

**CATALYTIC HYDROGENATION OF ACETIC ACID TO
ETHANOL IN HOMOGENEOUS AND
HETEROGENEOUS PHASES**

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**DEPARTMENT OF CHEMICAL ENGINEERING
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ETHANOL IN HOMOGENEOUS AND
HETEROGENEOUS PHASES**

by

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Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy

to the



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Dedicated to my beloved parents

CERTIFICATE

This is to certify that the report titled “**Catalytic Hydrogenation of Acetic Acid to Ethanol over Homogeneous and Heterogeneous Phases**” is a bonafide record of the project work carried out by **Mr. Pranab Kumar Rakshit** (2012CHZ8414) under our supervision and guidance, in fulfilment of the requirements for the award of the degree of **Doctor of Philosophy**. Further, to the best of our knowledge this has not been submitted to any other University or Institute for the award of any degree or diploma.

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Abstract

Increase in the cost of petroleum products and growing concerns of environmental impact of fossil fuel combustion are prompting researchers across the world to investigate alternative routes of fuel production from biomass. Among the many possible routes of conversion of biomass to fuel, ethanol has emerged as one of the major alternatives to fossil fuels along with few other alternatives such as biodiesel, green diesel, DME and Fischer- Tropsch product. Ethanol can be used as a gasoline additive to increase octane number and reduce CO_x, NO_x, and SO_x emissions. World ethanol production is currently around 23 billion gallons per year out of which 85% is consumed as fuel. Presently, ethanol is commercially produced by fermentation of sugars derived from grains of plant crops. Fermentation route of ethanol production is a biological conversion process and hence produces ethanol water mixture as the final product. Production of fuel grade ethanol (moisture free) from fermentation route requires separation of ethanol from water using distillation columns which are energy intensive and hence expensive. Furthermore, fermentation rates are usually much slower compared to any other industrial thermochemical conversion rates. Due to this the sizes of large ethanol fermentation plants are quite big. Apart from this, the commercial fermentation-based ethanol plants can only convert the agricultural grains to ethanol and can't convert the remaining woody biomass. Hence, in a ton of biomass only a fraction of carbonaceous feedstock is converted to ethanol, remaining carbon remains unutilized. In contrast to biological process, thermochemical route uses gasification to convert the entire biomass to synthesis gas (CO + H₂) thereby significantly increasing the carbon utilization compared to fermentation process. Syngas so produced is further processed to remove contaminants such as H₂S, NH₃, COS and tar. Clean syngas is then converted to liquid fuels or chemicals using complex processes involving heterogeneous catalysts.

In the case of homogenous catalysts, many organometallic complexes have been reported for conversion of carboxylic acids to corresponding alcohol. However, there is no one to one comparison exists between the reported catalyst. Detailed kinetics of homogenous catalyst are not even reported. Conversion of acetic acid to ethanol over impregnated catalysts have been widely reported but the basis for choosing the active metals are not clearly explained. Some catalyst showed reasonable activity and selectivity towards ethanol synthesis, but no explanation exists why they gave good yields and while others did not. There is no quantitative analysis done on the effect of support and their interaction with active metal on acetic acid conversion. Overall, a holistic view on what characteristics of catalyst and support are suitable for acetic acid hydrogenation is not clearly brought out. Finally, a plausible route to arrive at a robust process towards conversion of acetic acid to ethanol is not clearly brought out. In this work, we attempt to present a reasonable explanation towards these observations and substantiate them by credible evidences.

