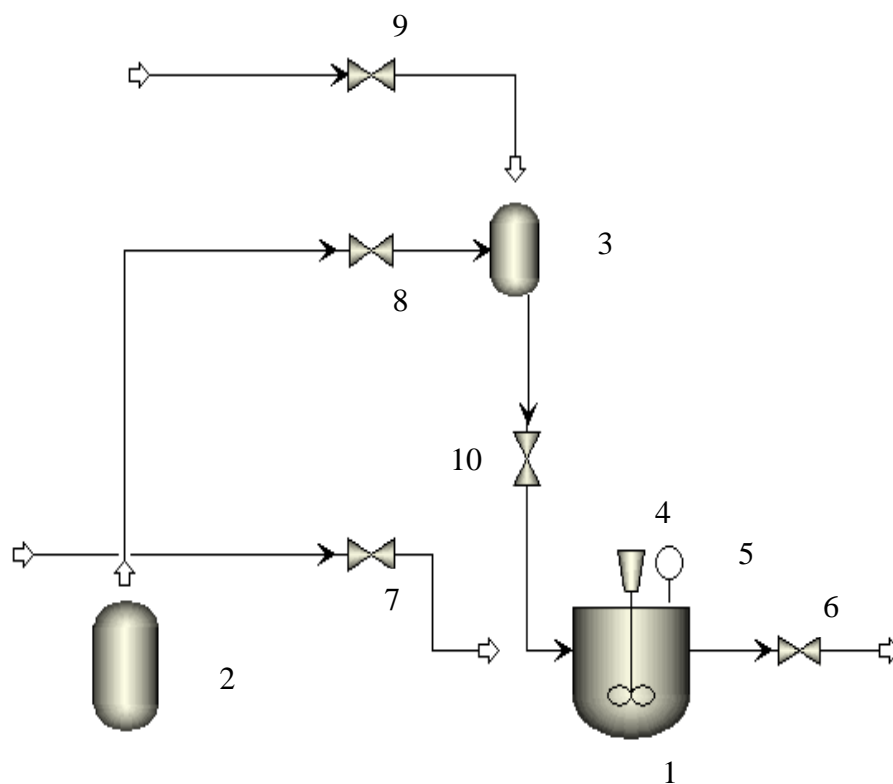


Figure 4.2 Process Flow Diagram of reactor set-up: 1, reactor; 2, Gas Cylinder; 3, sample cylinder; 4, Stirrer; 5, pressure gauge; 6,7,10 needle valves; 8,9 ball valves.



Figure 4.3 Experimental set-up of reactor.

5. CATALYST CHARACTERIZATIONS

5.1. SURFACE AREA, PORE VOLUME AND PORE SIZE

To determine the BET surface area and pore volumes, nitrogen adsorption was employed and then measured by a Micromeritics 3-Flex instrument at liquid nitrogen temperature. Before the measurements, all the samples were degassed in separate instrument, Smart Vacprep, under vacuum at 250 °C for 12 hours at the rate of 10 °C/min. The surface areas were taken from the isotherms in the P/P₀ relative pressure range of 0.05-0.3 and the pore volumes were determined at P/P₀ of 0.1. The pore diameter was estimated using the Barret-Joyner-Halenda (BJH) model. High purity grade helium, hydrogen and liquid nitrogen were obtained from the Airgas Company.

5.2. POWDER X-RAY DIFFRACTION (XRD)

To identify the structures of the catalyst and to evaluate the degree of crystallinity X-ray diffraction was used. The measurements were carried out in PANalytical X'Pert Materials Research Diffractometer using Cu K α as the source of radiation. Powdered samples of the catalysts are bombarded with x-rays at different angles. Diffraction patterns were measured in the range of $5^\circ \leq 2\theta \leq 50^\circ$ using the step size of 0.1°.

5.3. AMMONIA-TEMPERATURE PROGRAMMED DESORPTION (NH₃-TPD)

Micromeritics 3-Flex instrument connected with the mass spectrometer was used to characterize the amount and strength of the acid sites within the developed catalysts on a Micromeritics 3-Flex instrument connected with the mass spectrometer having MS detector. In a typical process, a sample of 0.1 g was measured and pretreated at 500 °C

for 1 h in flowing He (99.999%). The sample was then cooled down to 100 °C before being treated with 5% NH₃/He at 100 °C for 1 h. Again the sample was flushed with He for 0.5 h to remove the physically adsorbed NH₃. Subsequently, the temperature increased from 100 °C to 850 °C at 10 °C/min in the flowing He. The desorbed NH₃ was then detected using the mass spectrometry with mass measurement number of 17.

5.4. FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

FT-IR was carried out using the instrument Nexus 470 FT-IR made by Nicolet, to figure out the functional group (qualitative analysis of Bronsted and Lewis acid sites) within the catalysts and obtained organic compounds. Highly pure Potassium Bromide (KBr) powder was dried at 110 °C overnight to remove the moisture from it and then mixed 0.50 mg of solid catalyst to make the pellets. The pellet is then placed on the magnetic holder and then set in the FTIR sample chamber to do the rest of the procedure.

For organic compounds, the sample preparation is done by placing the few drops of liquid sample in between the silica discs and the setting the sample holder in the chamber as done for solid samples.

