# SYNTHESIS OF HIGHER CARBON NUMBER ALCOHOLS FROM ETHANOL

## A SYNOPSIS

# Submitted by

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in partial fulfillment of the requirements for the degree of

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#### 1. INTRODUCTION

Currently, around 80% of global total primary energy is derived from fossil resources, like oil, natural gas and coal (1), which are non-sustainable. Emission of CO<sub>2</sub> by burning of fossil fuels is responsible for the global warming and other associated ecological issues. Bio-fuels, based on renewable bio-mass resources, have emerged as the viable and sustainable alternatives, with a potential to reduce the global warming. The firstgeneration biofuels, biodiesel from vegetable oils and ethanol from corn and sugars (2), though effective in their applications, have issues related to food Vs fuel imbalances, with respect to the raw materials, their availability and cost, besides the consequent environmental impacts. The second-generation biofuels, derived from lignocellulosic/plant bio-mass feedstocks, are free from such limitations, abundant in different types and at lower cost. Typical second-generation biofuels are, cellulosic ethanol, fuels from bio-mass derived syngas and bio-oil, butanol and other higher carbon number alcohols. Advances in the chemistry, catalytic processes and engineering aspects related to the conversion of bio-mass into transportation fuels and value-added chemicals have been covered in excellent reviews (3,4). While both methanol and ethanol are used for blending with fuels and in the manufacture of fuel additives and oxygenates (5,6) n-butanol is considered as the next generation biofuel, with several advantages over ethanol, such as, higher energy density, lower volatility and solubility in water and non-corrosive nature (7). Besides, butanol blends well with gasoline and with higher air to fuel ratio, renders more efficient combustion. Currently, butanol is produced by the Oxo process, using propylene, a raw material derived from non-renewable resources and involves application of high pressure, energy inputs and cost of production and hence lacks sustainability. Though an alternative bio-based fermentation process (ABE process) is in practice, a number of factors, like, low yield of butanol, higher cost of substrates and product recovery and





solvent toxicity to the *Clostridium* stains, restrict its application on larger scale (8). In this context, conversion of ethanol to butanol and higher alcohols, using the classical Guerbet condensation reaction (9), has emerged as an attractive proposition. Especially, with the plentiful availability of bioethanol, processes for its conversion to butanol and other higher alcohols are being explored globally with keen interest, resulting in the revival of Guerbet alcohol chemistry and catalysts. Excellent reviews (10), covering various stages of developments in the heterogeneous as well as homogeneous catalytic processes for the conversion of ethanol to butanol and higher alcohols, based on the Guerbet chemistry, have been published. Studies on various types of catalyst systems, based on MgO, Mg-Al-O mixed oxides, Cu/CeO<sub>2</sub>, basic zeolites, hydroxyapatite, solid acid supported Cu, alumina and carbon supported metal (Ni, Cu, Co, Pd, Ru, Au) catalysts have been explored along with thermodynamic aspects and plausible reaction pathways for the major as well as minor products (11,12). Reactions have been carried out in batch as well as continuous modes, at different pressures. Higher selectivity for butanol and higher alcohols could be achieved mostly at lower ethanol conversion levels. For example, while Jordison et al. (13) could achieve 55% conversion of ethanol and 71% selectivity for total higher alcohols (~ 50% selectivity to butanol) at 230°C under autogenous pressure (800-1500 psia) on 8% Ni on Al<sub>2</sub>O<sub>3</sub> support (modified with 9% La<sub>2</sub>O<sub>3</sub>) after 10 hrs on stream period, Chistyakovet al. (14) observed 35% conversion and 62% butanol selectivity on Ni-Au-alumina at very high temperature and pressure (275°C and 150 bar). Thus, achieving higher selectivity/yield for butanol and higher carbon number alcohols, at higher ethanol conversion, under moderate reaction conditions, remains a challenge. Present investigation aims at addressing this challenge through a systematic study.

