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Research Article
International Journal of Pharmacy and Engineering (IJPE)
ISSN 2320-849X

HYDROGENOLYSIS OF GLYCEROL OVER NICKEL (Ni), PLATINUM (Pt), RUTHENIUM (Ru) AND COPPER (Cu) LOADED ON HYDROXYAPETITE TO FORM 1,2-PROPANDIOL AND ETHYLENE GLYCOL

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1. Abstract

The hydrogenolysis of glycerol (15 wt %) is investigated over Ni, Pt, Ru, Cu supported on hydroxyapetite(HAP) at 220 ºC and 60 bar pressure in hydrogen. The catalysts are prepared by loading the metals by impregnation methods and reducing at 400 °C prior to use in the hydrogenolysis reactions. The general conditions of the hydrogenolysis experiments are in the temperature, 220 °C; pressure 60 bar; and run duration 6 – 12 h. The activity of the metal is dependent on the support; Ni is most active when supported on HAP. The influence of process parameters, addition of $Ca(OH)_2$ and influence of solvents, such as isopropanol, water, on the activity and selectivity of Ni catalysts is presented.

Received: August 1st , 2014, Revised: August 10th , 2014, Accepted: August 15th , 2014.

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1.1 Introduction

1.1.1 Biomass for production of fuels and chemicals

In some regions of the world, production of bio-ethanol is already cost competitive with gasoline [1] and this demonstrates the potential of biomass as a renewable raw material. Though widespread use of biomass as a raw material for biofuel production remains controversial from both economical and ecological perspectives, it is undisputable that eventually alternatives to the fossil resources for producing chemicals and materials will need to be found [2-4]. If the amount of biomass available is not sufficient to substitute fossil resources in all applications, then the transformation of biomass into value-added chemicals will represent the optimal use of biomass. This is because, most chemicals are significantly

more valuable than transportation fuels, and the use of renewable resources as a feedstock for the chemical industry will lead to significantly higher reductions in the emission of green-house gases than can be achieved by production of biofuels. It is noteworthy that, today, the cost of glucose is comparable to the cost of crude oil (on a mass-to mass basis) [5].

Fossil resources are certainly limited and the demand is growing. At the same time, it is becoming increasingly clear that the emission of CO_2 that follows the use of fossil resources is threatening earth's climate.

Together, this makes the development of a chemical industry based on renewable resources one of the most important challenges of the present century. This challenge has two different facets. One is the discovery and development of methods to use renewable resources to supply suitable energy carriers, in sufficient quantities at acceptable costs, and with minimal impact on the environment. The other is the discovery and development of new ways to provide all the chemicals needed to sustain a modern society. Whereas, there are several possible energy scenarios that do not involve carbon containing energy currencies, it is difficult to envisage how one could make the required chemicals and materials without relying on carbon-containing compounds.

Thus, to develop a chemical industry that does not depend on fossil resources, there are only two alternative carbon sources, namely CO_2 and biomass. Since transformation of CO_2 into useful chemicals always requires a significant energy input, it appears attractive to instead utilize biomass as the dominant feedstock for chemical industry. In this way, it is possible to harvest the energy input from the Sun which is stored by photosynthesis in the C–C, C–H, C–O, and O–H bonds of the biomass.

Clearly, a shift from fossil resources to renewable resources as the preferred feedstock in chemical industry is a formidable challenge. Interestingly, these processes often rely on the availability of biological catalysts whereas processes for conversion of hydrocarbons use mostly heterogeneous catalysts. However, to explore the full potential of biomass as a feedstock in chemical industry, it is necessary to integrate processes that rely on biological catalysts with processes that use heterogeneous or homogeneous catalysts to develop new, cost-competitive and environmentally friendly technologies. [6]