The spectral range was kept from 400-4000 cm⁻¹. The IR spectrum was recorded by KBr disc method under ambient conditions.

6. RESULTS AND DISCUSSIONS

6.1. CATALYST CHARACTERIZATIONS

The activated catalysts prepared in Section 4, have been characterized by N₂ sorption, XRD, FT-IR, and NH₃-TPD. The results of these characterizations are discussed below.

6.1.1 Surface Area, Pore Volume and Pore Size. The BET surface area, pore volume and pore diameter of the catalysts are listed in the Table 6.1. For pure zeolite H-Beta, the surface area was 483.61 m²/g, and the pore volume was 0.1535 cm³/g. After loading the zeolite Beta with 5 wt%, 10 wt%, 15 wt% and 20 wt%, there is a slight decrease in the surface area. The type I isotherm indicates the presence of strong micropores which can be confirm from the figure below. The same trend in the surface area we can observe in other prepared bi-metallic catalysts which are loaded with metals like 5wt% (Cu-Zr), 5wt% (Zn-Zr), 5wt% (Zn-Zr) and 5wt% (Ni-Zr). But all the surface areas are above 400 m²/g, which is a good indication that the catalysts is having the surface area closer to pure zeolite H-Beta and it is comparatively higher than other metal catalysts used by other researchers.

The zeolite Beta corresponds to the group with high pore volume and pore size. That is the reason it has been used in many reactions like alkylation, cracking, isomerization, disproportionation and glycerol dehydration. From the Table 6.1, we can infer that the pore volume of pure zeolite Beta was 0.1535 cm³/g, which is in accordance with the pure commercial zeolite Beta. In addition to that, loading the zeolite beta with metal zirconium at different wt% shows slight decrease in pore volume. The largest pore

volume was found on 5wt%Zr-zeolite-Beta ($0.1510 \text{ cm}^3/\text{g}$) while the smallest pore volume was found on 5wt% (Cu-Zr)/zeolite-Beta ($0.1226 \text{ cm}^3/\text{g}$). The pore diameter is almost unaffected which according to the previous studies [74] is favorable condition to prevent the catalyst from deactivation from coke but at the same time it is contrary to the increase in the steric hindrance.

Table 6.1 Textural properties of developed catalysts.

Catalysts	S_{BET}¹ (m²/g)	Pore Volume² (cm³/g)	D_p³ (nm)
Pure Beta	484	0.1535	16.9
5%Cu-5%Zr-ZBeta	477	0.1226	18.9
5%Ni-5%Zr-ZBeta	407	0.1262	18.3
5%Sr-5%Zr-ZBeta	447	0.1479	18.5
5%Zn-5%Zr-ZBeta	420	0.1323	17.8
5%Zr-ZBeta	445	0.151	18.8
10%Zr-ZBeta	408	0.1349	18.9
15%Zr-ZBeta	434	0.142	17.3
20%Zr-ZBeta	416	0.1356	16.6

