Hydro-deoxygenation of Octanol Over Supported Bimetallic Catalysts

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Dedicated to my parents

CONTENTS

ABSTRACT

Now-a-days, utilization of fuel is increasing day by day and sources are gradually decreasing. By using these crude fuels, emission of chlorofluorocarbons and products which are hazardous to environment are also increasing. Because of the decrease in sources of energy, the cost of energy fuels are increasing. Thus, it is necessary to look for alternative sources which can minimize the above mentioned problems. Fuels from renewable sources have drawn a considerable attention in recent years as these sources are environmental friendly. Bio mass can be considered as carbon dioxide neutral because using bio mass means recycling mobile carbon instead of liberating fixed carbon from combustion of fossil fuels. For example, bio fuels like bio-oil, ethanol, methanol, biodiesel can be produced from renewable sources and they have gained popularity due to their sustainability, low contributions to the carbon cycle, and low production of greenhouse gases. Specifically the oxygen content of bio-oils is a limitation for utilisation as transport fuel since the high oxygen content of bio-oils causes high viscosity, poor thermal and chemical stability, corrosivity and immiscibility with hydrocarbon fuels. Thus bio-oils cannot be used as transportation fuels directly without up gradating to hydrocarbon like fuels. Also oil produced from pyrolysis has low heating value and high corossivity. The hydrodeoxygenation of bio oils is very important technology to produce hydrocarbons from bio-oils for application as transportation fuels. In the present work, the hydrodeoxygenation of aliphatic alcohols was studied using 1-octanol as model compound in a high pressure batch reactor using supported bimetallic catalysts in the presence of hydrogen. Silica alumina mixed oxide supports of different SiO_2/Al_2O_3 molar ratios (1:1, 1:2 and 2:1) were synthesized by supramolecular templating method using Pluronic (P123) as structure directing agent. 15wt% nickel catalyst supported on these mixed oxide support were prepared by incipient wetness impregnation method. The HDO of 1-octanol was performed with the silica-alumina mixed oxide supported nickel catalysts and 1Si1Al was found to be best support. The bimetallic catalysts of several metals combination such as NiMo, NiFe, NiCo were prepared on 1Si1Al mixed oxide support composition obtained by co-impregnation method. The HDO of octanol was performed over these bimetallic catalysts to understand the promotional effect of the secondary metal. It was concluded from these HDO studies over bimetallic catalysts that addition of secondary metal affects the octanol conversion and product distribution.

Specifically, molybdenum favours the formation of octane and cobalt increase the 1-octanol conversion and amount of oligomerized product. The Ni/Mo molar composition was varied to understand the effect of catalyst composition on HDO activity of 1-octanol and product distribution. A series of supported xNiyMo/1Si1Al (x:y = 1:0, 8:1, 4:1, 2:1, 1:1, 1:2, 0:1) were prepared using co-impregnation method and reduced in the presence of hydrogen at 823 K for 4 hours. The reduced catalyst was characterized by using BET and XRD. BET results revealed that the surface area of the catalyst was decreased by the presence of molybdenum. XRD results confirmed the presence of bulk nickel over bimetallic catalysts. HDO of 1-octanol over xNiyMo/1Si1Al confirmed that the product distribution of 1-octanol was more or less independent of molar composition of nickel and molybdenum. However presence of high amount of molybdenum suppressed the conversion of 1-octanol and 8Ni1Mo/1Si1Al was found to be the best catalyst considering 1-octanol conversion and amount of HDO product. Effect of Cobalt metal loading on conversion and product distribution 1-octanol was studied and the results revealed that the rate of oligomerization was independent of metal loading. The effect of process parameters such as temperature, catalyst loading, 1-octanol concentration on HDO of 1-octanol and product distribution was studied using 8Ni1Mo/1Si1Al catalyst. The conversion of 1-octanol and octane selectivity was increasing with temperature and catalyst loading, but decreasing with increase in concentration of 1-octanol. A comprehensive mechanism was proposed based on the product distribution obtained under different experimental condition. The spent catalysts were regenerated and used for reusability studies; results were found to be comparable with the fresh catalyst suggesting that the catalytic activity was unchanged.

NOMENCLATURE

TETD	Tetradecane
HEXD	Hexadecane
DOE	Dioctyl ether
OO	Octyl octanoate
OC	Octyl caprylate
OA	Octanoic acid
Ni/1Si1Al	15 wt% Ni/1SiO_2-1Al_2O_3
Ni/1Si2Al	15 wt% Ni/1SiO_2-2Al_2O_3
Ni/2Si1Al	15 wt% Ni/1SiO_2-1Al_2O_3
Ni/Al	15 wt% Ni/ Al_2O_3
Ni/Si	15 wt% Ni/SiO_2
NiCo/1Si1Al	15 wt% Ni-Co/1SiO_2-1Al_2O_3
NiFe/1Si1Al	15 wt% Ni-Fe/1SiO_2-1Al_2O_3
NiMo/1Si1Al	15 wt% Ni-Mo/1SiO_2-1Al_2O_3
8Ni1Mo/1Si1Al	15 wt% 8Ni-1Mo/1SiO_2-1Al_2O_3
4N1iMo/1Si1Al	15 wt% 4Ni-1Mo/1SiO_2-1Al_2O_3
2Ni1Mo/1Si1Al	15 wt% 2Ni-1Mo/1SiO_2-1Al_2O_3
1Ni1Mo/1Si1Al	15 wt% 1Ni-1Mo/1SiO_2-1Al_2O_3
1Ni2Mo/1Si1Al	15 wt% 1Ni-2Mo/1SiO_2-1Al_2O_3
Mo/1Si1Al	15 wt% Mo/1SiO_2-1Al_2O_3
10Co/1Si1Al	10 wt% Co/1SiO_2-1Al_2O_3
15Co/1Si1Al	15 wt% Co/1SiO_2-1Al_2O_3
20Co/1Si1Al	20 wt% Co/1SiO_2-1Al_2O_3
25Co/1Si1Al	25 wt% Co/1SiO_2-1Al_2O_3

LIST OF TABLES

LIST OF FIGURES

1. INTRODUCTION

Now-a-days, utilization of fuel is increasing day by day and sources are gradually decreasing. By using these crude fuels, emission of chlorofluorocarbons and products which are hazardous to environment are also increasing. Because of the decrease in sources of energy, the cost of energy fuels are increasing. Thus, it is necessary to look for alternative sources which can minimize the above mentioned problems. Fuels from renewable sources have drawn a considerable attention in recent years as these sources are environmental friendly. Bio mass can be considered as carbon dioxide neutral because using bio mass means recycling mobile carbon instead of liberating fixed carbon from combustion of fossil fuels. For example, bio fuels like vegetable oils, ethanol, methanol, biodiesel and hydrogen fuels can be produced from renewable sources and they have gained popularity due to their sustainability, low contributions to the carbon cycle, and low production of greenhouse gases. But above mentioned fuels are first generation bio fuels which are directly produced from biomass like forestry and agricultural products, vegetable oils, animal fats, wastes and residues produced from food related resources. Generally first generation bio-oils are composed of a complex mixture of oxygen-containing compounds. Second generation bio-fuels can be produced from lingo cellulosic biomass or woody crops, agricultural residues. In case of synthetic crudes, those derived from coal, the oxygen content may be well in excess of 10 wt%, in fact in feeds derived from biomass, oxygen content may approach 50 wt%. The oxygen compounds present in feed readily polymerize and cause fuel instability that lead to poor performance during the fuel combustion. These compounds contribute to the oxygen content of the oil in the form of hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids and esters, and aliphatic and aromatic alcohols in which oxygen content is very high up to 50 wt%. The oxygen content of bio-oils is a limitation for utilisation as transport fuel since the high oxygen content of bio-oils causes high viscosity, poor thermal and chemical stability, corrosivity and immiscibility with hydrocarbon fuels. So cannot be used as transportation fuels directly without some pre treatment. Oil products from pyrolysis have low heating value and high corossivity, so improvements are needed. Some upgrading of bio-oils is required for first and second generation bio-oils, so that they can be directly used for transportation purpose. Table 1.1 shows the physical properties of bio-oils and upgraded bio-oils [George W. Huber et al, 2006].

Table 1.1: Physical properties of Bio-oils and upgrades Bio-Oils

Elemental analysis	High pressure Liquifaction	Flash pyrolysis	Hydro-deoxygenated biooils
Carbon (wt%)	72.6	43.5	85.3-89.2
Hydrogen (wt%)	8.0	7.3	10.5-14.1
Oxygen (wt%)	16.3	49.2	0.0-0.7
Sulfur (wt%)	<45	29.0	0.005
H/C atom ratio (dry)	1.21	1.23	1.40-1.97
Density (g/mL)	1.15	24.8	0.796-0.926
Moisture (wt%)	5.1	24.8	0.001-0.008
HHV (MJ/kg)	35.7	22.6	42.3-45.3
Viscosity (cP)	15000(61oC)	59(40oC)	1.0-4.6(23oC)
Octane number			77

The reaction occurs during hydro-processing of Bio feeds is mainly HDO. HDO means hydrodeoxygenation which is same as hydrodesulfurization. In HDO, oxygenated compounds are converted into pure hydrocarbons by eliminating oxygen in the form of water in presence of hydrogen and acidic catalyst. During HDO, oxygen in the feed is converted to water which is environmentally benign.HDO plays a major role for conventional feeds particularly derived from biomass. Hydrodeoxygenation (HDO) is the process to produce second generation bio fuels with very less oxygen content, and thermal stability volatility can be increased and even viscosity can be decreased. HDO has attracted attention because hydro-processing may convert waste plastics and other o-containing wastes to unstable products [Edward F., 2000]. Knowledge of reaction mechanism plays crucial role for design of suitable catalysts for cost effective HDO of bio-oils. Some of carbon derived liquids have a low HDO reactivity. Therefore a higher H_2 pressure and higher temperature are necessary for their conversion to o-free compounds. Understanding mechanism of HDO of whole bio-oils is however highly challenging because of its diverse functionalities (phenolics, aldehydes, ketones, alcohols, organic acids, and others).

There is so much literature is available on aromatic oxygenates and some aliphatic oxygenates. HDO includes many reaction mechanisms like etherification to get ethers, dehydration to get hydrocarbons, dehydrogenation to get aldehydes, decarbonylation and in some cases oligomerization to get higher hydrocarbons. And these reaction mechanisms depend on the type of catalyst used. Generally on highly acidic catalysts give activity towards etherification reaction. And moderate amount of acidic sites on catalysts favour the formation of hydrocarbons in dehydration reaction. Many types of supported metallic and bimetallic catalysts are used in HDO of oxygenates. In those catalysts, supports like Al_2O_3, SiO_2, and zeolites are used for acidity, and metal gives the promotion and inhibition effects. Many catalysts like Ni, Co, Fe, Mo supported over zeolites, silica, alumina and bimetallic catalysts like alumina supported CoMo, NiMo, NiFe are used for HDO of different oxygenates. Some are favourable for conversion into ethers and some are favourable towards conversion into pure hydrocarbons [O. I. Senol et al, 2007]. Generally in HDO many reactions like hydrogenation, dehydration, dehydrogenation, etherification, esterification, decarbonylation, decarboxylation, oligomerization etc takes place [V.C.S. Palla et al, 2014]. Reaction parameters like pressure, temperature, amount of catalyst, feed composition plays key role in HDO of oxygenates. High temperatures favours the conversion of feed into pure hydrocarbons and even inhibits the formation of oxygen compounds like aldehydes, ethers etc. High amount of catalyst increases the amount of active sites so HDO also increases. HDO depends on the composition of different metals used in bimetallic catalysts.

The present work was therefore commenced to explore fundamental understanding of HDO of 1-octanol as a model aliphatic alcoholic functionality of bio-oil. Understanding the mechanism of HDO of bio-oils is highly challenging because of its diverse functionalities like phenolics, aldehydes, ketones, ethers, alcohols, organic acids and others. Very less research has been done on HDO of 1-octanol. So present work is to understand and explore the functionality of HDO of 1-octanol in a high pressure batch reactor. The feed was mixture of 1-octanol and isooctane where isooctane was used as solvent which was inert during the reaction. The catalysts used were Ni supported over different molar ratios of silica and alumina, NiMo/1Si1Al. Effects of reaction parameters like temperature, catalyst loading and composition of feed were also studied.

In this report chapter 2 explains the literature review on HDO studies, HDO of aliphatic alcohols, catalysts used for HDO of aliphatic alcohols, mechanism of HDO etc. Chapter 3 explains the objectives of this thesis work. Chapter 4 gives the experimental part of the thesis work. This includes characterization techniques required for catalyst testing, preparation of catalyst, procedure of the experiment etc. Chapter 5 gives the results and discussions of the project and finally chapter 6 will give conclusions of overall work.

2. LITERATURE REVIEW

2.1. HDO studies

During HDO studies, conventional hydro processing catalysts like $CoMo/Al_2O_3$ or $NiMo/Al_2O_3$ were used most extensively. Liquids derived from lingo cellulosic biomass will give mostly phenols (almost one fourth of liquids) and remaining oxygenated compounds includes alcohols, ketones, aldehydes, carboxylic acids, esters and ethers. For removal of oxygen from oxygenated compounds, several chemical bonds have to be broken and presence of hydrogen pressure plays an important role in HDO process. Edward F. et al, 2000 had performed research on HDO of phenol and told that Toluene and cyclohexane were main products and minor amount of methylcyclohexane was formed. They also found that the complexity of HDO depends on the feed origin. HDO plays minor role in the hydro processing of conventional crudes, whereas it plays major role in hydro processing of coal derived compounds. Even W. Y. Wang et al, 2010 had performed the reaction studies of HDO of Phenol to find characterization and catalytic properties of Ni-Mo-B amorphous catalysts. They had done the reactions on Ni-Mo-B catalysts taking Mo/Ni ratio as 1:1 to 3:1 and found that the conversion of phenol and selectivity of cyclohexane increased firstly and then decreased where as the selectivity of cyclohexane and benzene increased gradually. Also observed that the total selectivity of pure hydrocarbon products increased firstly and then decreased little. Finally they concluded that the more MoO_2 existed on the catalyst surface, the higher selectivity of the pure hydrocarbon products would have for the HDO of phenol was verified again. The HDO of phenol could be interpreted as follows: the hydrogen molecule was adsorbed on the site of Ni and dissociated to free hydrogen, the MoO_2 existed in the form of Mo-OH and acted as bronsted acid adsorption sites and adsorbed the phenol molecule. And many researchers have done experiments on hydro deoxygenation of phenol as model compound for oxygenated bio-oil and concluded that Mo based materials are active and promising materials for establishing selectivity control in HDO of bio-oils.

