

# **Bioethanol oxidation to value added products**

## **PhD Synopsis**

Submitted to

GUJARAT TECHNOLOGICAL UNIVERSITY

For the Degree

Of

*Doctor of Philosophy*

*In*

***CHEMICAL ENGINEERING***

***BY***

**Paresh Haribhai Rana**

(Enrollment Number: 129990905003)

Supervisor: **Dr. Parimal A. Parikh**

Professor, Chemical Engineering Department

Sardar Vallabhbhai National Institute of Technology, Surat

### **DPC Members**

**Dr. Ranjan A. Sengupta**

Professor, Department of Chemical Engineering

Faculty of Technology and Engineering

Maharaja Sayajirao University, Vadodara

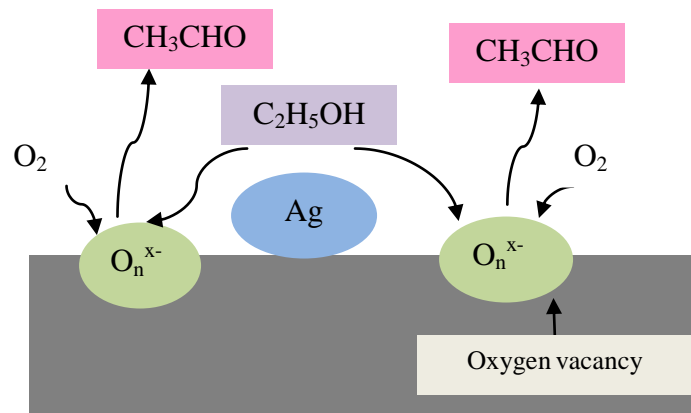
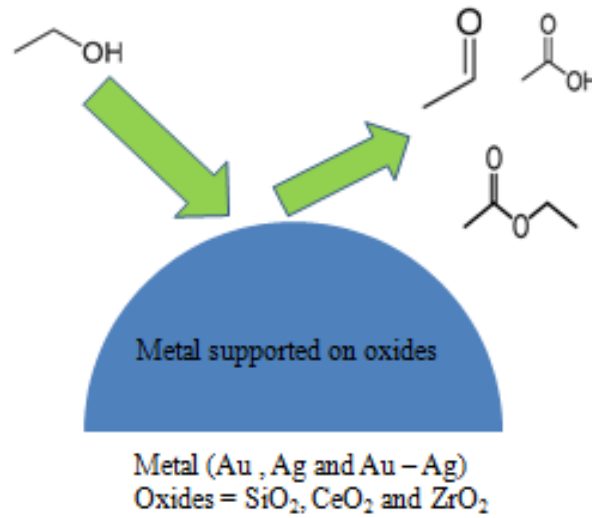
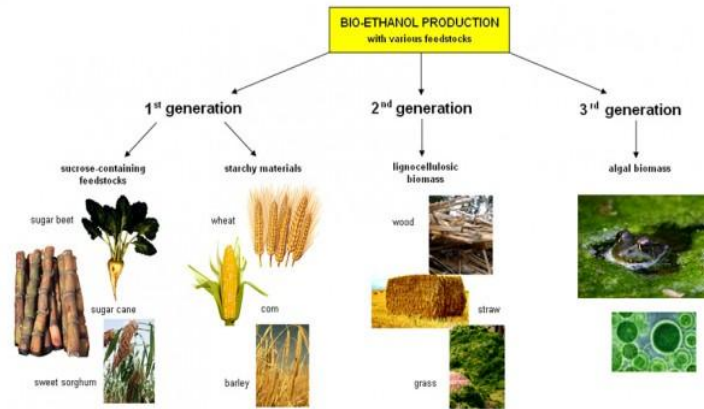
**Dr. Jagannath Das**

Assistant Vice President

Reliance Industries Limited

Vadodara

# Graphical Abstract



## **Title: Bioethanol oxidation to value added products**

**Abstract:** Coal energized the 19<sup>th</sup> century while oil worked for the 20<sup>th</sup> century. The question that remains pending is the future energy source. With the expanding population, growing demands from industrialization and rising concern for environment preventative measure, total dependence on fossil fuel resources is not sustainable. Hence there is an urgent need for a green and sustainable fuel provoked research into biomass as an alternative to fossil fuels. There is a need to identify a suitable biomass derived species, which can provide high value outputs in order to replace conventional fossil fuel resources. Bioethanol is one of such biomass derived platform molecule which has a potential to be a sustainable feedstock of variety of commodity chemicals. For instance, Acetaldehyde which majorly produced from the oxidation of ethylene (Wacker process) can be produced via one - step gas phase conversion of bioethanol. With the growing availability of bioethanol, oxidation of bioethanol to value added chemicals has been considered as feasible process.