¹BET surface area calculated by using BET equation

² Pore volume is calculated by using the Langmuir equation

³ Pore diameter calculated by using the t-plot curves

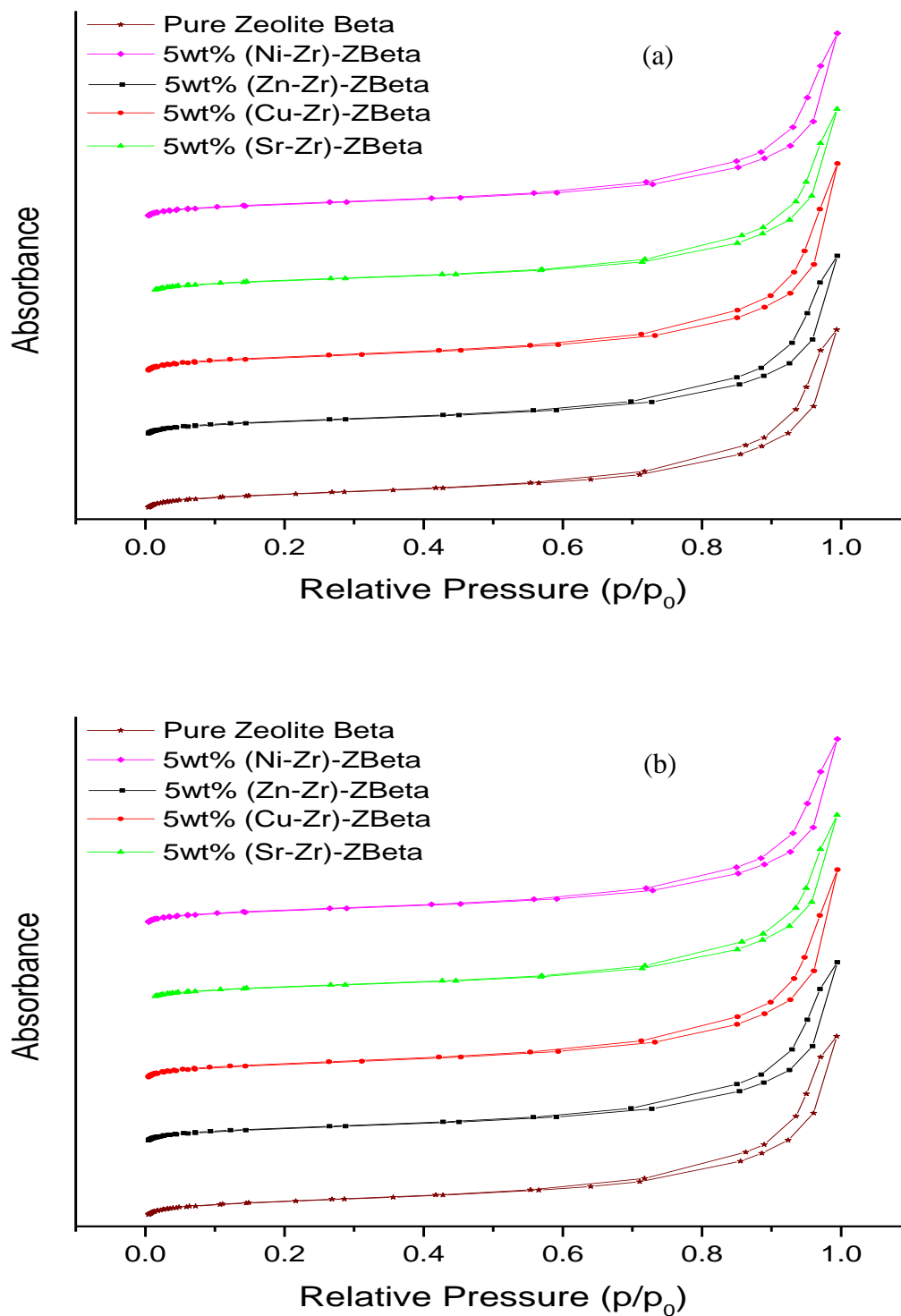


Figure 6.1 N_2 adsorption-desorption isotherms of a) pure H-Beta zeolites and modified H-Beta zeolites with various metals b) H-Beta zeolites with different wt% loading of Zr metal.

6.1.2 Powder X-ray Diffraction (XRD). Figure 6.2 (a) shows the XRD pattern of the pure H-Beta zeolite and also of zeolite beta loaded with metals which are Cu, Ni, Sr and Zn. The peaks assigned to the zeolite beta loaded with metals showed the same peak as that of pure H-beta zeolite. This similarity in the peaks indicates that the crystal structure are maintained even after loading H-Beta zeolite with the different metals or in other terms, we can infer from the graph that metal loading does not destroy the zeolites structure [56]. This can be also explained as, there was proper dispersion of all the metals individually on the H-Beta zeolite. However there is a slight decrease in the intensity of the peaks in comparison with pure H-Beta zeolite. This is because of the fact that some ions i.e. H^+ , Al^{3+} are replaced by the metal species which leads to destruction of the zeolites framework to a certain extent [55]. This change in the structure can be seen in the peaks of all the prepared catalysts. The Ni loaded zeolite beta has slightly sharp peaks at 38° and 44.6° which may be due to the reflection of the Ni metal because of the agglomeration.

XRD patterns for different Zr metal loading of 5, 10, 15 and 20 wt% on H-Beta zeolite are shown in Figure 6.2 (b). From the below figure, we can clearly see that the characteristic peaks of H-Beta zeolite at 25° , 27° , 33° and 44.6° slightly weakened in the intensity with the increase of Zr metal loading. This decrease in the intensity of the peaks goes in the descending order from 5 wt % to 20 wt % i.e. 20 wt % showed the maximum decrease in the intensity of the peaks. However, in this batch of catalysts also the number of peaks have the similarity with H-Beta zeolite. This shows the crystal structure of the zeolite Beta is preserved.