S.T. Oyama et al, 2013 studied for the HDO of 2-methyltetrahydrofuran as model compound for aromatic oxygenatic hydrocarbon on different noble metallic catalysts and activity was $Ni_2P>WP>MoP>CoP>FeP>Pd/Al_2O_3$ and conversion was highest for Ni2P/KUSY sample and decreased steadily with Fe content. They also told that the metallic Ni catalyst has little ability to produce benzene or hexane but produces only phenol, cyclohexane, orcyclohexanol at different H_2 pressure. Metal sulfided catalysts had good deoxygenation activity and thus were also used to find the activity for HDO of bio-oil in

comparison with noble metal catalysts. In this comparison, high cost was the primary disadvantage of the noble catalysts. But the sulfidation process of these catalysts was carried out at high temperatures using H_2S or CS_2 as sulfiding agent, which was inevitable to exhaust poisonous gas H_2S.It could be concluded that high temperature was beneficial to the HDO of phenol on Co-Mo-B amorphous catalysts [W. Y. Wang et al, 2012]. Octanoic acid is selected as model compound for biomass derived carboxylic acid and HDO experiments were performed on Ni-Zro2. The products were mainly C8 alkane and when performed on 10Mo/Ni-ZrO2 catalyst, the major product as C7 alkane. So it could be concluded that the introduction of Mo to the Ni-ZrO2 catalyst was more economic, and Mo was beneficial to the conversion of fatty acids into hydrocarbons with the same carbon chain compared with the feed stock. Doping of Mo favoured the dehydration-hydrogenation reactions of octanol intermediate which inturn facilitated octanoic acid HDO to C8 alkane [Y. Duan et al, 2015].
Enormous research efforts have been made in the past on mechanistic understanding of HDO of whole bio-oil and various oxygenated compounds of bio-oil such as guaiacol, phenol, anisole, aromatic aldehydes like furfural, benzaldehyde, aliphatic aldehydes like heptanal, 2-phenylpropionaldehyde, 3-phenylpropionaldehyde, cinnamaldehyde, and 4-isopropylbenzaldehyde, and various ketones such as 6-undecanone, 2,4-dimethyl-3-petnanone, 2-dodecanone, cyclopentanone, 2,2,4,4-tetramethyl-3-pentanone, and methyl isobutyl ketone. However, very limited information is available in open literatures on HDO of aliphatic alcohols. B. Peng et al, 2012 studied HDO of aqueous 1- and 2-propanol in a batch reactor at 473 K and 40 bars of H2 pressure in presence of Pt/Al2O3 catalyst.The identified products were propane, ethane, CO2 and acetone.

2.2. Supported catalysts

When a catalytic active material is dispersed on the surface of other material, the material on which catalyst is dispersed is support of the catalyst. Support plays a secondary role in the catalysis. The most common supports used in industry are silicates, aluminum oxides, ceramics, silica gel, MgO, TiO2, ZrO2, activated carbon and zeolites. Generally, support improves the physiochemical properties of the catalyst (activity and selectivity) and its mechanical strength. It is very important to choose a support suitable for the specific metal used, because the rate of reaction and formation of products depends on the type of support used. Another consideration to take into account is that it should withstand the operating conditions (like temperature, pressure and flow of fluid). If the catalyst is used in liquid phase, the support must be inert in the solvent. The support loading and the support size are also determined according to the requirements of the process. Pellet supports are indicated in gas and liquid continuous process. But powders are often in batch liquid phase system. The support can also play a significant role in delaying catalyst deactivation by sintering because of its interactions with the active metal. These include electronic effects, the formation of new phases at the boundary surface, van der Waals forces and the formation of reduced support species on the metal surface. The supports for HDO should be fluid catalytic cracking materials with high Si-Al ratio of interest, because they have a biomodel mesoporous, microporous structure and are highly attrition resistant.

2.3. Catalysts used

The transition metal phospide catalysts are highly effective in oxygen removal from model bio-oil compounds [S.T. Oyama et al, 2013]. Many catalytic studies have been performed on HDO of Bio-Oils using supported Ni, W, Ti, V, Cr, Mn, Fe, Co using various supports like γ-alumina, silica, silica-alumina and Zeolites etc. In some cases P, Molybdenum carbide, phospide, nitrite Etc are also used and reported that these are promising materials for HDO of Phenols which are taken as model compounds for aromatic alcohols derived from bio-oils. But very less research has done on bi-metallic catalysts like NiMo, NiCo, NiFe etc (S. Boullosa et al, 2014). Table 2.1 shows the different catalysts used for HDO so far.

Table 2.1: Some reaction studies on HDO of different oxygenates

Feed	**Catalyst**	**Reaction Conditions**	**Reactor**	**Reference**
Phenol Benzaldehyde acetophenone	Co-Mo-B	523-548 K 4.0 MPa 0.1 gm 10 hours	Autoclave	W.Wang et al
Methyl hexanoate Methyl heptanoate Ethyl heptanoate 1-heptanol Phenol	NiMo/ γ -Al_2O_3 CoMo/ γ -Al_2O_3	523 K 7.5 MPa	Autoclave Fixed bed reactor	O.I.Senol et al

Cyclohexane Cyclohexanol Benzene				
1-octanol	$Ni/\gamma\text{-}Al_2O_3$ Ni/HZSM-5 Ni/SiO_2	488-533 K 1-10 bar TOS=240 min WHSV=3.99 h^{-1}	Fixed bed reactor	V.C.S.Palla et al
Phenol	MoP/TiO_2 MoN/TiO_2 Mo_2C/TiO_2 MoO_3/TiO_2	623-723 K 25 bar $WHSV=0.27g_{phenol}/cm^3_{cat}h$	Fixed bed reactor	S.B.Eiras et al
Cyclopentanone	$Pt\text{-}Pd/ZrO_2$ Pt/Zro_2 Pd/ZrO_2	433 K 60 bar 3 hours	Autoclave	Y.Jiang et al
Ethyl Heptanoate Methyl Heptanoate Phenol	$NiMo/\gamma\text{-}Al_2O_3$	523 K 7.5 MPa 1-5 hours 0.5 gm	Autoclave	E.M.Ryymin et al
Palm oil	Ni/SAPO-11	633 K 4.0 MPa TOS=6 hours LHSV=1.0 h^{-1}	Fixed bed reactor	Q.Liu et al
Phenol	Ni-W/AC Ni-W(Si) Ni-W(P)	412-513 K 1.5 MPa WHSV=0.5 h^{-1} 0.2 gm	Fixed bed reactor	S.Echeandia et al
2-methaxycyclohexanol	Pt, Rh, Pd, Ru over Al_2O_3, SiO_2-Al_2O_3, NAC, ZrO_2	523 K 40 bar 0.4 gm 1 hour	Stainless steel batch reactor	Ch.Lee et al
Anisole	Rh-, Rh-Co-, Ni-,	523-673 K	Fixed bed	V.A.Yakovlev

	Ni-Cu- over SiO_2, Al_2O_3, ZiO_2, CeO_2, CeO_2-ZrO_2	0.5-2.0 MPa LHSV=1-6 h^{-1}	flow reactor	et al
Guaiacol	Ni-Cu over Ceo_2-ZrO_2, Al_2O_3, SiO_2, ZrO_2-SiO_2-La_2O_3	593K 11MPa 1 gm 1 hour	Stainless steel batch reactor	M.V.Bykova et al
Stearic acid	Ni/ γ -Al_2O_3 Ni/HZSM-5 Ni/SiO_2	533-563 K 8 bar 0.5 gm	autoclave	P.Kumar et al
Octanoic acid	Ni-ZrO_2 Mo/Ni-ZrO_2	593 K 3 MPa 0.5gm 420 min	autoclave	Y.Duan et al

2.4. HDO of alcohols

So much of research was available on phenols as model compounds for aromatic alcohols. O.I. Senol et al. 2007, W.Y.Wang et al. 2012, S.B. Eiras et al. 2014, E.M. Ryymin et al. 2010, S. Echeandia et al. 2010 had done research on phenol over various catalysts at various reaction conditions, and concluded that conversion and rate of deoxygenation was improving with some addition of promoters like molybdenum. O.I. Senol et al. 2007 studied HDO of 1-heptanol and cyclohexanol over NiMo/γ-Al_2O_3 and CoMo/γ-Al_2O_3 at 523 K and 7.5 bars of hydrogen pressure by taking n-xylene and n-decane as solvents, and concluded that NiMo/γ-Al_2O_3 was giving higher HDO activity and hydrogenation over aliphatic alcohols than CoMo/γ-Al_2O_3. HDO studis were perfomed on 2-methoxycyclohexanol by Ch. R. Lee et al. 2012 by taking n-decane as solvent in stainless steel batch reactor at 523 K and 40 bars of hydrogen pressure over various catalysts like Pt, Rh, Pd, Ru over Al_2O_3, SiO_2-Al_2O_3, NAC, ZrO_2. He concluded that hydrogenation was happening over metals and deoxygenation was occurring over acid supported metal catalysts. To remove oxygen from oxygenates, acid supported bimetallic catalysts were essential which allow hydrogenation of alcohols followed by deoxygenation.

Very recently V. C. S. Palla et al. 2012 reported HDO of 1-octanol in a fixed bed reactor at various process conditions in presence of supported nickel catalysts on various

Supports like gamma alumina, silica, and HZSM-5 and concluded that HDO of 1-octanol follows two different pathways depending on the nature of catalyst. On acidic catalysts, the major products were observed as DOE, isomers of octane and n-octane. And on metallic catalysts, the primary products were isomers of heptene, n-heptane and 1-octanal. It was also observed that higher conversion and selectivity towards alkanes was there when H_2 pressure was used than that of N_2. Finally it was concluded that the optimum conditions for high conversion of 1-octanol and high selectivity towards n-heptene, 1-octanal and n-heptane were high temperature, low pressure and 15 wt% Ni/Al_2O_3.Reverse trend was followed for higher selectivity of DOE, n-octene, n-octane. Other than heptanol, octanol, propanol very less work was available on HDO of aliphatic alcohols.

When the mechanisms for HDO of alcohols were observed, octane were formed from 1-octanol by dehydration or by etherification followed by dehydration reaction. alkanes were formed by hydrogenation of alkenes. Dehydrogenation, decarboxylation, decarbonylation, dehydroformylation, esterification were also participates in the HDO of aliphatic alcohols. Sometimes oligemerization also take place to form higher hydrocarbons. Generally in HDO oxygen was removed from oxygenates in the form of CO, CO_2 and H_2O. HDO was improved by increasing the reaction temperature due to rise in activity of the catalyst during HDO. By increasing the amount of catalyst loading, active surface area availability would increase. So, by increasing the catalyst loading more conversion and rate of deoxygenation was observed during the study of HDO of 1-octanol. Metal loading was active towards hydrogenation reaction, so more alkanes would be formed by increasing the metal loading over acidic supports where acidic supports were favaorable for deoxygenation reaction.

2.5. Summary of Literature Review

The main objective of HDO of bio-oils is to remove oxygen from oxygenated compounds, because presence of oxygen will increase the boiling point of oxygenated compounds, low heating value and stability and high corrossivity which are not desirable for transportation fuels and to produce pure hydrocarbons. Presence of hydrogen plays an important role in HDO. Enormous research has done on HDO of phenol as model compound for oxygenated bio-oil and concluded that Mo base materials were active and promoting materials for establishing selectivity control in HDO of bio-oils. Metal sulphide catalysts had good deoxygenation activity in comparison with noble metal catalysts but high cost was the primary disadvantage [S. Ted et al. 2013]. Very less research is available on HDO of aliphatic alcohols. O.I. Senol et al has done research on mixture of some aliphatic compounds and concluded that NiMo/γ-Al_2O_3 was giving high HDO activity and hydrogenation over aliphatic alcohols than CoMo/γ-Al_2O_3. To remove oxygen from oxygenated compounds, acid supported bimetallic catalysts were essential which allow hydrogenation of alcohols followed by deoxygenation [Ch. R. Lee et al. 2012]. Research has been done on expensive metals like Pt, Mo etc but very less literature is available on inexpensive materials like Ni. Studies on HDO of 1-octanol by V.C.S. Palla et al. 2012 concluded that the optimum conditions for HDO of 1-octanol are low pressure and high temperature over 15Ni/γ-Al_2O_3. Nickel loading was increasing the selectivity of hepatnes and heptanes. Selectivity of DOE, octane and octene was high over pure support. So to convert DOE into octane, dehydration and hydrogenation should be improved. Addition of Mo, Co or Fe may improve the selectivity of octane in the HDO of 1-octanol.

3. Objectives

The HDO of primary alcohol (1-octanol) was performed in a high pressure batch reactor using different mono and bimetallic catalysts. The specific objectives of the present investigation were given below.

1. Silica alumina mixed oxide supports of different SiO_2/Al_2O3 molar ratios (1:1, 1:2 and 2:1) were synthesized by supramolecular templating method using Pluronic (P123) as structure directing agent. 15wt% nickel catalyst supported on these mixed oxide support were prepared by incipient wetness impregnation method and characterized by a number of techniques.
2. The HDO of 1-octanol was performed with the silica-alumina mixed oxide supported nickel catalysts to find best composition of silica alumina mixed oxide support.
3. The Bimetallic catalysts of several metals combination such as NiMo, NiFe, NiCo, CoMo were prepared on best mixed oxide support composition obtained by co-impregnation method.
4. The HDO of octanol was performed over these bimetallic catalyst to understand the promotional effect of the second metal.

5. The molar composition of the best performing bimetallic catalyst was varied to understand the effect of catalyst composition on HDO activity of octanol and product distribution.
6. All the prepared catalysts were characterized by a number of techniques.
7. The effect of process parameters such as temperature, catalyst loading, octanol concentration on HDO of octanol and product distribution was studied. A comprehensive mechanism was proposed based on the product distribution obtained under different experimental condition..
8. The spent catalysts were regenerated and used for reusability studies.

4. Experimental

4.1. Material preparation

4.1.1. Preparation of silica-alumina support

The silica-alumina mixed oxide supports of varying alumina content (SiO_2/Al_2O_3 molar ratio= 2/1, 1/1 and 1/2) were prepared by adapting the recipe as described by Morris et al. 2008. About 2.0 g of P123 [$(EO)_{20}(PO)_{70}(EO)_{20}$ MW= 5800 Da, Sigma Aldrich] triblock co polymer was dissolved in 20 mL of anhydrous ethanol and the solution was stirred for 8 h. 20 mmol of aluminium isopropoxide [$Al(O\text{-}(CH(CH_3)_2))_3$, Sigma Aldrich, >98% purity] was dissolved in 3.2 mL of nitric acid (68-70 wt%) and 10.0 mL of anhydrous ethanol and was stirred the solution for 8 h. 20 mmol of tetraethyl orthosilicate [TEOS ($Si(OC_2H_5)_4$, Sigma Aldrich, purity >98%] was dissolved in 3.2 mL of nitric acid and 10.0 mL of anhydrous ethanol and the solution was stirred for 8 h. All the separately prepared three solutions were combined and stirred for 12 h. The well mixed solution was kept in hot air oven maintained at 333 K for 48 h. The dried material was ground to powder and calcined at 823 K for 6h using a heating rate of 1K/min. The calcined silica-alumina mixed oxides were denoted as xSiAl, where x represents SiO_2/Al_2O_3 molar ratio.

4.1.2. Preparation of Supported mono and bimetallic catalysts

Several supported bimetallic catalysts were prepared by co-impregnation method and supported mono metallic catalysts were prepared by incipient wetness impregnation method. Various secondary metals such as iron, cobalt and molybdenum were perceived in the present studies. The metal precursor (s) solution was prepared by dissolving measured amount of metal precursor corresponding particular metal loading in incipient volume of distilled water.