With this back - ground, the main goal of the study is to investigate the effect of noble metals, metal oxides and metal/oxide loading on the conversion as a function of temperature for the oxidation of bioethanol in air. In the first part of this work liquid phase oxidation of bioethanol was carried out with Au and Ag supported on various type of zeolites. Reaction parameters like pressure, O<sub>2</sub>/ethanol molar ratio, effect of alkali and reaction time has also been studied. It was observed that presence of water hindered that catalytic activity of the catalysts which resulted into poor conversion of bioethanol.

The second part of this work described the preparation, characterization and catalytic study of Au, Ag and Au - Ag over SiO<sub>2</sub>, CeO<sub>2</sub> and ZrO<sub>2</sub> in the gas phase oxidation of bioethanol as a function of reaction temperature. Among the 1 wt% Au supported on SiO<sub>2</sub>, CeO<sub>2</sub> and ZrO<sub>2</sub> catalysts, Au/ZrO<sub>2</sub> was found to be very active for bioethanol oxidation. The improved catalytic performance of Au/ZrO<sub>2</sub> was due to the oxygen deficiencies generated by Au on ZrO<sub>2</sub> surface. Ag/ZrO<sub>2</sub> and Au-Ag/ZrO<sub>2</sub> showed low conversion than Au/ZrO<sub>2</sub> and Au/CeO<sub>2</sub>, because Ag is more prone to oxidation than Au. Due to inert nature of SiO<sub>2</sub>, Au/SiO<sub>2</sub> exhibited lowest ethanol conversion.

Later on Ag/CeO<sub>2</sub> was employed for this work and characterization results indicated that a part of Ag was inserted into the lattice of CeO<sub>2</sub> and expanded the support lattice led to increase the lattice oxygen mobility. Also the presence of Ag weakens the Ce-O bond and furthermore promotes the exchange between lattice oxygen and adsorbed oxygen. Stability tests of Ag/CeO<sub>2</sub> showed no sign of deactivation even after 36 h of time on stream. Besides that, the catalyst also showed higher selectivity towards acetaldehyde even at higher temperature. Ag/CeO<sub>2</sub> catalyst was found to outperform the reported catalyst systems.

A Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> mixed oxide catalyst, prepared by co precipitation method, was also tested in the oxidation of bioethanol. Remarkable effects of Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> and Au supported Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> was observed in the bioethanol oxidation. The results obtained from catalyst characterization indicated that solid solution of Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> mixed oxide was formed. Role of oxygen in bioethanol oxidation was inevitable and Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> mixed oxides are known for their higher thermal stability and high oxygen mobility. In this work, oxygen storage capacity (OSC) of the catalysts was found to enhance the conversion of bioethanol. This could be due to incorporation of zirconium to ceria framework which improved OSC of catalysts. OSC of Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> mixed oxides further increased upon impregnation of Au as Au reduced supports.

### **Brief description on the state of the art of research topic:**

Biomass is one of the most significant, clean and environmentally friendly source from renewable energy. Worldwide, biomass is the fourth largest energy resources after coal, oil and gas, estimated to be about 16 % of global primary energy[1]. Biomass is primary alternative compared to expensive fossil oil resources and also a source of sustainable energy to curtail green-house gas emissions. It is possible to convert biomass derived chemicals to essentially high-value commodity chemicals currently available from fossil resources. It is more advantageous to produce some chemicals more easily in fewer steps from biomass derived feedstocks than from fossil resources.