#### 2. AIM AND SCOPE OF THE INVESTIGATION

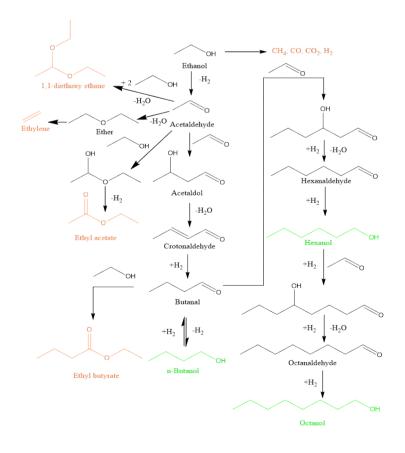




The key steps involved in the Guerbet process for ethanol conversion to higher alcohols are (10,11):

- i. Dehydrogenation of ethanol to acetaldehyde
- ii. Aldol condensation of acetaldehyde followed by dehydration to yield crotonaldehyde
- iii. Stepwise hydrogenation of crotonaldehyde to butyraldehyde and further to n-butanol

Similar surface transformations between butyraldehyde and acetaldehyde leads to the formation of hexanol and so on, as shown in Scheme.1. A bifunctional catalyst, having metal sites for dehydrogenation-hydrogenation functionalities and basic-acidic site pairs for condensation and dehydration functionalities, would be the ideal choice for this process. However, an effective integration of the primary active sites and surface transformations and balancing of acidity-basicity (type, population and strength) therein are







Scheme.1 Possible surface transformations in Guerbet process with ethanol the key issues to be addressed, in order to minimize possible side reactions (Scheme 1 in red) and achieve higher selectivity. Based on the literature data (10-14), 8% (w/w) Ni/Al<sub>2</sub>O<sub>3</sub> has been chosen as the base catalyst and both active metal phase and the support compositions have been modified in order to improve ethanol conversion and higher alcohol selectivity under moderate process conditions. Investigations in detail include the following aspects/ modifications in the base catalyst, Ni/Al<sub>2</sub>O<sub>3</sub>:

- a) Modifications in the alumina support, by addition (5% w/w each) of metal oxides, namely, La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>, MgO and TiO<sub>2</sub> as promoters. Besides tuning the acid-base characteristics of alumina, these promoters could influence the metal (Ni) dispersion, its electronic state and modulate metal-support interactions and hence activity and selectivity.
- b) Modifications in the active phase Ni, by addition of second metal, namely, Co, Cu, Pd, Au & Ru. Bimetallic catalysts are expected to display synergistic effects, depending on their nature, influence the electronic state of Ni and hence dehydrogenation-hydrogenation reactions on Ni/second metal,

Accordingly, the scope of the investigations includes studies on the conversion of ethanol to butanol and higher alcohols on different catalysts, as enumerated below:

- a) Influence of support characteristics on Ni/M<sub>x</sub>O<sub>y</sub>-Al<sub>2</sub>O<sub>3</sub> (M=La, Ce, Zr, Mg and Ti) catalysts
- b) Bimetallic Ni-Co catalysts with varying Ni and Co loadings and supported on CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> mixed oxide
- c) Bimetallic Ni- Cu catalysts with varying Ni and Cu contents and supported on CeO<sub>2</sub>- Al<sub>2</sub>O<sub>3</sub> mixed oxide
- d) Ni-based bimetallic catalysts containing noble metals (Pd/ Au/Ru) and supported on CeO<sub>2</sub>- Al<sub>2</sub>O<sub>3</sub> mixed oxide.





All the catalysts prepared by wet impregnation method have been evaluated for the conversion of ethanol to butanol and higher alcohols and subjected to characterization by XRD, Electron microscopy, TPR, XPS and DRS techniques and acidity and basicity measurements by ammonia and CO<sub>2</sub> TPD methods and textural characteristics by nitrogen adsorption at 77K. Reactions were carried out in 100 ml Parr reactor, in batch mode, under autogenous pressure, at 200-220°C for 8hrs, after pressurization with nitrogen up to 10 bar. Observed activity and selectivity patterns have been rationalized in terms of the characteristics of the catalysts.