The required amount of silica-alumina support was added into the precursor solution and mechanically agitated for 2h. The wet material was kept for drying at room temperature overnight followed by at 383 K in hot air oven for 12 h. The dried material was calcined at 823 K for 6h. The calined catalysts were reduced in presence of hydrogen in a tubular furnace at 823 K for 3h. The reduced catalysts were denoted as xM_1yM_2 /SiAlr, where M_1 and M_2 represent primary and secondary metals and r represents SiO_2/Al_2O_3 molar ratio.

4.2. Catalyst characterization

4.2.1. BET surface area measurement

The N_2 adsorption/desorption studies were performed at 77K in a Micromeritics ASAP 2020 physisorption analyser to determine the surface area and pore volume of pure supports and supported catalysts. Prior the analysis, all the samples were degassed under vacuum (5×10^{-6} mmHg) at 423 K for 6 h. The surface area was calculated from the adsorption isotherm data using multipoint BET equation in the relative pressure (P/P_0) range of 0.05 to 0.3. The volume of adsorbed nitrogen at relative pressure of ca.1.0 was considered as the pore volume of catalyst.

4.2.2. Powder X-ray diffraction

XRD patterns were recorded on a Philips P-analytical X-Pro diffractometer (PANalytical, X'pert Pro) using Cu Kα radiation (λ=1.5418 A0),15kV and 30 mA current at 2θ interval of 10 to 90° with a scanning speed of 1°/min.

4.3. Reaction studies

4.3.1. Experimental setup and procedure

The hydrodeoxygenation of 1-octanol was performed in a high pressure batch reactor. The schematic of the reactor setup is shown in Figure 4.1. The reactor consists of a 400 mL stainless steel vessel (Amar Equipments Pvt. Ltd.) equipped with a six bladed paddle type impeller . The reactor assembly was placed in a furnace and the temperature was controlled with in ±1K using temperature controller. The stainless steel reactor vessel was charged known vol% of 1-octanol in isooctane and catalyst. Then the reactor was pressurized to 10 bar with hydrogen. The reactor was heated to desired reaction temperature while stirring at constant speed of 1100 rpm. The first sample was collected as soon as the desired reaction temperature was attained and the collected sample was considered as zero min. All calculations were performed using this initial value. Product samples were collected for every 60 min. The effect of various process parameters such as temperature, catalyst composition, catalyst loading, metal loading and octanol concentration on hydrodeoxygenation of octanol was studied.

4.3.2. Product analysis

The liquid products were analysed by using GC (Shimadzu, GC-2014) equipped with flame ionization detector (FID) connected to capillary column (ZB-5HT Inferno, Phenomenex, 30 m×0.32 mm×0.10 mm). The following GC oven temperature programming was used to obtain well resolved chromatogram: Initially oven was kept at 313 K for 3 min and then temperature was increased to 493 K with a ramping rate of 15 K/min, and held at this temperature for 3 min. Injector and detector were maintained at 493 K and 523 K respectively. The material balance was checked for all experimental runs and errors were within ±3%. Gas products were analysed by GC equipped with TCD detector using packed

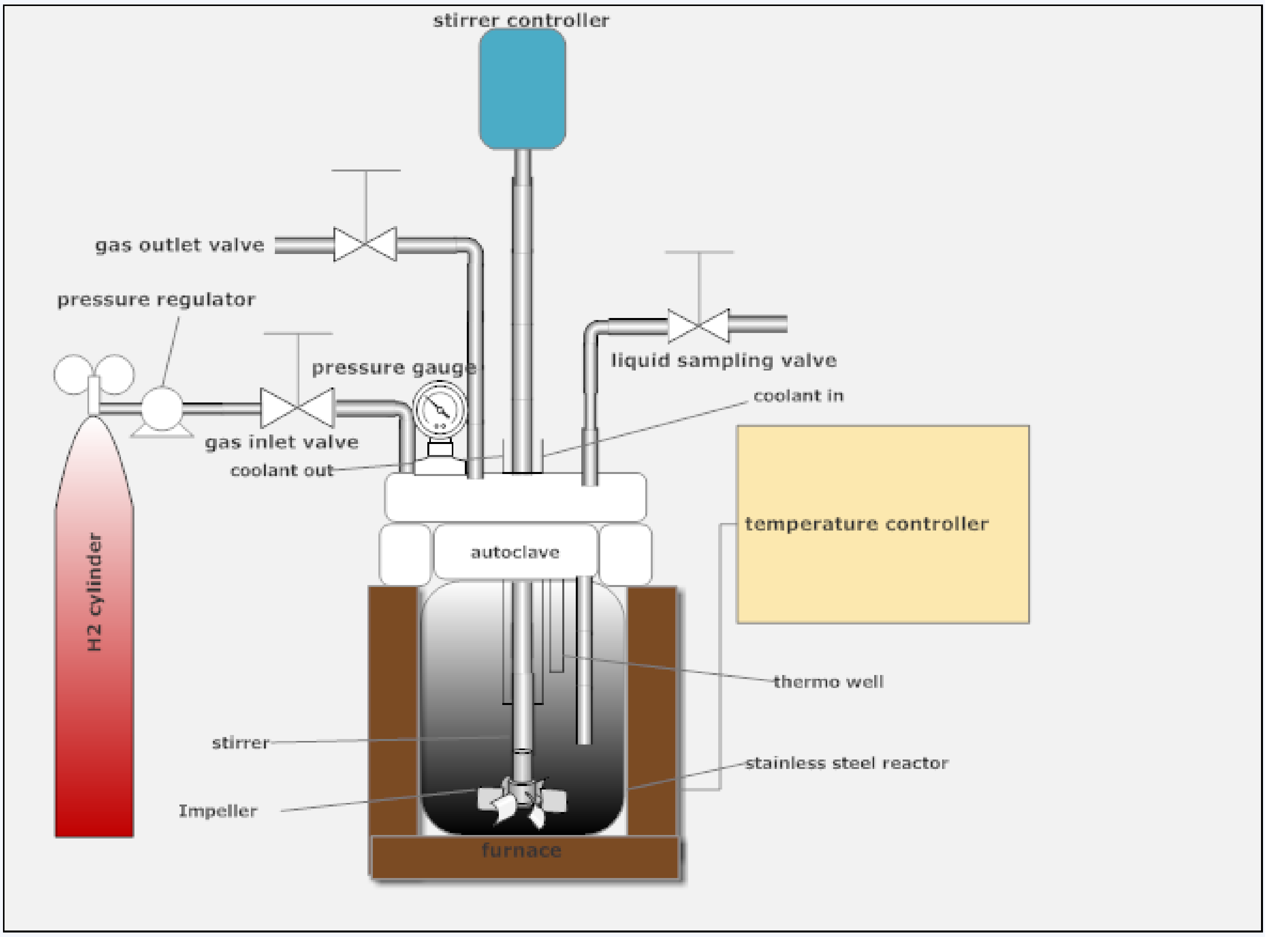


Figure 4.1: Reaction setup for HDO of 1-octanol over supported bimetallic catalysts.

column and argon as carrier gas (Chromatopak-Carboseive-S2, 1/8 and 3 m length). The column temperature was programmed with an initial temperature of 373 K for 15 min, increased at a rate of 30 K/min to 473 K and held there for 7 min. The injector and detector temperatures were maintained at 378 K and 523 K respectively. Liquid products were identified by comparing the data with calibrated standard data in GC-MS.

4.3.3. Calculations

Conversion of 1-octanol is calculated by taking number of moles of 1-octanol at 0th min and number of moles of 1-octanol at a particular time.

$$X_{1-octanol} = \frac{moles\ of\ 1 - octanol\ reacted}{initial\ moles\ of\ 1 - octanol}$$

Product Distribution is calculated by using the following formula at a particular time

$$p_i = \frac{n_i}{\sum_{i=1}^{m} n_i}$$

Where

$$p_i = product\ distribution\ of\ ith\ compound$$

$$n_i = number\ of moles\ of\ ith\ compound$$

5. RESULTS AND DISCUSSIONS

5.1. Characterization of Support and supported metal catalyst

The BET surface area and pore volume of bimetallic catalysts and pure supports was determined by N_2 adsorption/desorption method. The results were shown in the Table 5.1. The surface area of pure supports was decreased with increase in molar ratio of silica. The surface area of supported catalysts was lower that the respective pure support. The decrease in surface area might be due to pore blockage phenomena. In case of bimetallic catalyst higher molybdenum content decrease the surface area of the catalyst.

XRD patterns of reduced supported bimetallic and monometallic catalysts are shown in Fig. 5.1 and 5.2. XRD patterns of reduced mono metallic and bimetallic catalysts showed peaks at 44.5^o (1 1 1) and 51.8^o (2 0 0) and 76.5 (2 2 0) [PDF#701849] due to the presence of nickel metal. However, no peaks were identified for the secondary metals (Mo, Co and Fe) in the bimetallic catalysts suggesting that the secondary metals might be present as dispersed form.

Table 5.1: BET surface area and pore volume of Silica alumina supports

Support	Surface Area, m^2/gm	Pore Volume, mL/gm
1Si2Al	282	0.56
1Si1Al	155	0.39
2Si1Al	111	0.36
1Ni2Mo/1Si1Al	63	0.16
1Ni1Mo/1Si1Al	124	0.23
2Ni1Mo/1Si1Al	111	0.25
4Ni1Mo/1Si1Al	138	0.25

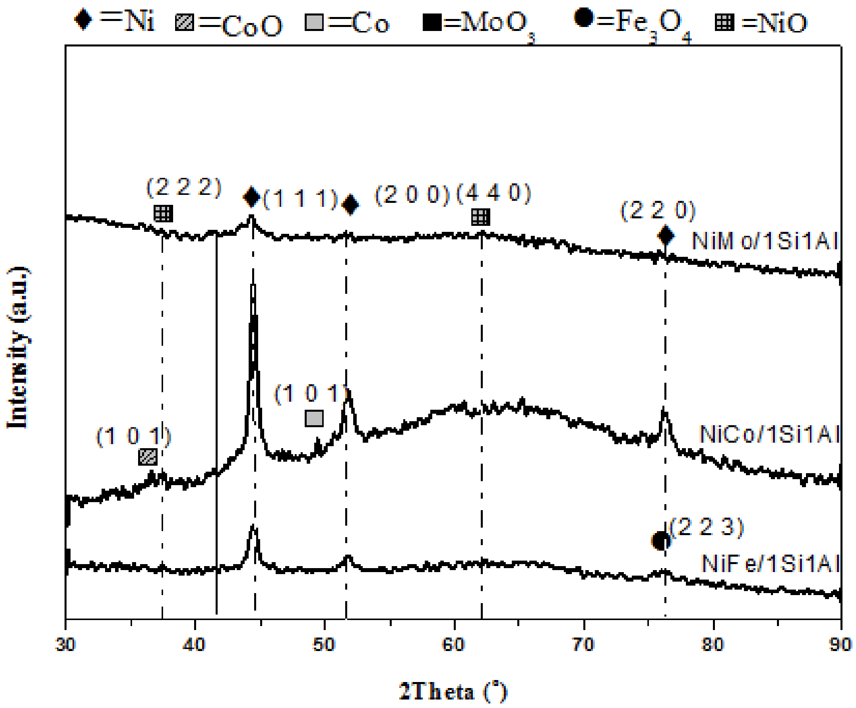


Figure 5.1: XRD patterns of different silica alumina supported bimetallic catalysts

The intensity of characteristic diffraction peak of nickel was increased with increase in nickel content. For Mo/1Si1Al catalyst, diffraction peaks at 2θ of 26.0° (1 1 1), 36.8° (2 0 0) and 53.87° (2 2 2) [PDF#761807] were identified and are assigned to the MoO_2 species as shown in Fig 5.2. The MoO_2 peaks were identified due to the incomplete reduction of molybdenum oxide. The XRD patterns of Mo/1Si1Al catalyst, also revealed peak due to the molybdenum metal at 2θ of 41.8 (1 10), 60.4° (2 0 0) and 73.2° weak (2 1 1) [PDF#89516]. Thus reduced bimetallic catalysts were associated with only metals. Figure 5.3 shows the XRD patterns of Co/SiAl with different metal loadings.

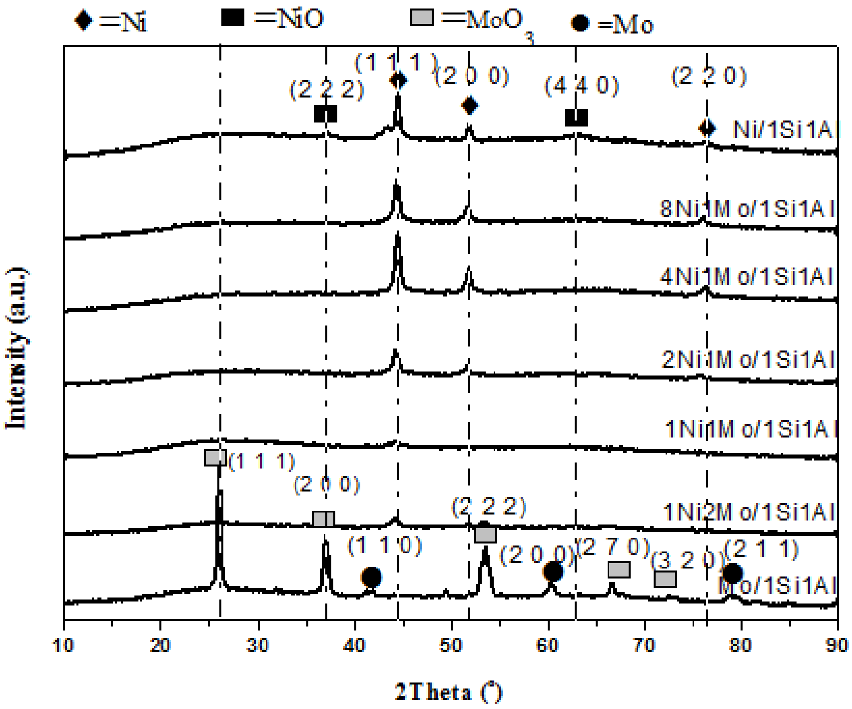


Figure 5.2: XRD patterns of xNiyMo/1Si1Al catalysts

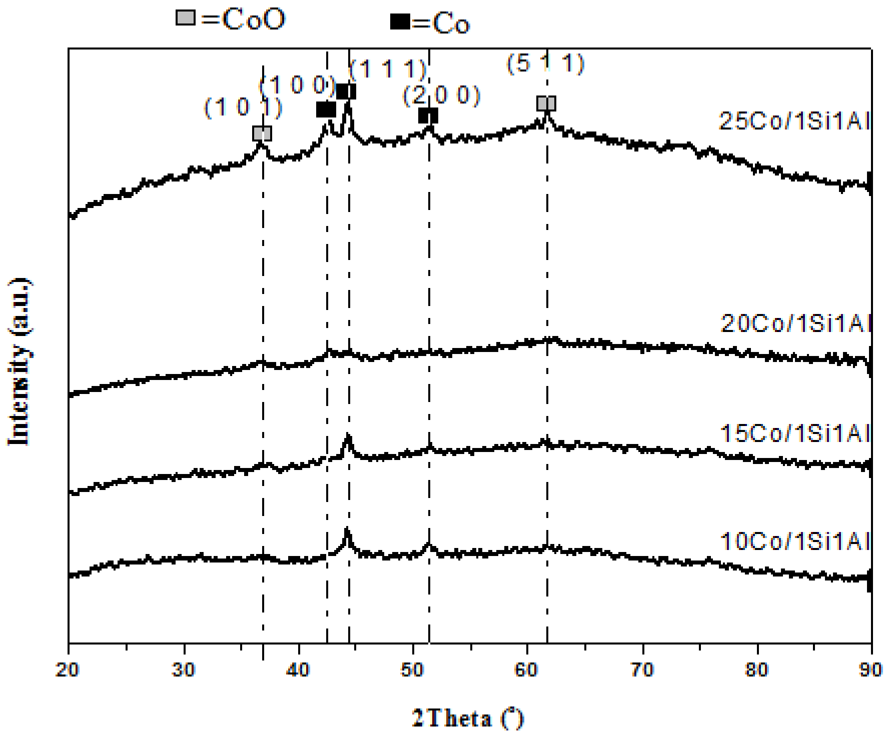


Figure 5.3: XRD patterns of xCo/1Si1Al catalysts.