Over the past couple of decades FAME derived from vegetable oil and animal fat have assumed importance as potential diesel fuel extenders known as ''biodiesel''. For every 9 kg of biodiesel produced, about 1 kg of a crude glycerol by-product is formed; and today, biodiesel production plants are in need of methods to realize increased income from this glycerol. If crude natural glycerol could be converted to propylene glycol, this technology could be used in biodiesel production plants to increase profitability. Preferred technology would convert crude natural glycerol at moderate temperatures and pressures. [7]

Catalytic conversion of renewable biomass to fuels and commodity chemicals becomes more and more important because of the worldwide energy and environmental problems. Glycerol is one of the top-12 building block chemicals that can be derived from plant sources [8]. In addition, the production of biodiesel by the transesterification of vegetable oils and animal fats makes large quantities of glycerol available as a reaction co-product, 10 wt% of the biodiesel produced. [9]

1.1.2 Glycerol

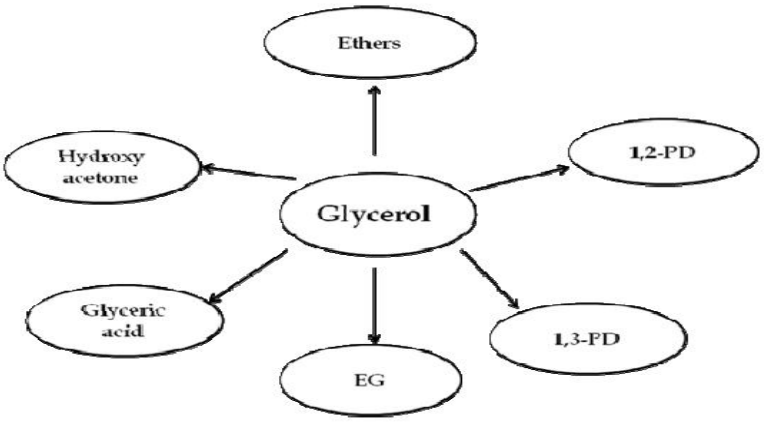

Figure 1 is a schematic representation of the conversion of glycerol into valuable chemicals. [10]

Glycerol possesses two (identical) primary alcohol functionalities and one secondary. Consequently, there exist a multitude of possible products from the oxidation reaction. Catalytic selectivity is therefore a central factor to consider in developing this chemistry.
The main products possible from glycerol oxidation are glyceric acid orglycerate, DHA, and glyceraldehyde. Under acidic conditions, oxidation of glycerol usually leads to the formation of DHA. In initial experiments performed at pH of 2–4, platinum on charcoal showed low catalytic activity for oxidation of the secondary hydroxy group of glycerol with a 4% yield of dihydroxyacetone at a glycerol conversion of 37% [11]. Several promoters were tried, including bismuth, tellurium, lead, tin, and selenium for this reaction [12]. On addition of bismuth a drastic increase of selectivity was seen for DHA, which increased from 10% to 80%. Glycerol was oxidized into glycerate and glyceric acid in presence of NaOH. The selective oxidation of a 50% aqueous solution of glycerol was performed at 50 °C with an oxygen/glycerol ratio of 2, in a continuous fixed bed process using a Pt–Bi catalyst supported on charcoal, and a DHA selectivity of 80% at a conversion of 80% was obtained [13]. Under basic conditions, oxidation of glycerol mainly leads to the formation of glycerate.
Glycerol is the major byproduct of vegetable oil transesterification and accounts for 10 wt. % of the biodiesel product. Therefore, the utilization of glycerol to produce high value-added chemicals may partially compensate for the production costs of biodiesel. [14]. As the amount of glycerol production has increased due to the increased production of biodiesel, developing new technologies for utilizing this glycerol by converting it into valuable chemicals has become a priority.
Among the value-added chemicals, propylene glycol, i.e. 1, 2-propanediol (1, 2-PDO), can be used as biodegradable functional fluids in applications such as de-icing reagents, antifreeze and coolants, and as precursors in the syntheses of unsaturated polyester molecules and pharmaceuticals. Therefore, the catalytic hydrogenolysis of glycerol to 1, 2-PDO has great potential for a cost effective process. [15].