Particularly, the oxidation of alcohols to carbonyl compounds is a fundamental transformation in organic chemistry as these compounds are widely used as intermediates for fine chemicals[2]. For oxidation of alcohols conventionally inorganic oxidants, such as permanganate and dichromate are used. However, they are known to toxic in nature and produce a large amount of

waste. The separation and disposal of this waste material increases cost in chemical processes. Hence, from both economic and environmental benign, there is a need for greener and more efficient methods that will replace traditional toxic oxidants. In this regards, catalytic oxidation of alcohols with air has attracted significant attention as a “green” chemistry reaction in catalysis[3].Molecular oxygen is a nonpoisonous and inexpensive oxidant for the oxidative transformation of alcohols.

Bioethanol can be easily produced from agricultural products by fermentation and typically contains about 8-10 vol % of ethanol[4]. The anhydrous process of this ethanol is energy intensive. The worldwide production of ethanol was 14.1 billion gallons in 2007[5], which is expected to reach around 30 billion gallons in 2016[6]. In compared to global demand of commercial chemicals like acetaldehyde, acetic acid, ethyl acetate, hydrogen, 1-3 butadiene, butanol etc., sufficient amount of bioethanol is produced to have a significant impact, even if only part of it is used as a chemical feedstock rather than a fuel additive.

Ethanol oxidation to value added products has gain significant interest in last decades. Christensen and co-workers[3] were first to investigated ethanol oxidation with molecular oxygen on noble metal catalysts in water. The catalytic performance of Pd, Pt, and Au was compared by depositing them on the same support,  $MgAl_2O_4$ . The results showed that all catalysts had the same catalytic activity, but only difference was that Au catalyst showed a high selectivity to acetic acid. Tembe et al.[7] extended studied of Au supported on three oxide supports,  $TiO_2$ ,  $Al_2O_3$  and  $ZnO$ . The result revealed that  $Au/ZnO$  showed catalytic activity equivalent to that of  $Au/TiO_2$ . While  $Al_2O_3$  supported Au showed a somewhat poor performance in ethanol oxidation and evident leaching of Au into solution. On the other hand Sun et al.[8] have discussed the effect of size of Au nanoparticles for ethanol conversion supported on  $SiO_2$ . Au NPs with an average diameter of 5 nm showed higher activity than Au NPs with 3 and 10 nm. Muhler et al.[9] found that influence of pressure on reaction condition was negligible as long as there was an excess of oxygen. The selectivity to acetic acid was high at high mass of catalyst and less mass led to higher amount of acetaldehyde. A higher ratio of  $n(O_2)/n(ethanol)$  leads to higher conversion, while the selectivity to acetic acid is limited, presumably due to a higher tendency to total oxidation. Letichevsky et al.[10] employed  $PdO/Al_2O_3$  and  $PdO/m-ZrO_2$  catalysts for selective oxidation of ethanol to acetic acid and found that  $PdO/m-ZrO_2$  catalyst was

more active than PdO/Al<sub>2</sub>O<sub>3</sub> due to the adsorption and spillover of the oxygenate species from m-ZrO<sub>2</sub> to PdO and vice-versa. Long et al.[11] used Pt/Fe<sub>3</sub>O<sub>4</sub>@X (X = PPy, C or SiO<sub>2</sub>) catalysts for selective oxidation of ethanol to acetic acid where Pt/Fe<sub>3</sub>O<sub>4</sub>@PPY exhibited higher catalytic activity in comparison with other two catalyst.

Various researchers have studied the gas phase oxidation of ethanol over various catalysts like, molybdenum based catalyst, copper-chromium supported catalyst, Palladium and Platinum based catalyst, vanadium catalysts, multi component oxides catalyst, gold based catalyst, silver based catalyst and bimetallic catalyst etc. Among this catalyst, molybdenum based[12,13] and copper-supported catalyst[14,15] are highly selective for acetaldehyde and ethyl acetate rather than acetic acid While the Mo<sub>0.61</sub>V<sub>0.31</sub>Nb<sub>0.08</sub>O<sub>x</sub>[16] and MoVNbTe[17] catalyst are much more selective to acetic acid. However Au based catalysts [18–20] was found to be most promising for aerobic oxidation of ethanol mainly due to good stability against metal oxidation.