#### **3. STRUCTURE OF THE THESIS**

In accordance with the scope described above, the thesis has been structured in the following manner:

- Chapter 1 Introduction, Aim and scope of the investigation
- Chapter 2 Experimental methods
- Chapter 3 Conversion of ethanol to higher alcohols on Ni/M<sub>x</sub>O<sub>y</sub>-Al<sub>2</sub>O<sub>3</sub> (M=La, Ce, Zr, Mg &Ti) catalysts: - Influence of support characteristics
- Chapter 4 Ethanol condensation to butanol and higher alcohols over nickel and cobalt decorated CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> mixed oxide catalysts
- Chapter 5 Bimetallic Ni- Cu catalysts supported on CeO<sub>2</sub>- Al<sub>2</sub>O<sub>3</sub> for conversion of ethanol to higher alcohols
- Chapter 6 Investigations on Ni-based bimetallic catalysts containing noble metals (Pd, Au & Ru) and supported on CeO<sub>2</sub>- Al<sub>2</sub>O<sub>3</sub> for ethanol conversion
- Chapter 7 Summary and Conclusions

References

List of Publications and Presentations

Salient features of the Chapters are presented in the following pages.





#### 4. SALIENT FEATURES OF THE THESIS

#### 4.1. Chapter 1 Introduction

**Chapter 1** presents an overview of biofuels, classification of biofuels, alcohols as biofuels, especially, bio-ethanol, butanol and higher alcohols, advantages of butanol over ethanol, existing chemical and bio-chemical routes for production of butanol, relevance of Guerbet chemistry in the synthesis of butanol and higher alcohols and bio-jet fuels, mechanistic aspects of Guerbet process, influence of acidity, basicity, metal dispersion, comprehensive review of different catalysts, mono/bi/ multi metallic, for ethanol conversion and future directions for research in this area.

#### 4.2. Chapter 2 Experimental

**Chapter 2** deals with the experimental methods adopted for the preparation, systematic characterization and performance evaluation of all catalysts for ethanol conversion process. The catalysts were prepared by wet impregnation method and characterized by X-ray diffraction (XRD), Temperature programmed reduction (H<sub>2</sub>-TPR), N<sub>2</sub> adsorption/desorption isotherm, Temperature programmed desorption (NH<sub>3</sub>&CO<sub>2</sub>-TPD), X-ray photoelectron spectroscopy (XPS), High resolution transmission electron microscopy (HR-TEM), Scanning electron microscopy (SEM) and Diffuse Reflectance Spectroscopy (DRS). Brief description of the methods has been provided. A schematic representation of the reactor set up along with the procedure adopted for activity measurements and analysis of the product streams are presented.

# 4.3. Chapter 3 Conversion of ethanol to higher alcohols on Ni/M<sub>x</sub>O<sub>y</sub>-Al<sub>2</sub>O<sub>3</sub> (M= La, Ce, Zr, Mg &Ti) catalysts: - Influence of support characteristics

A new series of alumina supported nickel (8% w/w) catalysts, modified with promoters, La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>, MgO and TiO<sub>2</sub>, are found to be highly active





for the conversion of ethanol to butanol and higher alcohols, at 200°C-220°C, in batch mode (8 hrs), under autogenous pressure. Presence of small amounts acetaldehyde, butanal and crotonaldehyde in the product indicates that the process follows the Guerbet reaction pathway. XRD and XPS results indicate the presence of metallic Ni and Ni aluminate as the active phases. H<sub>2</sub>-TPR studies (Fig.1) reveal that the introduction of promoters improves nickel dispersion, reducibility and moderates the metal-support interactions. Maximum reducibility is observed with 8%Ni/5%CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>catalyst.

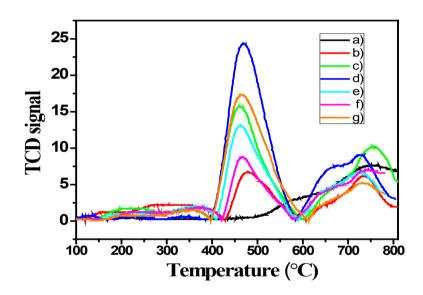


Fig.1 H<sub>2</sub> TPR profiles for Ni/M<sub>x</sub>O<sub>y</sub>-Al<sub>2</sub>O<sub>3</sub> (M=La, Ce, Zr, Mg &Ti) catalysts a) Al<sub>2</sub>O<sub>3</sub>, b) 8%Ni/Al<sub>2</sub>O<sub>3</sub>,c) 8%Ni/5%La<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>,d) 8%Ni/5%CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>,e) 8%Ni/5%ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>,f) 8%Ni/5%MgO-Al<sub>2</sub>O<sub>3</sub>,g) 8%Ni/5%TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>