Several review papers [16, 17-20] have appeared in recent literature focusing on the possible utilization of glycerol for chemicals and chemical building blocks. In this context, glycerol conversion to 1,2-propanediol (1,2-PDO) by catalytic hydrogenolysis [21-28] has emerged as one of the important processes because of the huge market of 1,2-PDO as an industrial solvent, antifreeze, deicing agent and approved additive in food, cosmetic and pharmaceutical industries.[29].

It is well-known that hydrogenolysis of glycerol to 1, 3-PDO involved dehydration of glycerol to 3-HPA on acidic sites followed by subsequent hydrogenation on metal center [30,31]. Thus, the appropriate combination of metal components and acidic species in reaction system is indispensable for the effective formation of 1, 3-PDO. The relatively feasible hydrogenolysis processes that have been reported employed $Pt/WO3/ZrO_2$ [32.33], $Rh/SiO_2 + H_2WO_4$ [34], $Pt/WO_3/TiO_2/SiO_2$ [35], Pt–sulfated zirconia [36], $Ir–ReOx/SiO_2 + H_2SO_4$ [37, 38] as catalysts. Most of previous studies have been performed in organic solvent or with liquid acids, which will greatly reduce environmental and economical viability.

As shown in Fig.2 the first step of glycerol hydrogenolysis requires acid sites for dehydration to acetol followed by metal catalyzed hydrogenation to 1, 2-PDO [39]. Hence, either monometallic catalysts with acid additives/supports or bifunctional catalyst systems have been extensively studied for glycerol hydrogenolysis. These include supported noble metals (Pd, Pt, Rh, Ru, Re, Au) and non-noble metals involving Cu in combination with one or more metals such as Zn, Ni, Cr, Ba, Mg and Co [40-44]. In spite of the higher activity exhibited by noble metals, 1, 2-PDO selectivity was affected due to higher extent of C-C cleavage [45, 46].Glycerol hydrogenolysis process to obtain 1, 2-PDO involves C-O bond dissociation and simultaneous addition of hydrogen[47]. Since hydrogenolysis uses hydrogen as a reactant, most of the published studies related to glycerol hydrogenolysis have been performed under hydrogen pressure, in liquid phase. [48]

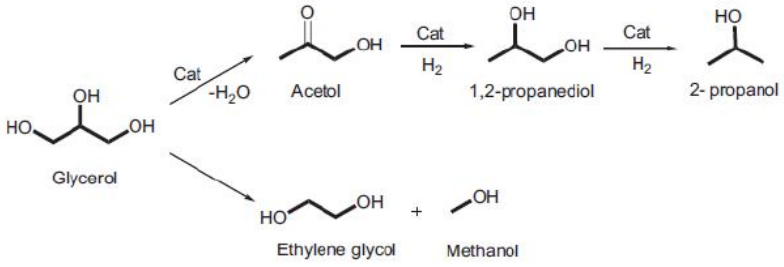

Fig.2 Hydrogenolysis of Glycerol[49]

1.1.3 Hydrogenolysis

C–C and C–O bond breaking by hydrogenolysis of different polyols namely glycerol, xylitol, erythritol and sorbitol has been investigated by Montassier et al. [50,51]. Predominantly ruthenium and copper-based charcoal catalysts were studied at 210–260 °C and 1–6 MPa of hydrogen pressures. The main products from aqueous glycerol conversions were propylene glycol over copper catalysts and ethylene glycol along with methane over ruthenium catalysts. The hydrogenolysis of glycerol to ethylene glycol and propylene glycol over ruthenium supported on a range of different supports at 180 °C and 5 MPa hydrogen pressure was investigated and the highest conversion was obtained on a TiO2 support [52]. Blanc et al.

reported the treatment of aqueous sorbitol solutions on CuO–ZnO catalysts at 180 °C and 130 bar hydrogen pressure to produce a variety of products [53].