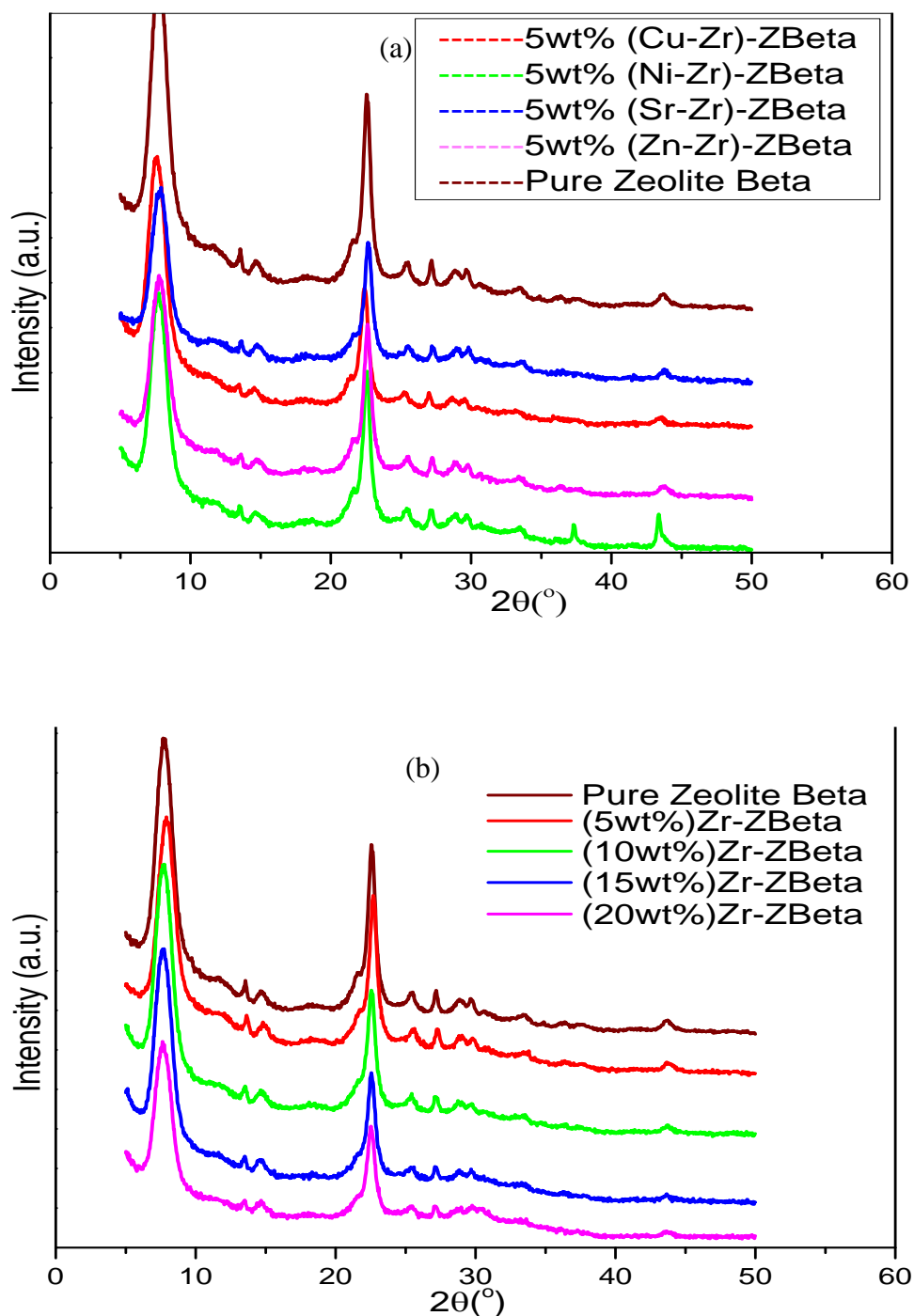


Figure 6.2 XRD patterns of a) pure H-Beta zeolites and modified H-Beta zeolites with various metals b) H-Beta zeolites with different wt% loading of Zr metal.

6.1.3 Fourier Transform Infrared Spectroscopy (FTIR). The FT-IR spectra of various H-beta supported various metals (5 wt%) are shown in Figure 6.3. The graphs

mainly consist of 4 bands at 1100 cm^{-1} , 1650 cm^{-1} , 3400 cm^{-1} and 3700 cm^{-1} . The peaks at 3400 cm^{-1} and 1650 cm^{-1} corresponds to the stretching and bending vibrations of the –OH groups. The additional peaks appeared in the region of 1100 cm^{-1} - 1350 cm^{-1} represents the presence of physisorbed water. The broad band at 3400 cm^{-1} - 3550 cm^{-1} is attributed to the bridging hydroxyl groups (Si-(OH)-Al) and the peak at 3700 cm^{-1} corresponds to the hydrogen bonded OH groups. The incorporation of the metal on H-Beta zeolite also produced a decrease in the intensity of the band at 1650 cm^{-1} .

6.1.4 Ammonia-Temperature Programmed Desorption (NH₃-TPD). Acidity plays one of the major roles in determining the catalytic performance of any catalyst in the process of glycerol hydrogenolysis. NH₃-TPD is the technique which is used to quantify the amount of acid sites present in the catalysts. The Figure 6.4 of zeolite Beta impregnated with metals shows the strong peak dominant at the temperature 200°C and above, which basically tells the presence of medium acid sites existed on the catalyst surface. Also, from the graph of zeolite beta with nickel and zinc, we can observe a small peak at about 500°C and 600°C respectively, which is assigned to ammonia desorption from the strong acid sites related to the framework Al atoms. From the reference graph of zeolite beta in Figure 6.4, the peak at about 380°C is assigned to ammonia desorption from strong acid sites. The peaks of strong acid sites shifted towards more high temperature which can be due to the addition of metals which are dispersed on the surface.

NH₃-TPD patterns for different loadings of zirconium are shown in Figure 6.4. The graph shows the peak for all the loadings at about 180°C which attributes to the