TPD of ammonia and CO<sub>2</sub> studies establish the strong influence of the promoter oxides on the strength and population of acidic and basic sites. Ethanol conversion at 200°C (Table 1) varies in a narrow range, 36-42%. CeO<sub>2</sub> and MgO modified catalysts display maximum selectivity towards butanol (48%) and higher alcohols, (81% and 75%) in comparison with the catalyst based on pristine alumina (28.9% and 40.5%). While the selectivity for butanol and higher alcohols is governed by the basicity of the catalysts, both metal function and basicity are required to drive ethanol conversion.





Cataysts	Conv. (%)	HA Selec. (%)	Butanol Selec. (%)
8%Ni/Al <sub>2</sub> O <sub>3</sub>	38.2	40.5	28.9
	45.5	78.7	45.7
8%Ni/5%La2O3-Al2O3	42.3	61.5	39.8
	65.0	80.3	40.4
8%Ni/5%CeO2-Al2O3	41.1	81.0	48.6
	65.7	79.0	40.4
8%Ni/5%ZrO2-Al2O3	39.6	69.3	45.8
	61.9	73.0	36.8
8%Ni/5%MgO-Al <sub>2</sub> O <sub>3</sub>	36.3	75.3	48.0
6 - 1	60.9	71.4	38.2

Table 1 Ethanol conversion and selectivity data on  $Ni/M_xO_y$ -Al<sub>2</sub>O<sub>3</sub>

(M= La, Ce, Zr, Mg &Ti) catalysts

36.2

63.1

46.1

55.1

33.5

28.4

8%Ni/5%TiO2-Al2O3

Moderation of acidity by promoters helps in minimizing the formation of ethylene and other C<sub>1</sub>-C<sub>5</sub> gaseous hydrocarbon products. Characterization of used catalyst indicates that the structural and active phase characteristics are retained during use. The catalysts display higher ethanol conversion (60-65%) at 220°C, but with lower butanol selectivity, possibly due to conversion to higher alcohols and increase in the formation of gaseous products. Increasing basicity of the catalysts with higher loading of ceria, improving metal function by addition of second metal with Ni and optimization of acidity-basicity to minimize side products formation are the useful strategies for achieving higher ethanol conversion activity and selectivity for butanol and higher alcohols. Since 8%Ni/5%CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst displayed maximum ethanol conversion, and selectivity for butanol and higher alcohols, all further studies are based on catalysts with 5% CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> as the support.





<sup>(</sup>Reaction conditions: Catalyst weight-1.83g, Ethanol feed- 20 g, Pressure 45-50 kg/cm<sup>2</sup>, Reaction time -8hrsTemperature- 200°C, 220 °C)

# 4.4. Chapter 4 Ethanol condensation to butanol and higher alcohols over nickel and cobalt decorated CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> mixed oxide catalysts

Improving metal function by introducing a second metal could be considered as one of the strategies for achieving higher ethanol conversion and selectivity. Based on this concept, a new series of bimetallic Ni-Co catalysts were prepared by step wise substitution of Ni (8% w/w) by Co, to get active phase compositions of 6%Ni-2%Co, 4%Ni-4%Co, 2.5%Ni-5.5% Co and 8% Co, supported on CeO<sub>2</sub>(5 % w/w)-Al<sub>2</sub>O<sub>3</sub> mixed oxide phase. XRD, TPR and

Table 2. Ethanol conversion and selectivity data on bimetallic

Catalysts	Conv. (%)	HA Selec. (%)	Butanol Selec. (%)
8%Ni/5%CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	52.6	46.4	29.2
6%Ni-2%Co/5%CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	42.2	51.4	34.2
4%Ni-4%Co/5%CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	55.0	50.1	30.0
2.5%Ni-5.5%Co/5%CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	52.7	53.4	32.7
8%Co/5%CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	43.6	20.7	17.0

