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Rational Synthesis to Optimize Ruthenium-Based Biomass Conversion Catalysts

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RATIONAL SYNTHESIS TO OPTIMIZE RUTHENIUM-BASED BIOMASS CONVERSION CATALYSTS

by

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DEDICATION

This work is dedicated to my beautiful wife, Yinghao Dong, who gives me a lovely family, always encourages and supports me, even at low points of my life, still stands on my side, and gives me strength to achieve anything that I pursue….

Be grateful, Be positive, Be persistent, Be humble…………
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ABSTRACT

With worldwide petroleum resources dwindling and greenhouse gas emissions rising, it is urgent to find renewable replacements for petroleum-derived products. A biomass-derived chemical with high potential as a platform intermediate, γ-valerolactone (GVL) can be readily synthesized by hydrogenation of levulinic acid (LA), itself a common biomass intermediate, using supported Ru catalysts. Overall, vapor phase hydrogenation is more energy sensitive as the higher boiling point of LA (~245°C) and requires a high energy input, comparable to liquid phase hydrogenation, which is more economical. To date the literature on many novel biomass conversion processes such as the hydrogenation of LA to GVL has focused more on the process and less on the catalyst. Therefore, many efforts have been given to develop the novel catalysts, to improve the activity, selectivity and stability for the hydrogenation of LA to GVL.

The purpose of this dissertation is to systematically study the effects of nanoparticle size, support, dopants including alkali metal, alkaline earth metal and Rhenium on ruthenium activity on the levulinic acid (LA) hydrogenation to γ-valerolactone (GVL), which could provides insight into optimizing commercial process for hydrogenation of LA to GVL by studying the structure-function relationships. The reactions were evaluated in a stainless steel EZE-Seal batch reactor with 100ml capacity. The first part of this work is to derive fundamental synthesis-structure-function
relationships of Ru catalysts for LA hydrogenation using carbon and alumina supported
Ru nanoparticles which have been synthesized in a rational, repeatable, scalable way. We have demonstrated that the method of strong electrostatic adsorption (SEA) yields well dispersed, homogeneously distributed Ru particles with tight particle size distributions over both types of supports. SEA synthesis of well dispersed nanoparticles results in higher activity than commercial Ru catalysts with higher Ru loadings. The dramatic, beneficial effect of potassium doping is reported for the first time. The carbon support yields higher inherent activity than alumina. Activity as a function of particle size appears to go through a maximum at about 1.5 nm for both supports and suggests hydrogenation of LA is structure sensitive on Ru particle size. Catalyst deactivation after 24 h occurs to significant extents (8 – 58%) mainly by nanoparticle sintering, but also by minor amounts of K loss in K-doped samples.

Secondly, a systematic study with alkali and alkaline earth elements was carried out to verify the origin of the promotion effect and the optimal ratio of dopant to Ru. Series of catalysts were prepared by impregnating various amounts of alkali onto 2% Ru/alumina (itself synthesized with high Ru dispersion by strong electrostatic adsorption) and were evaluated for LA hydrogenation. With the ratio of dopant to Ru constant, strong promotional effects of alkali and alkaline earth metals on the activity in terms of turnover frequency (TOF) were observed in the following order Na⁺<K⁺<Cs⁺ and Ba²⁺<Mg²⁺<Ca²⁺. To investigate the origin of the promotional effect, catalysts were characterized by H₂ chemisorption, X-ray photoelectron spectroscopy (XPS), CO-FTIR spectroscopy and Pyridine-FTIR. Characterization suggests that the promotion by the alkali metals is caused by electron donation and acidity effect whereas for the alkaline
earths, the promotion appears to stem from geometric and acidity effects. Furthermore, the effect of decomposition temperature of alkali and alkaline earth salts on Ru activity was investigated using potassium nitrate as a representative salt. The results suggest that higher reduction temperature (400°C) help redistribute the promoter on the metal surface and form more KOH, the active chemical state of potassium, leading to an increase of Ru activity.

Furthermore, we report the rational synthesis of bimetallic RuRe catalysts supported on VXC-72R carbon and γ-Al₂O₃ comparing co-strong electrostatic adsorption (co-SEA) to a more traditional method, co-dry impregnation (co-DI). We have found that the bimetallic catalyst exhibits an optimum activity with a Ru:Re atomic ratio of 2:1. In order to establish a correlation between catalytic properties and structure, selected catalysts were characterized by TPR-H₂, XRD, STEM/EDXS elemental mapping, XPS and CO-FTIR. The formation of a RuRe alloy along with segregated ReOₓ particles suggests that the geometric effect on activity promotion is more significant. XRD data of post reaction bimetallic catalysts indicate particle sintering and separated two metal particles for catalysts prepared by co-DI, but not for catalysts prepared by co-SEA.
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LIST OF ABBREVIATIONS

AAS..........................................................Atomic Absorption Spectroscopy
AM..........................................................Alkali Metal
AEM..........................................................Alkaline Earth Metal
BET..........................................................Brunauer-Emmett-Teller
BES..........................................................Binding Energy Shift
CPA..........................................................Chlorplatinic Acid
Cox..........................................................Oxidized Carbon
DI..........................................................Dry Impregnation
DFT..........................................................Density Functional Theory
Ea..........................................................Activation Energy
EXDS......................................................Energy Dispersive X-ray Spectroscopy
FID..........................................................Flame Ionization Detector
FTIR.......................................................Fourier Transform Infrared
FWHM.....................................................Full width at half maximum
Γ..........................................................Adsorption Density or Surface Coverage [μmol/m²]
GC..........................................................Gas Chromatography
GVL..........................................................γ-Valerolactone
HAADF....................................................High-angle Annular Dark-field
HDO..........................................................Hydrodeoxygenation
ID……………………………………………………………….………….Inside Diameter
ICP-AES………………………………………………………….Inductively Coupled Plasma-Atomic Emission Spectrometry
IW…………………………………………………………………Incipient Wetness
KIE………………………………………………………………..Kinetic Isotope Effect
LA……………………………………………………………..Levulinic Acid
PTA………………………………………………………………Platinum Tetraammine
PZC………………………………………………………………Point of Zero Charge
SEA…………………………………………………………….Strong Electrostatic Adsorption
SL…………………………………………………………….[m²/L]Surface Loading
STEM………………………………………………………..Scanning Transmission Electron Microscopy
TOF……………………………………………………………..Turnover Frequency
T……………………………………………………………….Temperature [°C]
TPR…………………………………………………………..Temperature Programmed Reduction
WI……………………………………………………………Wet Impregnation
XPS………………………………………………………………X-ray Photoelectron Spectroscopy
XRD………………………………………………………………X-ray Diffraction
CHAPTER 1
INTRODUCTION

1.1. BIOMASS CONVERSION OVERVIEW

With the worldwide petroleum resources dwindling, it is urgent to find renewable replacements for petroleum-derived products to accelerate the transition to renewable fuels to adapt to the increasing demand of our society. Several recent reports have underscored that biomass feedstocks are heavily used for the green catalytic conversion to renewable fuels and chemicals \(^1,2\).

In light of a report submitted to the US government in 2002 “The Roadmap for Biomass Technologies”, it has been predicted that by 2030, 20% of transportation fuel and 25% of value added chemicals will be produced from lignocellulosic biomass which is the only carbon source capable of supplanting fossil fuels \(^3\). As an alternative carbon source, lignocellulosic biomass has several advantages over petroleum. First of all, lignocellulosic biomass is invaluable and has widespread worldwide availability. It is reported that 1.3 billion tons of dry biomass can be produced per year in United States alone. Furthermore, the carbon source in lignocellulosic biomass is renewable and is converted into many valued added chemicals and fuels, such as reducing sugars, furfural, various carboxylic acids including levulinic acid (LA), lactic acids, etc. There are three main components of lignocellulosic biomass: cellulose (40-80wt %), hemicelluloses (15-30wt %) and lignin (10-25wt %) \(^4,5\). Structures of those components are shown in Figure
1.1. Cellulose is a crystalline glucose polymer unlike starch and consists of a linear polysaccharide with \( \beta-1,4 \) linkages of D-glucopyranose monomer, which occurs in association with hemicelluloses in the cell walls. There are about 10,000 and 15,000 glucopyranose monomer units in wood and cotton, respectively. Cellulose could be broken into glucose with complete acid hydrolysis. However, partial acid hydrolysis will result in the productions of cellobiose (glucose dimer), cellotriose (glucose trimer), and cellotetrose (glucose tetramer) the main component is xylose monomer unit in hemicelluloses, which is a complex amorphous sugar polymer because of its branched nature and is relatively easy to hydrolyze to its monomer sugars comparable to cellulose. Hemicelluloses consist of five different sugars, which are five-carbon sugars (xylose and arabinose) and six-carbon sugars (glactose, glucose and mannose). Lignin is also often associated with cellulose and hemicelluloses compounds in the cell walls of woody biomass and is typically composed of highly branched, substituted, mononuclear aromatic polymers. Lignin is an irregular polymer, which is formed by an enzyme-initiated free-radical polymerization of the alcohol precursors. Before converting biomass into biofuels, a variety of physical and chemical methods have been reported in order to overcome lignocellulose recalcitrance, where the approaches are commonly combined with pretreatment process, such as filtration, solvent extraction and distillation, those are necessary to employed to weaken the lignin protection and increase the susceptibility of crystalline cellulose to degradation, subsequently depolymerize cellulose and hemicelluloses by hydrolysis, thus, so that the sugars are isolated from the lignin fraction.
Figure 1.1 Structure of three main components in biomass (Cellulose, Hemicellulose, Lignin)\textsuperscript{4}, with permission.
Various approaches can be taken to the conversion of biomass into biofuels/liquid transportation fuel. The main pathways are presented in Figure 1.2, where three different processes or combination of them were utilized to achieve the goal of conversion to desired fuels, thermal routes (hydrolysis), biological routes (fermentation) and catalytic routes (catalysis). Non-food lignocelluloses feed stocks, such as forest wastes, agricultural residues like municipal paper wasters and corn stover, are usually with intrinsic recalcitrance and also with a high degree of chemical and structural complexity, therefore, the conversion of lignocelluloses is more complicate and employ a combination of different processes, in comparable to starch/sugars and lipids. In this dissertation, we will mainly discuss the pathways where lignocelluloses were converted to Jet fuels, Diesel and Gasoline. Converting Lignocelluloses into liquid hydrocarbon transportation fuels is often conducted by three major routes showing in Figure 1.2, which are gasification, pyrolysis and pretreatment-hydrolysis. However, because of the complexity of lignocelluloses, the first step is to transform it into simpler fractions that could follow by more easily converted to a variety of valuable chemicals, which is similar to biorefinery process in conventional petroleum refineries. Basically, lignocelluloses are converted to gaseous and liquid fractions, which could follow by upgrading to liquid hydrocarbon fuels during these three major processes. First process is gasification, also known as biomass to liquids (BTL), which converts solid biomass to synthesis gas (syngas) consisting of valuable mixture of CO and H₂, subsequently Fischer-Tropsch reaction was utilized to covert the mixture to liquid hydrocarbon fuels. The second one is pyrolysis, which could transform lignocellulosic biomass into bio-oil, subsequently various catalytic processes were employed to upgrade bio-oil to hydrocarbon fuels. The
last one is pretreatment-hydrolysis, which allows achieving the aqueous solution of C_5 and C_6 sugars that can be subsequently aqueous solution processing to targeted liquid hydrocarbon fuels. Liquid hydrocarbon fuels are normally unfunctionalized compounds. A number of reactions involving oxygen removal, such as hydrogenation, dehydration, and hydrogenolysis, combining with C-C coupling, such as aldol condensation, ketonization and oligomerization, are required for converting biomass derivatives into liquid hydrocarbon transportation as biomass derivatives, such as sugar, which derived from glucose, are molecules with –OH, -C=O and –COOH groups and maximum number of carbon atoms limited to six. The liquid hydrocarbon transportation fuels also could be synthesized by biological process, which includes anaerobic digestion for biogas production and fermentation for alcohol. The advantages of this process are: low capital cost, low energy requirement, no chemical requirement, and mild environments condition. However, the limitation is that the rate of hydrolysis is very slow. For the process efficiency, thermal conversion (pyrolysis) had 35% energy loss versus 45% energy loss for biological conversion. Compared to thermal and biological processes, catalytic process is required less energy input, and also is more controllable process for the desired products. Therefore, catalytic conversion of biomass has received increased attention in recent years. As we know, the catalytic process could be optimized by reaction process and catalysts. Catalysts play a significant role in improving reaction rates and selectivity to the desired products. The development and optimization of catalysts are crucial for the potential commercialized process for biomass conversion.
Figure 1.2 Route for the conversion of biomass into liquid transportation fuels. Red arrows refer to thermal routes, green arrows refer to biological routes, and blue arrow refer to catalytic routes \(^5\), with permission.
Levulinic acid (LA) is inexpensive and can be obtained through the decomposition of cellulose feedstock: glucose. It is a well-known product of hexose acid hydrolysis and its chemical properties were reported in the literature. In addition, it is a low molecular weight carboxylic acid with a ketonic carbonyl group. Therefore, it is used as the starting material for the production of many useful C₅-based compounds such as GVL, 2-methyltetrahydrofuran (MTHF) and other derivatives.

The production of LA could be achieved by catalytic routes for the aqueous-phase conversion of sugars and derivatives, where LA can be further upgraded to liquid hydrocarbon fuels. The main aqueous-phase routes are showing in Figure 1.3, hydroxymethylfurfural (HMF) and furfural are important compounds obtained from chemical dehydration of biomass-derived sugars and can be used as platform chemicals for the production of liquid hydrocarbon fuels by oxygen removal reactions, such as dehydration, hydrogenation and aldol-condensation reactions. LA can be obtained from sugars/HMF through chemical dehydration processes, followed by being hydrogenated to form γ-Valerolactone (GVL). Those two important biomass derivatives could be used to produce liquid hydrocarbon fuels through catalytic processes. It is conventional that LA was produced by cellulose deconstruction using dilute of mineral acids. The challenge for the commercializing the process is to separate the mineral acid from the reaction product, which will cause a negative impact on the production of GVL, thus neutralization, separation, and purification were required. Recently, Dumesic et al.⁷,⁸ have developed a streamlined process for making and extracting LA from aqueous solutions. Typically, LA is produced by deconstruction of biomass via acid catalysts in aqueous solutions, where LA is extracted by using alkylphenol solvents (insoluble in
water), subsequently, can be separated from the solvent by distillation. By doing so, firstly, it avoids the costly evaporation steps and the use of expensive catalysts. Secondly, Alkylphenols allows catalytic conversion of intermediates without purification. Thirdly, water and acid catalysts could be recycled for further biomass deconstruction as Alkylphenols solvents do not extract water or acids catalysts. Lastly and most importantly, it does not need the evaporation and reduced the energy demands since water does not need to be removed from reaction products. However, additional steps such as recovering and recycling of the solvent and purifying products (distillation) are introduced into the overall process. The developments of the processes have been under study to emphasize on commercialization.

Figure 1.3 Main catalytic routes for the aqueous-phase conversion of sugars and derivatives into liquid hydrocarbon transportation fuels \(^5\), with permission.
1.2. LA HYDROGENATION TO GVL OVERVIEW

As the one of major products of plant biomass, γ-valerolactone (GVL) has attracted considerable attention because it is renewable, safe to store, and could be used as (1) precursor of gasoline and diesel fuels, such as C_8-C_{16} alkenes, C_9-C_{18} alkanes, C_9 alkanes, valeric esters, or butane isomers, (2) food additives, green solvents, mixed with conventional gasoline in a capacity similar to ethanol and (3) as an intermediate in the synthesis of many value added chemicals, such as, 1,4 pentanediol, α-methylene γ-valerolactone and pentenoate esters \(^9\text{--}^{11}\). The synthesis of γ-valerolactone (GVL) commonly consists of the hydrogenation of levulinic acid (LA) using either using homogeneous or heterogeneous catalysis \(^12\). Homogeneous Ru catalysts have been confined in an aqueous phase in order to recycle the catalyst effectively. However, only one catalyst recycle cycle was used, which leads to a remarkable decrease in the conversion of LA. Recently, the manufacturing of GVL has mainly relied on the use heterogeneous catalysts\(^10\). \(^13\). Now, the question has moved to the pursuit of the best metal support catalyst in order to improve the conversion, selectivity and stability.