The XRD patterns of supported cobalt catalyst revealed peaks at 2θ of 44.3° (1 1 1) and 51.5° (2 0 0) [PDF#894307] and confirm the presence of bulk cobalt. The diffraction peaks at 2θ of

36.7^o and 61.66 (5 1 1) [PDF#781970] confirm the presence of dispersed cobalt oxide. Thus the supported cobalt catalysts were associated with both the metallic cobalt and cobalt oxides.

5.2. Activity tests

The HDO of 1-octanol was studied in batch reactor over pure alumina, silica alumina and silica supported mono (Ni, Co, Mo) and bimetallic (NiCo, NiFe, NiMo, CoMo) catalysts at 10 bars of initial hydrogen pressure under wide range of temperatures(473-548 K),catalyst loading (0-2.0 g), and concentration of 1-octanol (05-100 v/v%). The final pressures were observed as 18-35 bars at different temperatures. Octane isomers and dioctyl ether were observed as primary products and heptanes, 1-octanal, tetradecane, hexadecane, octyl octanote were observed in small quantities. Conversion was calculated by using equation 1 in all calculations and product distribution was calculated by using equation 2. Concentration of zero minute samples was taken as initial concentration and all calculations were performed based on the initial octanol concentration.

5.2.1. Role of support

The role of supports on conversion of 1-octanol and product distribution was studied over nickel catalysts of similar loading (15wt %) supported on SiAl mixed oxides (SiAl ratio: 1:2, 1:1 and 2:1) and respective pure supports and results are shown in Table 5.2 and Fig 5.4, 5.5. The 1-octanol conversion was higher in case of pure supports (SiO_2 and γ-Al_2O_3) compared to mixed oxides supported nickel catalysts. In case of pure supports, 1-octanol undergoes dehydration and etherification reaction and produces octane and DOE as major products. The octenes formed due to the dehydration reaction of 1-octanol was readily converted to octane in presence of nickel under hydrogen pressure. The 1-octanol conversion over silica-alumina mixed oxide supported nickel catalysts was found to be low compared to the respective pure supports. Moreover, the octanol conversion depends on the silica-alumina composition and higher octanol conversion was obtained over 15Ni/1Si1Al catalyst. However, selectivities towards HDO products were higher for 1Si1Al mixed oxide supported nickel catalysts. The octane was the foremost hydrocarbon formed during HDO of 1-octanol over these catalysts (Table 5.2 and Fig 5.5). The DOE was formed as major oxygenated product together with small amount of octanal for SiAl mixed oxide supported nickel catalysts. The amount of DOE and octanal formed in case of 15Ni/1Si1Al was lower compared to the rest of catalysts. This results indicates that octanol dehydrogenation leading to the formation of octanal followed by decabonylation reaction was suppressed over SiAl supported mixed oxide catalysts. The decabonylation of octanal produces heptanes together with carbonmonoxide as gaseous product. Analysis of gaseous products confirmed the formation of carbonmonoxide as gaseous product.

Table 5.2: Role of Supports on HDO of 1-Octanol at 240 min

Catalyst	Conversion of 1-octanol, %	Product distribution, mole%						
		Heptane	Octane	Octanal	TETD	DOE	HEXD	OO
Ni/Al	49.6	4.9	23.3	11.3	0.7	47.3	12.2	0.3
Ni/1Si2Al	8.3	3.0	20.6	13.1	1.5	55.4	4.8	1.6
Ni/1Si1Al	27.9	1.6	48.6	6.1	1.0	39.5	2.6	0.6
Ni/2Si1Al	10.3	2.6	35.5	12.0	1.4	42.4	5.0	1.1
Ni/Si	31.1	3.6	8.8	18.6	0.8	65.5	1.8	0.9

Reaction Conditions: Pressure = 10 bar, Temperature = 523 K, Catalyst Loading = 1 gm., Batch Time = 240 min., Metal Loading = 15 wt% of catalyst, Octanol concentration (20 (v/v)%)

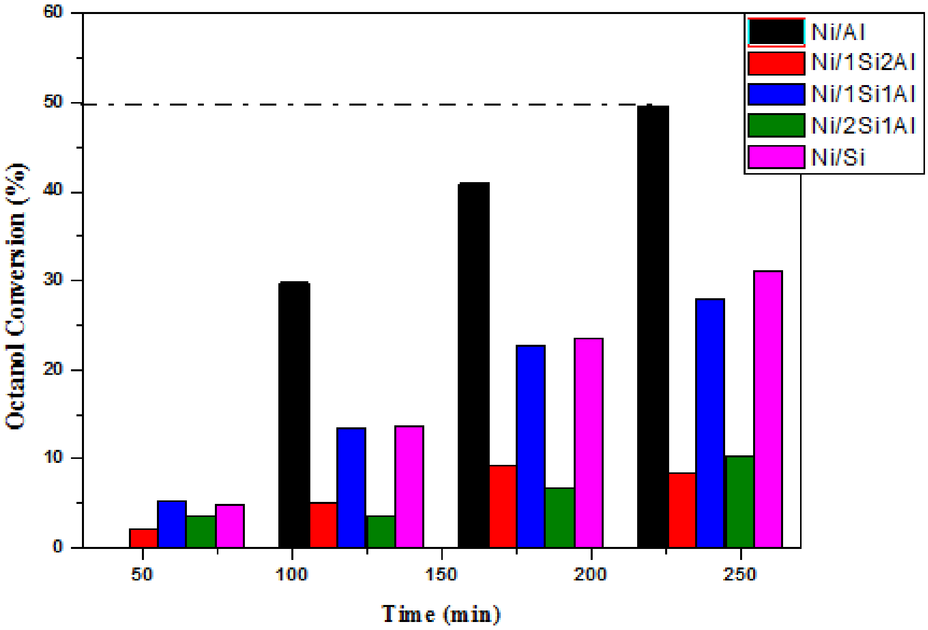


Figure 5.4: Conversion of 1-Octanol varying with time over supported nickel catalysts for HDO of 1-Octanol, Reaction conditions: Pressure = 10 bar, Temperature = 523 K, Catalyst Loading = 1 gm., Batch Time = 240 min., Metal Loading = 15 wt% of catalyst, Octanol concentration (20 (v/v)%)

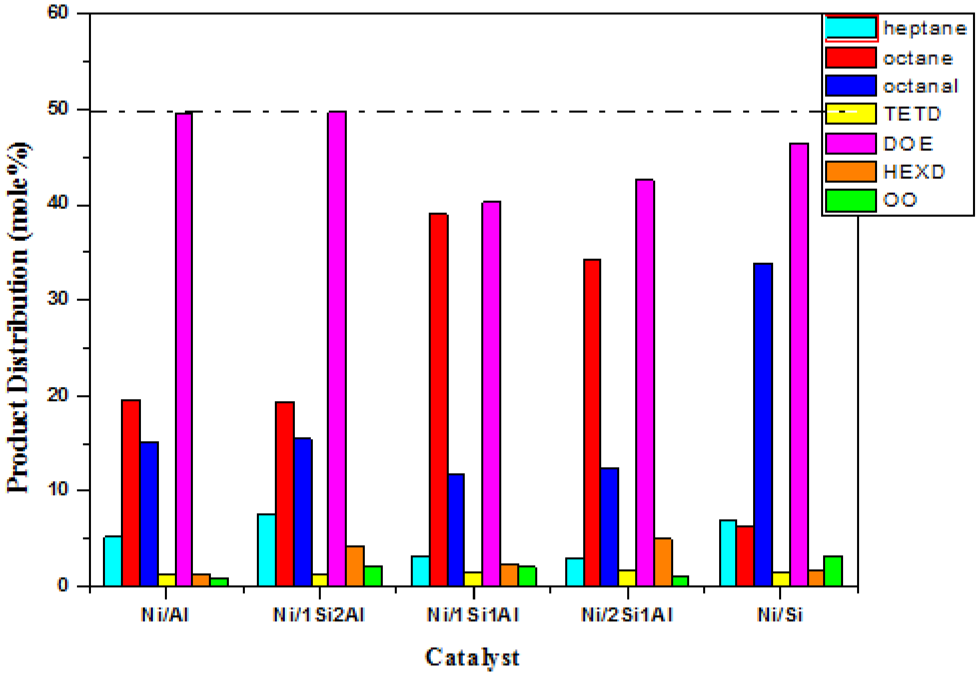


Figure 5.5: Product distribution for HDO of 1-octanol over supported nickel catalysts at a conversion of 9%. Reaction conditions: Pressure = 10 bar, Temperature = 523 K, Catalyst Loading = 1 gm., Batch Time = 240 min., Metal Loading = 15 wt% of catalyst, Octanol concentration (20 (v/v)%)

5.2.2. Performance of bimetallic catalysts

Several nickel based bimetallic (NiFe, NiMo and NiCo) catalysts with a metal loading of 15 wt% of catalyst equivalent to nickel were investigated for HDO of 1-octanol under similar experimental condition to understand the role of secondary metal on octanol conversion and the results are shown in Table 5.3 and Fig. 5.6. In this particular study the metal mole ratio was kept same for all bimetallic catalysts. From Table 5.3 it is evident that incorporation of secondary metals affects the octanol conversion and products distribution. The highest octanol conversion was achieved with 1Ni1Co/1Si1Al and trend in octanol conversion as follows: 1Ni1Co/1Si1Al> 1Ni1Mo/1Si1Al> 1Ni1Fe/1Si1Al. Interestingly, products distribution was different for different catalysts. The octane was the major product for NiMo catalysts whereas NiCo catalysts produced significant amount of octane and oligomerized product HEXD. The formation of HEXD over NiMo was significantly low compared to NiCo catalysts. The NiFe catalysts exhibited lowest activity in the above mentioned series of catalysts. However, formation of oligomerized product for NiFe catalyst was more compared to NiMo catalyst (Fig. 5.7). Similar, trend in octanol conversion and products distribution was observed at different reaction time as shown in Table 5.4 and Fig 5.8. In case of bimetallic catalyst selectivity for the formation of DOE was low for NiFe catalysts and highest for NiCo catalyst. The formation of octanal and hetane was higher for NiFe catalysts. It can be concluded that dehydrogenation of octanol leads to the formation of octanal which undergoes decabonylation reaction to produce hepetens. The heptenes further converted to heptane. The relatively high selective of heptane confirms this results. Further, studies were continued with NiMo bimetallic catalysts to understand effect of Ni/Mo mole ratio and various process parameters on octanol conversion and product distribution. Since, significant amount oligomerized product, HEXD was formed for NiCo catalysts, a separate investigation was performed with Co/1Si1Al catalyst to improve the yield of oligomerized product. Due to limited time, detailed study of NiCo catalyst was kept as future studies with the same expectation of improving the oligomerized product yield.

Table 5.3: Performance of bimetallic catalysts on HDO of 1-Octanol at 120 min

Catalyst	Conversion of 1-octanol, %	Product distribution, mole%						
		Heptane	Octane	Octanal	TETD	DOE	HEXD	OO
NiFe/1Si1Al	1.0	10.1	23.9	34.3	7.4	7.2	7.9	9.2
NiCo/1Si1Al	38.6	2.1	24.4	27.1	3.7	28.4	10.1	4.2
NiMo/1Si1Al	5.1	2.2	57.5	16.2	2.3	17.3	3.3	1.2

Reaction Conditions: Pressure = 10 bar, Temperature = 523 K, Catalyst Loading = 1 gm., Batch Time = 240 min, Octanol concentration (20 v/v%)

Table 5.4: Performance of bimetallic catalysts on HDO of 1-Octanol at 240 min

Catalyst	Conversion of 1-octanol, %	Product distribution,%						
		Heptane	Octane	Octanal	TETD	DOE	HEXD	OO
NiFe/1Si1Al	4.8	7.6	30.2	25.5	7.5	9.4	8.1	11.7
NiCo/1Si1Al	65.5	2.5	28.3	21.8	3.4	25.4	17.8	0.8
NiMo/1Si1Al	17.5	1.8	64.7	9.6	2.4	17.7	3.2	0.6

Reaction Conditions: Pressure = 10 bar, Temperature = 523 K, Catalyst Loading = 1 gm., Batch Time = 240 min., Octanol concentration (20v/v%)

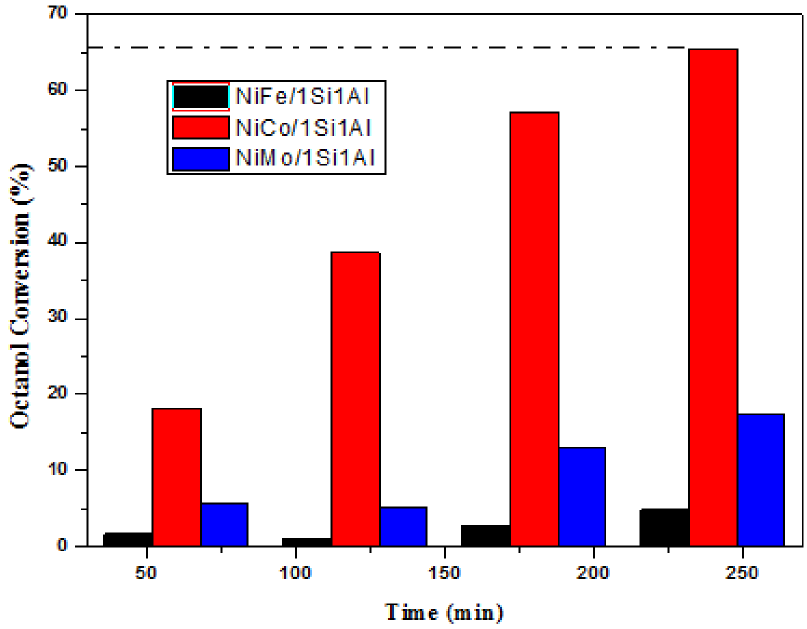


Figure 5.6: Conversion of 1-Octanol varying with time over supported bimetallic catalysts for HDO of 1-Octanol, Reaction conditions: Pressure = 10 bar, Temperature = 523 K, Catalyst Loading = 1 gm., Batch Time = 240 min., Octanol concentration (20 (v/v)%)

