Synopsis of thesis entitled

SELECTIVE CATALYTIC HYDROGENOLYSIS OF GLYCEROL TO 1,2-PROPANEDIOL

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BY

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1. Introduction

Fossil resources have been used as the main raw material for the current economy and life style. The transportation fuels and petrochemicals have been produced predominantly from the finite petroleum resources so far. The consumption of these products over the past decades has resulted in the depletion of fossil resources. In addition, burning fossil fuels creates carbon dioxide, the most important greenhouse gas contributing to global warming and eventually to adverse climate change. The emerging economical, political and environmental factors forced to look for alternative fuels. It is imperative to develop energy-efficient processes for the sustainable production of fuels and chemicals. In this respect, plant biomass is sustainable source for fuels and chemicals. Biofuels, fuels derived from plant biomass, are the only current sustainable source of liquid fuels. Biofuels generate significantly less greenhouse gas emissions than the fossil fuels. A variety of liquid biofuels such as bioethanol, biodiesel, bio-methanol and Fischer-Tropsch diesel can be produced from biomass resources. Ethanol and biodiesel comprise a majority of the manufactured biofuels. One such bio-based fuel that is being widely commercialized is biodiesel.

Biodiesel is produced by transesterification of edible, non-edible vegetable oils or animal fats. During the preparation of biodiesel glycerol will be formed as a co-product. Glycerol is normally generated at a rate of 1 mol for every 3 mol of methyl esters synthesized; approximately 10 wt% of the total product. Now a day’s biodiesel production is increasing globally at the average annual growth rate of 42%, which provides around 4 billion gallons of glycerol. There is a glut of glycerol in the global market due to increased production of biodiesel in the world. It is a big challenge to use low-grade glycerol obtained from biodiesel production. Today, there is a need to develop processes or technologies for the value-addition of glycerol which helps to improve the economics of biodiesel production. With a focus on recent developments in the conversion of glycerol into value-added chemicals, new chemistry of glycerol is going to play a crucial role in future bio-refineries.

Glycerol is a highly functionalized molecule; a variety of value-added chemicals can be produced by catalytic conversion of glycerol through different reactions via different reaction routes, such as oxidation, hydrogenolysis, dehydration, pyrolysis, steam reforming, etherification, esterification, oligomerisation and polymerization. Among all approaches, hydrogenolysis of glycerol to propanediols is one of the useful approaches to prepare value added chemicals from glycerol. The hydrogenolysis of glycerol gives several products such as 1,3-propanediol, 1,2-propanediol, 1-propanol, 2-propanol and ethylene glycol. The present thesis focus is mainly on the study related to the hydrogenolysis of glycerol to 1,2-propanediol. The conversion of glycerol into selective chemicals by hydrogenolysis utilize green catalytic processes is a challenging area of research. It is required to develop highly active heterogeneous catalysts to produce the desired chemical from crude glycerol.

1,2-propanediol or propylene glycerol is a three-carbon diol with a stereogenic center at the central carbon atom. It is an important medium-value commodity chemical with a 4% annual growth in the global market. It is used for making polyester resins, liquid detergents, pharmaceuticals, cosmetics, tobacco humectants, flavor and fragrance agents, personal care items, paints, animal feed, antifreeze compound, etc. There has been a rapid expansion of the market for 1,2-propanediol as antifreeze and de-icing agent because of the growing concern over the toxicity of ethylene glycol based products to humans and animals. Presently, the propylene glycol market is under severe pressure due to increase in oil and natural gas costs. Glycerol can be converted selectively to 1,2-propanediol using heterogeneous, homogeneous or biocatalysts. Among all these, heterogeneous catalytic conversion of glycerol is economically and environmentally attractive. The catalytic process of glycerol hydrogenolysis was investigated both in liquid phase (in batch setups) and vapor phase (normally in continuous setups).

Hydrogenolysis of glycerol to 1,2-propanediol can be produced over various transition metals-based catalysts like noble and non-noble metals such as Zn, Cu, Mg, Co, Mo, Pd, Ni, Ru and Pt. Among all these metals non-noble metal catalysts are highly selective toward 1,2-propanediol as compared to noble metal catalysts due to its lower activity for C-C bond cleavage. Among various different catalysts Cu and Ni catalysts showed low activity and selectivity to 1,2-propanediol even at longer reaction times. A limited number of studies were performed using Co and Cu catalysts in liquid phase glycerol hydrogenolysis. No detailed studies have been found over bimetallic catalysts for continuous/vapor phase glycerol hydrogenolysis. There are still many issues arising from these reports which highlight the need for development of new catalytic materials. Taking into account all the above mentioned features, there is a need for the development of new catalysts which should be highly active, selective and stable for both the liquid and vapor phase glycerol hydrogenolysis.