Ni-Co/5%CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	catalysts
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(Reaction conditions: Catalyst weight-1.83g, Ethanol feed- 20 g, Pressure 45-50 kg/cm<sup>2</sup>, Reaction time -8hrs, Temperature- 200°C)

XPS studies reveal the formation of Ni-Co alloys at specific compositions which modifies the electronic structure of bimetallic catalysts. DRS studies indicate that majority of  $Co^{2+}$  ions are located in tetrahedral sites, while Ni<sup>2+</sup> ions in octahedral sites. As expected, changes in the composition of Ni-Co do not affect acidity/basicity of the catalysts. Maximum ethanol conversion of 55.1 % is achieved with the composition 4%Ni-4%Co, with C<sub>4+</sub> alcohols selectivity of 50.2%, which is higher than those realized for mono metallic Ni and Co catalysts. At slightly lower conversion of 52.8%, higher C<sub>4+</sub>alcohols selectivity (53.4%) is observed with the composition 2.5% Ni-5.5% Co.





Maximum reducibility is also observed with these two catalyst compositions (Fig.1). The catalytic process follows classical Guerbet alcohol chemistry pathway. Primary surface reaction involving of dehydrogenation of ethanol to acetaldehyde and hydrogenation of  $C_4$  and higher carbon number aldehydes to the corresponding alcohols are the crucial steps for ethanol conversion to butanol and higher alcohols. Ni-Co alloys in Ni-Co bimetallic catalysts function as efficient dehydrogenation-hydrogenation catalysts, thereby increasing ethanol conversion and  $C_{4+}$  alcohol selectivity vis-a-vis the mono metallic catalysts.

# 4.5 Chapter 5 Bimetallic Ni- Cu catalysts supported on CeO<sub>2</sub>- Al<sub>2</sub>O<sub>3</sub> for conversion of ethanol to higher alcohols

In order to improve the selectivity towards butanol, copper as the second metal along with Ni has been explored. Bimetallic Ni-Cu catalysts with varying proportions of the metals, bi-metallic 6% Ni-2%Cu, 4%Ni-4% Cu, 2.5%Ni-5.5% Cu and 8% Cu, 8% Ni mono metallic catalysts, supported on CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> have been prepared by wet impregnation and characterized by X-ray diffraction (XRD), TPR and XPS. No significant changes are observed in acidity/basicity

Catalysts	Conv.	HA Solog (%)	Butanol
8% Ni/5%CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	41.1	<b>Selec.(%)</b> 81.0	<b>Selec. (%)</b> 48.6
6% Ni-2% Cu/5%CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	45.1	62.4	44.1
4% Ni-4%Cu/5%CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	37.0	62.8	46.4
2.5% Ni-5.5%Cu/5%CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	32.2	77.3	55.6
8% Cu/5%CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	18.0	81.8	64.1

Table 3 Ethanol conversion on Ni-Cu/ 5%CeO2-Al2O3bimetallic catalysts

(Reaction conditions: Catalyst weight-1.83g, Ethanol feed- 20 g, Pressure 45-50 kg/cm<sup>2</sup>, Reaction time -8hrs, Temperature- 200°C)