Looking to reported literature, higher ethanol concentration and high O<sub>2</sub>/ethanol molar ratio were employed for ethanol oxidation. Hence despite the extensive research on ethanol oxidation in both liquid and gas phase reaction still there is a research gap and the present work addresses the same. With higher output of bioethanol (8 - 10 wt %), present study focuses on bioethanol oxidation to value added products with O<sub>2</sub>/ethanol molar ratio equal to unity. The present work also demonstrated higher catalytic activity and stability of the used catalysts. Also the catalysts used in this work exhibited higher selectivity towards acetaldehyde which a valuable chemical to fine chemistry.

### **Definition of the problem:**

The present doctoral work addresses the following problems:

- 1) To achieve higher conversion for bioethanol and higher selectivity for the products.
- 2) To evaluate effect of the performance of noble metals over various supports for bioethanol oxidation.

3) To study the effect of process parameters like temperature, O<sub>2</sub> pressure, ethanol concentration and time on stream studies.

It systematically studies each aspect of the problem to suggest the solution.

## **Objective and scope of work:**

### **Objectives:**

1. To undertake the performance of noble metals over different supports employed and explores the metal support interaction to achieve high conversion and high products selectivity for bioethanol oxidation.
2. To Study the effect of time on stream for the stability of catalyst at the reaction condition and its usefulness for the reaction.
3. To carry out effects various affecting parameters like temperature, pressure, O<sub>2</sub>/ethanol molar ratio etc.
4. To demonstrate the effect of mixed oxides and evaluate importance of its properties to enhance the rate of bioethanol conversion.

**Scope of work:** The present doctoral work addresses each objective as mentioned above and studies the Au and Ag noble metal supported on SiO<sub>2</sub>, CeO<sub>2</sub> and ZrO<sub>2</sub> to investigate the effect of noble metal type, metal oxide type and metal/oxide loading on the conversion as a function of temperature for the oxidation of bioethanol in air. It also demonstrates that strengthen interaction between Ag and CeO<sub>2</sub> resulted into higher bioethanol conversion and also show no sign of deactivation after long run. It studied the effect of Ce/Zr ratio in the performance of Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> and Au/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> catalysts for this reaction and found the way to increase the oxygen storage capacity of the supports which enhanced the bioethanol conversion.

### **Original contribution by the thesis:**

The original contribution is manifested by international peer-reviewed paper. One paper has already accepted for publication as mentioned below. Second paper of the work has been submitted and it is under review. Third paper is ready for submission.

1. Paresh H. Rana, Parimal A. Parikh, Bioethanol Valorization *via* its Gas Phase Oxidation over Au and/or Ag supported on various Oxides, Accepted for publication in Journal of Industrial and Engineering chemistry, doi:10.1016/j.jiec.2016.11.037, (**IMPACT FACTOR: 4.179**)

### **Papers submitted and to be submitted to International Peer-Reviewed Journal**

1. Paresh H. Rana, Parimal A. Parikh, Bioethanol Selective Oxidation to Acetaldehyde over Ag-CeO<sub>2</sub>: Exploiting Support Lattice Defects under review in New journal of chemistry.
2. Paresh H. Rana, Parimal A. Parikh, Effect of Ce/Zr ratio in the performance of Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> and Au/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> for bioethanol oxidation is to be submitted to ACS catalysis.

### **Presentation at International Conference**

1. Paresh H. Rana, Parimal A. Parikh, Gas phase oxidation of aqueous ethanol using Au supported cerium oxide catalyst. Sustainable Chemistry & Engineering sponsored by American chemical society & Royal society of chemistry, 8-9<sup>th</sup>, October, 2015.
2. Paresh H. Rana, Parimal A. Parikh, Review: Selective Oxidation of bioethanol to Produce Acetic acid. CHEMCOM 2013, 26-30<sup>th</sup>, December, 2013.

### **Methodology of research, results/comparison**

**Methodology of research:** The methodology involved the experimental as well as theoretical calculation work. Bioethanol oxidation was carried out in both liquid and gas phase reaction. Wet impregnation method was used to immobilize noble metals on the various supports in the hunt of higher bioethanol conversion and high selectivity towards products. For liquid phase reaction theoretical calculation was done to find out the activity coefficient by UNIFAC method to make sure the reactant must be in liquid phase at the reaction conditions. Calculated data of activity coefficient were validated by data available for this system as they were in close conformity.