2. Aims and objectives of the work

The present work aims at:

- ✓ Development of active heterogeneous catalysts for selective hydrogenolysis of glycerol to 1,2-propanediol.
- ✓ Preparation of Co based mixed oxide catalysts for the selective liquid phase glycerol hydrogenolysis to 1,2-propanediol.
- ✓ Preparation and evaluation of Cu based mixed oxide catalysts for the liquid phase hydrogenolysis of glycerol.
- ✓ Studying the effect of second metal on Cu and Ni catalysts for vapor phase/continuous glycerol hydrogenolysis.
- ✓ Understanding the surface and structural characteristics of the catalysts and correlating their properties with activity and selectivity.
- ✓ Investigating the reasons for high activity with respect to the nature of catalyst in glycerol hydrogenolysis.
- ✓ Optimization of reaction parameters to achieve maximum conversion and selectivity towards desired products.

3. Scope of the work

Selective hydrogenolysis of glycerol to 1,2-propanediol was studied over two types of catalysts. Co and Cu based mixed oxide catalysts are explored for the liquid phase glycerol hydrogenolysis. Co-ZnO, Co-MgO and Cu-ZrO_2-MgO mixed oxide catalysts were prepared and evaluated for liquid phase hydrogenolysis of glycerol. Continuous/vapor phase hydrogenolysis was studied over Ni based bimetallic catalysts. γ-Al_2O_3 supported bimetallic Ni-Cu and Ni-Ag catalysts were prepared. The effect of second metal is studied in detail to improve the activity of the catalyst. The effect of reaction parameters was studied in detail to establish optimum reaction conditions to yield the desired product. The catalysts were characterized thoroughly with various spectroscopic and non spectroscopic methods to establish structure-activity relationships.

4. Organization of the thesis

Chapter 1: General introduction

This chapter gives a brief introduction on the commercial importance of glycerol and its value added compounds. The various methods available for value-addition of glycerol are discussed. Among different possible chemicals, the advantages of glycerol hydrogenolysis and synthesis of 1,2-propanediol are discussed. A detailed account for the development of heterogeneous catalysts for selective glycerol hydrogenolysis is discussed. The scope, aims and objectives of the thesis are elucidated.

Chapter 2: Literature survey

This chapter describes about various catalysts developed and studied for both the liquid and continuous/vapor phase hydrogenolysis of glycerol. The related literature on noble metal catalysts, non-noble metal catalysts and combination of noble and non-noble metal catalysts with or without external hydrogen are discussed in this chapter. Various catalytic systems reported in patent literature for glycerol hydrogenolysis is also reviewed briefly. The reaction mechanisms proposed for these reactions over various catalytic systems are also described.

Chapter 3: Experimental

General procedures for catalyst preparations like impregnation and co-precipitation along with the methodologies followed in the present work are presented in this chapter. The basic concepts and experimental procedures of catalyst characterization techniques are described. The methodologies followed in the present work to evaluate the catalysts during glycerol hydrogenolysis are also discussed in detail. The preparation of cobalt and copper based mixed oxide catalysts such as Co-MgO, Co-ZnO and Cu-ZrO_2-MgO with varying Co/M_1, Cu/M_2/MgO (M_1=MgO, ZnO and M_2=ZrO_2) weight ratios discussed in detail. The preparation of γ-Al_2O_3 supported bimetallic Cu-Ni and Ni-Ag catalysts are illustrated.

The principles and the actual conditions used in characterization of catalysts are narrated. The characterization methods such as N_2 gas adsorption for BET surface area, X-ray diffraction, temperature programmed reduction, transmission electron microscopy, chemisorption, temperature programmed desorption of CO_2 and X-ray photo electron spectroscopy techniques are described in detail.

Results and discussion

Chapters 4 and 5 represent the results and discussion part of the thesis. They essentially deal with results obtained during the activity studies on both the liquid and vapor phase glycerol hydrogenolysis with different catalysts. Further, the characterization results of all these catalysts obtained by various techniques are correlated with the activity.