1.1.4 Hydrogenolysis mechanism for converting higher polyols into lower alcohols

C–C and C–O bond breaking by hydrogenolysis of different polyols has been studied by Wang et al. [54] using 1, 3-propanediol as the model compound. This mechanism requires a β-dicarbonyl as the bond cleavage precursor. Polyols hydrogenolysis reactions have generally been explained by either retro-Claisen or retro-Michael or retro-aldol mechanisms [55]. Among these, retro-aldol is considered to be the dominating C-C cleavage mechanism for the following reasons: First, both the retro-Claisen and retro-Michael mechanisms require a dicarbony1 precursor. The formation of a dicarbonyl presumably occurs through dehydrogenation of a monocarbonyl. As dehydrogenation is thermodynamically unfavorable at the reaction conditions, the dicarbonyl formed is unlikely to be significant relative to the monocarbonyl, the precursor of the retro-aldol reaction. Second, the dehydrogenation of the monocarbonyl is in competition with dehydration, the C-O cleavage reaction.
Since dehydration is both thermodynamically and kinetically (in the presence of bases) much more favorable than dehydrogenation, the hydrogenolysis products would have exclusively resulted from C-O cleavage, had either the retro-Claisen or the retro-Michael been the dominating mechanism of C-C cleavage in hydrogenolysis. In contrast, the retro-aldol reaction shares the same precursor as the dehydration, and has the ability to compete with the dehydration. On the basis of these reasons, Montassier et al. believe that the C-C cleavage occurs through the retro-aldol reaction. The reaction mechanism described in Scheme 1 proposed by Wang et al**.** can explain the reaction products found in the hydrogenolysis of sugars and sugar alcohols.

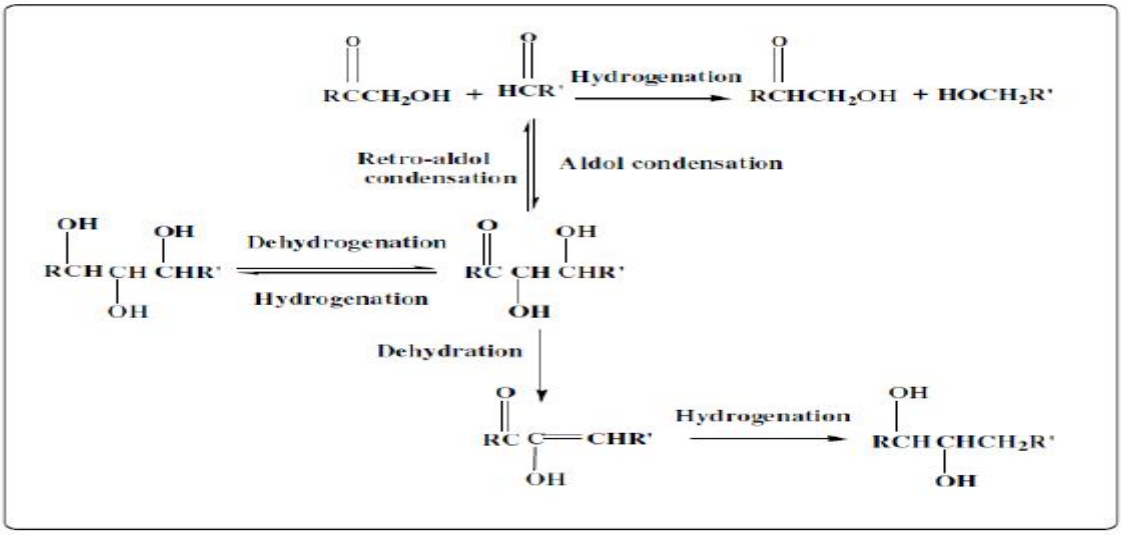

Fig.3 Hydrogenolysis of polyhydric alcohols in lower hydric alcohols [54

2.0 List of Abbreviations:

1, 2-PDO	1, 2-Propanediol
1, 3-PDO	1, 3-Propandiol
3-HPA	3-Hydroxypropaldehyde
EG	Ethylene Glycol
G	Glycerol
PG	Propylene Glycol
FAME	Fatty Acid Methyl ester
DHA	Dihydroxyacetone
HA	Hydroxyacetone
MeOH	Methanol
EtOH	Ethanol
HAP	Hydroxyapetite

3.0 Chemicals and materials used

The names and formulae of the chemicals and materials used in this project are given in the following table (Table 1.).
The source of the material / chemical and its purity are also given

Table: 1 Formula, purity and source of chemicals / materials used.