Gas phase oxidation of bioethanol as a function of reaction temperature was measured over Au, Ag and Au-Ag supported on SiO<sub>2</sub>, CeO<sub>2</sub> and ZrO<sub>2</sub>. Prior to entering the reactor, reactant (bioethanol, 10 wt %) was vaporized in a pre heater and mixed with synthetic air (21 % O<sub>2</sub>, 79% N<sub>2</sub>). The mixture passed through catalyst bed for 1 h before monitoring reaction product. Temperature inside the reactor was measured by an internally positioned thermocouple placed on the catalyst bed. Reaction products were analyzed by a gas chromatography with both a Flame ionization detector and thermal conductivity detector.

All the prepared catalysts were fully characterized by Scanning electron microscopy, Transmission electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, Energy-dispersive X-ray spectroscopy and Thermo gravimetric analysis. To evaluate the performance of the catalytic systems, conversions of ethanol ( $X_{\text{ethanol}}$ , %) and selectivity to products ( $S_i$ ) is defined as follow: ethanol conversion ( $X_A$ ) was calculated from ratio of the amount of ethanol converted and initial amount of ethanol. Selectivities to the reaction products such as acetaldehyde, ethyl acetate and acetic acid ( $S_i$ ) were calculated from the amount of the products formed divided by the amount of ethanol converted.

### **Outcomes of research work:**

- Initially Liquid phase reaction of bioethanol oxidation was carried out as different temperature, pressure, O<sub>2</sub>/ethanol molar ratio and time using Au and Ag supported on HZSM 5, HY and H $\beta$ . The obtained results on Ag/HZSM5 showed that ethanol conversion was less than 2 % at 150, 175 and 200°C at 4 and 8 h respectively. Catalyst displayed higher selectivity towards acetaldehyde and it was more than 78%, while acetic acid selectivity was around 22 %.
- We examined effect of exchange of alkali (Na) with H of Ag/HZSM5 in bioethanol oxidation. No change has occurred on bioethanol conversion and selectivity towards products. It remained about 2% and 80% bioethanol conversion and acetaldehyde selectivity respectively.
- As expected results are not obtained with Ag/HZSM5 and Ag/Na-HZSM5, we studied Au supported on HZSM5, HY and H $\beta$  at 200°C and 22 atm. However no drastic change has attended with these catalysts also. Bioethanol conversion is 8%, 10 % and 10 % for

Au/ HZSM5, Au/HY and Au/H $\beta$  respectively at the end of 6 h which was increased to 10 %, 15% and 17 % for Au/ HZSM5, Au/HY and Au/H $\beta$  respectively at the end of 24 h.

- But the products selectivity depended on the nature of support. Au/H $\beta$  gave 63%, 10% and 27% selectivities towards acetaldehyde, acetic acid and acetone respectively. Au/HY showed 14%, 33% and 53% selectivities towards acetaldehyde, acetic acid and acetone respectively. However Au/HZMS5 ratified 12%, 18% and 60% selectivities towards acetaldehyde, acetic acid and acetone respectively.
- As achieved higher conversion with Au/H $\beta$  in compared to Au/ HZSM5 and Au/HY, we further carried out bioethanol oxidation with Au/Na- H $\beta$ . Presence of Alkali didn't positively effect on conversion of bioethanol, while the selectivity was remaining almost constant.
- Ag/ZrO<sub>2</sub> has also been studied for liquid phase bioethanol oxidation with 10 wt % ethanol for 24 h and obtained bioethanol conversion was around 5 % and 90 % selectivity for acetic acid. To further studied the effect of reactant concentration, reaction was performed with 30 wt % for 6 and 24 h respectively. At 6 h conversion is 2 % and at end of 24 h, it is 30 % with 95 % selectivity towards acetic acid.
- An impressive result has not been obtained in liquid phase reaction may be due to the presence of water and lower Si/Al ratio. Zeolites are hydrophilic in nature at lower Si/Al ratio. Also due to hydrophilic in nature of zeolites water may block the active sites.
- Hence we decided to perform bioethanol oxidation in continuous mode operation with metal oxide as such SiO<sub>2</sub>, CeO<sub>2</sub> and ZrO<sub>2</sub>.
- We prepared Au, Ag and Au – Ag supported on SiO<sub>2</sub>, CeO<sub>2</sub> and ZrO<sub>2</sub> and prepared catalysts characterized by various techniques.
- Au supported on SiO<sub>2</sub> and CeO<sub>2</sub> exhibited 18% and 34% ethanol conversion and 70% and 83% acetaldehyde selectivity respectively. Au, Ag and Au - Ag nano particles supported on ZrO<sub>2</sub> shows 36, 27 and 23 % conversion of ethanol, respectively with more than 75 % selectivity towards acetaldehyde.
- Over all ethanol conversion followed the order: **Au/ZrO<sub>2</sub> > Au/CeO<sub>2</sub> > Ag/ZrO<sub>2</sub> > Au-Ag/ZrO<sub>2</sub> > Au/SiO<sub>2</sub>** , while acetaldehyde selectivity showed the trend: **Au/CeO<sub>2</sub> > Ag/ZrO<sub>2</sub> > Au-Ag/ZrO<sub>2</sub> > Au/ZrO<sub>2</sub> > Au/SiO<sub>2</sub>**