Ru has been proven to be the most active metal for hydrogenation of aliphatic carbonyl compounds \(^12, 14\). Consequently, the production of GVL relies on the use Ru based heterogeneous catalysts. The large metal weight loading required for commercial production is cost prohibitive as Ru is quite expensive, increased weight loadings lead to higher capital costs. It is then imperative to reduce the Ru weight loading and improve the catalyst activity and efficiency, either by optimizing the metal dispersion
or introducing a second metal to make bimetallic particles that can lead to a bimetallic effect that can increase selectivity and activity.

The reaction pathway for hydrogenation of LA to GVL has been proposed and was showing in Figure 1.4 by several groups\textsuperscript{15, 16}. In Pathway 1, 4-hydroxypentanoic acid (HPA) was formed by the hydrogenation of the ketone group in LA, followed by ring closure to form the thermodynamically favorable valerolactone (GVL) after dehydration step. In pathway 2, LA was dehydrated to form angelicalactones (AL), which is endothermic reaction. Subsequently, AL was rapidly hydrogenated with the presence of Ru catalysts and H\textsubscript{2}.

![Pathway diagram](image)

**Pathway 1**

**Pathway 2**

Figure 1.4 Schematic diagram of LA hydrogenation to GVL reaction pathway, with permission.
1.3. HETEROGENEOUS CATALYST FOR LA TO GVL OVERVIEW

The hydrogenation of LA into GVL with Ru supported on either carbon or Al₂O₃ catalysts has been reported by several groups\(^9,14,17,18\) and carbon shows higher activity than Al₂O₃\(^19,20\). Unfortunately, to our knowledge, the mechanism is not clear. In general, the smaller metal particle size leads to higher metal utilization during the reaction. Therefore, metal particle size plays an important role in the reaction. Furthermore, many impurities and by-products present in the real feedstock solution and would cause the low conversion and selectivity. Bimetallic catalysts offer a promising option for biomass feedstock upgrading as the interaction between metals can modify the surface properties of the catalyst, which could eliminate the negative effects from biomass-derived impurities and severe reaction conditions. Therefore, the optimized bimetallic catalysts would significantly improve the catalytic activity, modify the selectivity to the desired product, and increase the catalyst stability, so that lead to effective purification steps. Monometallic Ru and bimetallic Ru-Metal catalysts used for LA hydrogenation into GVL as well as Ru nanoparticle preparation was summarized in Table 1.1 and in Table 1.2, respectively.

Firstly, supported metal catalyst has been widely studied for the LA hydrogenation to GVL. Various metals supported on carbon were screened to find the most active metal for GVL synthesis by Manzer\(^14\). All catalysts were prepared by dry impregnation and the reaction is performed in 1.4 dioxane solvent at 150°C, with 800 psi H₂ pressure. Among the catalysts screened, Ru/C shows the highest activity yielding the highest conversion (80%). Ir, Rh, and Pd give the moderate activity (~35%). However, low LA conversions were obtained by Pt, Re and Ni system (less than 15%). Further
studies on the effect of metal and support are performed at milder condition by Hengne, all catalysts were also prepared by dry impregnation. Ru/C again gave the highest GVL conversion and carbon gives higher activity than Al₂O₃. Based on the reported finding, Ru/C is very active for GVL synthesis. Ru/C commercial catalysts were extensively utilized to study the reaction process at different conditions by many researchers. However, Ru particle size was reported by few groups (≈4nm), but not in the majority of the LA hydrogenation references.

Due to the important role of metal particle size in the reaction, Ru nanoparticle supported on carbon and Al₂O₃ preparation methods are summarized in Table 1.2, where wet impregnation is employed as the most common method to prepare Ru nanoparticle. Ru loading (1%, 2%, 5%) and the influence on the particle size was studied by Gavlvagno, who reported that particle size increases as the Ru loading increases. However, it is inconsistent with the claim made by Zheng, who prepared the same catalysts series as Gavlvagno did and observed the reverse phenomena. The same trend is also observed for Al₂O₃ support, even though the same precursor and methods were used for the preparation, very different particle size was obtained. Therefore, wetness impregnation is not reproducible and not necessarily the optimal method to prepare Ru nanoparticles.

Secondly, in the first study, we observed that the presence of potassium significantly enhances the Ru activity, TOF increased by a factor of 4 and 6 on carbon and alumina support, respectively with the addition of 3wt% potassium for LA hydrogenation. To our knowledge, the chemical state, physical location, and the role of alkali metal are not well understood. Research to date has proposed several mechanisms
for the role as promoters/poisons of alkali and alkaline earth metal for heterogeneous catalysis. Those suggested mechanisms can be summarized in two aspects. One is ascribed to the modification of metal surfaces, such as electron donation to or from the metal, geometric site blocking of active metal site, alkali-induced metal surface reconstruction and direct chemical interactions between promoter and adsorbate through-space interactions (e.g. dipole-dipole or electrostatic) and metal-modifier electronic interactions leading to changes in the strength. It is also reported that alkali and alkaline earth metal could form chemical compounds with many commonly used oxide supports, such as alumina, silica, or titania, which could be ascribed to the influence of the overall acidity or the basicity of the supported catalysts with the presence of promoters.

Lastly, a search of the literature to assess the application of supported bimetallic catalysts on the conversion of LA to GVL is discussed here. Dumesic et al. reported that RuRe/C catalyst with 3 to 4 RuRe atomic ratio shows significant higher activity than a traditional Ru/C catalyst with reaction streams comprised of LA, FA and H₂SO₄. The addition of Re improves the stability of catalysts in the presence of sulfuric acid. Under the same reaction condition, Wettstein et al. also reported that the addition of Sn improves the stability of Ru/C in RuSn/C system and selectivity towards to GVL. However, the addition of Sn caused the lower activity for bimetallic RuSn than monometallic Ru/C catalyst. Shimizu et al. tested a series of base metal (Ni, Co, Cu, and Fe) and metal oxides (Mo, V and W oxides) co-loaded carbon, Ni-MoOx/C showed 300 times higher rate than previously reported Noble- metal-free catalysts. Recently, Luo et. al found AuPd/TiO₂ gives 27 fold higher activity than its monometallic counter parts and also RuPd/TiO₂ shows excellent selectivity to GVL as the addition of Pd.
However, Lange et al.\textsuperscript{30} observed that PtRe and PtRu did not enhance activity comparing with monometallic Pt catalyst.

The purpose of this dissertation is to demonstrate strong electrostatic adsorption for the synthesis of well dispersed Ru nanoparticles on carbon and alumina and to use this precise synthesis as the basis for examining the effects of particle size, support type, and potassium dopant on ruthenium activity for LA hydrogenation to GVL; secondly, to investigate the effects that alkalis (Na\textsuperscript{+}, K\textsuperscript{+}, Cs\textsuperscript{+}) and alkaline earth (Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, Ba\textsuperscript{2+}) have on Ru activity for hydrogenation of LA in terms of electronic effect, site blocking, physical position and active chemical state of respective dopants; thirdly, to establish the correlations between structure and activity in order to have a fundamental understanding of the role alkali and alkaline earth metals play in improving the Ru activity for hydrogenation of LA; and lastly, to demonstrate a simple, scalable and reproducible way for the synthesis of bimetallic catalysts and the impact of synthesis methods on the stabilities of catalysts.
Table. 1.1 Summary of Ru-based catalysts for LA hydrogenation to GVL.

<table>
<thead>
<tr>
<th>Support</th>
<th>Metal</th>
<th>Metal wt%</th>
<th>Method</th>
<th>PZ (nm)</th>
<th>Precursor</th>
<th>Condition</th>
<th>LA Conv./GVL sel./GVL yield</th>
<th>Rates (mol GVL/g metal/h)</th>
<th>Ref.</th>
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<td>14</td>
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<tr>
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<td>DI</td>
<td>n.r.</td>
<td>n.r.</td>
<td></td>
<td>12%/80%/--</td>
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<td>DI</td>
<td>n.r.</td>
<td>n.r.</td>
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<td>30%/90%/--</td>
<td>n.r.</td>
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<td>DI</td>
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<td>n.r.</td>
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<td>39%/95%/--</td>
<td>n.r.</td>
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<tr>
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<td>8%/80%/--</td>
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<td>n.r.</td>
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<td>18</td>
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<td>RuCl₃</td>
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<td>DI</td>
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<td>RuCl₃</td>
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<td>2.7h,MeOH</td>
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<td>75.5%/81.5%/61.1%</td>
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<td></td>
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<td></td>
<td>2.7h,Ethanol</td>
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<tr>
<td>Carbon</td>
<td>Ru</td>
<td>5</td>
<td>Com.</td>
<td>n.r.</td>
<td>130°C,174psi H₂</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>48.6%/81.7%/39.7%</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.7h,Butanol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

31 32 10 20 19
<table>
<thead>
<tr>
<th>Material</th>
<th>Metal</th>
<th>Cat.</th>
<th>Cnt</th>
<th>Temp</th>
<th>Press</th>
<th>Time</th>
<th>Solvent</th>
<th>Yield</th>
<th>δ</th>
<th>Ref.</th>
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</thead>
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<tr>
<td>Carbon Ru 5 Com. n.r. n.r. 130°C,174psi H₂ 2.7h,1,4 Dioxane 98.8%/97.7/95.9% 1.24</td>
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<td></td>
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</tr>
<tr>
<td>Carbon Ru 5 Com. n.r. n.r. 130°C,290psi H₂ 2.7h,Butanol 100%98.3%/98.3% 1.24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Carbon Ru 5 Com. n.r. n.r. 130°C,174psi H₂ 2.7h,water 99.5%/86.6%/86.2% 1.08</td>
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<td></td>
</tr>
<tr>
<td>Al₂O₃ Ru 5 Com. n.r. n.r. 130°C,174psi H₂ 2.7h,Ethanol 37.7%/85.8%/32.3% 0.98</td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>SiO₂ Ru 5 Com. n.r. n.r. 130°C,174psi H₂ 2.7h,Ethanol 82.9%/92.8%/77% 0.98</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon Ru 5 Com. n.r. n.r. 150°C,508psi H₂,150h --/---/--- solvent free ---/---/--- 0.0034 33</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
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</tr>
<tr>
<td>Carbon Ru 5 Com. &lt;4.0 n.r. 220°C, 507psi H₂ 300h,SBP --/77%/-- n.r. 27</td>
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</tr>
<tr>
<td>Material</td>
<td>Metal/Metal</td>
<td>Ratio</td>
<td>IWI</td>
<td>Conversion</td>
<td>Selectivity</td>
<td>Reaction Conditions</td>
<td>Results</td>
<td>Notes</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>Ru/Re</td>
<td>15 (molar ratio 3:4)</td>
<td>IWI</td>
<td>n.r.</td>
<td>5%RuC Com.&amp; HReO₄</td>
<td>150°C, 508 psi H₂, 150h</td>
<td>&gt;80.0%/-/-/---</td>
<td>0.014</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>Ru/Sn</td>
<td>molar ratio 3.6:1</td>
<td>IWI</td>
<td>&lt;4</td>
<td>5%RuC Com.&amp; HReO₄</td>
<td>220°C, 507 psi H₂</td>
<td>98%/95%/93%</td>
<td>0.36</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>Ru/Pd</td>
<td>1</td>
<td>Modified IWI</td>
<td>1.2</td>
<td>RuCl₃/PdCl₃</td>
<td>200°C, 580 psi H₂</td>
<td>&gt;99%/99.6%/-/-/---</td>
<td>17.2</td>
<td>29</td>
<td></td>
</tr>
</tbody>
</table>

(Note: PZ-Particle size-, DI- dry impregnation, Conv.-Conversion, Sel.-Selectivity, Com.-Commercial, Immo.-Immobilization, n.p.-non-reported and rates are obtained from ref.13.)
Table 1.2 Summary of Ru nanoparticle preparation.

<table>
<thead>
<tr>
<th>Support</th>
<th>Metal</th>
<th>Metal wt%</th>
<th>Method</th>
<th>PZ (nm)</th>
<th>Precursor</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active Carbon</td>
<td>Ru</td>
<td>5</td>
<td>WI</td>
<td>6.0</td>
<td>RuCl₃</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>Ru</td>
<td>2</td>
<td>DI</td>
<td>3.9ᵃ</td>
<td>RuCl₃</td>
<td>35</td>
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<tr>
<td></td>
<td>Ru</td>
<td>1</td>
<td>DI</td>
<td>6.0</td>
<td>RuCl₃</td>
<td></td>
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<tr>
<td></td>
<td>Ru</td>
<td>2</td>
<td>DI</td>
<td>7.4</td>
<td>RuCl₃</td>
<td>21</td>
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<td>Ru</td>
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<td>DI</td>
<td>10.6</td>
<td>RuCl₃</td>
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<td></td>
<td>Ru</td>
<td>10</td>
<td>DI</td>
<td>16.8</td>
<td>RuCl₃</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ru</td>
<td>5</td>
<td>WI</td>
<td>1.7</td>
<td>RuCl₃</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>Ru</td>
<td>1</td>
<td>WI</td>
<td>2.5</td>
<td>RuCl₃</td>
<td>22</td>
</tr>
<tr>
<td>Active Carbon</td>
<td>Ru</td>
<td>WI</td>
<td>2.0</td>
<td>RuCl₃</td>
<td></td>
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<td>---------------</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Active Carbon</td>
<td>Ru</td>
<td>WI</td>
<td>1.5</td>
<td>RuCl₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Active Carbon</td>
<td>Ru</td>
<td>DI</td>
<td>1.5-2.2</td>
<td>Ru(NO)(NO₃)₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>Ru</td>
<td>WI</td>
<td>1.5</td>
<td>Ru(NO)(NO₃)₃</td>
<td></td>
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</tr>
<tr>
<td>Carbon</td>
<td>Ru</td>
<td>WI</td>
<td>3.3</td>
<td>RuCl₃</td>
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<tr>
<td>Carbon</td>
<td>Ru</td>
<td>WI</td>
<td>1.0-10</td>
<td>RuCl₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>Ru</td>
<td>WI</td>
<td>4.2</td>
<td>RuCl₃</td>
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<tr>
<td>γ-Al₂O₃</td>
<td>Ru</td>
<td>WI</td>
<td>5.0</td>
<td>RuCl₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>Ru</td>
<td>DI</td>
<td>1.6-2.4</td>
<td>RuCl₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>Ru</td>
<td>WI</td>
<td>0.84</td>
<td>Ru(NO)(NO₃)₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>Ru</td>
<td>WI</td>
<td>10.8</td>
<td>Ru(NO)(NO₃)₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>Ru</td>
<td>WI</td>
<td>1.7-2.3</td>
<td>Ru(NO)(NO₃)₃</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: WI-wetness impregnation, a- particle size analyzed by H₂-O₂ chemisorption, all others determined by electron microscopy.
CHAPTER 2
EXPERIMENTAL TECHNIQUES

2.1 CATALYST PREPARATION

A wide variety of catalyst preparation methods has been developed for satisfying the increased demand of industry as the use of catalyst in chemical processes increases. The three most common and important methods of catalyst synthesis employed for industrial production are impregnation, adsorption, and precipitation. Among all preparation methods of metal supported catalyst, impregnation is the simplest, least expensive, and most prevalent. The most common types of impregnation can be classified as wet or dry. This depends on the volume of impregnating solution and the pore volume of support. If the volume of metallic precursor solution is equal to the pore volume of support, it is termed dry impregnation (DI). If the volume of impregnation solution is considerably larger, it is termed as wetness impregnation (WI). Either DI or WI is a simple method since the pH of the solution does not need to be adjusted. In addition, little to no precursor will be wasted during the impregnation process and precise metal weight loadings can be achieved. Since the pH of impregnation solution is not controlled, the pH of the metal precursor solution can change dramatically and often adjusts to the point zero charge (PZC) of the support, where no interaction occurs between metal and support sites. For this reason, it is difficult to obtain a uniform metal distribution throughout the whole support. After impregnation, drying and pretreatment steps are used to remove the
ligands from the metal precursor and reduce the metal to metallic state. During this pretreatment process if no metal–support interaction occurs the metal complex will be very mobile and tend to sinter, which will result in the increase of metal particle size. Adsorption has recently been used for heterogeneous catalyst impregnation. A landmark work reported by Brunelle was demonstrated that the adsorption of noble metal complexes onto common oxides supports was essentially colomic in nature. In principle, adsorption is an impregnation method that creates a strong electrostatic interaction between the ionic metal precursor and hydroxyl groups on the surface of support. This strong interaction can ensure the metal precursor strongly adsorbs on the surface of support leading to increased metal particle dispersion.