of the catalysts. Mono metallic Ni displays ethanol conversion of 41%, with a selectivity of 48.6% towards butanol. Substitution of Ni with Cu up to 2% increases ethanol conversion to 45% with butanol selectivity at 44%. On increasing Cu loading to 4%, conversion decreases to 37% and butanol selectivity increases to 46.4%. Further increase of Cu loading to 5.5% results in higher butanol selectivity of 55.6 % with further decease in conversion to 32.2%. Whereas mono metallic Cu catalyst under identical reaction conditions displays high butanol selectivity, (64%) but very low ethanol conversion (18%). Thus, by optimization of Cu & Ni composition, it is possible to maximize butanol selectivity with optimum conversion level. XPS and TPR studies indicate Ni-Cu alloy formation, especially in the composition range 4% Ni-4% Cu, and 2.5% Ni-5.5% Cu. With increase in Cu loading part of Cu<sup>2+</sup> is reduced at higher temperature along with Ni<sup>2+</sup> indicating Ni-Cu alloy formation. With 2.5% Ni-5.5% Cu, higher selectivity to butanol (55.6%) is observed in comparison with 48.6% for mono metallic Ni catalyst, Ethanol butanol process involves initial dehydrogenation of ethanol to to acetaldehyde, its condensation to crotonaldehyde, which gets hydrogenated to yield butanol. While ethanol conversion decreases with the increase in Cu loading, Ni-Cu alloys facilitate the hydrogenation of crotonaldehyde and higher aldehydes, thereby improving the selectivity for butanol/higher alcohols. Sun et al (15) have reported ethanol conversion of 56% and butanol yield of 22% on Ni-Cu supported on Mg-Al hydrotalcite at higher temperature (320°C) in batch mode. In the present work Ni-Cu catalysts supported on CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> display comparable performance at lower temperature (200°C)'

4.6. Chapter 6 Investigations on Ni-based bimetallic catalysts containing noble metals (Pd, Au & Ru) and supported on CeO<sub>2</sub>- Al<sub>2</sub>O<sub>3</sub> for ethanol conversion





Nickel based bimetallic catalysts containing noble metals like, Pd, Au and Ru as the second metal have been investigated for conversion of ethanol. Catalysts containing 7% w/w Ni with 1% w/w of each noble metal and supported on CeO<sub>2</sub>- Al<sub>2</sub>O<sub>3</sub> have been prepared and characterized by XRD, textural properties, TPR, and TPD of ammonia and CO<sub>2</sub>. TPR studies indicate that the addition of noble metals improves reducibility and dispersion of Ni<sup>2+</sup>. Ethanol conversion and butanol and higher alcohol selectivity data for the catalysts are presented in Table.4. It is observed that the addition noble metals (especially Au & Ru) results in slight improvements in ethanol conversion with respect to mono metallic Ni catalyst, possibly due to increase in the Table 4. Ethanol conversion on Ni-M (M=Pd, Au, Ru)/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>

Catalysts	Conv. (%)	HA selec. (%)	Butanol selec. (%)
8% Ni/5% CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	41.1	81.0	48.6
1%Pd-7%Ni/5%CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	41.6	53.7	36.7
1%Au-7%Ni/5%CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	46.9	65.5	38.6
1%Ru-7%Ni/5%CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	55.9	59.2	32.7

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bimetallic	catalysts
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(Reaction conditions: Catalyst weight-1.83g, Ethanol feed- 20 g, Pressure 45-50 kg/cm<sup>2</sup>, Reaction time -8hrs, Temperature- 200°C)

dispersion of metallic Ni and acceleration of the first step, namely dehydrogenation of ethanol to acetaldehyde. However, selectivity for butanol and higher alcohols is lower than that observed for mono metallic Ni catalyst. Changes in the method of preparation of catalysts (reduction at temperatures < 500°C) may help to improve ethanol conversion and selectivity for butanol and higher alcohols