- Higher catalytic activity for Au/ZrO<sub>2</sub> can be due to the partial reduction of Zr surface from Zr<sup>4+</sup> to Zr<sup>3+</sup> which created oxygen deficiencies by Au on ZrO<sub>2</sub> surface. This oxygen actively participated in the catalytic activity and enhanced the overall bioethanol conversion.
- Au/SiO<sub>2</sub> showed the least bioethanol conversion among the used catalyst in this work which was due to the inert nature of SiO<sub>2</sub> support. With increase in temperature, selectivity towards acetic acid was increased at cost of decreased acetaldehyde selectivity.
- Ag/ZrO<sub>2</sub> and Au-Ag/ZrO<sub>2</sub> exhibited lower conversion was due to facile oxidation of Ag<sup>0</sup> to Ag<sup>+</sup> and also may be due weaker interaction between Ag and ZrO<sub>2</sub> than other metals.
- In case of Au/CeO<sub>2</sub>, CeO<sub>2</sub> was able to provide activate oxygen with concurrent creation of oxygen vacancies which could further played a role of activating reactant oxygen molecules reaching from the gas phase.
- Later on Ag/CeO<sub>2</sub> was employed for this reaction and obtained 38 % ethanol conversion with more than 85 % acetaldehyde selectivity.
- The higher bioethanol conversion in case of Ag/CeO<sub>2</sub> clearly indicated the stronger interaction of Ag with CeO<sub>2</sub> in comparison with Ag/ZrO<sub>2</sub>. High catalytical activity of Ag/CeO<sub>2</sub> due to the insertion of Ag into the lattice of CeO<sub>2</sub>.
- The cooperation of Ag<sup>δ+</sup> acid sites and base sites of ceria on the Ag - CeO<sub>2</sub> interface has imparted high activity to the catalyst in bioethanol oxidation. Also presence of Ag improved the OSC of CeO<sub>2</sub>, which may accelerate the activation of lattice oxygen in the reaction.
- Achieving comparable conversion with Au/ZrO<sub>2</sub> and Au/CeO<sub>2</sub>, we further decided to carry out bioethanol oxidation with mixed oxides of Ce<sub>x</sub>Ze<sub>1-x</sub>O<sub>2</sub>. We used co precipitation method for synthesis of Ce<sub>x</sub>Ze<sub>1-x</sub>O<sub>2</sub> and wet impregnation method was employed for anchoring of Au.
- XRD results showed that characteristic peak around 2θ = 28.5° ( JCPDS-34-0394) of Ce is shifted to 28.62° for Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> to 29.10° for Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> and 29.5° for Ce<sub>0.25</sub>Zr<sub>0.75</sub>O<sub>2</sub>. This is because of contraction of the lattice cell parameter by the insertion of ZrO<sub>2</sub> into the CeO<sub>2</sub> and has taken as formation of Ce - Zr solid solutions.