The mechanism of Strong Electrostatic Adsorption (SEA) is illustrated in Figure 2.1. An oxide surface contains the hydroxyl groups that can be protonated or deprotonated, depending on the pH of metal precursor solution. In order to understand this process the point zero charge (PZC) will be introduced, where the pH of the surface hydroxyl groups are neutral. At pH values below the PZC, the surface hydroxyl groups protonate and become positively charged. The surface can absorb anionic metal precursors and in the opposite way at pH values above the PZC, the surface hydroxyl groups become deprotonated and become negatively charged, the surface can adsorb cationic metal precursors. The PZC of the support can be acidic or basic. For instance, the PZC of SiO$_2$ is about 4, Al$_2$O$_3$ is about 8. Carbon is a special case; the PZC can be changed by the increasing or decreasing the amount of oxygen functional groups on the surface at mild or rigorous oxidation conditions. The PZC measurement of different carbons is presented in Figure 2.2. The PZC of Norit SX-ULTRA is around 8.1.
However, the PZCs of Darco KB-B and Norit CA-1 are 5.0 and 2.5, respectively.\textsuperscript{54-57} A low PZC support has a negatively charged surface, which can absorb cationic metal precursors, such as platinum tetraammine (PTA) \([\text{Pt(NH}_3\text{)}_4]^2+\). High PZC supports have positively charged surface, which can absorb anionic metal precursors, such as chloroplatinic acid (CPA) \([\text{PtCl}_6]^{2-}\). The greatest benefit of SEA is that a monolayer of adsorbed metal complexes on the surface can be reduced to form metal particles at very high dispersion.\textsuperscript{58}

![Figure 2.1 Mechanism of Strong Electrostatic Adsorption (SEA) for CPA and PTA system](image)

Figure 2.1 Mechanism of Strong Electrostatic Adsorption (SEA) for CPA and PTA system.\textsuperscript{49}
As the discussion above, the PZC measurement of the support is the first step to perform the method of SEA. To determine the PZC of a support, we can plot the PH shifts of the solution before and after contact with the support at high surface loading (SL)\(^{59}\). This is the surface area of the support per volume of solution,

$$\text{Surface loading } \left( \frac{m^2}{L} \right) =$$

$$\frac{\text{Mass of Support (g)} \times \text{Surface area of support} \left( \frac{m^2}{g} \right)}{\text{volume of solution (L)}}$$  \hspace{1cm} \text{Equation 2.1}

In the plot shown in Figure 2.3, a plateau is observed and corresponds to the PZC value of the support. Based on the PZC information of support, proper precursor can be selected for SEA method.
Figure 2.3 PZC measurement for a carbon and an alumina support.  

To find the optimal pH to obtain the maximum metal adsorbed on the support, a metal uptake survey should be performed. The varied concentration of metal precursor adsorbed onto the support at a desired surface loading though various pH values is exemplified in Figure 2.4 (a) and (b). A sharp volcano peak is observed. Figure 2.4 (a) shows CPA uptake over high PZC carbon (PZC=9.1), where the metal surface density is very low at pH=9.1. Figure 2.4 (b) shows PTA uptake over low PZC carbon (PZC=4), when pH=4, the metal surface hydroxyl density is zero. According to the mechanism of SEA no metal adsorption occurred when the pH of the metal precursor solution is equal to the PZC of the support for both cases. In addition, the maximum uptake appears at the range from 11 to 13 for PTA, 2 to 3 for CPA. The Revised Physical Adsorption (RPA) model has been developed to explain the mechanism of adsorption.
Due to the strong interaction between the metal precursor and the support highly dispersed metal particles can form after H$_2$ reduction. Strong electrostatic adsorption has its limitations, that is, the electrostatic attraction only allows one monolayer of metal precursor to be deposited onto the surface of the support due to the presence of a hydration sheath around the metal complex. Figure 2.5 shows how the hydration sheath impacts the maximum of metal loading on the support. The hydration sheaths around the metal set a boundary to the amount of molecules that can be positioned next to each other in a closed packed fashion.

Figure 2.4 (a) Final pH vs. uptake (Γ) plot for CPA on high PZC carbon (PZC=9.1) (b) Final pH vs. uptake (Γ) plot for PTA on low PZC carbon (PZC=4).
The SEA method also can be applied to the synthesis of bimetallic catalysts. The schematic of bimetallic synthesis by different methods presents in Figure 2.6. The cartoon of how dry impregnation works is shown in Figure 2.6 (a), where two metal precursors are mixed in the solution. However, as the DI normally ends up with PZC, where no good interaction between two metals and support, which results in the poorly dispersed and separated metal particles. However, if two metal precursors are mixed in the solution contacting with positively /negatively charged surface (Figure 2.6 (b)), a mixed monolayer of precursors will be adsorbed onto the charged surface, which ensures the better interaction between either two metals or metals and support. After reduction under H$_2$, it often gives well dispersed particles with tight particle size distribution and homogeneous alloyed particles. As two metal precursors are mixed simultaneously, this method is called co-SEA. Alternatively, if metal precursor is placed in the solution contacting with supports sequentially, that is called Sequential SEA. Sequential SEA can
be applied to synthesize core-shell morphologies nanoparticles. The core metal is initially deposited on the support by SEA, followed by oxidization. Depending on the PZC of support and oxidized core metal, proper precursor of the second metal is selected for the uptake by SEA. This method often offers a core-shell structure in bimetallic catalysts at low reduction temperature. However, high reduction temperature may result in the alloyed nanoparticles again. The aim of this dissertation is to introduce a simple, scalable, and reproducible way to synthesize catalysts to study the hydrogenation of LA to GVL. SEA will be employed to synthesize monometallic Ru catalysts and co-SEA for the synthesis of bimetallic RuRe catalysts in this work.

Figure 2.6 Schematic of hypothesis for bimetallic catalysts synthesis: (a) DI (b) co-SEA (c) sequential SEA \(^{63}\).
2.2. CATALYSTS CHARACTERIZATION

The characterization techniques used in this study are listed in Figure 2.7.

Figure 2.7 Schematic diagram of catalysts characterization.
2.2.1. BET surface area

BET surface area was measured using a Micromeritics ASAP 2020 system. The samples were first degassed at 110°C and 10⁻³ Pa. Then nitrogen was charged on the samples across a wide range of relative pressures at 77 K. This technique provides information about the type of isotherm, surface area and pore size distribution of the samples analyzed. The BET specific surface area was evaluated using the linear relation between \( P/P_0 \) and \( 1/ [v/(P/P_0 - 1)] \) with 8 points from 0-0.35 of \( P/P_0 \) values ⁶⁴-⁶⁶.

2.2.2. Inductively coupled plasma-atomic emission spectrometry (ICP-AES)

ICP-AES was performed using PerkinElmer. This is one of the most common techniques for elemental analysis. This technique is based on the measurement of the emission at one wavelength, which is highly selective for a specific element. The schematic diagram of a typical ICP-AES set-up is shown in Figure 2.8. When an aqueous sample solution is introduced into the spectrometer, it becomes atomized into a mist-like cloud. This mist is carried into the argon plasma with a stream of argon gas. The plasma (ionized argon) produces temperatures close to 7000°C, which thermally excites and emits light wavelengths characteristic of its elements. A mirror reflects the light through the entrance slit of the spectrometer onto a grating that separates the element wavelengths onto photomultiplier detectors ⁶⁷.

2.2.3. Atomic absorption spectroscopy (AAS)

AAS is an analytical method to determine quantitatively elements using the absorption of optical radiation by free atoms in the gaseous state. In principles, the
electrons of the atoms in the atomizer can be promoted in excited stage to higher orbital in nanoseconds by absorbing an energy, which corresponds to the radiation of wavelength. Particular elements have a specific electron transition that relates to the specific wavelength and energy. Firstly, liquid samples are atomized by flames, subsequently, atoms are irradiated by optical radiation. The radiation passes through a monochromator to separate the radiation coming from element from any other radiation emitted by the radiation source, which is measured by a detector.

2.2.4. Temperature Programmed Reduction (TPR)

TPR is widely used technique for the characterization of metal oxides dispersed on a support. By this method, quantitative information of the reducibility of the oxide’s surface and the heterogeneity of the reducible surface can be provided, which is very helpful to find the most efficient reduction conditions. For this study, TPR experiments were performed in a Quantachrome Instruments CHEBET 3000. First a reducing agent preferably a mixed gas of 10% hydrogen diluted in argon was applied on the sample while sample temperature was being increased linearly with time.

Figure 2.8 Schematic set-up of ICP-AES.
A thermal conductivity detector (TCD) was applied to measure changes in the thermal conductivity of the gas stream with temperature $^6, ^{68}, ^{69}$. If hydrogen is consumed, it could be easier to detect by TCD because hydrogen has the highest thermal conductivity among the common gases, the thermal conductivity of some common gases at 25°C has been summarized in Table 2.1.

Table 2.1 Thermal conductivity of some common gases at 250°C.

<table>
<thead>
<tr>
<th>Species</th>
<th>Thermal Conductivity W/(m*K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>0.0240</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.1680</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.0266</td>
</tr>
<tr>
<td>Argon</td>
<td>0.0160</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.0146</td>
</tr>
<tr>
<td>water</td>
<td>0.5800</td>
</tr>
</tbody>
</table>

2.2.5. X-Ray Diffraction (XRD)

XRD is primarily used for phase identification of a crystalline material and can provide unit cell information. X-rays are generated by a cathode ray tube, which is filtered to produce monochromatic radiation and then directed toward the sample. The interaction of the incident rays with sample produces constructive interference when the conditions satisfy the Bragg’s law.

$$n\lambda = 2d \sin \theta$$  

Equation 2.2
where \( n \) is an integer, \( \Theta \) is the wavelength of incident wave, \( d \) is the spacing between the planes in the atomic lattice and \( \Theta \) is the angle between the incident ray and the scattering plane. These diffracted X-rays are detected, processed and counted. All possible diffraction directions of the lattice were obtained after scanning the sample through a range of \( 2\Theta \) angle.

XRD is a bulk technique, which is suited for identification of crystal structure of an unknown material and measurement of the average particle size. However, this method does have some limitations. Firstly, the large amount of sample is required for XRD experiment. Secondly, if the particle size is less than 2nm, it will not be identified by the detector. In general, the larger the particle is, the sharper intensity signal is. Lastly, if the metal weight loading is less than 1%, XRD may not be able to detect that metal. X-ray diffraction (XRD) analysis for all catalysts was performed using a Rigaku MiniFlex II bench top system at \( 2\Theta = 10^\circ \text{C}-80^\circ \text{C} \). The XRD patterns were compared to JCPDS reference spectra using PDXL software. The radiation source was Cu K\( \alpha \) (\( \lambda = 1.5405 \) Å) at operating conditions of tube voltage of 30 KV and a current of 15mA. All spectra were taken at a scan rate of 0.5°/min and a sampling width of 0.02°. According to the XRD pattern, the particle size was calculated from the Scherrer Equation.

\[
d = \frac{K\lambda}{B \cos \Theta}
\]

Equation 2.3

where \( d \) is the average crystal particle diameter, \( K \) is a constant (usually between 0.9-1), \( \lambda \) is the X-ray wavelength, \( B \) is the width in radians at half the maximum intensity of the peak and \( \Theta_B \) is the position of the peak at maximum intensity.\(^{64, 68, 71}\).
2.2.6. Scanning Transmission Electron Microscopy (STEM)

STEM is a powerful technique for viewing metal particles deposited on the support. Scanning transmission electron microscopy (STEM) was used to image the materials with a JEOL 2100F 200kV FEG-STEM/TEM equipped with a CEOS Cs corrector on the illumination system. The geometrical aberrations were measured and controlled to provide less than a \( \pi/4 \) phase shift of the incoming electron wave over the probe-defining aperture of 17.5 mrad. High angle annular dark-field (HAADF) STEM images were acquired on a Fischione Model 3000 HAADF detector with a camera length such that the inner cut-off angle of the detector was 50 mrad. The scanning acquisition was synchronized to the 60 Hz AC electrical power to minimize 60Hz noise in the images and a pixel dwell time of 15.8\( \mu \)s was used \(^{64,68}\).

2.2.7. Energy dispersive X-ray spectroscopy

EDXS is an analytical technique used for the elemental analysis of a sample. Each element has a unique atomic structure resulting in the special peaks on its X-ray emission spectrum. The energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer.

2.2.8. H\(_2\)-chemisproton

Chemisorption refers to the chemical adsorption and desorption phenomena by which gas or vapor molecules bond to or are released from the solid surface of sample materials. The method is the most sensitive to count metal surface atoms because all surface atoms are independent of crystallite size and probed at the molecular level. In
addition, since the strong chemisorption is irreversible on the reduced metal surface, it is widely applied for support catalysts, especially when a significant fraction of small particles (less than 2 nm) are present which are difficult to detect by XRD. In this method, firstly, the surface of the catalyst was cleaned and reduced to metallic state, which was treated at proper temperature with flowing H\textsubscript{2} and then exposed to O\textsubscript{2} in order to cover the metal surface with oxygen at room temperature. Finally, H\textsubscript{2} was used to titrate the precovered oxygen atoms at proper temperature. Since the amount of consumed H\textsubscript{2} is known, the amount of oxygen atom covered on the metal surface and the number of metal atoms on the surface can be determined by the adsorption stoichiometry\textsuperscript{68,72}.

2.2.9. X-Ray Photoelectron Spectroscopy (XPS)

XPS is a surface sensitive technique that is used to obtain the chemical information about the surfaces of solid materials, such as the elemental composition and the chemical state of surface component. The peak position and peak area obtained from XPS are used to evaluate the composition, while the peak shape provides the information about chemical shifts or chemical bonds of the elements. XPS measurements were conducted using a Kratos AXIS Ultra DLD XPS system equipped with a monochromatic Al K source. The energy scale of the system is calibrated using a Au foil with Au4f scanned for the Al radiation and a Cu foil with Cu2p scanned for Mg radiation resulting in a difference of 1081.70 ± 0.025 eV between these two peaks. The binding energy is calibrated using an Ag foil with Ag3d\textsubscript{5/2} set at 368.21 ± 0.025 eV for the monochromatic Al X-ray source. The monochromatic Al K source was operated at 15 keV and 120 W.
The pass energy was fixed at 40 eV for the detailed scans. A charge neutralizer (CN) was used to compensate for the surface charge \(^\text{64, 68}\).

2.2.10. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a surface technique that can result in positive identification (qualitative analysis) of every different kind of materials. As atoms vibrate with frequencies in the IR range, probe molecules, such as carbon monoxide and pyridine, could be used to employ the active metal sites and acidic sites, respectively.

2.2.11. Gas Chromatography (GC)

GC is a method for separating the components of a solution that can be vaporized without decomposition to measure their relative quantities. Typically, this technique is used for purification and reaction solution analysis. In a typical GC operation system presented in Figure 2.9, an inert carrier gas (typically, helium or nitrogen) carries the vaporized compounds through a column at different rates depending on their various chemical and physical properties and their interaction with the walls of the stationary column. Sample components are separated based on their boiling points and relative affinity for the stationary phase, which is most often a viscous liquid within the column. The higher a component's affinity for the stationary phase, the slower it comes off the column. This causes each compound to elute at a different time, known as the retention time of the compound which is then detected and identified electronically and represented as peaks on a chromatogram. Other parameters that can be used to alter the order or time of retention are the carrier gas flow rate, column length and the temperature \(^\text{73}\).
The precision of repeated injections in GC is not particularly good, either by autosampler injection or manual injection, certainly worse than the loop injectors used in HPLC. Therefore, internal standard is primarily used to improve the accuracy and precision of quantitative analysis that have large inherent variability. In general, an internal standard is a known concentration of a substance that is present in every sample analyzed. A compound similar to the analyte of interest is added to the sample and run. By having the analyte and the standard elute in the same run, the run to run variability is eliminated giving more precise results, where the internal standard is to behave similarly to the analyte but to provide a signal that can be distinguished from that of the analyte. Ideally, any factor that affects the analyte signal will also affect the signal of the internal standard to the same degree. Thus, the ratio of the two signals will exhibit less variability than the analyte signal. 

Figure 2.9 Schematic diagram of gas chromatography.
Activities were calculated by three ways (time was selected when the conversion of LA reached to 10%, number of active sites is measured by STEM/chemisorption).

\[
\text{TOF} = \frac{\text{Number of reacted LA}}{\text{Number of active sites} \times \text{time}} \quad \text{Equation 2.4}
\]

\[
\text{Rate/g metal} = \frac{\text{Mol of reacted LA}}{\text{g metal} \times \text{time}} \quad \text{Equation 2.5}
\]

\[
\text{Rate/g catalyst} = \frac{\text{Mol of reacted LA}}{\text{g catalyst} \times \text{time}} \quad \text{Equation 2.6}
\]

More details for the operation parameters will be given in the experiments session for each chapter.