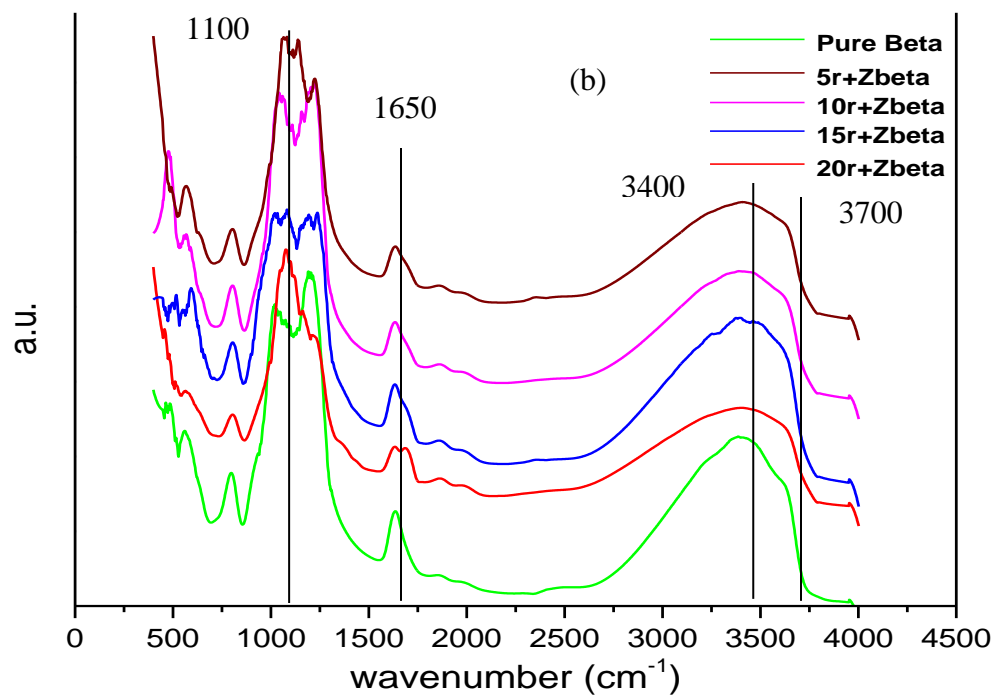
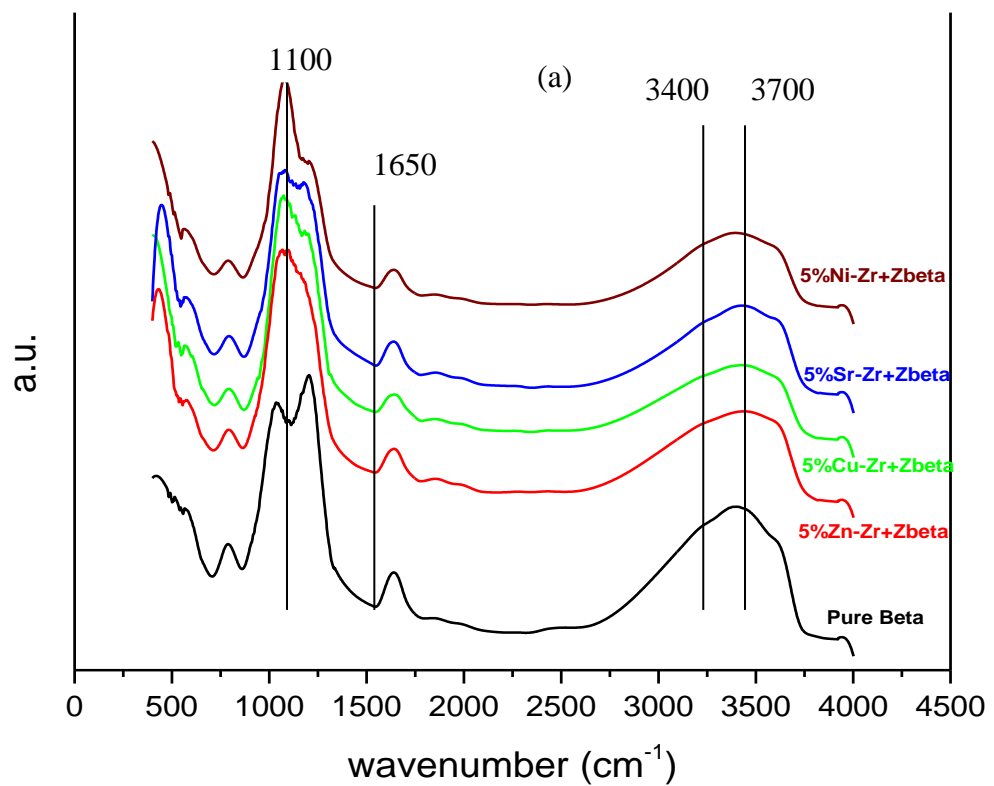


Figure 6.3 FT-IR patterns of a) pure H-Beta zeolites and modified H-Beta zeolites with various metals b) H-Beta zeolites with different wt% loading of Zr metal.

weak acid sites which confirms after the comparison with the graph of zeolite beta. But all of them also show a weak peak at about 380 °C which belongs to the strong acid sites. Overall, we can say that the prepared catalysts are having the moderate combination of weak and strong acid sites which make it reasonably appropriate catalyst.

6.2. GAS CHROMATOGRAPHY ANALYSIS

As mentioned in Section 5, all the catalysts tested at 200 °C and hydrogen pressure 600 psi for 10 h, their obtained organic products were collected in the glass vials to further do the analysis on Varian-3800 gas chromatography equipped with flame ionization detector. DB wax column (30m x 0.25mm x 0.5µm) was used for separation.