Chemical Name	Molecular Formula	Purity	Source
Calcium hydroxide	$Ca(OH)_2$	LR(90%)	Sigma Aldrich Chem.Co, India.
Ethylene glycol	$C_2H_6O_2$	AR(99%)	Sisco Res.Lab, India.
Glycerol	$C_3H_8O_3$	AR (99%)	Sisco Res.Lab, India.
Methanol	CH_3OH	AR(99%)	S.D.Fine-Chem Ltd, India.
Ethanol	CH_3CH_2OH	AR(99%)	S.D.Fine-Chem Ltd, India.
Nickel nitrate hexa hydrate	$Ni(NO_3)_2.6H_2O$	AR(99%)	Central drug house (p) Ltd, India.
Ruthenium chloride	$RuCl_3 \cdot nH_2O$	LR(39%)	Loba Chemie Pvt.Ltd, India.
platinum(II) chloride hydrate	$Cl_2.XH_2O$		Chem.Co, India.
1,2-Propanediol	$C_3H_8O_2$	AR(99%)	Sisco Res.Lab.India.

4.0 Hydrogenolysis Experiments

Glycerol hydrogenolysis was carried out in a 300 mL stainless steel (SS) autoclave (Parr 4843) with a solution of 15 wt% sorbitol. After the solution of glycerol was introduced into the autoclave, the H_2-reduced catalyst (powder) was added. The sealed autoclave was purged by flowing H_2 at room temperature. The contents were then stirred (500 rpm) and the autoclave pressurized with H_2 to 50 bars and heated to the reaction temperature. Once the desired temperature was reached, the pressure was adjusted to 60 bars and timing was started. During reaction, the H_2 pressure in the autoclave was kept constant by periodic addition of small amounts of hydrogen. After the required run duration (generally, 6 h), the autoclave was

cooled rapidly with cold water. The product mixture was then collected, weighed, filtered and analyzed.

5.0 Results and Discussions

5.1 Effect of different metal loading

Glycerol hydrogenolysis was carried out with 15 % glycerol in isopropanol; temperature, 220°C; pressure, 60 bar; run duration, 6 h; stirring speed, 500 rpm. The results of the reaction over all the supported metal catalysts are presented in

Table2. The performance (conversion and product selectivity) of individual metals over different supports

Catalyst	Glycerol conversion (%)	Selectivity (%)			
		1,2-PDO	EG	MeOH+EtOH	HA
Ru(1% HAP	7.8	16.6	_	83.3	_
Pt(1%)-HAP	9.4	31.8	_	68.1	_
Ni(6%)-HAP	1.8	_	_	100	_
Cu(6%)-HAP	6.9	_	27.7	72.2	_
Ni(12%)-HAP	33.7	5.5	8.8	65.4	20.0

Reaction conditions: 15 wt% glycerol in isopropanol; catalyst: 0.2g; temp: 220 □C; pressure: 60 bar; duration of run: 6h; stirring speed: 500 rpm;

Examining product selectivity over the catalysts, the selectivity for Methanol+Ethanol is rather large over most catalysts. Ni(12%) supported on HAP gives the highest conversion (33.7%) with 65.46 % selectivity for Methanol+Ethanol and 5.55% selectivity towards 1,2-propandiol.The order of activity: Ni(12%) > Pt(1%) > Ru(1%) > Cu (6%) > Ni(6%).