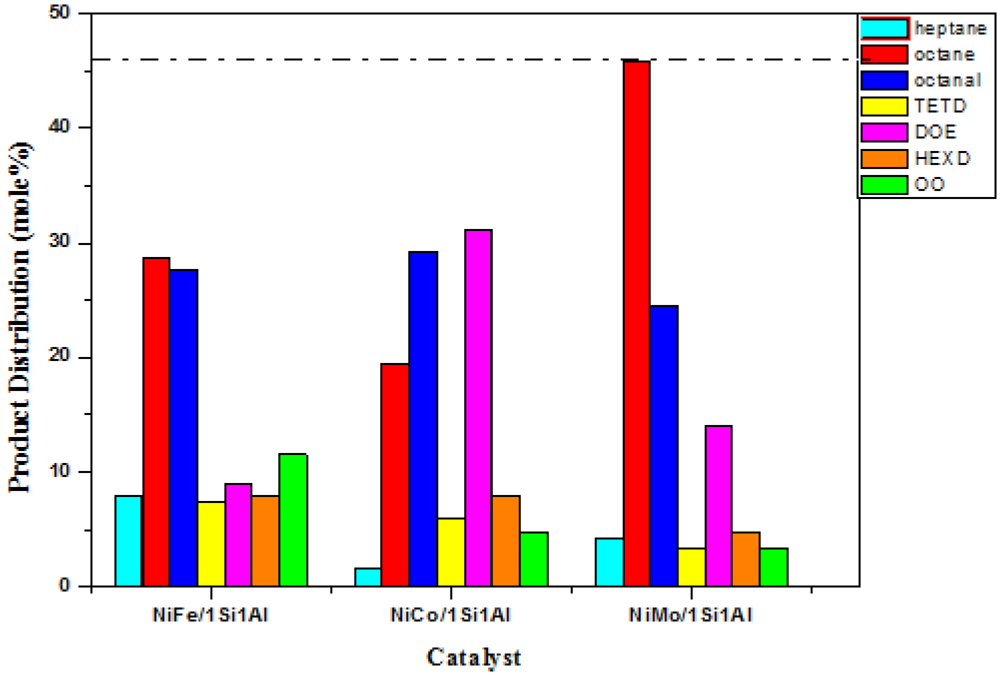


Figure 5.7: Product distribution for HDO of 1-octanol over various bimetallic catalysts at a conversion of 4%, Reaction conditions: Pressure = 10 bar, Temperature = 523 K, Catalyst Loading = 1 gm., Batch Time = 240 min., Octanol concentration (20 (v/v)%)

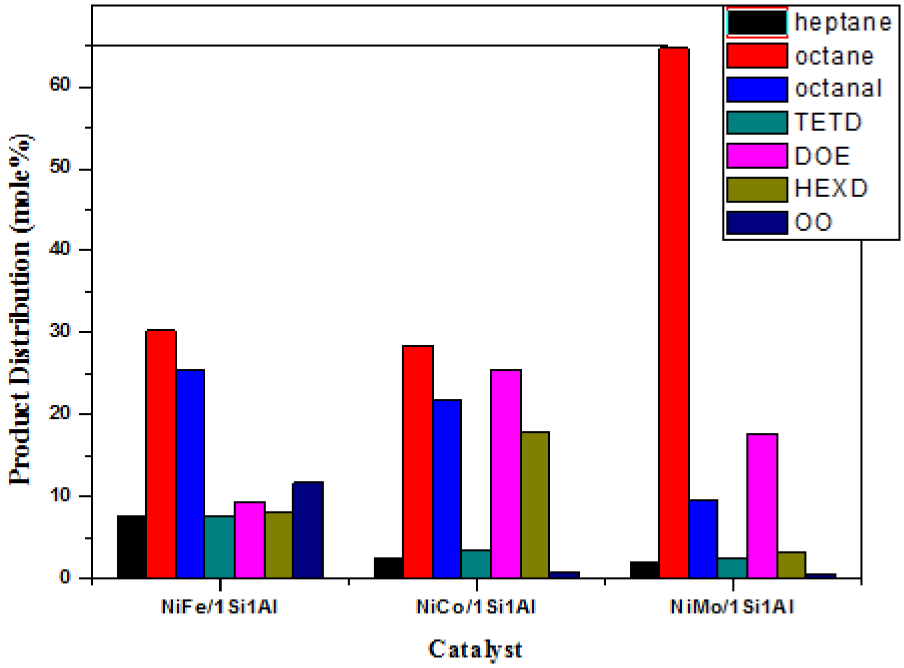


Figure 5.8: Product distribution for HDO of 1-octanol over various bimetallic catalysts at 240 min, Reaction conditions: Pressure = 10 bar, Temperature = 523 K, Catalyst Loading = 1 gm., Batch Time = 240 min., Octanol concentration (20 (v/v)%)

5.2.3. Effect of Ni/Mo molar ratio

The HDO of octanol was studied over various NiMo catalysts of varying Ni/Mo mole ratio and metal loading of 15 wt% of catalyst equivalent to nickel was investigated at 523 K temperature and other process parameters were kept similar for all catalysts. The activity and product distribution data are shown in Table 5.5 and 5.6. From Fig 5.9, it is evident that the octanol conversion increases with increase in nickel content in the bimetallic catalyst. The trend in octanol conversion as follows: 8Ni1Mo/1Si1Al >4Ni1Mo/1Si1Al >2Ni1Mo/1Si1Al >1Ni1Mo/1Si1Al >1Ni2Mo/1Si1Al >Mo/1Si1Al. However, product distribution was observed to different for bimetallic catalyst compared to supported nickel catalyst. Incorporation of small amount of molybdena in the bimetallic catalysts improved the octane selectivity compared to supported nickel catalyst (Fig 5.10). The octanol conversion for supported nickel catalyst and 8Ni1Mo catalyst is similar. However, higher octane selective was obtained for 8Ni1Mo catalyst. Moreover, the formation DOE was low for molybdena modified supported nickel catalyst. From these results it can be concluded that in presence of molybdenum degree of dehydration increase which leads to the formation of octenes and octenes are readily converted to octane over nickel metal. Further, studies were performed over 8Ni1Mo/1Si1Al catalyst.

Table 5.5 Effect of Molar ratio of NiMo on SiAl on HDO of 1-Octanol at 120 min

Catalyst	Conversion of 1-octanol, %	Product distribution,%						
		Heptane	Octane	Octanal	TETD	DOE	HEXD	OO
Ni/1Si1Al	13.5	3.7	42.8	9.1	1.1	40.0	2.2	1.1
8Ni1Mo/1Si1Al	15.4	1.0	68.6	8.9	2.0	15.6	3.6	0.3
4Ni1Mo/1Si1Al	9.6	2.5	67.3	9.3	1.5	14.7	4.4	0.3
2Ni1Mo1Si1Al	8.5	1.4	66.5	12.1	2.0	14.7	3.1	0.2
1Ni1Mo/1Si1Al	5.1	2.2	57.5	16.2	2.3	17.3	3.3	1.2
1Ni2Mo/1Si1Al	10.5	3.3	65.1	11.0	1.9	15.8	2.6	0.3
Mo/1Si1Al	9.2	3.0	56.2	19.5	3.3	14.4	3.4	0.2

Reaction Conditions: Pressure = 10 bar, Temperature = 523 K, Catalyst Loading = 1 gm., Batch Time = 240 min., Octanol concentration (20 (v/v)%)

Table 5.6: Effect of Molar ratio of NiMo on SiAl on HDO of 1-Octanol at 240 min

Catalyst	Conversion of 1-octanol, %	Product distribution,%						
		Heptane	Octane	Octanal	TETD	DOE	HEXD	OO
Ni/1Si1Al	27.9	1.6	48.6	6.1	1.0	39.5	2.6	0.6
8Ni1Mo/1Si1Al	27.7	0.7	71.2	5.2	2.2	16.9	3.7	0.1
4Ni1Mo/1Si1Al	20.0	2.0	70.7	6.1	1.5	15.1	4.4	0.2
2Ni1Mo1Si1Al	20.1	0.8	71.9	6.9	1.8	15.5	2.9	0.2
1Ni1Mo/1Si1Al	17.5	2.0	64.6	9.6	2.4	17.7	3.2	0.5
1Ni2Mo/1Si1Al	20.0	1.6	69.9	6.8	1.9	16.6	2.9	0.3
Mo/1Si1Al	13.6	1.9	62.6	12.6	3.0	16.6	3.2	0.1

Reaction Conditions: Pressure = 10 bar, Temperature = 523 K, Catalyst Loading = 1 gm., Batch Time = 240 min., Octanol concentration (20 (v/v)%

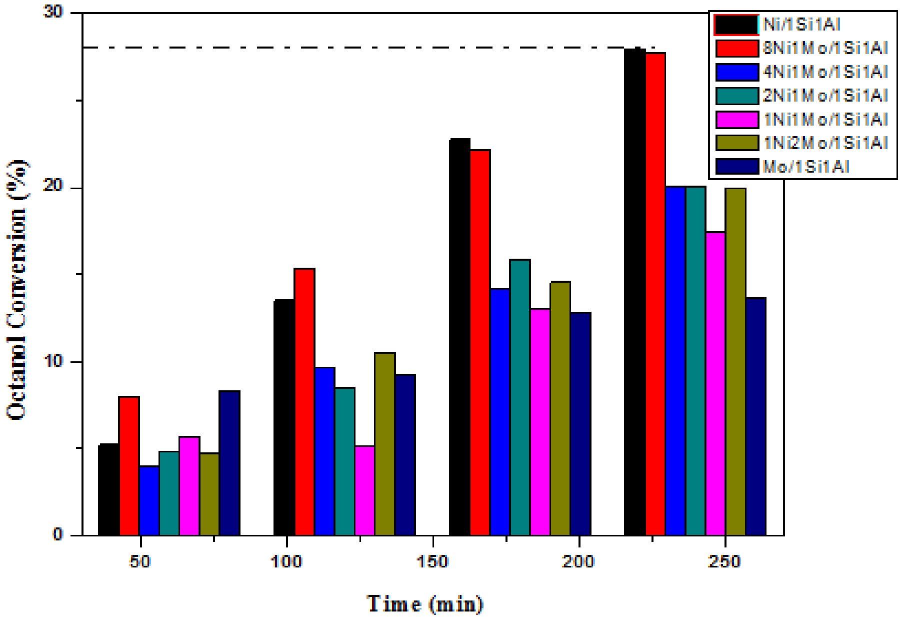


Figure 5.9: Conversion of 1-Octanol varying with time over supported NiMo catalysts for HDO of 1-Octanol, Reaction conditions: Pressure = 10 bar, Temperature =523 K, Catalyst Loading = 1 gm., Batch Time = 240 min., Octanol concentration (20 (v/v)%)

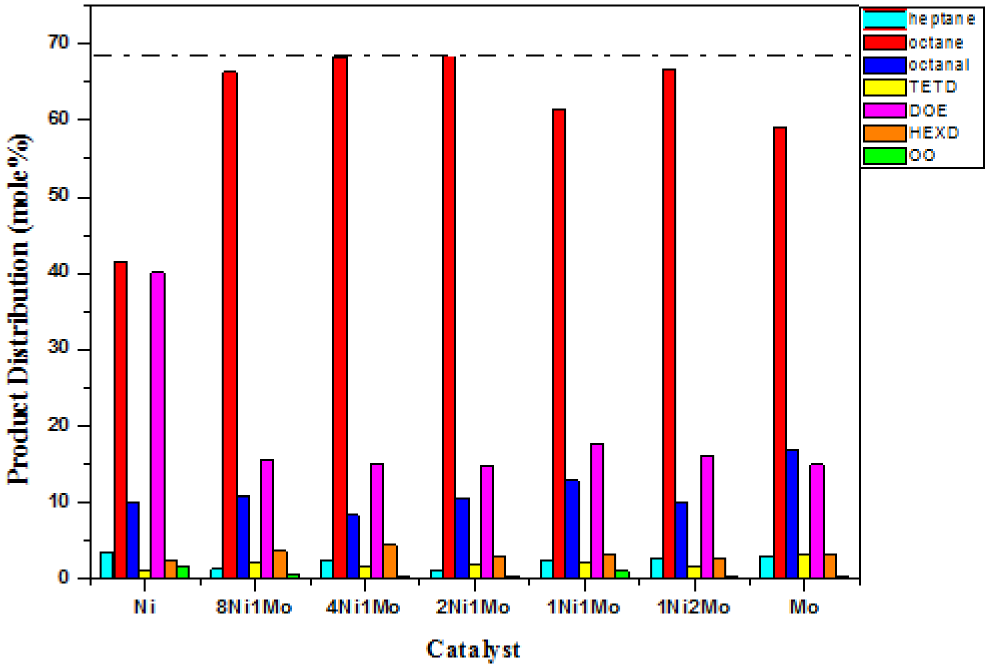


Figure 5.10: Product distribution for HDO of 1-octanol over supported NiMo catalysts at a conversion of 12%, Reaction conditions: Pressure = 10 bar, Temperature = 523 K, Catalyst Loading = 1 gm., Batch Time = 240 min., Octanol concentration (20 (v/v)%)

5.2.4. Effect of cobalt metal loading

The effect of cobalt metal loading on the conversion and product distribution of 1-octanol was studied with four different metal loadings (10, 15, 20 and 25 % of catalyst) over 1Si1Al support and the results are shown in Table 5.7 and Fig. 5.11, 5.12. The octanol conversion was high for 15Co/1Si1Al and 25Co/1Si1Al. The amount of octane was increased with increase in metal loading where as octanal and DOE was decreased with increase in metal loading. Selectivity of heptanes and HEXD was high for 15Co/1Si1Al among all metal loadings. The results indicate that the decrease in amount of DOE confirms that dehydration of octanol and followed by hydrogenation over metal catalyst was the major route for the formation of octane at high metal loadings. The HEXD was formed due to the oligomerization of octenes. Tetradecane was not noticeable and also selectivity of octanal was low compared to other product suggesting dehydrogenation of octanol followed by decabonylation is not favourable reaction over supported cobalt catalyst.