सार

पेट्रोलियम उत्पादों की लागत में वृद्धि और जीवाश्म ईंधन के दहन के पर्यावरणीय प्रभाव की बढ़ती चिंताओं ने दुनिया भर के शोधकर्ताओं को बायोमास से ईंधन उत्पादन के वैकल्पिक मार्गों की जांच करने के लिए प्रेरित किया है। ईंधन के लिए बायोमास के रूपांतरण के कई संभावित मार्गों में, इथेनॉल कुछ अन्य विकल्पों जैसे बायोडीजल, डीएमई, एफटी वैक्स के साथ जीवाश्म ईंधन के प्रमुख विकल्पों में से एक के रूप में उभरा है। इथेनॉल का उपयोग ऑक्टेन संख्या को बढ़ाने और CO_x, NO_x और SO_x उत्सर्जन को कम करने के लिए एक गैसोलीन एडिटिव के रूप में किया जा सकता है। विश्व इथेनॉल का उत्पादन वर्तमान में प्रति वर्ष लगभग 23 बिलियन गैलन है, जिसमें से 85% ईंधन के रूप में खपत होती है। वर्तमान में, इथेनॉल व्यावसायिक रूप से अनाज से प्राप्त चीनी के किण्वन द्वारा उत्पादित किया जाता है। इथेनॉल उत्पादन का किण्वन मार्ग एक जैविक रूपांतरण प्रक्रिया है और इसलिए अंतिम उत्पाद के रूप में इथेनॉल पानी के मिश्रण का उत्पादन करता है। किण्वन मार्ग से ईंधन ग्रेड इथेनॉल (नमी मुक्त) के उत्पादन में आसवन तकनीक का उपयोग करके पानी से इथेनॉल को अलग करने की आवश्यकता होती है जो ऊर्जा गहन प्रक्रिया है और इसलिए महंगी होती है। इसके अलावा, किसी अन्य औद्योगिक थर्मोकैमिकल रूपांतरण दरों की तुलना में किण्वन दर आमतौर पर बहुत धीमी होती है। इसके कारण बड़े इथेनॉल किण्वन रिएक्टरों के आकार काफी बड़े हैं। इसके अलावा, वाणिज्यिक किण्वन-आधारित इथेनॉल संयंत्र केवल कृषि अनाज को इथेनॉल में बदल सकते हैं और शेष वुडी बायोमास को परिवर्तित नहीं कर सकते हैं। इसलिए, बायोमास के एक टन में केवल कार्बन वाले फीडस्टॉक का एक अंश इथेनॉल में बदल जाता है, शेष कार्बन अप्रयुक्त रहता है। जैविक प्रक्रिया के विपरीत, थर्मोकैमिकल मार्ग पूरे बायोमास को संश्लेषण गैस (CO + H₂) में परिवर्तित करने के लिए गैसिफिकेशन का उपयोग करता है जिससे किण्वन प्रक्रिया की तुलना में कार्बन उपयोग में काफी वृद्धि होती है। उत्पादित सिनगैस को H₂S, NH₃, COS और टार जैसे दूषित पदार्थों को हटाने के लिए आगे संसाधित किया जाता है। स्वच्छ सिनगैस को विषम उत्प्रेरक से युक्त जटिल प्रक्रियाओं का उपयोग करके फिर तरल ईंधन या रसायनों में परिवर्तित किया जाता है।

समरूप उत्प्रेरक के मामले में, कार्बोक्जिलिक एसिड को संबंधित अल्कोहल में परिवर्तित करने के लिए कई ऑर्गनोमेटलिक कॉम्प्लेक्स की सूचना मिली है। हालांकि, रिपोर्ट किए गए उत्प्रेरक के बीच कोई भी एक तुलना मौजूद नहीं है। समरूप उत्प्रेरक के विस्तृत कैनेटीक्स की भी रिपोर्ट नहीं की गई है। संसेचन उत्प्रेरकों पर एसिटिक एसिड का इथेनॉल में रूपांतरण व्यापक रूप से बताया गया है लेकिन सक्रिय धातुओं को चुनने का आधार स्पष्ट रूप से नहीं बताया गया है। कुछ उत्प्रेरक ने इथेनॉल संश्लेषण के प्रति उचित गतिविधि और चयनात्मकता दिखाई, लेकिन कोई स्पष्टीकरण मौजूद नहीं है कि उन्होंने अच्छी पैदावार क्यों दी और जबकि अन्य ने नहीं दी।