For preparation of the GC samples, a solution of internal standard was prepared and used for analysis. The standards of glycerol are prepared at different concentrations using methanol (HPLC grade) as solvent. These different concentrations were then run on GC-FID to get the calibration curve of the glycerol. The concentrations prepared were 7500 ppm, 9000 ppm, 12000 ppm and 13500 ppm using the pure methanol in 2 ml vial. The oven temperature program consists of: start at 50 °C for 0 min, ramp at 20 °C per min to 250 °C. The temperature was then holding at 250 °C for another 7 min. One micro liter of the sample was injected into the column. Before and after every run, pure methanol was injected to clean the column. The graph is obtained and the retention time of the glycerol peak is observed at 12.2 min. The data of the calibration curve is shown in Table 6.2. The calibration curve is made between the area counts of the glycerol peak on the y-axis and the concentration of the standards on the x-axis. The trend line is drawn and the

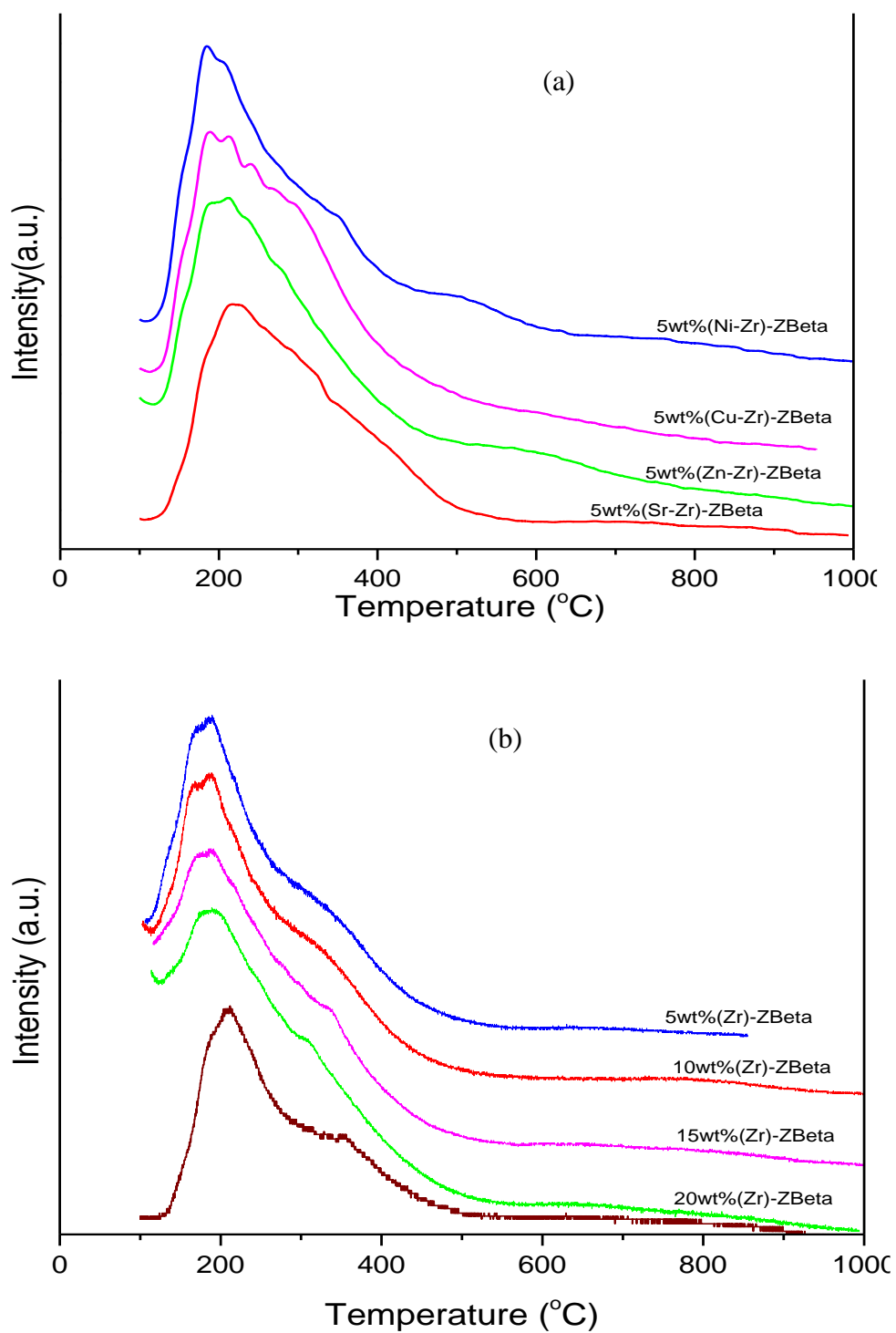


Figure 6.4 NH_3 -TPD patterns of a) pure H-Beta zeolites and modified H-Beta zeolites with various metals b) H-Beta zeolites with different wt% loading of Zr metal.

equation is calculated. The R-squared value obtained was 0.9831 which is very close to the 1. This calculations and R-squared value concludes that the calibration curve for the glycerol standards is within the acceptable range.