2.3. CATALYSTS EVALUATION

Hydrogenation reactions of LA were performed in a stainless steel EZE-Seal batch reactor with 100ml capacity from autoclave Engineers, which is equipped with a K-type thermocouple, a pressure gauge and a stirring motor from SpeedMaster. Water was connected with the motor for cooling purposes. Importantly, the batch reactor was modified by putting a four-port valve associated two-way valves and metal tubing allowed purging of the gas and sampling of the liquid reaction mixture to minimize liquid loss during sampling at different time intervals. This type of batch reactor can be operated at the temperature range from -29°C to 450°C and at pressure up to 3300psi. A picture of batch reactor is shown in Figure 2.7. Under this operation condition, only GVL was observed (100% selectivity) for all catalysts in this work.
In a typical reaction, reaction was run at 200 psi H\textsubscript{2} and 220°C with the impeller speed of 1000rpm, which ensure no internal and external mass transfer limitations (shown in Figure A.1 and Figure A.2 in Appendix A). For the solvent, nonpolar, aprotic 1,4 dioxane was employed so that the catalytic activity could be attributed entirely to the metal sites. The reactor was loaded with 54g solvent, 13 to 36 mg catalyst, 200 μl diglyme as an internal standard. After sealing, a leak check using 200psi H\textsubscript{2} was performed three times, subsequently three vent cycles in order to remove the residual oxygen from the system. The temperature of the liquid in the reactor was monitored by the thermocouple with the maximum deviation of 1-2°C. Prior to the reaction, catalysts were reduced in dioxane in flowing H\textsubscript{2} at 220°C for 1 h. After 1 h, the reactor was filled with H\textsubscript{2} to a total pressure of 422psi, with the partial (i.e., vapor) pressure of dioxane at 220°C being 222 psi. To initiate the reaction, the mixture of 3.0 g LA+ 3.0 g 1,4 Dixoane
was pumped (in 10 sec) into the reactor with a high pressure HPLC pump. Liquid samples (0.25 ml) were taken periodically and analyzed by GC.

The sample collected from the batch reactor at different reaction times were injected automatically with a Hi-Tech 300A liquid auto sampler from Overbrook Scientific. The quantitative analysis of the product mixture was performed using a Hewlett Packard 5890 Series gas chromatograph with a flame ionization detector (FID), equipped with an HP-5 capillary column (30 m length, 0.32 mm inside diameter, 0.25 μl film, 5% phenyl methyl silicone from Agilent J&W Technologies). The temperature of injector and detector are both at 250°C. The temperature program for GC furnace is shown in Figure 2.11. The retention time is following this order: Dixoane, Diglyme, GVL and LA.

![Temperature vs time for GC operation](image)

**Figure 2.11** Furnace Temperature vs time for the GC operation.
CHAPTER 3

RATIONAL NANOPARTICLE SYNTHESIS TO DETERMINE THE EFFECTS OF SIZE, SUPPORT AND POTASSIUM DOPANT ON RU ACTIVITY FOR HYDROGENATION OF LEVULINIC ACID

3.1 INTRODUCTION

With worldwide petroleum resources dwindling (even with the temporary windfall of shale oil and gas) and especially with greenhouse gas emissions rising, it is urgent to find renewable replacements for petroleum-derived products. Several recent reports have underscored the potential of biomass feedstocks for green catalytic conversion to renewable fuels and chemicals\textsuperscript{1,2}. Levulinic acid (LA) is inexpensive and can be obtained through the decomposition of biomass and can be used as the starting material for the production of many useful C\textsubscript{5} based compounds such as \(\gamma\)-valerolactone (GVL), 2-methyltetrahydrofuran (MTHF) and other derivatives\textsuperscript{6}. GVL has attracted considerable attention as a platform chemical because it is renewable, safe to store, and could be used as (1) a precursor of gasoline and diesel fuels, such as C\textsubscript{8}-C\textsubscript{16} alkenes, C\textsubscript{9}-C\textsubscript{18} alkanes, C\textsubscript{9} alkanes, valeric esters, or butane isomers, (2) for food additives, green solvents, or mixed with conventional gasoline in a capacity similar to ethanol and (3) as an intermediate in the synthesis of many value added chemicals, such as, 1,4 pentanediol, \(\alpha\)-methylene \(\gamma\)-valerolactone and pentenoate esters\textsuperscript{10,11,75}.

GVL is commonly synthesized by hydrogenation of levulinic acid (LA) using supported metal catalysts. Literature results are summarized in the Section 1.3 in Table
1.1. Various metals supported on carbon were screened by Manzer et al.\textsuperscript{14} using dioxane as solvent. All catalysts were prepared by dry impregnation (DI) (also known as incipient wetness or pore filling). Ru/C showed the highest activity; Ir, Rh, and Pd gave moderate activity, and lowest LA conversions were obtained over Pt, Re and Ni. Studies on the effect of metal and support were performed at milder condition by Hengne et al\textsuperscript{18}, who also employed dry impregnation. Ru/C again gave the highest GVL conversion, and carbon yielded higher activity than Al\textsubscript{2}O\textsubscript{3} using methanol as solvent. A number of studies utilized commercially obtained Ru/C catalysts at different conditions and solvents\textsuperscript{19,20,32}. The above studies are more concerned with the process of LA hydrogenation to GVL, and are not focused on catalyst optimization; the particle size of any single metal catalyst has been given for (~5.0 nm and ~3.3nm) in few reports\textsuperscript{9,15}. A search of the literature to assess the impact of preparation methods on Ru nanoparticle size, independent of the reaction for which the carbon or alumina supported Ru was employed is summarized in Table 1.2 in Section 1.3. Impregnation is the predominant method to prepare Ru nanoparticles. Ru loading (1.0\%, 2.0\%, 5.0\%) and the influence on the particle size was studied by Galvagno\textsuperscript{21}, who reported that particle size increases as the Ru loading increases. However, this is inconsistent with the claim of Zheng\textsuperscript{22}, who prepared a similar catalyst series with the same method, but observed that particle size decreased as metal loading increased. Inconsistent trends are also seen for Al\textsubscript{2}O\textsubscript{3} supports\textsuperscript{33, 37-40}; even though the same precursor and methods were used for the various preparations, very different particle sizes are obtained.

It appears that the methods used to date for the synthesis of supported Ru catalysts are far from reproducible and frequently yield large, poorly dispersed Ru nanoparticles.
Earlier work from this laboratory has demonstrated a simple, reproducible, scalable method to make well dispersed Ru nanoparticles supported on silica based on strong electrostatic adsorption (SEA). The purpose of this paper is to demonstrate strong electrostatic adsorption for the synthesis of well dispersed Ru nanoparticles on carbon and alumina and to use this precise synthesis as the basis for examining the effects of particle size, support type, and potassium dopant on ruthenium activity for LA hydrogenation to GVL.

3.2. EXPERIMENTAL METHODS

3.2.1. Materials

Hexaammineruthenium(III) chloride (Ru (NH₃)₆Cl₃), potassium hexacyanoruthenate(II) hydrate K₄Ru(CN)₆, levulinic acid (98%), 1,4 dioxane (99.8%) and potassium nitrate (>99.9%) were purchased from Sigma-Aldrich. Commercial 5.0% Ru on activated carbon and 5.0% Ru Al₂O₃ catalysts were obtained from Strem Chemicals and Alfa Aesar, respectively. Vulcan XC 72 (surface area 250 m²/g, PZC ~ 8.2) and SBA-200 gamma alumina (surface area 189 m²/g, PZC ~ 8.3) were obtained from Cabot and Aerosil, respectively.

3.2.2. Ruthenium catalyst preparation

The carbon support was oxidized to lower its PZC in order to enable the adsorption of Ru cations. Ten grams of VXC72 was refluxed in concentrated nitric acid (>70%) 3 h near its boiling temperature (90°C). Subsequently, the mixture was washed with deionized water until the pH of the wash solution reached 5.0, and was dried
overnight at room temperature. The sample was calcined for 1 h at 300°C in order to collapse micropores, from which surface oxygen groups are not removed\textsuperscript{55,58}.

To determine the pH at which maximum metal uptake could be achieved, adsorption experiments were conducted over a range of pH as has been done previously\textsuperscript{52,59,61}. A series of 50-ml pH adjusted (using HCl or NaOH) solutions with desired metal concentrations were prepared from the stock and then each was placed in a 60-ml polypropylene bottle. The adsorption surveys are given in the next section. Reproducibility of the inductively couples plasma (ICP) measurements was better than 5.0%.

Once the pH of strongest electrostatic adsorption was determined, about 2.0 g of catalyst was synthesized at this condition by scaling up the volume. 1.5 wt% Ru/C was prepared with 100 ppm Ru(NH\textsubscript{3})\textsubscript{6}Cl\textsubscript{3} at a surface loading (SL) = 1000 m\textsuperscript{2}/l at optimal initial pH of 11.6 and for 2.0% Ru/Al\textsubscript{2}O\textsubscript{3} catalysts, 100 ppm K\textsubscript{4}Ru(CN)\textsubscript{6} at SL = 500 m\textsuperscript{2}/l at optimal initial pH of 1.95 was employed. Prior to reduction, the samples were dried at room temperature for 48 h, and then at 100°C overnight. A 4.4% Ru/C catalyst was prepared by repeating the SEA sequence 3 times with intermittent drying and reduction at 250°C to decompose the adsorbed precursor. For comparison, catalysts with the same Ru metal loadings were prepared by dry impregnation (DI) (also known as pore filling or incipient wetness). On selected samples, dry impregnation was used to dope potassium (in the form of KNO\textsubscript{3}) into the SEA-prepared catalysts at 3.0wt% as well as the 2.0% Ru γ-Al\textsubscript{2}O\textsubscript{3} DI sample. To study Ru particle size effect, two methods were applied to vary Ru particle size. For carbon support, catalysts were treated under the reaction condition for 6h and 24h to grow the Ru particle size, then filtrated and dried for the evaluation. For
alumina support, the 2.0% Ru $\gamma$-Al$_2$O$_3$-SEA sample, the Ru particles were sintered by varying pretreatment condition. A summary of catalysts is given in Table 3.1. The numbers preceding the components are weight percents and the supports are represented by C or Al for carbon and alumina. For example, a 3.0 wt% K, 1.5 wt% Ru/carbon catalyst prepared by SEA is abbreviated 3K-1.5RuC-SEA.

Table 3.1 Nomenclature of carbon and alumina-supported catalysts synthesized.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>support</th>
<th>precursor</th>
<th>Method, pretreatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5RuC-SEA</td>
<td></td>
<td>Ru(NH$_3$)$_6$Cl$_3$</td>
<td>SEA, 250°C reduc. 1h</td>
</tr>
<tr>
<td>1.2RuC-SEA</td>
<td>oxidized Vulcan XC72 (Cabot)</td>
<td></td>
<td>SEA, 220°C reduc.1h</td>
</tr>
<tr>
<td>1.5RuC-DI</td>
<td></td>
<td></td>
<td>DI, 300°C reduc.1h</td>
</tr>
<tr>
<td>4.4RuC-SEA</td>
<td></td>
<td></td>
<td>3X: SEA, 250°C reduc.</td>
</tr>
<tr>
<td>3K-1.5RuC-SEA</td>
<td></td>
<td></td>
<td>Ru SEA, 250°C reduc., K$^+$ DI, 250°C reduc.1h</td>
</tr>
<tr>
<td>5.0RuC-com</td>
<td>(commercial) Strem Chemicals</td>
<td></td>
<td>250°C reduc.1h</td>
</tr>
<tr>
<td>alumina</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0RuAl-SEA</td>
<td></td>
<td></td>
<td>SEA, 520°C reduc.1h</td>
</tr>
<tr>
<td>2.0RuAl-DI</td>
<td></td>
<td>K$_4$Ru(CN)$_6$</td>
<td>DI, 650°C reduc.1h</td>
</tr>
<tr>
<td>3K-2.0RuAl-SEA</td>
<td>SBA-200 $\gamma$-alumina (Aerosil)</td>
<td></td>
<td>Ru SEA, 520°C reduc., K$^+$ DI, 650°C reduc.1h</td>
</tr>
<tr>
<td>2.0RuAl-SEA-C100</td>
<td></td>
<td></td>
<td>SEA, cal.100°C 1h, then 300°C reduc 1.5h</td>
</tr>
<tr>
<td>2.0RuAl-SEA-C200</td>
<td></td>
<td></td>
<td>SEA, cal.200°C 1h, then 300°C reduc 1.5h</td>
</tr>
<tr>
<td>2.0RuAl-SEA-</td>
<td></td>
<td></td>
<td>SEA, cal.300°C 1h, then</td>
</tr>
</tbody>
</table>

45
<p>| | | |</p>
<table>
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<th></th>
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</thead>
<tbody>
<tr>
<td>C300</td>
<td>300°C 1.5h</td>
<td></td>
</tr>
<tr>
<td>2.0RuAl-SEA-R520</td>
<td>SEA, 520°C reduc. 24h</td>
<td></td>
</tr>
<tr>
<td>5.0RuAl-com</td>
<td>(commercial) Alfa Aesar</td>
<td>Pre-reduc.</td>
</tr>
</tbody>
</table>

3.2.3. Catalyst characterization

Surface areas were obtained with a Micromeritics 2020 ASAP instrument. The concentration of Ru in the solution was determined by inductively coupled plasma-atomic emission spectrometry. Temperature programmed reduction (TPR) of all catalysts were performed on a ChemBET 3000 station (Quantachrome Instruments). Powder X-ray diffraction (XRD) analysis was performed using a Rigaku MiniFlex II system. The XRD patterns were compared to JCPDS reference spectra using JADE software. The radiation source was Cu Kα (λ=1.5405 Å) at operating conditions of tube voltage of 30 KV and a current of 15 mA. All spectra were taken at a scan rate of 0.5°/min and a sampling width of 0.02°. The Scherrer equation was used to calculate the particle size from XRD in the limited number of cases that Ru nanoparticles were large enough to be observed. The Ru metal particle size also was measured by scanning transmission electron microscopy (STEM). STEM was performed on the reduced catalyst samples with a JEOL 2100F microscope equipped with a field emission electron gun source and operated at 200 kV and with an extracting voltage of 4.5 kV. Around 1000 Ru particles were used for particle size analyses. XPS measurements were conducted with a Kratos AXIS Ultra DLD XPS system equipped with a monochromatic Al K source operated at 15 keV and 120 W. The samples were analyzed under identical conditions and the resulting spectra were fitted by applying a Shirley-type background subtraction and a charging correction with reference
to carbon 1s at 284.5 eV. Fourier Transform Infrared (FTIR) spectroscopic studies of adsorbed CO on the catalysts were conducted in transmission mode on a Thermo Electron model 4700 spectrometer with a liquid nitrogen-cooled MCT detector. Spectra were collected in the single beam mode, with a resolution of 2 cm\(^{-1}\). Samples consisted of 0.050g of catalyst pressed into pellets with a diameter of 0.5 in. and thickness of approximately 20mg/cm\(^2\). All experiments were performed in a stainless cylindrical steel sample cell, which can be heated externally and cooled by flowing water. A gas flow rate of 70ml/min entered the cell in front of the pellet and exited behind the pellet. Prior to each experiment the samples were reduced in H\(_2\) for 2h at 250°C, held in He for 0.5h at 250°C, cooled to RT in He (3K-2RuAl was pre-reduced in the reduction furnace at 400°C for 1h). At this point a background spectrum was acquired. The samples were then exposed to 1% CO/He, and then flushed with pure He until all of the gas phase CO and any physisorbed CO had been removed. Spectra were taken during this procedure and until the signal was unchanged.

3.2.4. Reactivity evaluation

The hydrogenation of LA was performed in a stainless steel EZE-Seal batch reactor with 100ml capacity from autoclave Engineers with the stirring speed of 1000 rpm to avoid external mass transfer limitations (see Figure A.1 in Appendix A). Reactions were run for 6 h at 200 psi H\(_2\) and 220°C. For the solvent, nonpolar, aprotic 1,4 dioxane was employed so that the catalytic activity could be attributed entirely to the metal sites. Catalyst amounts ranged from 13 to 36 mg. Diglyme in the amount of 200 μl was added as an internal standard. Prior to the reaction, catalysts were reduced in dioxane in flowing H\(_2\) at 220°C for 1 h. After 1 h, the reactor was filled with H\(_2\) to a total
pressure of 422 psi, with the partial (i.e., vapor) pressure of dioxane at 220°C being 222 psi. To initiate the reaction, 3.0 g LA was pumped (in 10 sec) into the reactor with a high pressure HPLC pump. Liquid samples (0.25 ml) were taken periodically and analyzed by GC. The only product observed in all runs was GVL (i.e., selectively was 100%). Blank runs with carbon and γ-Al₂O₃ exhibited negligible activity.