एसिटिक एसिड रूपांतरण पर सक्रिय धातु के साथ समर्थन और उनके प्रभाव के प्रभाव पर कोई मात्रात्मक विश्लेषण नहीं किया गया है। कुल मिलाकर, एसिटिक एसिड हाइड्रोजनीकरण के लिए उपयुक्त उत्प्रेरक और समर्थन की विशेषताओं पर एक समग्र दृष्टिकोण स्पष्ट रूप से सामने नहीं लाया गया है। अंत में, एसिटिक एसिड को इथेनॉल में बदलने की दिशा में एक मजबूत प्रक्रिया पर पहुंचने के लिए एक प्रशंसनीय मार्ग स्पष्ट रूप से सामने नहीं लाया गया है। इस काम में, हम इन टिप्पणियों के प्रति एक उचित स्पष्टीकरण प्रस्तुत करने का प्रयास करते हैं और विश्वसनीय साक्ष्य द्वारा उन्हें प्रमाणित करते हैं।

Table of contents

1. Introduction.....	1
1.1 Background.....	1
1.2 Motivation for the present work.....	8
1.3 Research objectives.....	9
1.4 Thesis Organization	10
2. Literature review	15
2.1 Introduction.....	15
2.2 Thermodynamic Considerations	16
2.3 Reaction Mechanism.....	20
2.4 Catalyst Types.....	24
2.4.1 Heterogeneous Catalysts	24
2.4.2 Homogenous Catalysts.....	26
2.5 Reaction rates.....	31
2.6 Reactor design.....	33
2.7 Summary	35
3. Liquid phase hydrogenation of acetic acid using Triphos ligand based homogenous phase catalysts.....	46
3.1 Introduction.....	46
3.2 Experimental Section	47
3.2.1 Catalyst preparation	47
3.2.2 Catalyst characterization	50
3.2.3. Catalyst evaluation.....	51
3.3 Results and Discussion	53
3.3.1 Spectroscopic and diffraction analysis.....	53
3.3.2 Activity testing.....	59
3.3.3 Effect of catalyst precursor	63
3.3.4 Effect of catalyst additive on ethanol selectivity	64
3.3.4 Kinetic study	66

3.4 Conclusions.....	72
4. Selective hydrogenation of acetic acid over silica supported Co-Pt and Ni-Pt catalysts to renewable fuel ethanol	77
4.1 Introduction.....	77
4.2 Experimental section.....	79
4.2.1 Catalyst preparation	79
4.2.2 Catalyst characterization	80
4.2.3 Catalytic activity testing.....	82
4.3 Results and discussion	83
4.3.1 Catalyst characterization	83
4.3.2 Catalytic activity testing.....	89
4.3.3 Acetic acid TPD of catalysts	91
4.4 Conclusion	93
5. Pt-Sn bimetallic catalyst catalyzed hydrogenation of acetic acid: Effect of acidity on ethanol selectivity	98
5.1 Introduction.....	98
5.2 Experimental section.....	101
5.2.1. Catalyst Preparation	101
5.2.2. Instrumentation	101
5.2.3. Catalyst evaluation.....	103
5.3 Results and discussion	105
5.3.1 Physical properties	105
5.3.2 XRD and TEM analysis	106
5.3.3 Reduction behaviour	111
5.3.4 Hydrogenation of acetic acid	115
5.3.5 Effect of catalyst acidity on ethanol selectivity	120
5.4 Conclusion	128
6. Kinetics of Acetic acid hydrogenation reaction over bimetallic Pt-Sn catalyst.....	137
6.1 Introduction.....	137

6.2 Materials and methods	139
6.2.1 Catalyst preparation	139
6.2.2 Catalyst testing	139
6.3 Hydrogenation of acetic acid	140
6.4 Kinetics of acetic acid hydrogenation reaction	144
6.5 Mathematical model of fixed bed reactor for acetic acid hydrogenation.....	149
6.5.1 One Dimensional (1D) pseudo-homogeneous model	149
6.5.2 Two-Dimensional (2D) pseudo-homogeneous model	152
6.6 Conclusion	155
7. Design of multi-tubular reactor for carrying out gas-solid exothermic reactions.....	160
7.1 Introduction.....	160
7.1.1 Conventional ethanol process	163
7.2 Methods.....	164
7.2.1 Overview	165
7.2.2 Reactor	166
7.2.3 Simulation studies	168
7.3 Results and Discussion	169
7.3.1 Mass and energy balances.....	169
7.3.2 Effect of pressure, temperature and space velocity on isothermal reactor.....	170
7.3.3 Heat duty of isothermal reactor.....	172
7.3.4 Ethanol reactor with constant coolant temperature – Non-isothermal operation.....	174
7.3.5 Effect of tube diameter.....	175
7.3.6 Effect of heat transfer coefficient.....	177
7.3.7 Estimation of optimum reactor size	177
7.4 Conclusion	180
8. Conclusions and future recommendations	184
8.1 Conclusions.....	184
8.2 Future recommendations.....	185