- Incorporation of Zr to Ce frame work led to enhance the OSC of the as prepared catalysts. The OSC order is as follow :  $Ce_{0.25}Zr_{0.75}O_2 > Ce_{0.5}Zr_{0.5}O_2 > Ce_{0.75}Zr_{0.25}O_2$  and Au further reduced surface of  $Ce_xZr_{1-x}O_2$  which led to increase oxygen mobility in order of:  $Au/Ce_{0.25}Zr_{0.75}O_2 > Au/Ce_{0.5}Zr_{0.5}O_2 > Au/Ce_{0.75}Zr_{0.25}O_2$ . This trend indicated that surface is more reduced at higher Zr content which implies that oxygen availability at surface is increased.
- Bioethanol conversion increased with increase of Zr content in Ce framework and vice versa.
- In comparison to Au supported  $ZrO_2$  and  $CeO_2$ ,  $Au/Ce_xZr_{1-x}O_2$  showed better performance for bioethanol oxidation due to higher oxygen storage capacity. Also it exhibited higher selectivity towards acetaldehyde which is a valuable chemical for fine chemical industry.

Bioethanol (derived from biomass) has potential to be a sustainable feedstock. This work demonstrated that bioethanol (10 wt %) converted into valuable chemicals with good conversion and high product selectivity using air as oxidant. This work also highlighted the important of supports and metals in bioethanol conversion and product selectivities. Used catalysts are also exhibited high catalytic stability (40 h) at the reaction condition.

### Achievements with respect to objectives:

Objective	Published Paper for the objective
❖ To undertake the performance of noble metals over different supports employed to achieve high conversion and high products selectivity for bioethanol oxidation.	Paresh H. Rana, Parimal A. Parikh, Bioethanol Valorization <i>via</i> its Gas Phase Oxidation over Au and/or Ag supported on various Oxides, Accepted for publication in Journal of Industrial and Engineering chemistry, doi:10.1016/j.jiec.2016.11.037
❖ To explore the metal support interaction and the effect of time on stream for the stability of catalyst at the reaction condition and its usefulness for the reaction.	Paresh H. Rana, Parimal A. Parikh, Bioethanol Selective Oxidation to Acetaldehyde over Ag-CeO <sub>2</sub> : Exploiting Support Lattice Defects under review in

❖ To carry out effects various affecting parameters like temperature and WHSV etc.	New Journal of Chemistry.
❖ To demonstrate the effect of mixed oxides and evaluate importance of its properties to enhance the rate of bioethanol conversion.	Paresh H. Rana, Parimal A. Parikh, Effect of Ce/Zr ratio in the performance of $Ce_xZr_{1-x}O_2$ and Au/ $Ce_xZr_{1-x}O_2$ for bioethanol oxidation is to be submitted to ACS catalysis.

**Conclusion:** All the mentioned objectives are full filled and one peer reviewed, international paper with impact factors has been published. Second research paper has been submitted to New journal of chemistry and currently it is under review. Third research paper of this work is to be submitted to peer reviewed, International journal. Thus, the synopsis of doctoral work is hereby, submitted to Gujarat Technological University.

### **Copies of papers published and a List of all publications arising from the thesis:**

Copies of the papers published are attached herewith.

1. Paresh H. Rana, Parimal A. Parikh, Bioethanol Valorization *via* its Gas Phase Oxidation over Au and/or Ag supported on various Oxides, Accepted for publication in Journal of Industrial and Engineering chemistry, doi:10.1016/j.jiec.2016.11.037, (**IMPACT FACTOR: 4.179**)

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2. Paresh H. Rana, Parimal A. Parikh, Bioethanol Selective Oxidation to Acetaldehyde over Ag-CeO<sub>2</sub>: Exploiting Support Lattice Defects under review in New Journal of Chemistry.

3. Paresh H. Rana, Parimal A. Parikh, Effect of Ce/Zr ratio in the performance of  $Ce_xZr_{1-x}O_2$  and Au/ $Ce_xZr_{1-x}O_2$  for bioethanol oxidation is to be submitted to ACS catalysis.

### Presentation at International Conference

4. Paresh H. Rana, Parimal A. Parikh, Gas phase oxidation of aqueous ethanol using Au supported cerium oxide catalyst. Sustainable Chemistry & Engineering sponsored by American chemical society & Royal society of chemistry, 8-9<sup>th</sup>, October, 2015.
5. Paresh H. Rana, Parimal A. Parikh, Review: Selective Oxidation of bioethanol to Produce Acetic acid. CHEMCOM 2013, 26-30<sup>th</sup>, December, 2013.

### Patents – Nil

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