3.3. RESULTS AND DISCUSSION

3.3.1. Ruthenium adsorption surveys on carbon and γ-Al₂O₃

The Ru uptake curves on carbon and alumina are shown in Figure 3.1. The surface density of Ru anions adsorbing over the oxidized carbon assumes a volcano-shaped peak typical of SEA and has an optimal final pH value near 9.9, which corresponds to an initial pH value of 11.6 of the [Ru(NH₃)₆]³⁺ containing solution. The maximum Ru surface density of 0.88 μmol/m² corresponds to a Ru weight loading of about 1.5 wt%.
Figure 3.1 Adsorption surveys of (a) cationic Ru over oxidized carbon and (b) anionic Ru over alumina.

For the γ-Al₂O₃ support shown in Figure 1b, the maximum uptake of the anionic Ru precursor, [Ru(CN)₆]⁴⁻, is 1.3 μmol/m² and occurred at a final pH of 2.1, which corresponds to an initial pH of 1.95. For both experiments, the pH shift of the metal containing solution was essentially identical to metal-free control experiments (not shown), which is another indication that the adsorption mechanism is electrostatic and not chemical ⁵²,⁶¹.

3.3.2. Catalyst synthesis and characterization

Once the optimal conditions for SEA were determined, the adsorption experiment was simply scaled up to yield enough catalyst for characterization and testing. SEA performed at the optimal pH in one liter of solution yielded 4.0 grams of catalyst for both the carbon and alumina supports.
The TPR traces of dried Ru precursors produced from both SEA and DI are shown in Figure 3.2. Two obvious peaks were observed for both carbon supported catalysts in Figure 3.2 (a). The lower temperature peak was assigned to the reduction of Ru\(^{3+}\) to metallic Ru\(^0\)\textsuperscript{53}. The broad high temperature peak is assigned to methanation, confirmed by mass spectrometry. For the TPR profile of 1.5RuC-SEA, an additional small peak appears at 300°C. This might be explained by a small amount of poorly dispersed Ru precursor having little or no interaction with the surface. In the case of the TPR profiles of Ru/γ-Al\(_2\)O\(_3\) in Figure 3.2 (b), only one peak is observed which indicates that Ru\(^{3+}\) is directly reduced to metallic Ru. Over both supports the SEA-deposited Ru precursor exhibited a lower reduction temperature than the DI-deposited precursor, as seen in a previous work \textsuperscript{53}.

![Graph showing TPR profiles](image-url)
Figures 3.3 (a) and (b) show the XRD patterns of Ru catalysts supported on carbon and γ-Al₂O₃, respectively. In Figure 3.3 (a), the diffraction peaks of metallic Ru phase (2θ=38.4°, 42.2°, 44.0°, 58.3° and 69.4°, JCPDS 06-0663) appeared in the XRD patterns of 1.5RuC-DI and 5.0RuC-com. The sharper peaks of the 5.0RuC-com sample imply a larger Ru particle size compared to 1.5RuC-DI. On the other hand, Ru peaks were not observed for 1.5RuC-SEA catalyst. The number average size detection limit of the silicon strip detector on this Rigaku Miniflex instrument is about 1.5nm, suggesting that the Ru particles of the SEA-derived catalysts are smaller than that limit.

In Figure 3.3 (b), metallic Ru peaks appear only for the 5.0RuAl-com catalyst, and additional peaks located at 2θ = 45.7 and 46.0 are seen which correspond to a small amount of delta Al₂O₃ in the gamma alumina. The crystallite sizes of metallic Ru determined from the Scherrer formula are shown in Table 3.2.
Figure 3.3 (a) XRD patterns of Ru based catalysts on Carbon after reduction treatment. (b) XRD patterns of Ru based catalysts on γ-Al₂O₃.
Figures 3.4 and 3.5 display representative STEM images for various catalysts and their corresponding particle size distributions. The number average Ru particle size\(^{53}\) (\(d_{\text{avg}}=\sum_i n_i d_i / \sum_i n_i\) Equation 3.1) was obtained by counting over 1000 Ru particles. The value of \(d_{\text{avg}}\) varied on carbon as: 1.5RuC-SEA (1.30 nm) < 4.4RuC-SEA (1.50 nm) < 1.5RuC-DI (2.06 nm) < 5.0RuC-com (2.52 nm). It is notable that cycling SEA three times to achieve a Ru weight loading of 4.4 wt% did not cause a significant increase in particle size. The same result was achieved after cycling the SEA of Pt complexes onto a carbon support\(^{78}\). In the case the Al\(_2\)O\(_3\) catalysts, size increased as: 2.0RuAl-SEA (0.92 nm) < 2.0RuAl-DI (1.31 nm) < 5.0RuAl-com (4.82 nm). In general, very small and homogeneously distributed Ru particles with narrow size distributions were achieved via SEA method. The DI and commercial catalysts had broader particle size distributions and less homogeneous distributions of the metal particles on the support surface, especially in the case of carbon. The STEM results (this time calculated as volume averages for XRD comparison) are in good agreement with XRD data as shown in Table 3.2.
Figure 3.4 STEM micrographs of carbon supported samples: (a) 1.5RuC-SEA, (b) 4.4RuC-SEA, (c) 1.5RuC-DI, and (d) 5.0RuC-com.
Figure 3.5 STEM micrographs of alumina supported samples: (a) 2.0RuAl-SEA, (b) 2.0RuAl-DI, (c) 5.0RuAl-com.
The XPS spectra of the Ru 3d region for 1.5RuC-SEA are presented in Figure 3.6. Due to the overlapping of the Ru 3d$_{3/2}$ peak with the carbon 1s peak (284.5 ev), the binding energy of the Ru 3d$_{5/2}$ peak was used to determine the oxidation state of Ru present on the surface. For the sample reduced at 250° C in the pretreatment chamber, the most intense doublet peaks at 280.2 ev and 284.2 ev ($\delta=4.0$ ev) are attributed to metallic Ru$^{79}$. On the other hand, for the sample reduced in the reduction furnace at same temperature and then exposed to air, a doublet peak was also observed yet the peak corresponding to Ru 3d$_{5/2}$ is shifted to a higher binding energy of about 281.6 ev, which indicates that Ru is oxidized at room temperature, likely forming RuO$_2$.$^{80}$ Similar results were observed in the Ru 3p region of both samples. Shown in Fig. 6b is the XPS spectrum for the Ru 3p region of the same 1.5RuC-SEA sample. A doublet peak is noticeable in the spectrum with peak binding energy of Ru 3p$_{3/2}$ at 462.7 ev and Ru 3p$_{1/2}$ at 484.9 ev, indicating that metallic Ru is formed and that Ru in the 1.5RuC-SEA catalyst can be completely reduced at 250° C$^{81}$. After ambient exposure to air, Ru 3p$_{3/2}$ shifted to higher binding energy, again implying the formation of RuO$_2$. 
Figure 3.6 XPS spectra for (a) Ru 3d regions of 1.5RuC-SEA after reduction (upper spectrum) and 1.5% Ru CoX SEA after reduction then exposed to air (lower spectrum), (b) Ru 3p regions of 1.5RuC-SEA after reduction (upper) and after air exposure (lower).

To study the support effect and avoid the influence of particle size effect on it, a similar Ru particle size on carbon and alumina catalysts (4.4RuC-SEA-1.50nm, 1.5RuC-SEA-1.30nm and 2.0RuAl-SEA-C100-1.10nm) were selected for in-situ XPS (catalysts were treated in pretreatment chamber as described above). The Ru 3d<sub>5/2</sub> peaks of those catalysts are shown in Figure 3.7. The peak binding energy of Ru 3d<sub>5/2</sub> in 2.0RuAl-SEA-C100 appears at 280.9ev. On the other hand, for 4.4RuC-SEA and 1.5RuC-SEA samples, much lower binding energies of Ru 3d<sub>5/2</sub> were observed about 280.1ev and 280.2ev, respectively, which indicates metallic Ru in both catalysts and the electronic effect between Ru particle and supports are different.
Figure 3.7 Support effect on the Ru binding energy. XPS of spectra of Ru 3d for (A) 4.4 RuC-SEA, (B) 1.5RuC-SEA, (C) 2.0RuAl-SEA-C100 (right hand figure is expanded vertically).

Finally, XPS was further used to explore presence and effects of potassium in the alumina-supported DI catalyst, which based on the synthesis method retains all of the components of the $K_4Ru(CN)_6$ salt. The 2.0RuAl-DI XPS spectra are compared to those of the 2.0RuAl-SEA catalyst in Figure 3.8. A doublet peak located at 292.7 ev (K $p_{3/2}$) and 295.5 ev (K $p_{1/2}$) was observed ($\delta=2.8$ ev) for the DI sample, while potassium was not evident after the SEA preparation. SEA employs a great excess of solution so the potassium would have remained in solution and been filtered away from the SEA catalyst. These results also reveal that the presence of potassium causes a lowering of the
Ru binding energy as seen in both the Ru 3d5/2 peak and the Ru 3p doublet in Figure 3.8 (b). Ru is presumed fully oxidized in both cases, as it was exposed to ambient air.

Figure 3.8 K affects on the Ru binding energy (a) XPS of spectra of Ru 3d for 2.0RuAl - DI and 2.0RuAl-SEA (b) XPS of spectra of Ru 3p for 2.0RuAl -DI and 2.0RuAl-SEA.
Figure 3.9 shows IR spectra of CO adsorbed on different Ru particle sizes supported on alumina and K-promoted-2.0RuAl-SEA catalysts. From the IR spectrum of largest Ru particle size (2.70 nm), several main features can be identified. A relatively weak band centered at 2141 cm⁻¹ is assigned to Ru tricarbonyl species. The broad and strong band appears in the 1900-2120 cm⁻¹ region, where several overlapping bands with local peaks and shoulders are attributed to a combination of linear CO (2035 cm⁻¹) and Ru dicarbonyl species (2061 and 2070 cm⁻¹). In addition, a very weak and broad band is also observed in the 1800 cm⁻¹ region attributed to bridged-bond CO on Ru. These peaks and assignments are in close agreement with published spectra in the literature. The absolute intensities of the spectra substantially decreased as the particle size increased due to the decrease in the number of available Ru surface sites and thus adsorbed CO molecules. Comparing the spectral area of the 0.92 nm sample with that of the 2.70 nm sample shows a decrease of 65%. Similarly, the intensity of the shoulder at 2061 and 2070 cm⁻¹ decreased and at 2035 cm⁻¹ band increased. These changes are caused by the presence of more low coordinated Ru sites (e.g., edges, corners, kinks, etc.) in the smaller particle sample. For the 3K-promoted catalyst (f), the IR spectrum was significantly different than the unpromoted 2.0RuAl-SEA catalyst. The intensity of the band at 2141 cm⁻¹ almost disappeared and the linear CO peak shifted to 2008 cm⁻¹, which is 27 cm⁻¹ lower than the unpromoted catalyst. These features were previously reported by the work of Blackmond 83, who proposed that the absence of Ru tricarbonyl species in K-promoted samples is due to the formation of the adsorbed gem dicarbonyl species. After the “corrosive” 83 or oxidative chemisorption of CO on Ru, this species may form though its reaction with the surface hydroxyl groups on the alumina support. The carbonyl
species break away from Ru particle as partially oxidized monometallic Ru tricarbonyl entities. In addition, corrosive chemisorption is more favorable on small particles with low coordination sites. Thus, if sites with low coordination are blocked by the addition of K, the formation of these tricarbonyl species would be prevented.

![FTIR spectra](image)

Figure 3.9 FTIR spectra of different size of Ru particle supported on Alumina and K-promoted catalysts. (a) 2.0RuAl-SEA, (b) 2.0RuAl-SEA-C100, (c)2.0RuAl-SEA-C200, (d) 2.0RuAl-SEA-R520-24h, (e) 2.0RuAl-SEA-C300, (f) 3K-2.0RuAl-SEA.

3.3.3. Activity and stability of ruthenium catalysts

Hydrogenation of LA to GVL was evaluated over all Ru catalysts to determine the effects of particle size, support type (carbon or alumina) and potassium dopant. The chemical equation of this reaction is
C₃H₅O₃ (LA) + H₂ → C₅H₈O₂ (GVL) + H₂O \quad \text{Equation 3.2}

An Arrhenius plot for the 5.0RuC-com catalyst was made for the temperature range of 50 – 220°C and revealed a straight line with a slope corresponding to activation energy of 35 kJ/mol, as seen in Figure 3.3S (Appendix A). Prior studies have reported activation energies over supported Ru ranging from 34 to 64 kJ/mol for cinnamaldehyde, D-lactone, D-glucose, and arabinonic acid hydrogenation. The other two activation energies of LA hydrogenation reported in the literature are a value of 48 kJ/mol for a supported Ru catalyst and 33 kJ/mol for a supported Pd catalyst. Therefore, 35 kJ/mol is considered as the reasonable activation barrier for hydrogenation of LA over Ru/C. The linearity of the Arrhenius plot and the similarity of these activation energy values suggest that the current results are free from internal mass transfer limitations, which is also consistent with a calculation of the Weisz-Prater criteria (CWP). For 5.0RuC-com and 2.0RuAl-SEA, CWP are 0.17 and 0.68, respectively, indicating no internal mass transfer limitation at 220°C. However, our result is different from those of Bond and co-workers, where two regimes were observed when water was used as solvent. In low temperature region (50°C-100°C), internal mass transfer limitations were absent, but not in high temperature region. The difference could be due to a variety of factors, including catalyst support pore structure, catalyst particle size used in the reaction, and the increased solubility of H₂ in 1,4 dioxane.
In Table 3.2, catalytic activity is reported in four ways: a first order rate constant, reaction rates based on mass of Ru and mass of catalysts, and turnover frequencies (TOF) calculated from STEM estimates of dispersion. Rates were obtained at the times corresponding to 10% LA conversion. The tabulated values are the averages of two to four runs made for each sample. Error bars will be given and further analysis of this data will be made in several graphs in the discussion.

The unexpectedly high activity of the 2.0Al-DI catalyst and the XPS analysis of Figure 3.8 led to the suspicion that potassium promoted the reaction. Several SEA-prepared samples purposefully doped with K⁺ (3K-1.5RuC-SEA and 3K-2.0RuAl-SEA) confirmed this hypothesis by exhibiting higher activity than their K-free analogs. The 3K-1.5RuC-SEA sample was over two and a half times as active as the K-free analog, and potassium doping of 2.0RuAl-SEA led to a six-fold increase in activity.

Four catalysts were selected for a durability study: 1.5RuCSEA, 3K-1.5RuCSEA, 2.0RuAlSEA and 3K-2.0RuAlSEA. Catalysts were aged at reaction conditions for 6 h and 24 h, then recovered by filtration and dried overnight at 120°C. XRD and STEM were employed for post-aging characterization. XRD patterns of all used catalysts were virtually indistinguishable from those of the fresh catalysts, which implies that no significant particle sintering occurs. STEM imaging gave more detailed data on sintering and STEM-derived particle sizes of the aged catalysts are summarized in Table 3.2. The 1.5RuC-SEA particle size increased from 1.30 to 1.70 nm after aging 24 hours, and the 3K-1.5RuC-SEA particle size increased negligibly after 6 hours, but sintered to 1.80 nm after 24 hours. From ICP analysis of the liquid phase, small amounts of potassium had dissolved such that the initial 3.0 wt% K fell to 2.8% after 6 hours and to 2.7% after 24
hours of aging. The 2.0RuAl-SEA catalyst sintered from 0.92 to 1.80 nm after 24 hours aging. The K-doped alumina-supported sample did not appear to sinter after 6 hours, but after 24 hours the size had increased to 2.01 nm. The potassium content decreased slightly from 3.0 to 2.9% after 6 hours, and to 2.8% after 24 hours. The trends on metal sintering and potassium loss will be discussed in the next section.