List of figures

Figure 1.1: Biological route of ethanol production.....	1
Figure 1.2: Thermochemical route of ethanol production	2
Figure 1.4: Acetic acid production and import data (Source: DGFT, Govt. of India).....	7
Figure 2.1: Gibbs free energy changes in the conversion of Acetic acid to ethanol, ethyl acetate, acetaldehyde and methane	17
Figure 2.2: Equilibrium conversion and selectivity of ethanol, ethyl acetate and acetaldehyde with variation of temperature at 15 bar and Hydrogen/Acetic acid ratio =4	18
Figure 2.3: Equilibrium conversion and selectivity of ethanol, ethyl acetate and acetaldehyde with variation of pressure at 280 ⁰ C and Hydrogen/Acetic acid ratio =4.....	19
Figure 2.4: Equilibrium conversion and selectivity of ethanol, ethyl acetate and acetaldehyde with variation of Hydrogen/Acetic acid ratio at 280 ⁰ C and 15 bar	20
Scheme 2.1: Elementary reactions of acetic acid hydrogenation [4].....	21
Scheme 2.2: Reaction mechanism of acetic acid hydrogenation over Pt-Sn catalyst [40]	22
Scheme 2.3: Reaction mechanism of acetic acid hydrogenation over Wilkinson type catalyst. P ₃ is the tridentate ligand attached with metal M of the complex, S is solvent.....	23
Figure 3.1: Glove box and associated equipment employed for catalyst synthesis.....	47
Scheme 3.1: Synthesis of the organometallic catalysts	48
Figure 3.2: ORTEP plots of synthesized catalysts.(ref for HA4: Korstange et. al [18])	50
Figure 3.3 : High pressure Batch reactor system employed for catalyst performance evaluation.....	52
Figure 3.4: XRD pattern of synthesized Ni, Pt and Ru based Triphos ligand catalysts	53
Figure 3.5: Infrared spectra of catalysts HA1, HA2 and HA3.....	55
Figure 3.6: ³¹ P NMR of catalyst HA1	56
Figure 3.7: ¹³ C NMR of catalyst HA1	57
Figure 3.8: ¹ H NMR of catalyst HA1	57
Figure 3.9: ³¹ P NMR of catalyst HA2.....	57
Figure 3.10: ¹³ C NMR of catalyst HA2	58
Figure 3.11: ¹ H NMR of catalyst HA2	58
Figure 3.12: ³¹ P NMR of HA3 catalyst.....	58
Figure 3.13: ¹³ C NMR of catalyst HA3	59
Figure 3.14: ³¹ P NMR of catalyst HA4.....	59