5.2 Effect of percentage of metal loading

Table 3: The influence of percentage of metal loading was investigated using Ni(6%) and Ni(12%) over HAP:

Catalyst	Glycerol conversion (%)	Selectivity (%)			
		1,2-PDO	EG	MeOH+EtOH	HA
Ni(6%)-HAP	1.8	_	_	100	_
Ni(12%)-HAP	77.7	.72	3.2	95.3	.75

Reaction conditions: 15 wt% glycerol in isopropanol; catalyst: 0.2g; temp: 220 □C; pressure: 60 bar; duration of run: 6h; stirring speed: 500 rpm;
The effect of increase in percentage of metal loading was investigated using Ni(6%)-HAP and Ni(12%)-HAP. Conversion is found to increase with increase in the percentage of metal loading. However, the selectivity for 1, 2-PDO increases slightly only.

5.3 Effect of Reaction time

Table 4: (a) Influence of reaction time in the hydrogenolysis of glycerol over Cu(6%)-HAP

Catalyst	Run time (h)	Glycerol conversion (%)	Selectivity (%)			
			1,2-PDO	EG	MeOH+EtOH	HA
Cu(6%)-HAP	6h	6.9	_	27.7	72.2	_
Cu(6%)-HAP	12h	8.3	_	32.7	62.2	5.0

Reaction conditions: 15wt% glycerol in isopropanol; catalyst: 0.4g; temp: 220 °C; pressure: 60 bar; stirring speed: 500 rpm.

The effect of run time on glycerol hydrogenolysis was investigated using Cu(6%)-HAP and the results are presented in Table.2 Conversion is found to increase linearly with increasing reaction time from 6 h to 12 h, the increase being from 6.9 % at 6h to 8.3 % at 12 h. The selectivity for EG increases during the period (6h to 12h). Even though conversion is higher at larger run duration, all the studies reported earlier over the different catalysts were carried out at 6 h run duration mainly for a better comparison of the activity of the different metal-support combinations.

Table 4: (b) Influence of reaction time in the hydrogenolysis of glycerol over Ni(12%)-HAP

Catalyst	Run time(h)	Glycerol conversion (%)	Selectivity (%)			
			1,2-PDO	EG	MeOH+EtOH	HA
Ni(12%)-HAP	6h	23.2	35.0	5.3	59.6	_
Ni(12%)-HAP	12h	77.7	.72	3.2	95.3	.75

The effect of run time on glycerol hydrogenolysis was investigated using Ni(12%)-HAP with 1:1 ration of H_2O and isopropanol with base, and the results are presented in Table.3 Conversion is found to increase sharply with increasing reaction time from 6 h to 12 h, the increase being from 23.2 % at 6h to 77.7 % at 12 h. However the selectivity for EG decreases sharply during the period (6h to 12 h), with increase in selectivity for Methanol+Ethanol. Even though conversion is higher at larger run duration, all the studies reported earlier over the different catalysts were carried out at 6 h run duration mainly for a better comparison of the activity of the different metal-support combinations

5.4 Effect of addition of Base $Ca(OH)_2$

Table 5: The effect of adding $Ca(OH)_2$ (0.4 g) to the reaction mixture investigated using Ni(12%)-HAP as the catalyst.

Catalyst	Glycerol Conversion (%)	Selectivity (%)			
		1,2-PDO	EG	MeOH+EtOH	HA
Ni(12%)-HAP H_2O	9.8	59.2	3.6	22.3	14.7
Ni(12%)-HAP H_2O+$Ca(OH)_2$	96.7	_	_	100	_
Ni(12%)-HAP H_2O+IPA(50 50)	35.6	1.6	44.4	53.9	_
Ni(12%)-HAP H_2O+IPA(50 50)+ $Ca(OH)_2$	23.2	35.0	5.3	59.7	_
Ni(12%)-HAP IPA	33.7	5.5	8.8	65.4	20.0
Ni(12%)-HAP IPA+ $Ca(OH)_2$	28.2	23.7	5.8	66.8	6.0