Table 3.2 Summary of Ru particle size and catalytic activity.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Particle size (nm)</th>
<th>k_{rxn} liter/(gRu h psi)</th>
<th>Rate^{10^3} (mol LA)/(g Ru^s)</th>
<th>Rate^{10^7} (mol LA)/(g cat^s)</th>
<th>TOF/s^{-1}</th>
</tr>
</thead>
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<tr>
<td></td>
<td>XRD</td>
<td>STEM a</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Carbon</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>1.5RuC-SEA</td>
<td>&lt;1.50</td>
<td>1.30</td>
<td>0.0557</td>
<td>1.70</td>
<td>2.49</td>
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<td>1.2RuC-SEA</td>
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<td>1.08</td>
<td>0.0482</td>
<td>1.56</td>
<td>2.35</td>
</tr>
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<td>3K-1.5RuC-SEA</td>
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<td>0.121</td>
<td>4.40</td>
<td>6.70</td>
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<td>4.4RuC-SEA</td>
<td>&lt;1.50</td>
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<td>0.0911</td>
<td>3.10</td>
<td>14.0</td>
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<td>1.5RuC-DI</td>
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<td>2.06</td>
<td>0.0128</td>
<td>0.430</td>
<td>0.650</td>
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<tr>
<td>5.0RuC-com</td>
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<td>2.52</td>
<td>0.0219</td>
<td>0.540</td>
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<td>Alumina</td>
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<td>0.0219</td>
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<td>0.965</td>
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<td>3K-2.0RuAl-SEA</td>
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<td>0.0836</td>
<td>3.10</td>
<td>6.10</td>
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<td>2.0RuAl-DI</td>
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<td>1.31</td>
<td>0.0319</td>
<td>0.880</td>
<td>1.81</td>
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<td>5.0RuAl-com</td>
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<td>4.82</td>
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<td>0.440</td>
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<td>Aged catalyst</td>
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<tr>
<td>1.5RuC-SEA -6h</td>
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<td>1.63</td>
<td>2.20</td>
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<td>4.10</td>
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<td>3K-1.5RuC-SEA 24h</td>
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<td>2.30</td>
<td>3.40</td>
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</tr>
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<td>Catalyst</td>
<td>d \text{avg}</td>
<td>d_{0.5}</td>
<td>k_{0.5}</td>
<td>k_{1.5}</td>
<td>k_{2.0}</td>
</tr>
<tr>
<td>--------------------------</td>
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</tr>
<tr>
<td>2.0RuAl-SEA 24h</td>
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<td>1.80</td>
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<td>4.80</td>
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<td>&lt;1.50</td>
<td>1.65</td>
<td>2.10</td>
<td>9.20</td>
<td>0.350</td>
</tr>
</tbody>
</table>

Sintered catalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>d \text{avg}</th>
<th>d_{0.5}</th>
<th>k_{0.5}</th>
<th>k_{1.5}</th>
<th>k_{2.0}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2RuAl-SEA-C100</td>
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<td>1.81</td>
<td>3.63</td>
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<tr>
<td>2RuAl-SEA-C200</td>
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<td>0.26</td>
</tr>
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<td>2RuAl-SEA-C300</td>
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<td>2.70</td>
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<td>0.79</td>
<td>0.08</td>
</tr>
<tr>
<td>2RuAl-SEA-R520-24h</td>
<td>&lt;1.50</td>
<td>1.60</td>
<td>1.33</td>
<td>2.66</td>
<td>0.21</td>
</tr>
</tbody>
</table>

**a.** Number average \( d_{\text{avg}} = \frac{\sum n_i d_i}{\sum n_i} \).

3.3.4. Activity of ruthenium catalysts, particle size effect, supports effect and Potassium effect.

A comparison of measured rate constants, corrected to the same temperature, can be made with the previous studies of this reaction employing dioxane as solvent \(^{19, 32}\). (The linearity of the Arrhenius plot, Figure 3.2S, over the temperature range 50 – 220°C supports this extrapolation.) Over a 5 wt% Ru/C catalyst, Al-Shaal et al. \(^{19}\) reported a LA reaction rate of 1.24 mol LA/(g Ru h) with 174 psi H\(_2\) pressure and 0.42 molar LA at 130°C (Table 3.1S). Using the activation energy of 35 kJ/mol, this translates to a rate constant at 220°C of 0.075 liter/(gRu h psi), which is toward the high end of the rate constants calculated from the current study (Table 2). Values for the 3K-1.5RuC-SEA, 4.4RuC-SEA, and 3K-2.0RuAl-SEA catalysts were higher at 0.12, 0.091, and 0.084 liter/(gRu h psi), respectively. While the Ru weight loading of the Al-Shaal catalyst was
higher than those used here (5.0% versus 1.5, 4.4, and 2.0%), the promotion by K as well as high Ru dispersion of the current catalysts appears to more than make up for the lower Ru loading. Gong et al.\textsuperscript{32}, at 173 psi H\textsubscript{2} pressure and 0.36 molar LA at 130°C and 160 min, reported a conversion of 4.32% from which a rate constant of 0.00089 liter/(g Ru h psi) can be calculated. The value translated to 220°C is 0.0038 liter/(g Ru h psi), which about 4 times lower than the lowest value reported here. Gong et al. employed a 5.0% Ru/C commercial catalyst, but did not report Ru dispersion. The relatively low rate constant from their work suggests the Ru dispersion of their catalyst was low. Recently, Bond et al.\textsuperscript{15} reported that a 5.0% Ru/C commercial catalyst with 40.4% Ru dispersion gives a TOF of 0.17s\textsuperscript{-1} at 130°C, similar to the 5.0% Ru/C commercial catalyst used here (0.14s\textsuperscript{-1}). The effects of support type, particle size, and presence of potassium will now be discussed individually.

3.3.4.1 The effect of particle size

The effect of particle size can be explored with a calculation of turnover frequency and its variation with particle size. These calculations are shown for all K-free, in-house prepared catalysts in Figure 3.10. Plotting both the carbon and alumina supported catalyst TOFs versus nanoparticle size, there appears to be a sharp volcano and maximum in the activity of catalysts at 1.50 nm for both supports, which indicates the hydrogenation of LA is structure sensitive on Ru particle size. The sharp volcano peak with the narrow range of Ru particle size is very similar to the plot of activity (TOFs) versus Au particle size for CO oxidation observed by Goodman\textsuperscript{88}. For a structure sensitive reaction, an active site may consist of an ensemble of surface atoms arranged in a particular configuration. Structure sensitivity of supported Ru catalysts for ammonia
synthesis has been widely reported, for example, where so-called B5-type sites are believed to be extremely active and thus to dominate the reaction activity. B5-type active sites (an active site that is part of edges on small Ru crystals with only hcp (001) and (100) surfaces exposed and consists of 5 atom surfaces) are identified as the most active sites, as shown in Fig 12 (c). The formation of B5-types needs to fulfill two requirements: (1) the presence of a three-fold hollow site and a bridge site, which are exposed and close together (2) part of atoms have to be low-coordinated surface atoms such as edge and corner atoms. Thus, the probability of the presence of B5-types site on very low coordinated and small particles (1.50 nm and smaller) is significantly smaller than relatively larger and higher coordinated particles (1.50 to 2.50 nm). Consequently, the maximum value of activity was observed about at 1.50 nm for Ru particle size. Though B5 type sites are not necessarily operative for the current reaction, the active sites stemming from two different nanoparticle surfaces would exhibit a similar size dependency.

The relatively lower activity of alumina is manifested by those points being lower than the carbon-supported catalyst of the same size, the same result was observed by Martinelli. In particular, TOF of the 1.80 nm alumina-supported nanoparticles of the 2.0RuAl-SEA-24h aged catalyst is well below that of the 1.70 nm 1.5RuC-SEA-24h aged catalyst. However, the fact that both sets of data fall into the same trend suggests that the inherent activity difference in catalyst support is less than the difference in activity due to particle size.
Figure 3.10 TOF versus particle size estimated from STEM a) carbon supported catalysts (left side) and b) alumina supported catalysts (right side).(c) Fraction of edge atoms and active sites on small Ru crystals relative to the total number of atoms versus particle size, with permission.

To more quantitatively correlate the activity of these catalysts with certain types of Ru surface sites, the infrared spectra of Fig. 3.9 were fit in the much-cited manner of Chin et al. Figure 3.11 shows the results of this procedure for the 2.0RuAl-SEA and 3K-2.0RuAl-SEA samples, the detailed curve-fitting procedure and the fitted spectra of the other catalysts are discussed and shown in Table 3.3S (Appendix A). The plot of the ratio of reduced Ru to Ru\(^{n^+}\) (summation of peaks 4, 6, and 7 for reduced Ru; summation of peaks 8, 9, 10, 11, and 12 for Ru\(^{n^+}\)) versus particle size yields the same volcano shape as for the TOFs, as shown in Figure 3.12. This indicates a correlation between activity (TOF) and degree of Ru reduction, although the sharpness is somewhat muted for alumina. Since all catalysts were pretreated in a reducing environment, the oxidized Ru sites may be caused by the corrosive chemisorption discussed earlier. It is notable that the
relative fraction of $\text{Ru}^0$ to $\text{Ru}^{n+}$ significantly increases with addition of K, which indicates K helps to prevent Ru oxidation at the reaction temperature (220°C), so enhancing activity. The electron donating role of K will be discussed later.

Figure 3.11 Fitting of selected spectra (a) 2.0RuAl-SEA, (b) 3K-2.0RuAl-SEA.
3.3.4.2. Effect of support: carbon versus alumina

Reaction rates can be reported as moles of LA produced per gram of Ru per time (Figure 3.13 (a)), or moles of LA produced per gram of catalyst per time (Figure 3.13 (b)). For the undoped samples the carbon support appears to impart higher activity than alumina. Both the K-free and K-doped 1.5RuC-SEA and 3K-2.0RuC-SEA catalysts have higher per-g Ru activity than the alumina analogs, 2.0RuAl-SEA and 3K-2.0RuAl-SEA, in spite of being a bit more poorly dispersed (1.30 versus 0.92 nm). The 1.70 nm particle size of the 24 h aged 1.5RuC-SEA sample is much more active than the similarly sized (1.80 nm) 24 h aged 2.0RuAl-SEA sample (Table 3.2 and Figure 3.10, below). This agrees with the findings of Al-Shaal et al. 19 and Galletti et al. 20, who also found carbon to impart higher activity than alumina. They claimed, however, that the
enhancement is caused by the much higher surface area of Ru/C than Ru/Al$_2$O$_3$. Rode et al. $^{18}$ reported the same observation with the same interpretation. As there is no apparent direct role of the support in the reaction (both supports exhibited no activity in control experiments) the difference in surface area would not appear to be a primary cause for activity difference. We offer a different explanation based on electronic effects.

Two sets of catalysts with the similar Ru particle size, 4.4 RuC-SEA (1.50 nm) with TOF (0.47 s$^{-1}$), 1.5RuC-SEA (1.30 nm) with TOF (0.22 s$^{-1}$) and 2.0RuAl-SEA-C100 (1.10 nm) with TOF (0.19 s$^{-1}$), were further characterized by in-situ XPS to explore the support effect (Figure 7). The binding energy of Ru3d$_{5/2}$ in carbon (280.1 ev and 280.2) is lower than in Al$_2$O$_3$ (280.9 ev) which is consistent with metallic Ru particles on carbon being more difficult to oxidize under reaction conditions than on Al$_2$O$_3$. This is further supported by the FTIR data in Figure 12, where the higher ratio of (Ru$^0$/Ru$^{n+}$) or less corrosive chemisorption, is associated with higher activity with particle sizes ranging from 0.9 nm to 1.5 nm.

The K-doped alumina catalyst 3K-2.0RuAl-SEA has activity per mass Ru almost as high as the best carbon supported catalyst, which is also K-doped (the 3K-1.5RuC-SEA sample). The most active catalyst per gram catalyst is the 4.4RuC-SEA sample, which is highly loaded, well dispersed (1.50 nm average particle size by STEM) and supported on carbon. The utility of the SEA synthesis method is seen as the per g catalyst activity of the 4.4 wt% RuC-SEA catalyst (Figure 13b) with 10% less Ru is over five times more active than the two commmercial 5 wt% Ru catalysts, which have much larger particles.
Figure 3.13 Rates in terms of (a) mass of active metal and (b) mass of catalyst.
3.3.4.3 The effect of potassium

The effect of potassium was first observed as a higher activity of the 2.0RuAl-DI compared to the 2.0RuAl-SEA catalyst, even though the latter catalyst was better dispersed (Table 3.2, 0.92 nm versus 1.30 nm by STEM). With the K₄Ru(CN)₆/γ-Al₂O₃ synthesis, for SEA, only the [Ru(CN)₆]⁴⁺ complex was adsorbed onto the γ-Al₂O₃ support, as a great excess of liquid is used and is filtered from the solid at the conclusion of the contact time. The vast majority of potassium remains in the filtrate and is separated from the solid. In dry impregnation, however, potassium is doped into the support with the Ru(CN)₆⁴⁺ complex and stays there as the paste is dried.

It has been reported that potassium can enhance the activity and selectivity for some reactions, such as ammonia synthesis, CO hydrogenation, and Fischer-Tropsch synthesis (FTS)⁹¹-⁹³. The mechanism of K promotion for ammonia synthesis over Ru/C is suggested not only to significantly enhance the amount of adsorbed hydrogen, nitrogen and ammonia, but also to weaken the adsorption of strength of those molecules via electronic interaction of the promoter with Ru⁹⁴. In the current catalysts, the TPR data of the K-promoted and K-free (DI and SEA preparations, respectively) from Figure 3.2b shows that the K promoter actually retards reduction relative to the K-free preparation, which suggests a weaker interaction of hydrogen with the K-promoted surface. This observation is in good agreement with FTIR data showed in Table 3S, where the fraction of linear bonded CO is reduced from 0.18 to 0.14 with addition of K. This indicates that the presence of K may suppress H₂ chemisorption by blocking the low coordinate sites of Ru, thus leading to a weaker interaction.
On conductive supports such as graphite, the role of K in FTS has been reported as an electron conductor to facilitate the transfer of electrons from the potassium to the ruthenium \(^{91}\). The current results exhibit about the same enhancement of rate over both alumina and carbon supports, so it appears that at the current reaction conditions the promotional effect is not related to the conductivity of the support. In fact, the electronic effect on alumina supported Ru is seen in the XPS results of Figure 3.8. The binding energy of the Ru 3d\(_{5/2}\) peak shifts from 281.6 eV for the unpromoted catalyst to 280.9 eV for the K-promoted sample. The same trend also was observed in the Ru 3p doublet. These are consistent with the earlier postulation for FTS over Fe \(^{91,95}\) that the addition of K results in a decrease of activation energy by lowering the local ionization energy of Fe in the vicinity of an adsorbed K atom.

To our knowledge, the role and the active state of K in hydrogenation of LA has not been reported. However, many studies of alkali metal promotion effect for supported metal catalysts have suggested that alkali species may have significant electronic or dipole-dipole interactions with transition metals. These interactions result in modifications in the nature of adsorption of molecules such as CO on these metals. Indeed, new CO adsorption peaks appeared in the low frequency range in the K-promoted catalyst in Figure 3.11. This indicates that a strong, short-range interaction occurs between K and CO, which is similar to CO adsorbed on K-promoted Ni (111) \(^{83}\). Secondly, the peak around 2140 cm\(^{-1}\) (summation of peaks 1, 2 and 3) almost disappeared, resulting in an increase of the ratio of reduced Ru to Ru\(^{n+}\). Finally, XPS data shows that K lowers the binding energy of Ru to make it more “metallic”. In summary, the role of K in enhancing the activity can be ascribed to the increase of electron donation from K to Ru.
3.3.4.4. Catalyst Durability

Significant deactivation was seen in all catalysts and was more pronounced for the K-doped samples. The K-free 1.5RuC-SEA catalyst deactivated 18% after 24 h aging (Table 3.2, from 1.70 to 1.42 x 10^{-3} mol LA/(g Ru s). The K-free 2.0RuAl-SEA catalyst deactivated 8%, from 0.490 to 0.430 x 10^{-3} mol LA/(g Ru s) after 24 h. On the other hand, the 3K-1.5RuC-SEA deactivated 44% over 24 h, from 4.40 to 2.30 x 10^{-3} mol LA/(g Ru s), and the 3K-2.0RuAl-SEA deactivated 58% over 24 h, from 3.10 to 1.30 x 10^{-3} mol LA/(g Ru s).

The mechanism of deactivation can be better understood by a consideration of the turnover frequencies of the four aged catalysts, shown in Figure 14 as a function of aging time. For the carbon support, the 24 h aged 1.5RuC-SEA catalyst sintered from 1.30 to 1.70 nm, but the TOF remained essentially the same as these two particle sizes have about the same TOF (Figure 3.14). The K-doped sample, 3K-1.5RuC-SEA, did not sinter appreciably after 6 hours, but sintered to about the same extent (to 1.80 nm versus 1.70 nm) as the K-free sample. It appeared to lose 0.2 wt% K after 6 hours (as determined by ICP), and another 0.1 wt% at 24 hours. The TOFs of the 6 and 24 hour aged samples did decrease, and this can be attributed to the loss of potassium.