Table 6.2 Calibration data from the GC-FID for glycerol standards.

ppm ¹	gm/ml	Area ²	R.T. ³
7500	7.5	40066	12.2
9000	9	182020	12.2
12000	12	689768	12.2
13500	13.5	1039287	12.3

¹ppm refers to parts per million

²Area refers to area counts of the glycerol peak

³R.T. Refers to retention time of the peak

The samples (reaction products) for GC injection were prepared by using 60 mg of glycerol in 1 ml of methanol mixed together into a 2 ml glass vial. The same amount of these samples i.e. one micro liter injected into the column with alternate injection of pure methanol. Again, the only purpose of injecting the pure ethanol after every sample injection is to keep the column clean. Through the area counts obtained from the GC-FID graphs and the calibration curve obtained previously, the concentrations of the samples were calculated. After calculating the concentration we can then calculate the amount of glycerol actually present in our samples or in other words this calculation will give the amount of glycerol remained in the sample after the reaction is over. To do the further calculations for conversion and selectivity, the amount of glycerol present in the feed or entering the reactor before reaction is calculated. Now knowing the amount of glycerol

before the reaction and glycerol left after the reaction the conversion was then calculated using the equation mentioned below:

Conversion

$$(\%) = \left(\frac{\text{Amount of glycerol in feed (mg)} - \text{Amount of glycerol in product (mg)}}{\text{Amount of glycerol in feed (mg)}} \right) \times 100 \quad (3)$$

After the conversion, the peaks for the products which are 1,3-PDO, 1,2-PDO and 1-propanol were obtained. The retention time for these products was observed at 8.9 min, 7.8 min and 4.0 min respectively. Also, to calculate the selectivity of the desired compounds, the total areas of all the peaks are calculated from the obtained GC-FID graph. For one particular compound, the selectivity of it is calculated as mentioned in the equation below:

$$\text{Selectivity (\%)} = \frac{\text{Area of the desired product}}{\text{Total area of all the peaks}} \times 100 \quad (4)$$

The conversion and selectivity is calculated for all the 8 samples and reported in the Table 6.3 below.

From the data shown in the table we can see that among the mixed metal catalyst, conversion for catalyst containing mixture of Cu and Zr with H-Zeolite Beta showed the maximum conversion of 73.1% and the catalyst with Ni and Zr showed the minimum conversion of 67.1%. Zn metal mixed catalyst showed the small improvement in conversion in comparison to the Ni mixed catalyst. The conversion order for these catalysts goes in the following way: Cu>Zn>Sr>Ni. The selectivity towards 1,3-PDO was

Table 6.3 GC-FID results for product conversion and selectivity.

Catalysts	Conversion (%)	Product Selectivity (%)		
		1,3-PDO	1,2-PDO	1-propanal
5 wt%Ni-Zr-ZBeta	67.1	7.9	3.4	88.7
5 wt%Sr-Zr-ZBeta	70.0	1.8	0.5	97.7
5 wt%Zn-Zr-ZBeta	68.0	4.3	14.2	81.5
5 wt%Cu-Zr-ZBeta	73.1	2.7	0.7	96.6
5 wt%Zr-ZBeta	70.0	2.4	0.7	96.9
10 wt%Zr-ZBeta	69.1	2.2	0.0	97.8
15 wt%Zr-ZBeta	69.6	1.8	0.0	98.2
20 wt%Zr-ZBeta	69.4	1.5	0.0	98.5

shown highest by the Ni mixed catalyst which is 7.9% and minimum was for Sr metal which is 1.8%. The selectivity order goes in the following way: Ni>Zn>Cu>Sr. For 1,2-PDO, Zn metal mixed catalyst showed the maximum selectivity with 14.2 % and other catalysts did not show good results.

Apparently, it was observed that all the prepared catalysts showed very good selectivity for 1-propanol. The selectivity calculated for Sr metal mixed catalyst came out to be 97.7 % which was much higher than the results reported by other researchers. 1-propanol selectivity order goes in the following way: Sr>Cu>Ni>Zn.

The catalytic performance for the catalyst by increasing the metal loading on the catalyst is even worse than the mixed metal catalyst. The conversion of all the different metals weight loadings were quite similar with the mixed metals which was mostly

around 69%. But the selectivity for 1,3-PDO and 1,2-PDO were less than 3% for all the catalyst and no selectivity were shown for 1,2-PDO by any of the catalysts. But from the table we can see that selectivity towards 1-propanol is following the increasing trend as the metal wt% loading was increased from 5 wt% Zr to 20 wt% Zr. The selectivity trend for 1-propanol using the catalysts with increasing metal loadings followed the trend as: 20 wt% > 15 wt% > 10 wt% > 5 wt%.

In comparison with some previous results, one of the studies by Friedrich et al., they reported the selectivity towards 1-propanol (1-PO) up to 35.3% using Ni/Al₂O₃ and 42.8% using Ni/SiO₂. The high selectivity towards 1-PO can be because of hydrogenation of the acrolein which was generated when reactant, which is glycerol, reacts with the H-beta zeolite [71].

G. Shi et al. in their work prepared the Ni₃P catalyst at different annealing temperatures to test the conversion of glycerol. They found the best glycerol conversion to be 5 % only and the selectivity to be 86.4% for 1,2-PDO and 5.7% for 1,3-PDO [41]. In this study, we prepared the catalysts using the H-beta zeolite and the mixed metals together.

Up to date nobody previously used this combination of catalysts for glycerol conversion. The results shown in above table, the conversion of glycerol, using the catalyst with Ni and Zr metal mixed with H-beta zeolite, is 67.1% which indicates the good performance of the prepared catalysts and the selectivity towards 1,3-PDO, 1,2-PDO and 1-propanol is also better than the results which were reported previously. Musolino et al. co-precipitated the Pd with Ni and also with several different metals such as PdFe, PdZn to increase the conversion of glycerol and selectivity of 1,2-PDO. PdNi

showed the selectivity of 84% and the conversion of more than 90% while for other metals selectivities were 71% and 59% respectively [43].