Figure 3.15: Effect of stirring speed on reaction rates (H_2 pressure, 80 bar, catalyst loading 0.05 mol%, temperature $100\text{ }^\circ\text{C}$, reaction time, 3 hrs, Initial concentration of acetic acid: 1M and 2M)	61
Figure 3.16: ^{31}P NMR of HA2 reaction mixture.....	62
Figure 3.17: Concentration vs time profile at different initial concentrations of acetic acid ..	65
Figure 3.18: Concentration vs time profile at different initial concentrations of acetic acid ..	67
Figure 3.19: Rate of acetic acid hydrogenation for 0.6M, 1.0M and 1.5M initial concentration of acetic acid during the reaction study ($T=100\text{ }^\circ\text{C}$, 80 bar, Catalyst loading: 0.5mol%)	68
Figure 3.20 Plot between $\log r$ and $\log C_{a0}$	69
Figure 3.21: Arrhenius plot for acetic acid hydrogenation over HA4 catalyst.....	69
Figure 3.22: Effect of pressure on acetic acid conversion over HA4 catalyst.....	70
Figure 3.23: Effect of reactor pressure on selectivity of ethanol.....	71
Figure 3.24: Effect of catalyst loading on acetic acid conversion and ethanol selectivity	72
Scheme 4.1. Schematic diagram of a high-pressure fixed-bed reactor for acetic acid hydrogenation	83
Figure 4.1. XRD patterns of the prepared catalysts: (a) Co-based catalysts and (b) Ni-based catalysts.....	86
Figure 4.2. HR-TEM images of (a) $1\text{Co}-0.1\text{Pt}/\text{SiO}_2$ and (b) $1\text{Ni}-0.1\text{Pt}/\text{SiO}_2$ catalysts	87
Figure 4.3: TPR profiles of the prepared catalysts (a) Co-based (b) Ni-based catalysts.....	88
Figure 4.4: Conversion of AA and selectivity to products at various temperatures over: (a) $1\text{Co}/\text{SiO}_2$, (b) $2\text{Co}/\text{SiO}_2$, (c) $5\text{Co}/\text{SiO}_2$, (d) $1\text{Co}-0.1\text{Pt}/\text{SiO}_2$, (e) $2\text{Co}-0.1\text{Pt}/\text{SiO}_2$, and (f) $5\text{Co}-0.1\text{Pt}/\text{SiO}_2$	90
Figure 4.5: Conversion of AA and selectivity to products over: (a) $1\text{Ni}/\text{SiO}_2$, (b) $2\text{Ni}/\text{SiO}_2$, (c) $5\text{Ni}/\text{SiO}_2$, (d) $1\text{Ni}-0.1\text{Pt}/\text{SiO}_2$, (e) $2\text{Ni}-0.1\text{Pt}/\text{SiO}_2$, and (f) $5\text{Ni}-0.1\text{Pt}/\text{SiO}_2$	90
Figure 4.6: AA-TPD profiles of the prepared catalysts	91
Scheme 5.1. Schematic representation of the test setup for acetic acid hydrogenation.....	104
Figure 5.1: XRD diffraction pattern of SA1 supported Pt-Sn catalysts in calcined state.....	107
Figure 5.2: XRD diffraction patterns of $3\text{Pt}-3\text{Sn}-\text{SA1}$ catalyst sample in reduced state.....	108
Figure 5.3: TEM images and corresponding particle size distribution of (A) $3\text{Pt}-3\text{Sn}-\text{SA1}$ and (B) $3\text{Pt}-\text{SA1}$	109
Figure 5.4: HRTEM image of $3\text{Pt}-3\text{Sn}-\text{SA1}$ catalyst sample reduced at $400\text{ }^\circ\text{C}$	110
Figure 5.5: Temperature reduction profile of Pt-Sn catalysts.....	111

Figure 5.6: Effect of catalyst particle size on acetic acid conversion at 270 °C, 2.0 MPa pressure, WHSV=3 hr ⁻¹ and H ₂ to Acetic acid molar ratio 10	114
Figure 5.7: Product analysis of over calcined 3Pt-3Sn-SA1 catalyst sample. (A) Liquid products and (B) Gaseous products. Reaction conditions: Temp. 270 °C; Press. 1 MPa; WHSV 5 hr ⁻¹ ; H ₂ /acetic acid ratio~10.....	117
Figure 5.8: Reactor effluent composition of in-situ reduced 3Pt-3Sn-SA1 catalyst sample. Reaction conditions: Temp. 270 °C; Press. 1 MPa; WHSV 5 hr ⁻¹ ; H ₂ /acetic acid ratio~10.....	118
Figure 5.9: FTIR spectra of as received silica alumina supports.....	121
Figure 5.10: NH ₃ -TPD profile of 3Pt-3Sn-SiO ₂ -Al ₂ O ₃ catalyst over different supports.....	122
Figure 6.1: Thermodynamic analysis of acetic acid hydrogenation. (A) Gibbs free energy changes in the conversion of Acetic acid to ethanol, ethyl acetate, acetaldehyde and methane. Variation in conversion of acetic acid and selectivity of ethanol, ethyl acetate, acetaldehyde and methane with process parameters, (B) Temperature, (C) Pressure and (D) Hydrogen to acetic acid molar ratio	142
Figure 6.2: Acetic acid conversion to ethanol using 3Pt-3Sn-SiO ₂ catalyst at varying reaction conditions: (A) Temperature, (B) Pressure, (C) LHSV and (D) H ₂ /Acetic acid molar ratio	143
Figure 6.3: Acetic acid conversion w.r.t bed length at inlet temp of 270 deg C and 20 bar pressure	150
Figure 6.4: Axial variation of bed temperature at inlet temp of 270 deg C and 20 bar pressure	151
Figure 6.5: Acetic acid concentration w.r.t bed length at inlet temp of 270 deg C and 20 bar pressure	151
Figure 6.6: Axial and radial variation of catalyst bed temperature for acetic acid hydrogenation	153
Figure 6.7: Axial and radial variation of acetic acid concentration for acetic acid hydrogenation	154
Figure 6.8: Sensitivity of catalyst bed temperature with variation of reactor inlet temperature	155
Scheme 7.1: Block diagram of the process.....	165
Figure 7.1: Effect of temperature and space velocity on conversion at (A) 10 bar and (B) 20 bar. (C) Catalyst content at maximum conversion for a given temperature and pressure. (D) Conversion per kg catalyst as a function of temperature	171