For the alumina support, the undoped sample sintered significantly (from 0.92 to 1.80 nm), representing a loss of 50% of the active area, but the TOF increased due to the larger particle size. This mitigated the decrease in activity per g Ru (resulting in only the 8% decrease). The drop of the TOF of the K-doped sample aged 6 hours, which did not sinter, may be attributed to a loss of potassium. The 24 h aged sample
had about the same TOF as the 6 h aged sample; presumably the loss of more potassium was balanced by the higher TOF of the larger Ru particle size. In general it appears that the loss of activity is mainly due to nanoparticle sintering, accompanied by some K loss.

(a) carbon
Figure 3.14 TOF versus aging conditions for catalysts supported on a) carbon and b) alumina.

3.4. CONCLUSION

Well dispersed Ru particles were achieved by applying the SEA method to oxidized carbon and $\gamma$-Al$_2$O$_3$ supports. The surface of oxidized carbon in the solution above its PZC (4.0), becomes deprotonated and negatively charged and is able to absorb cationic $[\text{Ru(NH}_3)_6]^{3+}$. On the other hand, the surface of $\gamma$-Al$_2$O$_3$ in solution at pHs below its PZC (8.1), becomes protonated and positively charged and able to absorb anionic
[Ru(CN)₆]⁴⁻. The maximum uptake of [Ru(NH₃)₆]³⁺ on oxidized carbon occurs at the final pH of 9.9 and of [Ru(CN)₆]⁴⁻ on γ-Al₂O₃ occurs at the final pH 2.1. The maximum surface densities over the respective supports correspond to Ru metal loadings of 1.5 wt% for Ru/C and 2.0 wt% for Ru/γ-Al₂O₃. The Ru (number) particle size after reductions were 1.30 nm for Ru/C and 0.92 nm for Ru/Al₂O₃ as observed with STEM. The high dispersion of these Ru nanoparticles on carbon and their promotion by potassium on carbon and alumina has led to the highest reported activity (per g Ru, per g catalyst, and TOF) of Ru catalysts for LA hydrogenation to GVL. Aging in the reaction medium for 24 h led to significant deactivation; up to 18% for the undoped catalysts due to nanoparticle sintering, and up to 58% for the K-doped alumina and carbon catalysts due to both sintering and K loss.

Several other trends were revealed by this rational synthesis of Ru nanoparticles. First, carbon supported catalysts were generally more active than alumina catalysts because of more formation of metallic Ru in carbon than alumina. Second, the presence of potassium significantly enhances the activity over either support, due to a significant decrease in the electron binding energy of Ru in the presence of K⁺. Finally, LA hydrogenation is structure sensitive and depends on Ru particle size, with a maximum in particle size about 1.5 nm.
CHAPTER 4

A SYSTEMATIC STUDY OF ALKALI AND ALKALINE EARTH METAL PROMOTION OF ALUMINA SUPPORTED RUTHENIUM FOR HYDROGENATION OF LEVULINIC ACID TO GAMMA-VALEROLACTONE

4.1. INTRODUCTION

With the dramatic increase of the global consumption of fossil fuels and the associated problem of global warming caused by the rising amount of greenhouse gas emissions, it is urgent to find renewable replacements for petroleum-derived products. The potential of lignocellulosic biomass for green catalytic conversion to renewable fuels and valuable chemicals has been underscored by several recent reports \(^1\), \(^4\), \(^5\), \(^96\), \(^97\). Levulinic acid (LA) is an inexpensive, versatile and viable platform chemical and can be produced efficiently through the decomposition of lignocellulosic biomass, which has recently become a commercial-scale process. LA may be used as the starting material for the production of many useful C\(_5\) based compounds such as \(\gamma\)-valerolactone (GVL), 2-methyltetrahydrofuran (MTHF) and other derivatives. The former compound, GVL, has been identified by the US DOE as the key target molecule to be derived from biomass for its many applications as a renewable/green solvent, a precursor to alkene based transportation fuels, food additives, and a conventional gasoline additive in a capacity similar to ethanol \(^1\), \(^6\), \(^98\). GVL is commonly synthesized by hydrogenation of LA using ruthenium supported catalyst \(^13\), \(^14\), \(^19\), \(^20\).
In the past few decades, alkali metals (AM) have been widely used as promoters in many industrial catalytic processes, such as Fischer-Tropsch Synthesis \(^{99,100}\), alcohol synthesis from syngas \(^{101,102}\), water gas shift \(^{103,104}\), and ammonia synthesis \(^{105-107}\). When alkalis were added to supported metal catalysts, activity is increased, the selectivity of desired product is enhanced and catalyst stability is improved. Less is known about alkaline earth metal (AEM) promoters. Enhanced methanol selectivity on a magnesia-Pd/SiO\(_2\) catalyst was reported by Driessen \(^{108}\). Lietz et al also found that the role of magnesia in promoting Pd activity is to significantly increase the dispersion of the metallic component \(^{109}\). A similar promotion effect was found for calcium doping of Pd/SiO\(_2\) in methanol synthesis \(^{110-113}\).

In our earlier work \(^{23}\), we reported that the presence of potassium significantly enhances the Ru activity, TOFs for LA hydrogenation increased by a factor of 4 and 6 on carbon and alumina support, respectively, with the addition of 3wt\% potassium. To our knowledge, the chemical state, physical location, and the role of alkali metal have not been reported for this reaction. Research to date has proposed several mechanisms for the role as promoters/poisons of alkali and alkaline earth metal for Fischer-Tropsch synthesis and CO hydrogenation for methanation \(^{24,25}\). Those suggested mechanisms can be summarized in two aspects, which are the modification of metal surfaces and the modification of support. Modification of metal surfaces could be achieved by electron donation to or from the metal, geometric site blocking of active metal site, alkali-induced metal surface reconstruction and direct chemical interactions between promoter and adsorbate through-space interactions (e.g. dipole-dipole or electrostatic) and metal-modifier electronic interactions leading to changes in the strength. Modification of
support could take place when alkali and alkaline earth metal form chemical compounds with many commonly used oxide supports, such as alumina, silica, or titania, which could be ascribed to the influence of the overall acidity or the basicity of the supported catalysts with the presence of promoters.

The aim of this work was to investigate the effects that alkali \( \text{Na}^+, \text{K}^+, \text{Cs}^+ \) and alkaline earth \( \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Ba}^{2+} \) metals have on Ru activity for hydrogenation of LA in terms of electronic effects, site blocking, physical position and active chemical state of respective dopants. It was also desired to study how support modification affects Ru activity.

4.2. EXPERIMENTAL METHODS

4.2.1. Materials

Potassium hexacyanoruthenate(II) hydrate \( \text{K}_4\text{Ru(CN)}_6 \), levulinic acid (98%), 1,4 dioxane (99.8%), potassium nitrate (>99.9%), potassium hydroxide (Laboratory, Pellet), sodium nitrate (99.9%), cesium nitrate (99.9%), magnesium nitrate (99.9%), calcium nitrate (99.0%) and barium nitrate (99.0%) were purchased from Sigma-Aldrich. SBa-200 gamma alumina (surface area 189 m\(^2\)/g, PZC \(~\)8.3) was obtained from Aerosi.

4.2.2. Ruthenium and promoted catalysts preparation

The details of the synthesis and characterization of 2wt% Ru on alumina catalyst (2RuAl-SEA) by strong electrostatic adsorption (SEA) has been reported in our previous paper \(^23\). A large amount of 2RuAl-SEA (\(~\)20g) was synthesized for the
preparation of all promoted catalysts. The alkali metal (AM) / alkaline earth metal (AEM) were introduced to 2RuAl-SEA catalyst by dry impregnation, and were dried overnight at room temperature, then reduced at 220°C (or 400°C, based on the need of experiments) for 1h at a heating rate of 2.5°C/min. For simplicity reasons, the base catalyst (2 wt% Ru/alumina-SEA) is not included in the catalyst names since it is the same for all. The numbers proceeding AM and AEM are weight percentages and represent doped catalysts. For example, 3 wt% KNO\textsubscript{3} or 3 wt% KOH, doped on 2 wt% Ru/alumina catalyst prepared by SEA pretreated at 220°C is abbreviated 3K-220°C and 3KOH-220°C, respectively. Nomenclature of catalysts synthesized is given in Table 4.1.

4.2.3. Catalyst characterization

X-ray Photoelectron Spectroscopy (XPS) was conducted with a Kratos AXIS Ultra DLD XPS system with a monochromatic Al K source at 15 keV and 120 W. Spectra were fit by applying a Shirley-type background subtraction and a charging correction with reference to carbon 1s at 284.6 eV. Powder X-ray diffraction (XRD) analysis was performed using a Rigaku MiniFlex II system. The XRD patterns were compared to JCPDS reference spectra using JADE software. The radiation source was Cu Kα (λ=1.5405Å) at a tube voltage of 30kV and current of 15 mA. All patterns were taken at a scan rate of 0.5°/min and a sampling width of 0.02°. Ruthenium dispersion was determined with chemisorption using hydrogen pulse titration of oxygen-precovered Ru with a Micromeritics Autochem II 2920 automated chemisorption analyzer. Prior to titration, approximately 0.1g of sample was pretreated in flowing H\textsubscript{2} for 3hrs at 250°C and then purged with flowing Ar for 0.5hr to remove chemisorbed hydrogen from the
metal surface before cooling to 40°C in Ar. A gas flow of 10% O₂/balance He was passed over the samples for 30mins to form O-covered Ru surface species. After purging with pure Ar flow for 30mins to remove residual gas phase weakly adsorbed O₂, the sample was ready for pulse flow H₂ titration. At 250°C, pulses of 10%H₂/balance Ar were dosed and repeated at 5min intervals until all surface adsorbed atomic oxygen reacts with H₂ to form H₂O and Ru-H surface species, assuming Ru:H adsorption stoichiometry is 0.4:1. The metal dispersion results were found to be reproducible within ±5%. Hydrogen consumption was quantitatively measured using a high sensitivity thermal conductivity detector (TCD) below the sample cell. Hydrogen pulses were continued until no further uptake of H₂ was observed. About 0.050g of ground sample was pressed into pellets with a diameter of 0.5 in. and thickness of approximately 20mg/cm² for Fourier Transform Infrared (FTIR) spectroscopic studies of adsorbed CO. Transmission FTIR spectra were collected in the single beam mode, with a resolution of 2 cm⁻¹, using a Thermo Electron model 4700 spectrometer with a liquid nitrogen-cooled MCT detector. All experiments were performed in a stainless steel cylindrical sample cell under a gas flow rate of 70ml/min. Prior to each experiment, the samples were reduced in H₂ for 2h at 400°C, held in He for 0.5h at 400°C (220°C depending on experiment), cooled to RT in He, exposed to 1% CO/He, and then flushed with pure He. The initial background spectra were taken before CO exposure. Finally, spectra were collected after purging with He to remove physisorbed and gas phase CO. Pyridine-FTIR experiments were conducted in the same IR cell at 150°C, using 30mg sample pellets. The samples were reduced in H₂ at 400°C (220°C) for 1.5h, then treated in He for 0.5h at the same temperature. The temperature was reduced to 150°C and held for 0.5h, the initial background spectra were
taken before pyridine-vapor exposure. Finally, the IR spectra was taken after purging pyridine for 0.5h at 150°C following purging He for 0.5h in order to remove physisorbed pyridine.

4.2.4. Reactivity evaluation

The hydrogenation of LA was performed in a 100 ml autoclave (Parr Instruments Co. USA) with the stirring speed of 1000 rpm to avoid external mass transfer limitations. The reaction was run for 2 h at 200 psi H₂ and 220°C with 36mg of promoted catalysts. Nonpolar, aprotic 1,4 dioxane was employed as the solvent so that the catalytic activity could be attributed entirely to the metal sites. More details of reaction operation are in the previous paper. The only product observed in all runs was GVL (selectivity was 100%). The intrinsic reaction rate is expressed in terms of turnover frequency (TOF s⁻¹), defined as moles of LA converted per surface Ru metal atom per second, at the time corresponding to 10% conversion of LA.

4.3. RESULTS AND DISCUSSION

4.3.1. Results

4.3.1.1. Catalyst characterization

Table 4.1 summarizes Ru dispersions and TOFs of the synthesized catalysts. The addition of alkali metal has a small effect on Ru dispersion, decreasing from 62.5% to 50% for the 3K-400°C catalyst. The Ru phase was XRD transparent (see Figure 4.1 for representative patterns). The number average size detection limit of the silicon strip detector on this Rigaku Miniflex instrument is about 1.5nm, suggesting that the Ru particles on the potassium catalyst are smaller than 1.5nm (> 66.7% dispersion). This is
in reasonable agreement with the chemisorption results of the K-free sample. There are no peaks of any potassium oxides compounds in the XRD patterns of the promoted catalyst. Thus, XRD suggests that potassium does not form a crystalline phase and at least some of it is present on the Ru surface. Na\(^+\) and Cs\(^+\) also impede chemisorption to a significant extent at the high Na\(^+\)/Ru ratios over half the surface appears to be blocked, even at low Cs\(^+\)/Ru ratios a significant portion of the surface appears blocked by bulky Cs ions.

Table 4.1 Nomenclature, Ru dispersion and TOF of Alkali metal (AM) promoted catalysts synthesized.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(AM/Ru) atomic ratio (nominal)</th>
<th>AM precursor</th>
<th>Ru dispersion (%)</th>
<th>TOF (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2RuAl-SEA</td>
<td>-</td>
<td>-</td>
<td>63</td>
<td>0.08</td>
</tr>
<tr>
<td>Alkali Metal (AM)</td>
<td></td>
<td>KNO(_3)</td>
<td>56</td>
<td>0.27</td>
</tr>
<tr>
<td>1K-220°C</td>
<td>1.3</td>
<td></td>
<td>50</td>
<td>0.47</td>
</tr>
<tr>
<td>2K-220°C</td>
<td>2.6</td>
<td></td>
<td>50</td>
<td>0.57</td>
</tr>
<tr>
<td>3K-220°C</td>
<td>3.9</td>
<td></td>
<td>50</td>
<td>0.29</td>
</tr>
<tr>
<td>4K-220°C</td>
<td>5.2</td>
<td></td>
<td>50</td>
<td>0.38</td>
</tr>
<tr>
<td>5K-220°C</td>
<td>6.5</td>
<td></td>
<td>50</td>
<td>0.50</td>
</tr>
<tr>
<td>1K-400°C</td>
<td>1.3</td>
<td></td>
<td>53</td>
<td>0.65</td>
</tr>
<tr>
<td>2K-400°C</td>
<td>2.6</td>
<td></td>
<td>50</td>
<td>0.52</td>
</tr>
<tr>
<td>3K-400°C</td>
<td>3.9</td>
<td></td>
<td>50</td>
<td>0.45</td>
</tr>
<tr>
<td>4K-400°C</td>
<td>5.2</td>
<td></td>
<td>63</td>
<td>0.43</td>
</tr>
<tr>
<td>5K-400°C</td>
<td>6.5</td>
<td></td>
<td>63</td>
<td>0.69</td>
</tr>
<tr>
<td>1KOH-220°C</td>
<td>1.3</td>
<td>KOH</td>
<td>48</td>
<td>0.47</td>
</tr>
<tr>
<td>3KOH-220°C</td>
<td>3.9</td>
<td></td>
<td>63</td>
<td>0.42</td>
</tr>
<tr>
<td>5KOH-220°C</td>
<td>6.5</td>
<td></td>
<td>63</td>
<td>0.66</td>
</tr>
<tr>
<td>1KOH-400°C</td>
<td>1.3</td>
<td></td>
<td>53</td>
<td>0.45</td>
</tr>
<tr>
<td>3KOH-400°C</td>
<td>3.9</td>
<td></td>
<td>53</td>
<td>0.45</td>
</tr>
<tr>
<td>5KOH-400°C</td>
<td>6.5</td>
<td></td>
<td>56</td>
<td>0.30</td>
</tr>
<tr>
<td>1Na-220°C</td>
<td>2.2</td>
<td>NaNO(_3)</td>
<td>46</td>
<td>0.47</td>
</tr>
<tr>
<td>3Na-220°C</td>
<td>6.6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
XPS was employed to identify whether the alkali nitrate precursors were decomposed after the reduction pretreatment step at 220°C. Fig. 1 displays the XPS survey scans of the catalyst series with high weight loading of AM dopants (5K-220°C, 7Na-220°C and 5Cs-220°C samples), which clearly indicate the presence of the promoters along with Al, O, and adventitious C. The N₁s peak (about 399ev) is not

<table>
<thead>
<tr>
<th>Sample</th>
<th>Intensity</th>
<th>Promoter</th>
<th>2θ Position</th>
<th>30°</th>
<th>0.59</th>
</tr>
</thead>
<tbody>
<tr>
<td>5Na-220°C</td>
<td>11.0</td>
<td></td>
<td></td>
<td>30</td>
<td>0.59</td>
</tr>
<tr>
<td>7Na-220°C</td>
<td>15.4</td>
<td></td>
<td>0.59</td>
<td>29</td>
<td>0.51</td>
</tr>
<tr>
<td>1Cs-220°C</td>
<td>0.4</td>
<td>CsNO₃</td>
<td>50</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>3Cs-220°C</td>
<td>1.2</td>
<td></td>
<td>50</td>
<td>0.79</td>
<td></td>
</tr>
<tr>
<td>5Cs-220°C</td>
<td>1.9</td>
<td></td>
<td>48</td>
<td>0.69</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.1 XRD patterns of gamma-alumina and 3K-400°C.
observed for these three catalysts, indicating that the nitrate precursors are substantially decomposed under 220°C in H₂ for 1h. ¹¹⁵

Figure 4.2 XPS survey scan spectra for 5Cs-220°C, 5K-220°C and 7Na-220°C.