Reaction conditions: 15 wt% glycerol; catalyst: 0.4 g of Ni(12%)-HAP;0.4 g of $Ca(OH)_2$; Pressure: 60 bar; temp: 220 °C; duration of run: 6 h

Conversion of glycerol is suppressed by the addition of $Ca(OH)_2$ in case of Ni(12%)-HAP with water+IPA in equal ratios and also with only IPA. However with Ni(12%)-HAP and only water the conversion increases sharply from 9.8% to 96.7%.However,the selectivity for 1,2-PDO increases with addition of the base sharply from 5.55 to 23.76 in with only IPA and from 1.6 to 35.02 with water+IPA in equal ratios. Also the selectivity for 1, 2-PDO reduces to 0 from 59.24 in Ni(12%)-HAP with only water by addition of $Ca(OH)_2$, with 100% selectivity for Methanol+Ethanol.
The reason for the suppression of activity by $Ca(OH)_2$ is not clear, but earlier workers have reported that Ca^{++} ion may form complexes with intermediates/product

5.5 Effect of Solvent

Table 6: The effect of different solvents investigated using Ni(12%)-HAP as the catalyst.

Solvent	Glycerol Conversion (%)	Selectivity (%)			
		1,2-PDO	EG	MeOH+EtOH	HA
H_2O	9.8	59.2	3.6	22.3	14.7
IPA	33.7	5.5	8.8	65.4	20.0
IPA+H_2O(50:50)	35.6	1.6	44.4	53.9	

Reaction conditions: 15 wt% glycerol; catalyst: 0.4 g of Ni(12%)-HAP; Pressure: 60 bar; temp: 220 °C; duration of run: 6 h.
Conversion of glycerol is maximum with H_2O+IPA in equal ratios (35.6%). However, the selectivity for 1,2-PDO is least with Ni(12%)-HAP with H_2O+IPA in equal ratios, being only 1.6% whereas, that for only water is 59.24%.The selectivity for Methanol+Ethanol is maximum for Ni(12%)-HAP with only IPA.

6.0 Conclusion

The study for hydrogenolysis of glycerol was carried out using different metal loading Ni(6%, 12%), Cu(6%), Pt(1%), Ru(1%) using Hydroxyapetite as the support for the conversion of glycerol in 1,2-propandiol and ethylene glycol.
The studies reveal that both the metal and the support influence the activity of the catalysts. The conversions are low (less than 10%) over most catalysts under the experimental conditions, selectivity for the desired products, 1, 2-propanediol and ethylene glycols are moderate only over a few catalysts. The order for conversion of the different metal supported catalysts with isopropanol as the solvent is Ni(12%) > Pt(1%) > Ru(1%) > Cu (6%) > Ni(6%).

The different reaction conditions were carried out using Ni(12%) supported on hydroxyapetite. Increase in reaction time in case of Ni(12%)-HAP increases conversion with sharp decrease in the selectivity for ethylene glycol. Also, increase in time for Cu(6%)-HAP from 6h to 12h causes increase in the conversion with moderate increase in selectivity for ethylene glycol. Addition of $Ca(OH)_2$ to the (catalyst Ni(12%)-HAP) causes increase in conversion and decrease in selectivity for 1,2-propanediol for the reaction mixture with only water and decreases in conversion and increase in selectivity for 1,2 propanediols in that with H_2O+isopropanol in equal ratios and also for only isopropanol.
Use of only water: Decrease in conversion; increase in selectivity for 1, 2-PDO
Use of H_2O+IPA(50 50):Increase in conversion; decrease in selectivity for 1,2PDO
Use of IPA: Increase in conversion; decrease in selectivity for 1, 2-PDO
The use of only water in the reaction mixture with Ni(12%)-HAP decreases the conversion with increase in selectivity for 1,2-propandiol.The use of equal ratios of water and isopropanol causes maximum conversion with maximum selectivity for ethylene glycol.

Acknowledgement

I acknowledge National Center for Catalysis Research for their help and financial support.

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