Table 5.7 Effect of Cobalt loading on HDO of 1-Octanol at 240 min

Catalyst	Conversion of 1-octanol, %	Product Distribution,%						
		Heptane	Octane	Octanal	TETD	DOE	HEXD	OO
10Co/1Si1Al	56.1	11.0	54.0	7.4	0.7	8.8	18.1	0.0
15Co/1Si1Al	71.9	19.3	50.5	7.2	0.8	4.6	17.6	0
20Co/1Si1Al	56.8	9.9	57.5	6.5	0.6	8.5	17.0	0.0
25Co/1Si1Al	74.1	8.9	64.5	5.1	0.6	5.0	15.9	0

Reaction Conditions: Pressure = 10 bar, Catalyst Loading = 1 gm., Temperature = 523 K, Batch Time = 240 min., Concentration of octanol (20 v/v %)

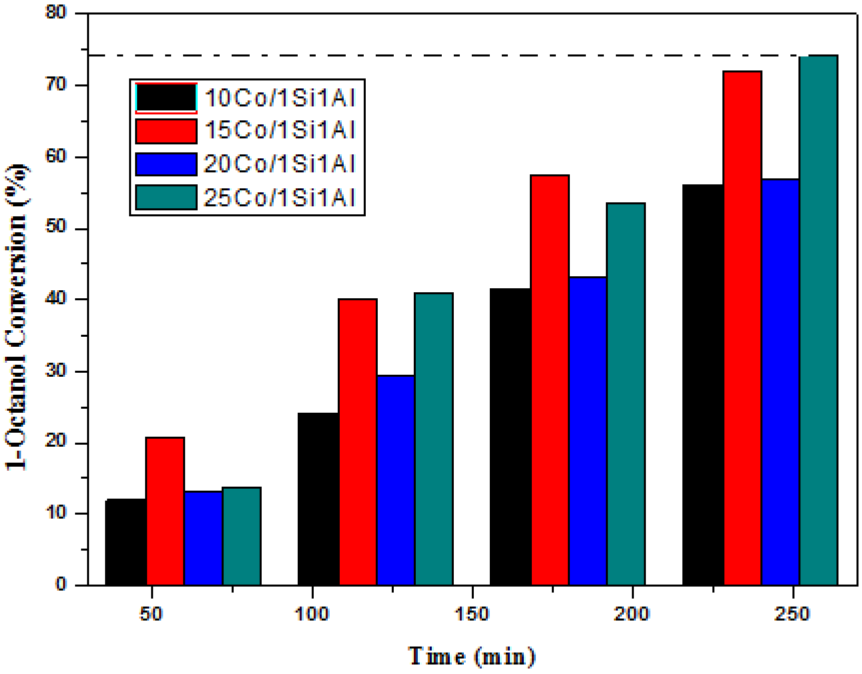


Figure 5.11: Conversion of 1-Octanol varying with time for HDO of 1-Octanol at various cobalt metal loadings, Reaction conditions: Temperature = 523 K, Pressure = 10 bar, Catalyst Loading = 1 gm, Batch Time = 240 min, Concentration of octanol (20 v/v %)

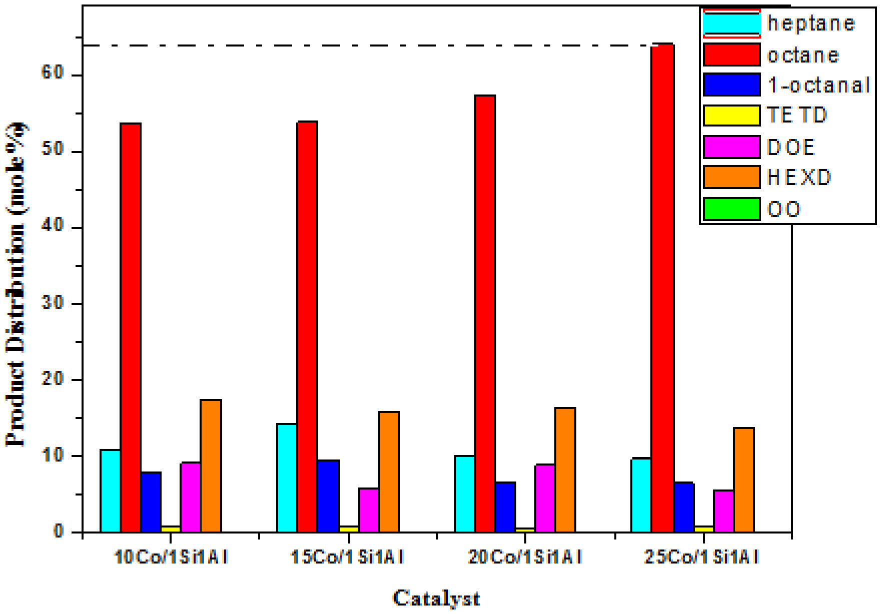


Figure 5.12: Product distribution for HDO of 1-octanol over Co/1Si1Al at a conversion of 50%, Reaction conditions: Temperature = 523 K, Pressure = 10 bar, Catalyst Loading = 1 gm., Batch Time = 240 min., Concentration of octanol (20 v/v %)

5.2.5. Effect of temperature

The effect of temperature on octanol conversion and product distribution was investigated at four different temperatures (473, 498, 523 and 548 K) over 8Ni1Mo/1Si1Al catalyst and the results are shown in Table 5.8 and 5.9. The octanol conversion was increased with increase in reaction temperature (Fig 5.13). The amount of octane was increased with increase in temperature whereas amount of heptanes octanal and DOE was decreased with increase in temperature (Fig 5.14). These results indicate that dehydrogenation of octanol leading to the formation of octanal was not favour at high temperature. Again dehydrofomylation reaction followed by hydrogenation reaction was not favoured at elevated temperature. The decrease in amount of DOE confirms that dehydration of octanol and followed by hydrogenation over metal catalyst was the major route for the formation of octane at high temperature. The decrease in amount of oligomerized product (HEXD) at high temperature indicate that hydrogenation of octenes is much faster reaction than oligomerization reaction of octenes. Similar trend was observed at different batch time as shown in Fig 5.15 and 5.16. Arrhenius type plot was drawn to know the activation energy for HDO of 1-octanol shown in Fig. 5.17.

Table 5.8 Effect of temperature on HDO of 1-Octanol at 120 min

Temp, K	Conversion of 1-octanol, %	Product Distribution,%						
		Heptane	Octane	Octanal	TETD	DOE	HEXD	OO
473	3.7	11.5	31.9	27.5	6.3	17.6	4.5	0.7
498	1.6	19.1	45.6	16.9	2.1	14.1	1.8	0.4
523	15.4	1.0	68.6	8.9	2.0	15.6	3.6	0.3
548	60.5	0.2	80.2	2.4	2.0	13.9	1.3	0

Reaction Conditions: Pressure = 10 bar, Catalyst = 8Ni1Mo/SiAl, Catalyst Loading = 1 gm., Batch Time = 240 min., Concentration of octanol (20 v/v %)

Table 5.9 Effect of temperature on HDO of 1-Octanol at 240 min

Temp, K	Conversion of 1-octanol, %	Product Distribution,%						
		Heptane	Octane	Octanal	TETD	DOE	HEXD	OO
473	3.9	8.9	41.0	20.4	4.5	20.6	4.0	0.6
498	6.2	10.8	59.1	7.7	2.1	18.0	2.1	0.2
523	27.7	0.6	71.3	5.2	2.2	16.9	3.7	0.1
548	88.1	0.1	82.4	1.2	2.0	13.3	1.0	0

Reaction Conditions: Pressure = 10 bar, Catalyst = 8Ni1Mo/SiAl, Catalyst Loading = 1 gm., Batch Time = 240 min., Concentration of octanol (20 v/v %)

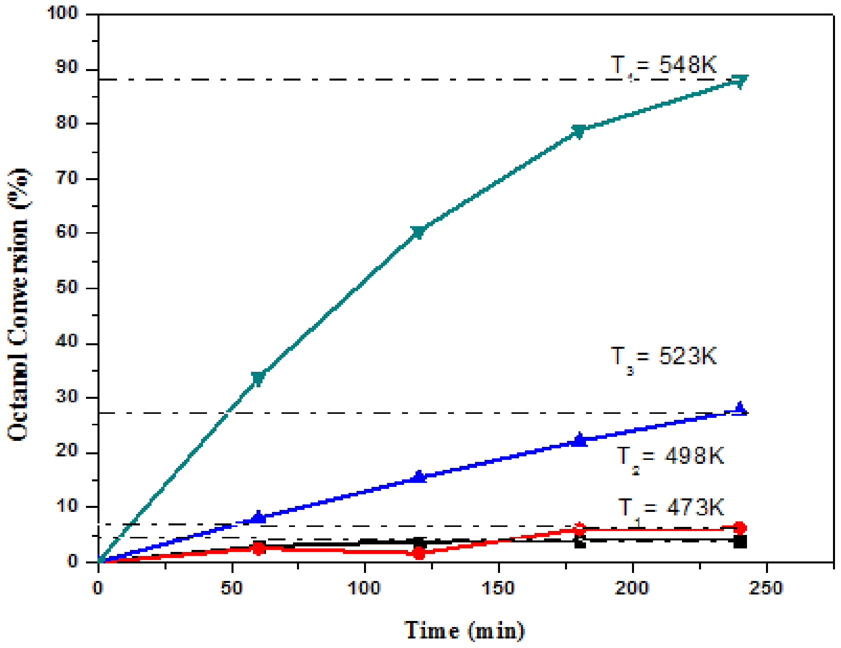


Figure 5.13: Conversion of 1-Octanol varying with time over 8Ni1Mo/1Si1Al catalyst for HDO of 1-Octanol at various temperatures, Reaction conditions: Pressure = 10 bar, Catalyst Loading = 1 gm., Batch Time = 240 min., Concentration of octanol (20 v/v %)

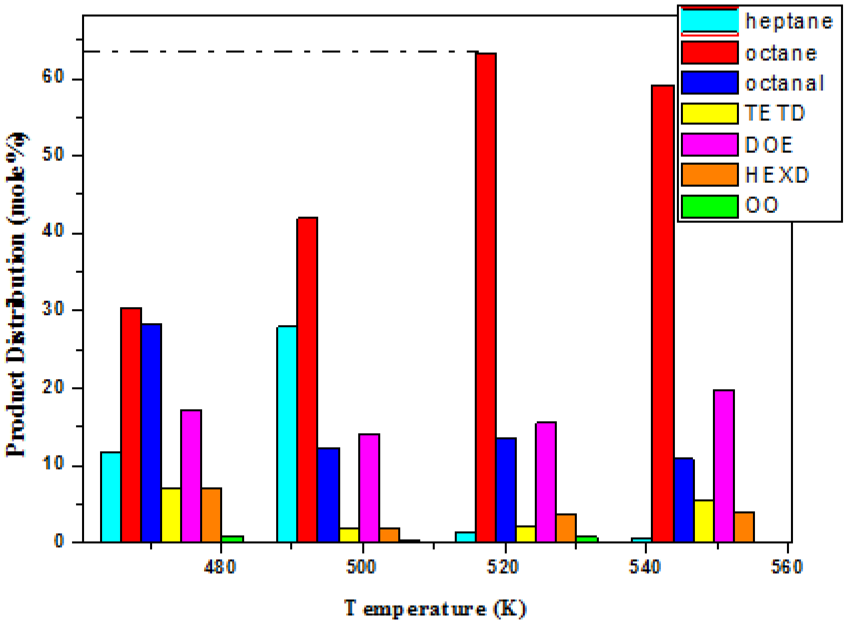


Figure 5.14: Product distribution for HDO of 1-Octanol at different temperatures over 8Ni1Mo/1Si1Al catalyst at a conversion of 3.5%, Reaction conditions: Pressure = 10 bar, Catalyst Loading = 1 gm., Batch Time = 240 min., Concentration of octanol (20 v/v %)

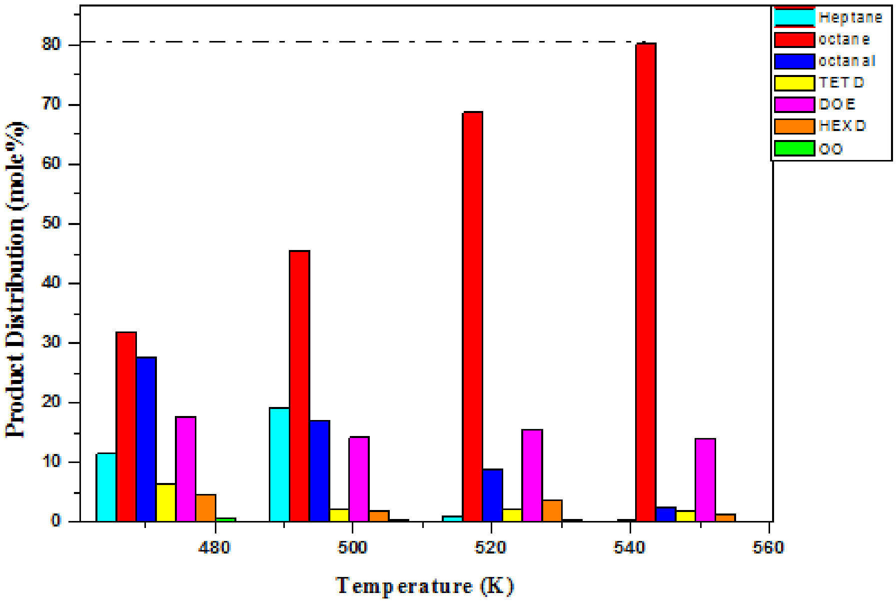


Figure 5.15: Product distribution for HDO of 1-Octanol at different temperatures over 8Ni1Mo/1Si1Al catalysts at 120 min, Reaction conditions: Pressure = 10 bar, Catalyst Loading = 1 gm., Batch Time = 240 min., Concentration of octanol (20 v/v %)

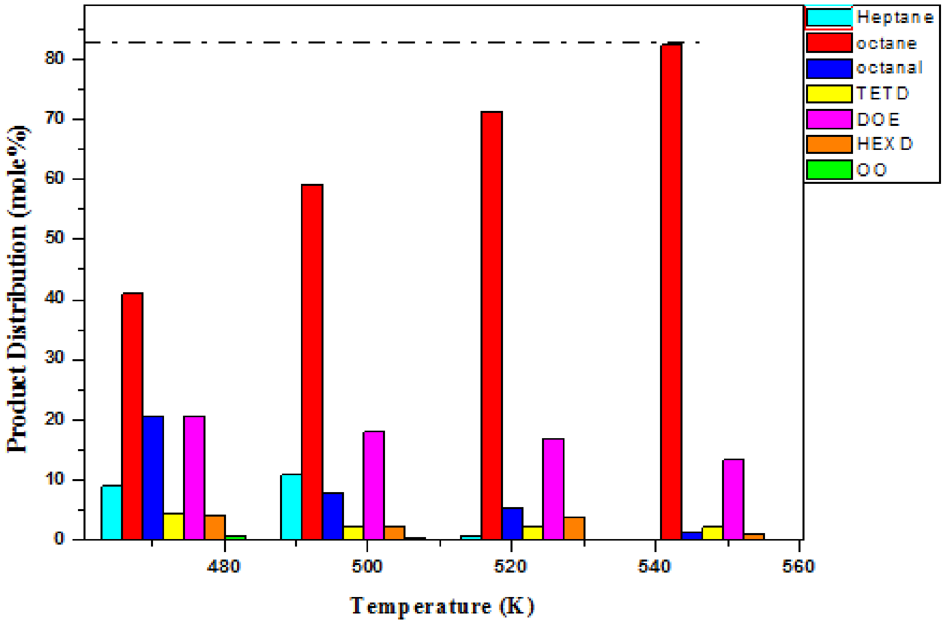


Figure 5.16: Product distribution for HDO of 1-octanol at different temperatures over 8Ni1Mo/1Si1Al at 240 min, Reaction conditions: Pressure = 10 bar, Catalyst Loading = 1 gm., Batch Time = 240 min., Concentration of octanol (20 v/v %)

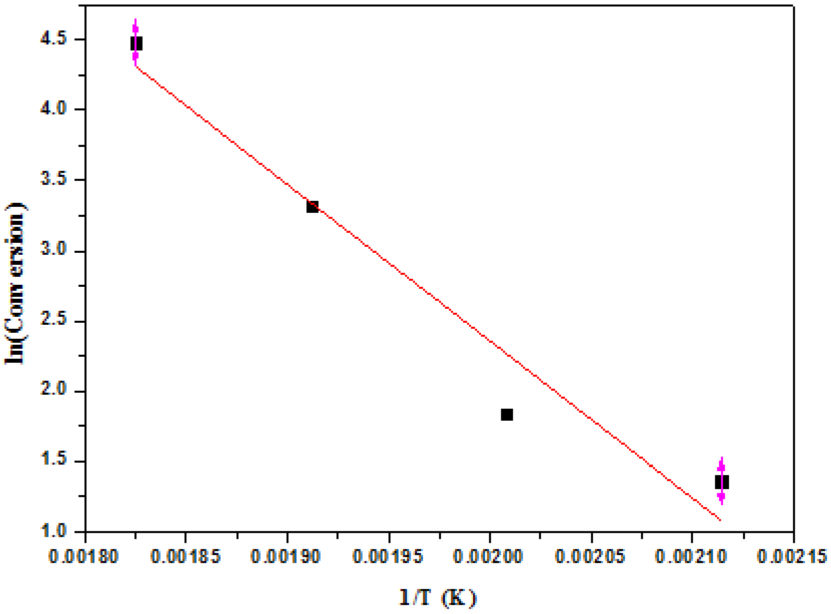


Figure 5.17: Arrhenius Plot for HDO of 1-octanol in the temperature range of 473 to 548 K over 8Ni1Mo/1Si1Al at 240 min, Reaction conditions: Pressure = 10 bar, Catalyst Loading = 1 gm., Batch Time = 240 min., Concentration of octanol (20 v/v %)

Arrhenius plot (ln(Conversion) vs 1/T) was drawn to know the activation energy for HDO of 1-octanol in the temperature range of 473 to 548 K. The conversion for different temperatures was taken at 240 m in of reaction. Activation energy E_a was calculated by using the following formula where slope is obtained from the plot and R is universal gas constant. The activation energy for this reaction was 92.722 kJ/mol.

$$\mathrm{Ea} = slope * R$$

5.2.6. Effect of catalyst loading

The effect of catalyst loading was studied by loading four different amount of catalyst and results are shown in Table 5.10 and Fig 5.18, 5.19. No conversion of octanol was observed for the reaction without catalyst. The octnol conversion was increased with increase in catalyst loading. However, no significant change in product distribution was observed with increase in catalyst loading. At higher catalyst loading the formation of hepatne and octanal became insignificant suggesting that dehydrogenation of octanol suppressed at high catalyst loading. Thus higher catalyst loading favours dehydration reaction than the dehydrogenation reaction.