#### 5. Chapter 7. SUMMARY AND CONCLUSIONS





- The objective of the thesis work is to develop supported metal catalysts that display high ethanol conversion with high selectivity for butanol and higher alcohols, under moderate process conditions
- Alumina supported nickel catalysts has been chosen as the base catalyst.
- Both active phase (Ni) and the support have been modified in order to improve the performance.
- All the catalysts were prepared by wet impregnation and subjected to extensive characterization by XRD, Electron microscopy, TPR, TPD of ammonia and CO<sub>2</sub>, XPS and DRS
- Modification of alumina support by addition of promoter oxides like, La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>, MgO and TiO<sub>2</sub> results in improvements in Ni metal dispersion, reducibility, modulation of metal-support interactions and variations in total acidity- basicity, and their distribution.
- Such changes in the characteristics of the catalyst influences the activity for ethanol conversion and selectivity for the formation of butanol and higher alcohols
- Nickel supported on ceria modified alumina displays maximum selectivity for butanol and higher alcohols
- In bimetallic Ni-Co / CeO<sub>2</sub> Al<sub>2</sub>O<sub>3</sub> catalysts, compositions 4% Ni-4%Co and 2.5% Ni-5.5% Co display higher ethanol conversion and selectivity to C<sub>4+</sub> alcohols compared to the mono metallic catalysts
- In the case of bi-metallic Ni-Cu// CeO<sub>2</sub> Al<sub>2</sub>O<sub>3</sub> catalysts, composition 2.5% Ni-5.5% Cu displays higher butanol selectivity in comparison with mono metallic Ni-Cu// CeO<sub>2</sub> Al<sub>2</sub>O<sub>3</sub>
- Formation of Ni-Co and Ni-Cu alloys in the respective bi-metallic catalysts, as evidenced by XRD, TPR and XPS studies, is responsible for the observed increase in ethanol conversion and C<sub>4+</sub> alcohol selectivity
- Bimetallic catalysts containing Ni with noble metals, Pd, Au and Ru exhibit higher ethanol conversion vis-à-vis mono metallic Ni





- Modification of the support by selection of suitable metal oxide promoter to balance the acidity and basicity functions and identification of effective bimetallic catalysts with optimum compositions are the two strategies that could be useful in increasing ethanol conversion and C<sub>4+</sub> alcohols selectivity
- Catalysts developed in this work are effective for ethanol conversion to higher alcohols under moderate process conditions

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# LIST OF PUBLICATIONS

## Journal publications

1. Vinayagamoorthi, R, Krishnamurthy, KR, Viswanathan, B & Shanthi, K, 'Ethanol condensation to butanol and higher alcohols over nickel and cobalt decorated CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> mixed oxide catalysts', Indian Journal of Chemistry, Vol.60A, pp. 386-396 (Impact Factor-0.489)





# Conferences

- 1. **R. Vinayagamoorthi,** K. Shanthi, K.R. Krishnamurthy and B. Viswanathan, Participated and presented a poster on "Ethanol conversion to Higher Alcohols" in RSC-NIT Symposium on "Heterogeneous Catalysis and Sustainable Chemistry" organized by National Institute of Technology, on November 5, 2016, Tiruchirappalli, India.
- R. Vinayagamoorthi, K. Shanthi, K.R. Krishnamurthy and B. Viswanathan, Participated and presented a poster on "Conversion Ethanol to higher alcohols over Ni/M<sub>x</sub>O<sub>y</sub>-Al<sub>2</sub>O<sub>3</sub> (M=La, Ce, Zr & Mg) catalysts: Influence of supports 23<sup>rd</sup> National Symposium on Catalysis (CATSYMP-23) organized by the Catalysis Society of India-Bengaluru Chapter, held at Royal Orchid Convention Centre, January 17-19, 2018, Yelahanka, Bengaluru, India.
- 3. **R. Vinayagamoorthi,** K. Shanthi, K.R. Krishnamurthy and B. Viswanathan, 2019, Participated and presented a poster on "Enhancement of 1-butanol selectivity in ethanol condensation over nickel and cobalt decorated Ce-Al mixed oxide" in National Conference on Recent Advances in Chemistry (RAC-19) organized by Anna University CEG, January 4,5 2019, Chennai, India.
- 4. **R. Vinayagamoorthi,** K. Shanthi, K.R. Krishnamurthy and B. Viswanathan, Participated and made oral presentation on 'Synthesis of butanol through sustainable process: Condensation of ethanol to butanol over bimetallic Ni-Cu catalysts." in One day National Conference on Sustainable Materials for Energy and Environmental Applications (SMEEM-19) organized by Anna University CEG, March 2, 2019, Chennai, India.
- 5. R. Vinayagamoorthi, K. Shanthi, K.R. Krishnamurthy and B. Viswanathan, Participated and presented a poster on "Catalytic upgrading of ethanol to n-butanol over Ni-Cu bimetallic catalyst supported on CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>" in 17<sup>th</sup> National Workshop on Catalysis for Clean energy and Sustainable future" organized by IIT-Delhi, 31<sup>st</sup> May-1<sup>st</sup> June, 2019, Delhi, India.