Figure 7.2: Heat duty of isothermal ethanol reactor at 240 °C and 20 bar	172
Figure 7.3: Ethanol reactor with constant coolant temperature of 240°C and 10 bar pressure	173
Figure 7.4A: Effect of coolant temperature on bed temperature	173
Figure 7.4B: Effect of coolant temperature on acetic acid conversion.....	174
Figure 7.5: Effect of tube diameter on (A) bed temperature (B) conversion.....	175
Figure 7.6A: Effect of overall heat transfer coefficient on bed temperature	176
Figure 7.6B: Effect of overall heat transfer coefficient on conversion.....	176
Figure 7.7: Effect of tube diameter on heat transfer coefficient and number of tubes required	179

List of Tables

Table 1.1: Reactions taking place in different routes of syngas conversion to Ethanol	4
Table 2.1: Selected heterogeneous catalyst results employed in acetic acid hydrogenation to Ethanol	37
Table 2.2: Selected homogenous catalyst results employed in carboxylic acid hydrogenation to Ethanol	38
Table 3.1: ³¹ P NMR and Infrared spectra of synthesized catalysts	54
Table 3.2: Catalyst activity and product selectivity of the synthesized catalysts	61
Table 3.3: Acetic acid conversion and product selectivity of the synthesized Co based catalysts with different Co precursors	63
Table 3.4: Effect of catalyst additives on ethanol selectivity	64
Table 3.5: Rate parameter estimation of acetic acid hydrogenation	67
Table 4.1. Composition of Co– based and Ni–based catalysts	80
Table 4.2. Surface properties of prepared Co-based catalysts	84
Table 4.3. Surface properties of prepared Ni-based catalysts	85
Table 4.4. Hydrogen and AA content on selected catalysts	92
Table 5.1: Physicochemical properties of Pt/Sn catalysts	105
Table 5.2: Hydrogen consumption of different catalyst samples during reduction	112
Table 5.3: Hydrogen uptake and H ₂ /Pt atomic ratio of 3Pt-SA1 and 3Pt-3Sn-SA1 catalyst	113
Table 5.4: Catalyst activity and selectivity of Pt/Sn catalysts	115
Table 5.5: Physical properties of the silica-alumina supported 3Pt-3Sn catalysts	120
Table 5.6: Isopropylamine (IPA) TPD of the SiO ₂ -Al ₂ O ₃ supported 3Pt-3Sn catalysts	123
Table 5.7: Catalytic performance of SiO ₂ -Al ₂ O ₃ supported 3Pt-3Sn catalysts	123
Table 5.8: Catalytic performance of bimetallic Pt-Sn catalysts	124
Table 6.1: Estimated kinetic parameters	147
Table 7.1: Parameters of the kinetic model	167
Table 7.2: Characteristics of the catalyst	167
Table 7.3: Mass balance	169
Table 7.4: Energy balance	170
Table 7.5: Reactor sizing details	178