Yin et al. reported the conversion of glycerol up to 100% and selectivity towards 1,2-PDO to 43% but at the same time there was almost no 1,3-PDO was produced in his reaction [77].

Also another reason for high selectivity towards 1-PO is the dehydration of 1,3-PDO and then the subsequent hydrogenation which then further goes the same reaction sequences of dehydrogenation. In one of the work, generation of CO₂ and ethane is also explained as the further decarboxylation during the reaction. In another work for glycerol hydrogenolysis to 1,3-PDO, catalyst used was SiO₂ supported Cu and H₄SiW₁₂O₄₀. The conversion for glycerol was reported to 83.4% and selectivity for 1,3-PDO and 1,2-PDO was 32.1% and 22.2% [62].

Dasari et al. in their paper, reported Cu chromite as one of the most effective catalyst for glycerol hydrogenolysis. In their paper they used different ranges of hydrogen pressure and reported the highest conversion of 65.3% for glycerol and 89.6% selectivity for 1,2-PDO at 300 psi H₂ pressure and 200 °C [34]. Quite similar results were shown by Vasiliadou and Lemonidou, where addition of Ru and Cu increased the conversion but at the same time there was decrease of selectivity towards 1,2-PDO which was reported to be 85.9% [42]. Liu et al. did the similar work using the CuRu over different supports and observed the selectivity to be 90% for 1,2-PDO using ZrO₂ as the support and 0% for the 1,3-PDO [39].

Jiang et al. reported that combination of Ru and Cu as mixed metal catalyst gives some of the most interesting results under specific reaction conditions. Their group

reported the selectivity for 1,2-PDO up to 87% at the reaction condition of 503 K, 100 bar H₂ pressure with 3:1 Ru:Cu ratio [78].

There is a very little research on the use of the zeolites till now. Jin et al. did the hydrogenolysis of glycerol over HY zeolite having Ru as the support. He proposed that HY support could present excellent hydrogenolysis activity because of the acidity and porosity property of it. It was found that catalyst with 5%Ru/HY with 1.0 concentration of HCl showed the best catalytic activity with 60.1 % glycerol conversion and 81.3% selectivity for 1,2-PDO under 435 psi H₂ pressure and 220 °C [19].

Also, Lin et al. in their study discussed about the combined use of the H-Beta zeolite and Ni/Al₂O₃ as catalysts for the hydrogenolysis of glycerol to achieve high selectivity to 1-propanol. During their experiments they reported the maximum conversion of glycerol to be 89.9 % and selectivity towards 1,3-PDO and 1,2-PDO were 2.6 % and 3.7 % respectively. But at the same time they reported very high selectivity for 1-propanol which was 60.3%.

Li et al. reported the effect of adding HZSM5 with different SiO₂/Al₂O₃ ratios to Ru/Al₂O₃ and Ru/SiO₂. They obtained the maximum glycerol conversion of 60.9 % and selectivity of 12.7 % for 1,2-PDO and 0.3% for 1,3-PDO with Si/Al ratio of 25 and using Ru with Al₂O₃ as support. They also reported the glycerol conversion of 38.8% and selectivity of 21.6% and 1.0 % towards 1,2-PDO and 1,3-PDO respectively [79].

Similarly, there are many reports on the use of zeolites like HZSM5, H-Beta and HY for glycerol conversion to acrolein. But there has been very few reports of glycerol conversion to 1,3-PDO and 1,2-PDO using these zeolites. In our study, we used the H-Beta zeolites with mixed metal oxide to know the effect of their combination which was

never tried before. As previously reported in the above table, the conversion for all the prepared mixed metal catalysts were appreciable and better than the conversion reported by other researchers. However, the selectivity towards 1,3-PDO and 1,2-PDO were low. Apparently, it was observed that all the catalyst was showing very good selectivity towards 1-propanol which is more than 90% for all of them.

7. CONCLUSION

In summary, various mixed bi-metallic catalysts have been synthesized using zeolite H-Beta as the catalyst support. The obtained catalyst exhibits the good characterization properties and also the conversion of glycerol is obtained in appreciable quantity but the reaction could not be able to give the good results for the selectivity of 1,3-propanediol and 1,2-propanediol. But the lower alcohols which is 1-propanol is obtained in good quantity which can be concluded on the basis that the acid sites obtained from the developed catalyst were not sufficient to move the reaction towards the production of 1,3-PDO and 1,2-PDO. Also we can conclude that as per the reaction mechanism, 3-hydroxypropanaldehyde which is thermodynamically unstable intermediate formed during the reaction is converting into the 1-propanol.

To further improve the reaction and selectivity towards the 1,3-PDO and 1,2-PDO we can suggest the treatment of transition metal with some acidic media or the other metals which comprises of good Bronsted acid characteristics. Further, we can also change the reaction conditions which could be by increasing the hydrogen pressure in the reactor during the reaction so that we can convert the 3-HPA immediately towards 1,3-PDO and constraining its conversion into some other products.

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