Table 5.10: Effect of catalyst loading on HDO of 1-Octanol at 240 min

Catalyst Loading, gm	Conversion of 1-octanol, %	Product Distribution,%						
		Heptane	Octane	Octanal	TETD	DOE	HEXD	OO
0.5	11.2	3.0	62.2	9.8	2.8	19.2	2.9	1
1.0	27.7	0.6	71.3	5.2	2.2	16.9	3.7	0.1
1.5	47.4	0.9	74.5	2.5	2.4	17.8	1.9	0
2.0	56.9	0.7	76.8	1.8	2.1	17.1	1.5	0

Reaction Conditions: Pressure = 10 bar, Catalyst = 8Ni1Mo/SiAl, Temperature = 523 K, Batch Time = 240 min., Octanol concentration (20 v/v %)

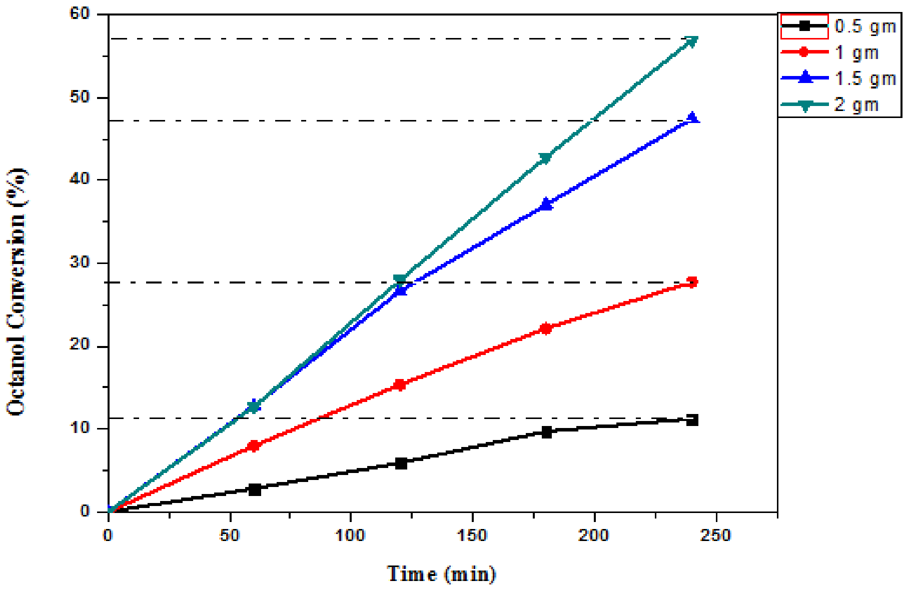


Figure 5.18: Conversion of 1-Octanol varying with time over 8Ni1Mo/1Si1Al catalyst for HDO of 1-Octanol at various catalyst loadings, Reaction conditions: Pressure = 10 bar, Temperature = 523 K, Batch Time = 240 min., Concentration of octanol (20 v/v %)

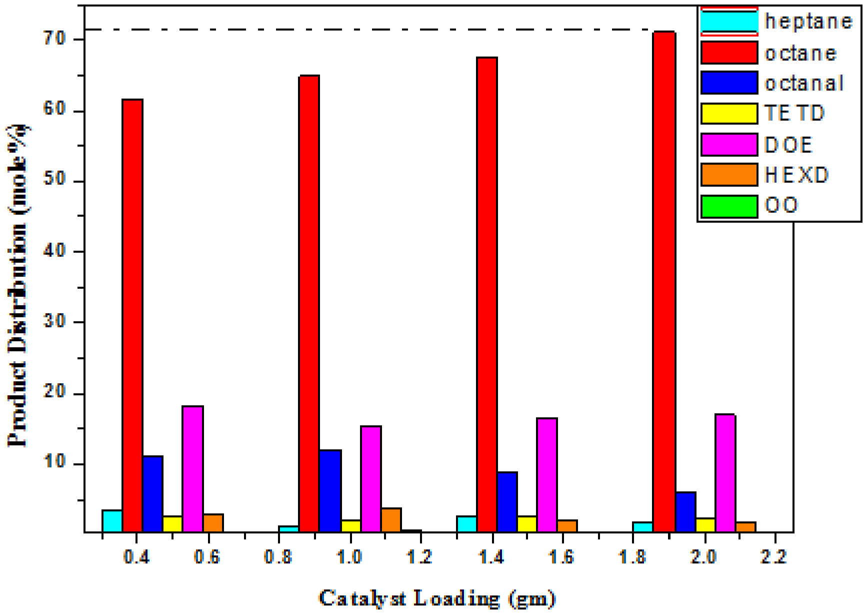


Figure 5.19: Product distribution for HDO of 1-octanol over 8Ni1Mo/1Si1Al at various catalyst loadings for HDO of 1-Octanol at a conversion of 10%, Reaction conditions: Pressure = 10 bar, Temperature = 523 K, Batch Time = 240 min., Concentration of octanol (20 v/v %)

5.2.7. Effect of feed composition

Effect of feed composition was studied by varying the volume percent of 1-octanol in the reaction mixture with 100%, 30%, 10% and 5% over 8Ni1Mo/1Si1Al catalyst. Table 5.11 shows the conversion and product distribution varying with feed composition. The octanol conversion was increased with decrease in the volume percentage of 1-octanol in reaction mixture (Fig 5.20). Figure 5.21 confirms that, a relatively small amount of isooctane (~1%) was formed during HDO of pure 1-octanol. In case of HDO of pure octanol, octanal was formed as major product followed by HEXD and TETD. The octenes produced due to dehydration of octanol was readily converted to oligomerized product, HEXD. Low octane selectivity confirm that rate of hydrogenation of octenes is much slower than oligomerization reaction leading to the formation of HEXD. Moreover, high selectivity of octanal confirms that dehydrogenation of octanol happens at much faster rate than the further conversion of octanal to heptanes due to decabonylation reaction. However, amount of octane was increased with decrease in octanol conversion.

Table 5.11: Effect of feed composition on HDO of 1-Octanol at 240 min

Octanol Concentration (v/v%)	Conversion of 1-octanol, %	Product Distribution,%						
		Heptane	Octane	Octanal	TETD	DOE	HEXD	OO
100/0	6.3	0.4	3.0	53.1	14.6	3.4	20.8	3.7
30/70	23.0	0.9	69.5	6.1	2.7	18.6	2.2	0
20/80	27.7	0.6	71.3	5.2	2.2	16.9	3.7	0.1
10/90	61.1	1.9	78.0	1.6	1.7	15.6	1.2	0
5/95	95.1	2.2	87.1	0.3	0.8	9.4	0.2	0

Reaction Conditions: Pressure = 10 bar, Catalyst = 8Ni1Mo/SiAl, Temperature = 250^{o}C, Batch Time = 240 min.

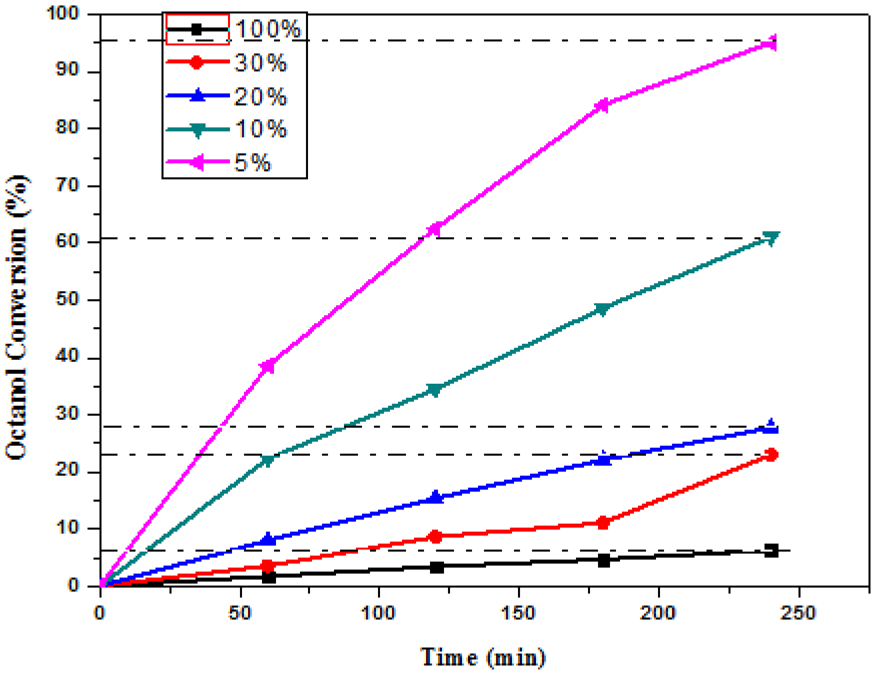


Figure 5.20: Conversion of 1-Octanol varying with time over 8Ni1Mo/1Si1Al catalyst for HDO of 1-Octanol at various feed compositions, Reaction conditions: Pressure = 10 bar, Temperature = 523 K, Batch Time = 240 min.

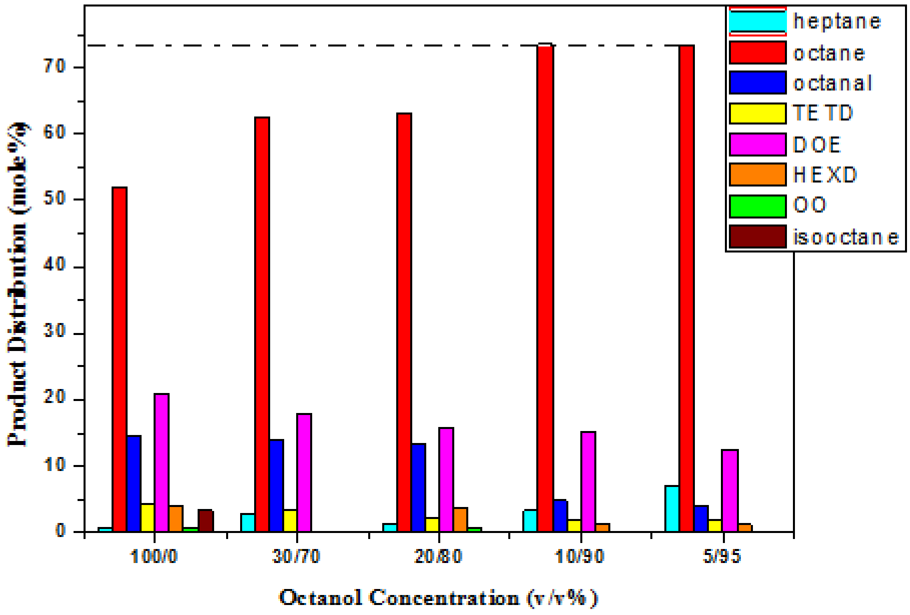


Figure 5.21: Product Distribution for HDO of 1-Octanol varying with different feed compositions over 8Ni1Mo/1Si1Al catalysts at a conversion of 5%, Reaction conditions: Pressure = 10 bar, Temperature = 523 K, Batch Time = 240 min.

5.2.8. Reusability test

The spent 8Ni1Mo/1Si1Al catalyst was recovered after the HDO of octanol. The wet catalyst was dried at 383 K and calcined at 823 K temperature. The calcined catalyst was reduced in a tubular furnace under the flow of hydrogen. Activity test was performed over this regenerated catalyst at the same reaction conditions (523 K temperature, 10 bars of hydrogen pressure, 1 gm of catalyst loading, octanol concentration 20 (v/v)%) and activity data are shown in Table 5.12 and Fig 5.22. From Table 5.12, the octanol conversion over regenerated catalyst was slightly more (~3%). However, slightly lower octane selectivity was obtained for regenerated catalyst.