Chapter 4: Liquid phase glycerol hydrogenolysis

This chapter consists of three sections. The individual sections describe the results obtained during liquid phase glycerol hydrogenolysis over Co and Cu based catalysts. In each section, the results obtained on these catalysts are discussed in detail. The effect of different reaction parameters are highlighted. The activity results are correlated with the physico-chemical properties of catalysts.

Section 4.1: Selective hydrogenolysis of glycerol to 1,2-propanediol over Co-ZnO mixed oxide catalysts

This section presents the Co-ZnO catalysts for liquid phase hydrogenolysis of glycerol. These catalysts are prepared by co-precipitation method and evaluated for liquid phase hydrogenolysis of glycerol to 1,2-propanediol. Co-ZnO catalyst can be used for selective hydrogenolysis of glycerol due to the acidic nature of ZnO and hydrogenation ability of Co in the Co-ZnO catalyst. The results suggested that with glycerol conversion increase with increase in Co content up to 50% and the activity decreases with further increase in Co composition. The optimum conversion was recorded for the catalyst with Co to Zn ratio of 50:50. It is found that the hydrogenolysis activity mainly depends on Co particle size and its dispersion.

Section 4.2: Selective hydrogenolysis of glycerol to 1,2-propanediol over Co-MgO mixed oxide catalysts

This section deals with the synthesis, characterization and catalytic evaluation of Co-MgO catalysts for liquid phase glycerol hydrogenolysis. As discussed in previous section, a selectivity to 1,2-propanediol of more than 70 % is achieved over Co-ZnO catalysts. However, the glycerol conversion is low. Therefore, hydrogenolysis is performed on Co-MgO catalysts prepared via co-precipitation with varying Co loading. Co-MgO catalyst is found to be more active than Co-ZnO catalyst. The results have been explained based on the reaction mechanism. Consequently, correlation of surface-structural features of the catalysts with glycerol hydrogenolysis activity is also discussed. Optimization of various reaction parameters were also discussed.

Section 4.3: Selective hydrogenolysis of glycerol to 1,2-propanediol over Cu-ZrO_2-MgO catalysts

The previous sections describes about the results obtained taking different cobalt based mixed oxide for glycerol hydrogenolysis. Co based mixed oxide catalysts showed less 1,2-propanediol selectivity under mild reaction conditions. Hence, there is a need to increase 1,2-propanediol selectivity under mild reaction conditions. Therefore, Cu-ZrO_2-MgO catalysts are prepared and evaluated for glycerol hydrogenolysis. The Effect of Cu/Zr weight ratio on glycerol hydrogenolysis is studied in detail. The results suggested that the glycerol conversion increased up to 20wt% Cu loading and the selectivity of 1,2-propanediol was improved to 96%. It is found that the catalyst having high metal surface area offered high activity. The correlation between structural features derived from characterization results such as X-ray diffraction, temperature programmed reduction, BET surface area, TPD of CO_2 and N_2O pulse chemisorption with that of activity results is discussed in detail. The effect of various reaction parameters such as effect reaction temperature, hydrogen pressure, glycerol concentration and reaction time are also studied to optimize the reaction conditions.

Chapter 5: Continuous/Vapor phase glycerol hydrogenolysis

This chapter is divided into two sections. The individual sections explain the continuous/vapor phase glycerol hydrogenolysis over bimetallic catalysts. The hydrogenolysis activity of γ-Al_2O_3 supported bimetallic Cu-Ni and Ni-Ag catalysts are discussed in detail. The effect of different reaction parameters is also presented. High activity of the catalysts is explained with the help of characterization results.

Section 5.1: Selective hydrogenolysis of glycerol to 1,2-propanediol over γ-Al_2O_3 supported bimetallic Cu-Ni catalysts

This section describes the results obtained on the studies made on γ-Al_2O_3 supported bimetallic Cu-Ni catalysts prepared by varying Ni content and keeping the copper loading constant. With increasing Ni content from 1 to 5 wt% in the catalyst, the glycerol conversion is found to be increased. The catalyst with 10%Cu-3%Ni/γ-Al_2O_3 gave about 72.6% of glycerol conversion with 46.5% selectivity towards 1,2-propanediol. The activity of this catalyst might be due to the presence of easily reducible metallic species at low temperature and also the amount of Ni content in the catalyst. The effects of various reaction parameters such as reaction temperature, glycerol concentration and weight hourly space velocity (WHSV) also discussed.

Section 5.2: Selective hydrogenolysis of glycerol to 1,2-propanediol over γ-Al_2O_3 supported bimetallic Ni-Ag catalysts

As discussed in previous section conversion and selectivity to 1,2-propanediol is less over Cu-Ni/γ-Al_2O_3 catalysts. In order to increase the conversion and selectivity towards 1,2-propanediol the Ni-Ag/γ-Al_2O_3 with a total metal loading of 20 wt% by varying Ni to Ag weight ratios catalysts are prepared. Influence of Ag loading on continuous/vapor phase glycerol hydrogenolysis is also studied. The catalyst with 5wt% of Ag showed reasonable conversion of 79.4% with 57.7% selectivity to 1,2-propanediol. The high activity of 10%Ni-5%Ag/γ-Al_2O_3 catalyst might be due to the presence of highly dispersed Ni and Ag species on γ-Al_2O_3. The catalyst is stable during the glycerol hydrogenolysis and showed consistent activity during the entire time of the study. The glycerol conversion also depends on the reaction parameters and optimum reaction conditions are established.

Chapter 6: Overall conclusions

This chapter describes the important conclusions drawn from the results obtained in the present work.

5. Highlights of the thesis

- Efficient heterogeneous catalysts were designed for the glycerol hydrogenolysis to achieve high yields of 1,2-propanediol.
- Adopted various catalyst synthesis techniques such as co-precipitation and impregnation to prepare mixed oxides and bi metallic catalysts.
- Evaluated the surface structural properties of the synthesized catalysts and their catalytic functionalities.
- Glycerol hydrogenolysis reaction was studied under liquid and continuous/vapor phase.
- Establishment of Co and Cu mixed oxide catalyst to achieve high selectivity to 1,2-propanediol.
- Catalytic activity of Co on different supports such as ZnO and MgO was studied for liquid phase glycerol hydrogenolysis.

- Optimized the Co metal content on ZnO for high glycerol hydrogenolysis activity and selectivity towards 1,2-propanediol.
- Studied the effect of metal content and its surface area on ZnO and MgO catalysts.
- Studied the Cu-ZrO_2-MgO catalyst activity by varying the Cu and ZrO_2 content and evaluated the catalytic properties for glycerol hydrogenolysis.
- Kinetic model was applied for glycerol hydrogenolysis and evaluated the activation energy.
- Studied the various reaction parameters such as reaction time, catalysts loading, temperature, hydrogen pressure and glycerol concentration etc. to optimize the reaction parameters.
- Bimetallic Ni-Cu and Ni-Ag catalysts were studied for continuous/vapor phase hydrogenolysis reaction.
- Studied the effect of Ni/Cu and Ni/Ag percentage on γ-Al_2O_3 catalysts for high selectivity of 1,2-propanediol.
- Evaluated the effect of WHSV, reaction temperature, catalyst loading and glycerol concentration on glycerol hydrogenolysis to selective formation of 1,2-propanediol.

List of Publications

1. Understanding the role of Co in Co-ZnO mixed oxide catalysts for the selective hydrogenolysis of glycerol.

   V. Rekha, C. Sumana, S. Paul Douglas, N. Lingaiah

   Applied Catalysis A: General 491 (2015) 155-162.

2. 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

   Applied Catalysis A: General 384 (2010) 107-114.

3. 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.

   Applied Catalysis A: General 354 (2009) 82-87.

4. Selective hydrogenolysis of glycerol to 1, 2 propanediol over Cu-ZnO catalysts.

   M. Balaraju, **V. Rekha**, P. S. Sai Prasad, R. B. N. Prasad, N. Lingaiah.

   Catalysis Letters 126 (2008) 119-124.