Table 5.12: Regeneration test on HDO of 1-octanol over 8Ni1Mo/SiAl at 240 min

Run	Conversion of 1-octanol, %	Product Distribution,%						
		Heptane	Octane	Octanal	TETD	DOE	HEXD	OO
I	27.7	0.6	71.3	5.2	2.2	16.9	3.7	0.1
II	30.8	1.3	69.8	4.6	2.0	19.9	2.4	0

Reaction Conditions: Pressure = 10 bar, Catalyst = 8Ni1Mo/SiAl, Temperature = 523 K, Batch Time = 240 min., Concentration of octanol (20 v/v %)

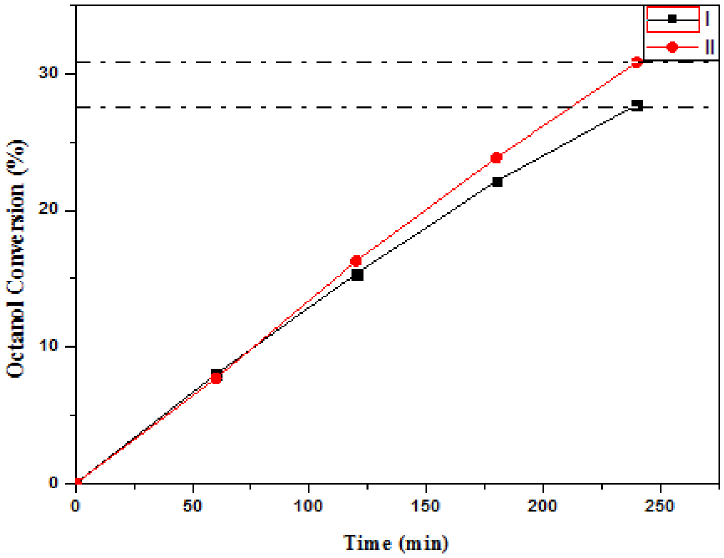


Figure 5.22: Conversion of 1-Octanol varying with time over pure and 8Ni1Mo/1Si1Al for HDO of 1-Octanol, Reaction conditions: Pressure = 10 bar, Temperature = 523 K, Batch Time = 240 min., Concentration of octanol (20 v/v %)

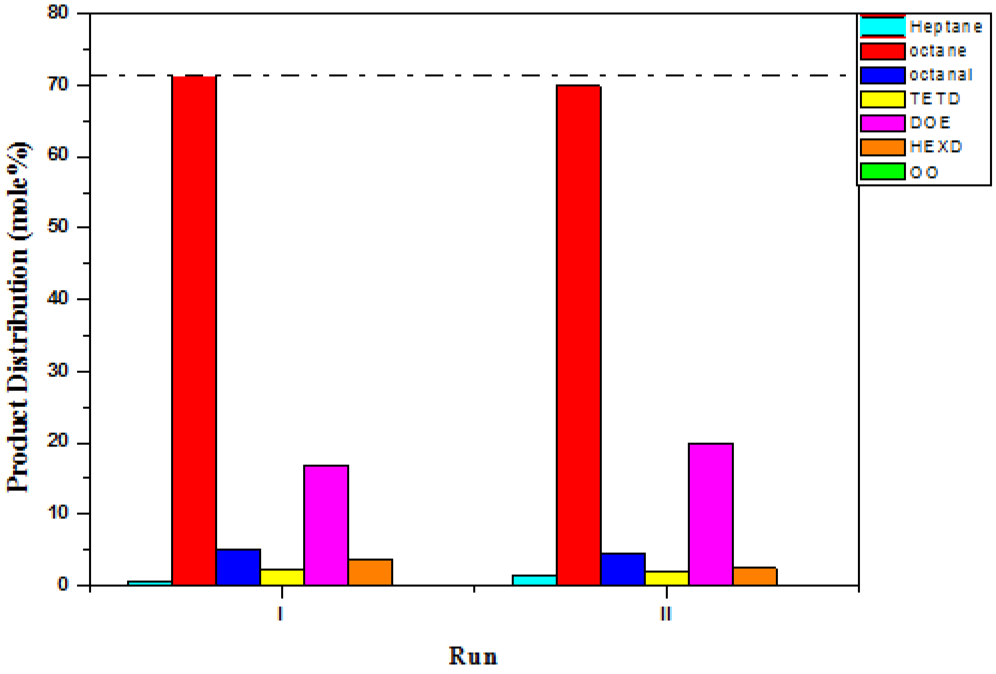
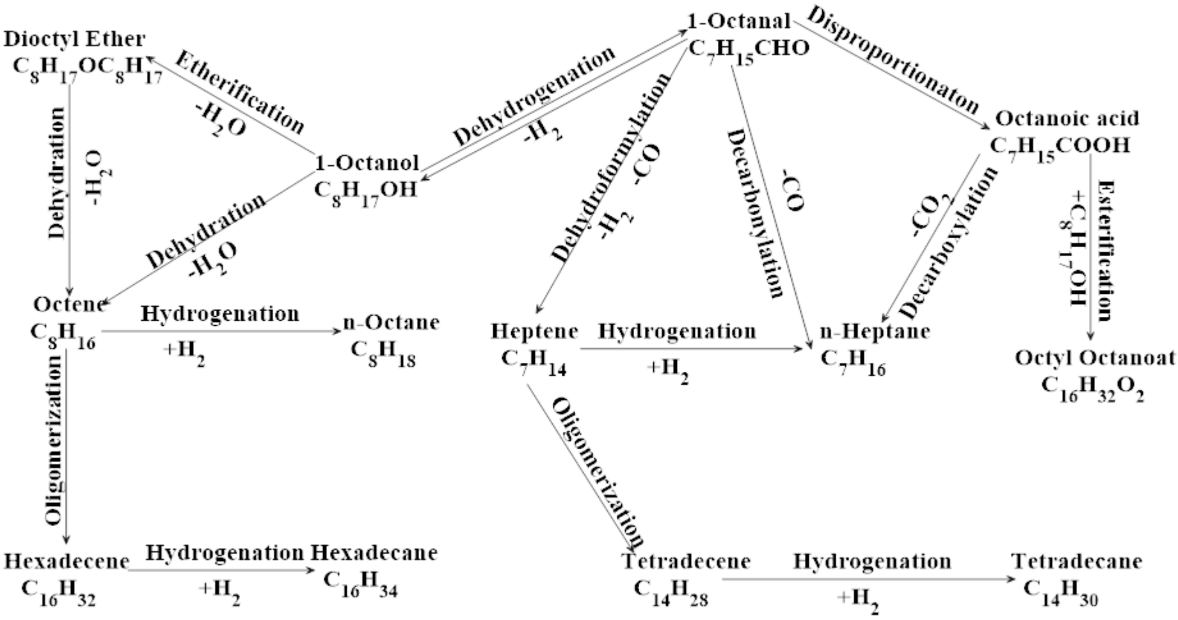


Figure 5.23: Product Distribution for HDO of 1-octanol over pure and spent 8Ni1Mo/1Si1Al catalysts at 240 min, Reaction conditions: Pressure = 10 bar, Temperature = 523 K, Batch Time = 240 min., Concentration of octanol (20 v/v %)

5.3. Reaction mechanism

The n-heptane, n-octane, 1-octanal, di-n-octyl ether (DOE), tetradecane (TETD), and hexadecane (HEXD) were identified in the liquid samples for HDO of 1-octanol under various experimental conditions. The octyl caprylate (OC) was also identified in small quantity. A comprehensive reaction mechanism of HDO of 1-octanol was proposed based on products distribution as shown in Scheme 1. The octane was formed by hydrogenation of octenes in presence metal catalysts. The octenes were formed either from direction dehydration of octanol or through the etherification followed by dehydration of ether route as shown in the scheme 1. However, octenes were not identified in the liquid sample suggesting that hydrogenation of octenes may happens readily in presence of metal catalysts. The octenes also undergores oligomerization followed by hydrogenation to HEXD. The acidic sites of catalysts might be responsible for etherification, dehydration, and oligomerization reactions. Alternatively, 1-octanol also undergoes dehydrogenation reaction over active metal sites of the catalysts leading to formation of 1-octanal. Subssequent, the 1-octanal is transformed to either n-heptane by decarbonylation reaction or heptenes by dehydroformylation reaction. The heptenes are then either hydrogenated to n-heptane or oligomerized followed by hydrogenated to TETD. Again, heptanes were also not identified in liquid samples. Analysis of gaseous product confirmed formation of both hydrogen and carbon monoxide. Formation of OA was however not well understood and might be formed by disproportination of 1-octanal. The OA formed further undergoes esterification reaction with 1-octanol producing OC.



Scheme 1: Reaction mechanism of HDO of 1-Octanol over different bimetallic catalysts.

6. CONCLUSIONS

The Hydrodeoxygenation of bio oils is very important to produce hydrocarbons for application as transportation fuels. In the present work, the hydrodeoxygenation of aliphatic alcohols was studied using 1-octanol as model compound in a high pressure batch reactor using supported bimetallic catalysts in the presence of hydrogen. Silica alumina mixed oxide supports of different SiO_2/Al_2O_3 molar ratios (1:1, 1:2 and 2:1) were synthesized by supramolecular templating method using Pluronic (P123) as structure directing agent. 15wt% nickel catalyst supported on these mixed oxide support were prepared by incipient wetness impregnation method. The HDO of 1-octanol was performed with the silica-alumina mixed oxide supported nickel catalysts and 1Si1Al was found to be best support. The bimetallic catalysts of several metals combination such as NiMo, NiFe, NiCo were prepared on 1Si1Al mixed oxide support composition obtained by co-impregnation method. The HDO of octanol was performed over these bimetallic catalysts to understand the promotional effect of the secondary metal. It was concluded from these HDO studies over bimetallic catalysts that addition of secondary metal affects the octanol conversion and product distribution. Specifically, molybdenum favours the formation of octane and cobalt increase the octanol conversion and amount of oligomerized product. The Ni/Mo molar composition was varied to understand the effect of catalyst composition on HDO activity of octanol and product distribution. A series of supported xNiyMo/1Si1Al (x:y = 1:0, 8:1, 4:1, 2:1, 1:1, 1:2, 0:1) were prepared using co-impregnation method and reduced in the presence of hydrogen at 823 K for 4 hours. The reduced catalyst was characterized by using BET and XRD. BET results revealed that the surface area of the catalyst was decreased by the presence of molybdenum. XRD results confirmed the presence of bulk nickel over bimetallic catalysts. HDO of 1-octanol over xNiyMo/1Si1Al confirmed that the product distribution of 1-octanol was more or less independent of molar composition of nickel and molybdenum. However presence of high amount of molybdenum suppressed the conversion of 1-octanol and 8Ni1Mo/1Si1Al was found to be the best catalyst considering octanol conversion and amount of HDO product. Effect of Cobalt metal loading on conversion and product distribution 1-octanol was studied and the results revealed that the rate of oligomerization was independent of metal loading. The effect of process parameters such as temperature, catalyst loading, octanol concentration on HDO of octanol and product distribution was studied using 8Ni1Mo/1Si1Al catalyst. The conversion of 1-octanol and octane selectivity was increasing with temperature and catalyst loading, but decreasing with increase in concentration of 1-octanol. A comprehensive mechanism was proposed based on the product distribution obtained under different experimental condition. The spent catalysts were regenerated and used for reusability studies; results were found to be comparable with the fresh catalyst suggesting that the catalytic activity was unchanged.

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8. APPENDIX

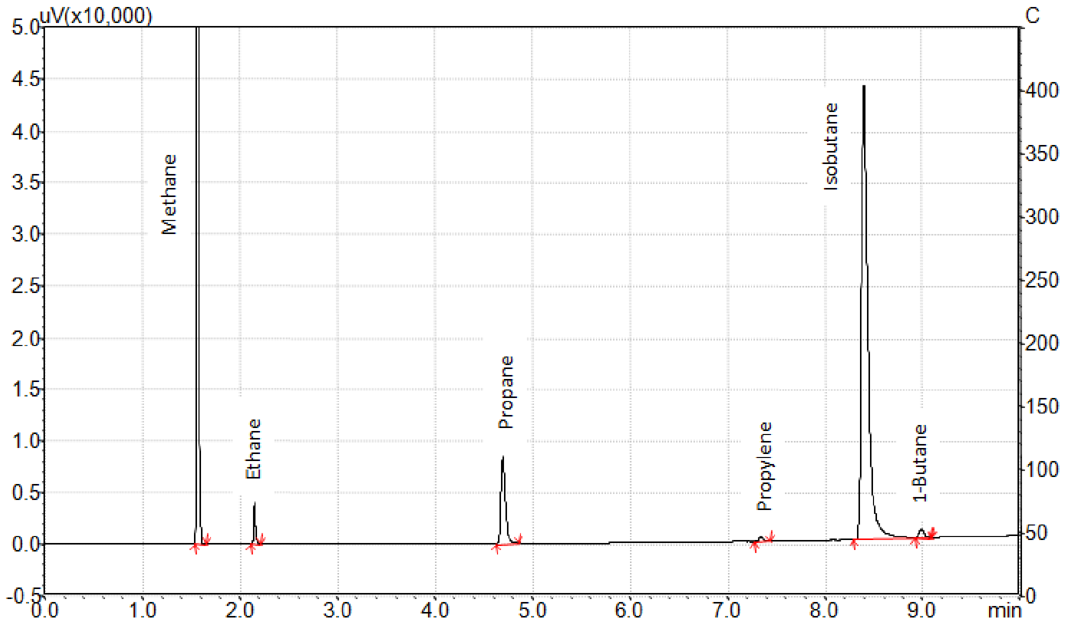

Figure 8.1: Chromatogram observed in GC analysis of gas products 8Ni1Mo/1Si1Al catalysts for HDO of 1-Octanol, Reaction Conditions: Pressure = 10 bar, Catalyst = 8Ni1Mo/SiAl, Catalyst Loading = 1 gm., Batch Time = 120 min., Metal Loading = 15 wt% of catalyst, Concentration of octanol (20 v/v %)

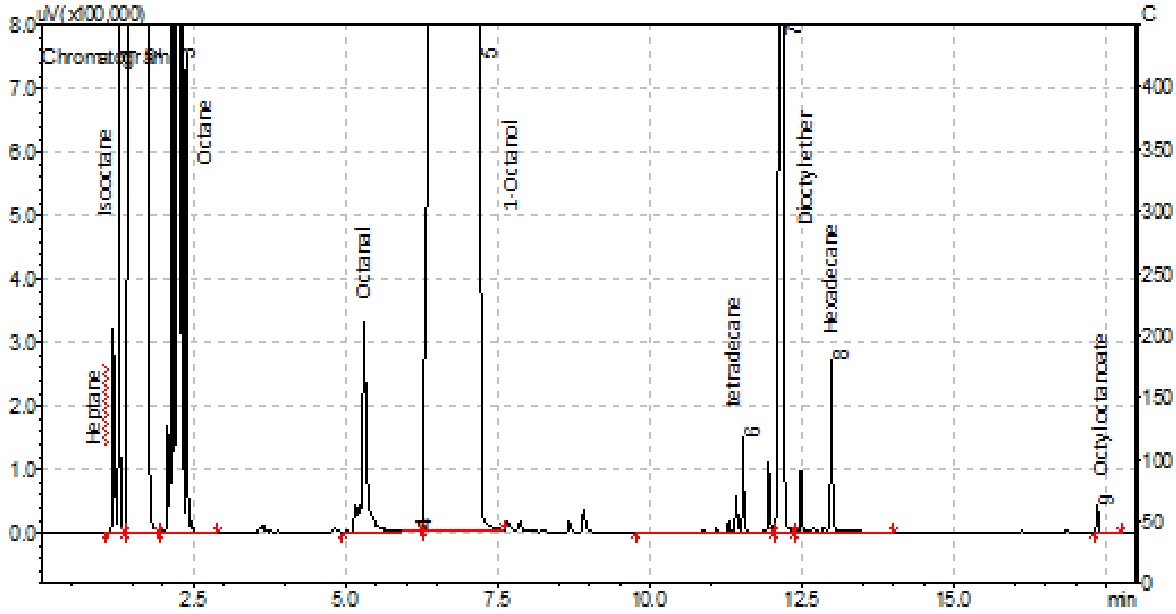

Figure 8.2: Chromatogram observed in GC analysis of liquid products 8Ni1Mo/1Si1Al catalysts for HDO of 1-Octanol, Reaction Conditions: Pressure = 10 bar, Catalyst = 8Ni1Mo/SiAl, Catalyst Loading = 1 gm., Batch Time = 120 min., Metal Loading = 15 wt% of catalyst, Concentration of octanol (20 v/v %)