Papers Communicated

5. Kinetics and Catalytic Hydrogenolysis of Glycerol to 1, 2-Propanediol over Cu-ZrO_2-MgO Catalysts.

   V. Rekha, N. Raju, C. Sumana, S. P. Douglas, N. Lingaiah (To be communicated)

6. Selective hydrogenolysis of glycerol over Co-MgO mixed oxide catalysts.

   V. Rekha, N. Raju, C. Sumana, S. P. Douglas, N. Lingaiah (To be communicated)

Oral presentations in national & international symposiums

1. Continuous hydrogenolysis of glycerol over alumina supported bi metallic Ni-Ag catalysts.

   V. Rekha, N. Raju, C. Sumana, P. S. Sai Prasad and N. Lingaiah,

   CHEMCON-2014, 67th Annual Session of Indian Institute of Chemical Engineers held in Chandigarh, December 27-30, 2014.

2. Selective Hydrogenolysis of Glycerol to 1, 2-Propanediol over Cu-MgO-ZrO_2 catalysts.

   V. Rekha, Ch. Ramesh Kumar, C. Sumana, P. S. Sai Prasad and N. Lingaiah

   CHEMCON-2013, 66th Annual Session of Indian Institute of Chemical Engineers, Mumbai during December 27-30, 2013.

3. Co-based mixed oxides as catalysts for selective hydrogenolysis of glycerol.

   V. Rekha, S. Paul Douglas, P. S. Sai Prasad and N. Lingaiah

   National seminar on recent trends and future perspectives in materials science 28th & 29th, June-2013, Andhra University, Visakhapatnam.

Poster presentations in national & international symposiums

4. Selective hydrogenolysis of glycerol over Co-MgO mixed oxide catalysts.

   V. Rekha, N. Raju, P. S. Sai Prasad and N. Lingaiah.

   22nd National Symposium on Catalysis, CATSYMP-22, Bhavnagar, held from Jan 7-9, 2015.

5. Supported cesium salts of heteropoly tungstate catalytic systems for liquid phase benzylation of anisole with benzyl alcohol.

   Ch. Ramesh Kumar, **V. Rekha**, P. S. N. Rao, P. S. Sai Prasad, N. Lingaiah

   16th National Workshop on Catalysis for Sustainable Development Symposium held at CSIR-NEERI, Nagpur during 4-5 February 2014.

6. Development of solid acid catalysts for the conversion of waste plastics into valuable fuel range hydrocarbons.

   V. Rekha and N. Lingaiah

   7th International Symposium on Feedstock Recycling of Polymeric Materials, 23rd - 26th October 2013, India Habitat Centre, New Delhi, India.

7. Vapor phase hydrogenolysis of glycerol over alumina supported Co-Ag bimetallic catalysts.

   V. Rekha, P. S. Sai Prasad and N. Lingaiah.

   International Conference on Emerging Trends in Oleo chemicals & Lipids Expo - 2013, at Hyderabad during 8-10th August 2013.

8. The role of catalysts in conversion of glycerol into value added chemicals.

   M. Srinivas, G. Parameswaram, **V. Rekha**, P. S. Sai Prasad and N. Lingaiah

   International Conference on Emerging Trends in Oleo chemicals & Lipids Expo - 2013, at Hyderabad during 8-10th August 2013.

9. Selective hydrogenolysis of glycerol to 1,2-Propane diol over Co-ZnO catalysts.

   V. Rekha, Rekha Sree, M. Balaraju, S. Paul Douglas, P. S. Sai Prasad and N. Lingaiah.

   21st National Symposium on Catalysis, CATSYMP-21, CSIR-IICT, Hyderabad during February 11-13, 2013.

10. Vapor phase hydrogenolysis of glycerol over alumina supported bi metallic catalysts.

    V. Rekha, K. Jagadeeswaraiah, P. S. Sai Prasad and N. Lingaiah

    2nd International Indo German Symposium on Green Chemistry and Catalysis for Sustainable Development to be held on October 29-31, 2012, Mumbai.

11. Selective hydrogenolysis of glycerol to propylene glycol over Cu based mixed oxide catalysts.

    V. Rekha, A. Sreevani, R. B. N. Prasad, P. S. Sai Prasad and N. Lingaiah.

    19th National Symposium on Catalysis, NCL, Pune, January 2009.

<u>Participation in national & international symposiums</u>

12. One day Seminar on Recent Trends In Progess Intensification Methods TEQIP-11 (Centre of Excellence) Osmania University, Hyderabad, Septmber, 2014.
13. Participated in the National Seminar on Student Centric Creative Research titled CREATIVE QUEST held at ST. Pious X degree & PG College for women held at Hyderabad, during 2-3rd august 2013.