XPS was also further used to explore electronic effects in the promoted catalysts. The XPS spectra of the Ru 3d region for the potassium doped catalysts with various potassium weights loading as representative example are presented in Figure 4.3, where the most intense doublet peaks at 280.1ev and 284.3ev (δ=4.2ev) are attributed to metallic Ru. ²³, ¹¹⁶ The carbon 1s (284.6ev) peak was used as an internal standard to confirm the position of the peaks. Due to the overlapping of the Ru 3d₃/₂ peak with the carbon 1s peak, the binding energy of the Ru 3d₅/₂ peak was used to determine the oxidation state of Ru present on the surface. However, a shoulder about 283ev in 4K-220°C and 5K-220°C samples become visible as the amount of adventitious carbon becomes lower comparing with 1K-220°C, 2K-220°C and 3K-220°C samples. In our previous study, the binding energy of the Ru 3d₅/₂ peaks in 2RuAlSEA was seen at
280.1ev, which was attributed to metallic Ru. Notably, a shift to lower binding energy of the Ru 3d_{5/2} peak was observed for all alkali promoted catalysts in comparison with the alkali free catalyst (2RuAlEA). Furthermore, this negative shift increased as the weight loading of potassium increased. The binding energy shift of Ru 3d_{5/2} peak of 5K-220°C at 279.14ev, is -0.96ev relative to the unpromoted Ru (280.1ev). Negative BE shifts are also observed in previous studies with the addition of alkali metal to Ru or other metals systems \textsuperscript{117-121}, and will be discussed later. For bimetallic catalysts, either the change of particle sizes or electronic interactions between the two metals could result in this BE shift as Ru particle size appears to be constant\textsuperscript{122,123}. In this study, the negative shift with increasing weight loading of alkali metal is most likely due to electronic interactions, with a net transfer of electron density from K\textsuperscript{+} to Ru.

Figure 4.3 XPS spectra of Ru 3d for potassium doped catalysts with various potassium wt loading (0%, 1%, 2%, 3%, 4% and 5%).
Figure 4.4 I shows IR spectra of CO adsorbed on alkali promoted catalysts (1Na-220°C, 2K-220°C and 5Cs-220°C) with a similar AM/Ru atomic ratio about 2.2. The shapes of these spectra are similar to those reported by Gonzalez et al.\textsuperscript{124} In the case of the unpromoted 2RuAlSEA catalyst, a broad and strong band appears in the 1900-2120 cm\textsuperscript{-1} region, where several overlapping bands with local peaks and shoulders are attributed to a combination of linear CO (2035 cm\textsuperscript{-1}) and Ru dicarbonyl species. A relatively weak band centered at 2141 cm\textsuperscript{-1} is assigned to Ru tricarbonyl species. In addition, a very weak and broad band is also observed in the 1800 cm\textsuperscript{-1} region attributed to bridged-bond CO on Ru. These peaks and assignments agree with published spectra in the literature\textsuperscript{83, 125}. The IR spectra of promoted catalysts were significantly different than the unpromoted catalyst. The addition of an alkali metal promoter results in a decreased intensity of the band at 2141 cm\textsuperscript{-1} and a shift to lower frequency. Furthermore, the spectra become broader and asymmetrical with a shoulder around 1995 cm\textsuperscript{-1} in the presence of an alkali metal promoter\textsuperscript{83, 124}. In our previous study, we have found that the degree of Ru reduction (the ratio of Ru\textsuperscript{0}/Ru\textsuperscript{n+}) displays the positive correlation on the Ru activity. The same procedure for the peak fitting was employed to explore the ratio of Ru\textsuperscript{0}/Ru\textsuperscript{n+} for these alkali promoted catalysts. The results of peak fitting were shown in Figure 4.4. II and the detailed curve-fitting procedure are discussed and shown in Table B.1.
Figure 4.4 FTIR spectra (I left side) and the results of peak fitting (II right side) of alkali promoted catalyst with the similar AM/Ru atomic ratio about 2.2 and unpromoted catalyst pretreated at 400°C in-situ (a) 5Cs, (b) 2K, (c) 1Na, and (d) 2RuAlSEA.

CO-FTIR spectroscopy was also used to explore the active chemical state of potassium by comparing the spectra of 3KOH-220°C with 3K-400°C, and also the effect that potassium weight loading by comparing the spectra of 1K-400°C, 3K-400°C and 5K-400°C samples. These spectra are shown in Figure 4.5 I. The intensity of the band centered at 2141 cm\(^{-1}\) decreased as the weight loading of potassium increased. In the spectra of 3K-400°C and 5K-400°C catalysts, the linear CO peak shifted to 2008 cm\(^{-1}\), which is 27 cm\(^{-1}\) lower than the unpromoted catalyst (2RuAlSEA), which was also observed in the literature. On the other hand, the shape of the spectrum for 3KOH-220°C sample is similar to that of the 3K-400°C sample, which implies that KNO\(_3\) may turn to KOH after reduction pretreatment. Once again, the results of peak fitting were shown in
Figure 4.4 II and the detailed curve-fitting procedure are discussed and shown in Table B.1.

Figure 4.5 FTIR spectra (I right side) and the results of peak fitting (II right side) of 2RuAlSEA dopant with various potassium nitrate wt% loading and unpromoted catalyst pretreated in-situ at 400°C as well as 3KOH pretreated in-situ at 220°C. (a) 5K, (b) 3KOH, (c) 3K, (d) 1K, and (e) 2RuAlSEA.

XPS was employed on a representative catalyst, 3K, to study the effect of reduction temperature (220°C and 400°C) on redistribution of alkali promoter. The catalysts were treated in a pretreatment chamber as described before, where the sample was pre-reduced under H₂ at 220°C and 400°C for 1h. As shown in Figure 4.6, the binding energy of the Ru 3d₅/₂ peak in the 3K pretreated at 220°C appears at 279.32ev. In contrast, the peak position of the Ru 3d₅/₂ peak shifts to a lower binding energy
(279.02ev) when the 3K was pretreated at 400°C. The surface compositions of the 3K catalysts are summarized in Table 4.2, the data shows that the surface concentration of K increases from 0.0616 to 0.0867 as the reduction temperature increased from 220°C to 400°C, which may suggest promoter components are being from the Ru surface to the support. Similar results are also observed in Cs promoted Ag on alumina catalyst by Monnier et al\textsuperscript{126}.

Figure 4.6 Reduction temperature effect on the Ru binding energy. XPS of spectra of Ru 3d for 3K-220°C and 400°C.
Table 4.2 Summary of the surface compositions for 3K-220°C and 3K-400°C catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Atomic concentration %</th>
<th>K2p/Al2p atomic ratio</th>
<th>Ru3p/Al2p atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ru3p</td>
<td>K2p</td>
<td>Al2p</td>
</tr>
<tr>
<td>3K-220°C</td>
<td>1.38</td>
<td>5.72</td>
<td>92.90</td>
</tr>
<tr>
<td>3K-400°C</td>
<td>1.46</td>
<td>7.86</td>
<td>90.68</td>
</tr>
</tbody>
</table>

The infrared analysis of pyridine adsorption was carried out to explore the effect of the higher reduction temperature of alkali metal caused on the acidity of the 3K catalyst. The IR spectra at 220°C and 400°C for the 3K as well as the unpromoted 2RuAlSEA sample are displayed in Figure 4.7. The bands characteristic of Bronsted (PyH+) and Lewis (L-Py) acid sites appear around 1540-1548 cm\(^{-1}\) and 1445-1460 cm\(^{-1}\), respectively \(^{127}\). In the IR spectrum of unpromoted catalyst (2RuAlSEA) an apparent and sharp band at around 1445-1450 cm\(^{-1}\) and weak band around 1540 cm\(^{-1}\) appear, indicating Lewis sites are dominant. The band centered at 1492 cm\(^{-1}\) is assigned to both acid sites. Finally, the bands appearing at 1596 and 1606 cm\(^{-1}\) are ascribed to pyridine adsorbed on Lewis acid sites. The addition of potassium causes a decrease of absolute intensity for the 3K-220°C catalyst, and it is even lower for the 3K-400°C catalyst. The decrease of the absolute intensity suggests a decrease of the surface acidity, which indicates that the higher temperature (400°C) causes the redistribution of K to the surface of the support. This is consistent with the surface concentration of potassium (Table 4.2) was increases after the higher temperature reduction.
4.3.1.2. Catalytic performance tests

Hydrogenation of LA was evaluated over all promoted Ru catalysts to determine the best alkali metal promoter and the optimum content for each. Reactivity results of the promoted catalysts in Table 4.1 show that the LA hydrogenation activity of Ru/Al₂O₃ catalysts depends strongly on the type and loading of alkali promoters. All promoted catalysts give a higher TOF than unpromoted 2RuAISEA catalyst and the volcano-type dependence of activity on alkali loading was observed for each of the three alkali-promoted catalysts series, which will be discussed in detail later. The chemical equation of this reaction is in Equation 4.1.
4.3.2. Discussion

4.3.2.1. Position of Alkali metal

The position of Alkali dopant on acidic $\text{Al}_2\text{O}_3$ supported Ru and on basic MgO supported Ru has been discussed by Murata Shuzo etc, el $^{128}$, and the mechanism of CsNO$_3$ disproportionation is proposed in Figure 4.8. Firstly, CsNO$_3$ decomposes on the Ru surface and migrates to the support. Since $\text{Al}_2\text{O}_3$ is acidic, it may attract more alkali than MgO does, resulting in less Cs$^+$ on Ru with $\text{Al}_2\text{O}_3$ support. However, Cs$^+$ remains more on Ru with MgO support, where two basic compounds, MgO support and alkali promoter (Cs$_2$O or CsOH) can interact well with Ru. To the contrary, some of the promoter interacts with Ru but most of it interacts with acidic $\text{Al}_2\text{O}_3$ support. Another indication of this mechanism, is that hydrogen adsorption significantly decreases on Cs doped Ru/MgO as the Cs$^+$ content is increased, suggest us that more Cs$^+$ covers the Ru surface. However, this effect is not so severe on Cs doped on Ru/$\text{Al}_2\text{O}_3$ sample. In this study, $\text{H}_2$-$\text{O}_2$ chemisorption data also suggests that most of the potassium remains on the alumina support since the same Ru dispersion (50.0%) was obtained for both 3K and 5K samples.
4.3.2.2. The volcano-type dependence of Ru activity on alkali loading

Activity at 220°C is plotted in Figure 4.9 (a), (b), and (c), where the TOF (s\(^{-1}\)) is plotted as a function of alkali weight loading. The alkali weight loading was also plotted vs BE shift on the secondary axis. In each of the three alkali doped catalyst series, a volcano curve of activity was observed, where TOF initially increases as promoter loading increases, goes through a maximum at a certain dopant level, and then decreases for higher alkali contents. The Na, K and Cs promoted catalysts reach a maximum activity (TOF = 0.59, 0.57 and 0.79 s\(^{-1}\)) at a wt% of 5, 3 and 3 respectively. These TOFs are much higher than that of unpromoted 2RuAlSEA catalyst (TOF=0.08s\(^{-1}\)). A similar dependence of catalytic activity on alkali loading has been reported in several studies. Huang et al\(^{129}\), who studied the effect of alkali metal on Ni/SiO\(_2\)-Al\(_2\)O\(_3\) catalysts for CO
methanation, found that the TOF increases with the increase of Na content and a maximum appears at 0.2wt% Na. The TOF was enhanced by a factor of 6 relative to the unpromoted catalyst. Kondarides et al.\textsuperscript{130} also observed a similar volcano trend for the Water Gas Shift (WGS) reaction, where 0.06wt% Na and 0.1wt% K on Pt/TiO\textsubscript{2} exhibited the highest activity in their respective series, compared to the alkali-free catalyst. Finally, similar results for the reduction of NO by propene over Pd/YSZ catalyst were observed by Yentekakis et al.\textsuperscript{131}, with 0.068% Na, the activity of was about 10 times higher than that of unpromoted Pd/YSZ. Above this number, a lower rate was obtained. The volcano-shape dependence of reaction rate on alkali loading, which is often observed in alkali doped catalysts, can be represented as the balance between underpromotion (not all sites are promoted) and overpromotion (surface is poisoned by excess promoter concentration, also called site blocking)\textsuperscript{132}.

![Graph showing TOF vs Na wt%]

\[ \text{TOF (s}^{-1}) \]

\[ \text{BE Shift (eV)} \]

\[ \text{Na wt}\% \]
Figure 4.9 TOF (left axis) and XPS BE shift (right axis) measured at 220°C versus wt% loading of alkalis (a) Na series, (b) K series, and (c) Cs series.
In each of the three series of promoted catalysts, results for H$_2$-chemisorption presented in Table 4.1 show that the catalysts, which are above optimum alkali loading, give the same Ru dispersion as the catalysts with optimum alkali loading. For example, 3K and 5K has the same Ru dispersion of about 50%. This was also the case for 3Cs and 5Cs samples as well as 5Na and 7Na samples. In aiming to correlate the effect of the BE shift of Ru on the catalyst activity, BE shift was plotted as a function of weight loading of alkalis in Figure 4.9. The BE shift increases with weight loading of alkalis for the K and Cs series. On the other hand, the BE shift of the Na catalyst series exhibits the same volcano trend as activity. However, the absence of a correlation of BE shift with activity for the other two AMs, suggests that BE shift is not the controlling factor on the catalytic activity. This evidence suggests that there are other factors that govern the Ru activity. In this regard, it was desired to explore the acidity effect, so Pyridine-FTIR was performed for the 3K and 5K promoted catalysts, 5K would be expected to exhibit lower surface acidity than 3K as shown in Figure 4.10, because most of the K stays on the alumina support. If such volcano-shape plots are caused by Ru site blocking, the same TOF values should be obtained for each of the following pairs of catalyst sets because the same Ru dispersion was seen in each set of catalysts, 3K and 5K, 3Cs and 5Cs, and 5Na and 7Na. The role of surface Mg$^{2+}$ sites in MgO based catalysts has been reported in the literature. For example, Mg$^{2+}$ could provide adsorption sites for acetone through its carbonyl group and stabilize the reaction intermediates, where Mesityl oxide adsorbs via C=O bond on Mg$^{2+}$ cation. In another study, Mg$^{2+}$ sites are also reported to provide adsorption sites for DMK through its carbonyl group and to stabilize the reaction intermediates. In the present study, the real active chemical state of each of the three alkali dopants (Na, K
and Cs) under reaction conditions is not in the metallic state, but in AM$^+$ state (AM$_2$O/AMOH), which will be discussed in detail later. According to the indication from the role of Mg$^{2+}$, we proposed that alkali dopant AM$^+$ may provide adsorption sites through carbonyl group, O (1) in levulinic acid shown in Equation 4. (1) and stabilize the reaction intermediates. Therefore, the volcano plot could ascribe to the surface basicity of the catalyst. The appropriate basicity could activate the adsorption process. On the other hand, if adsorption is too strong, desorption becomes more difficult and controls the rate, thus the rate goes down as the basicity is above the optimum level.

Figure 4.10 IR spectra of pyridine adsorbed on 2RuAlSEA, 3K and 5K catalysts.
4.3.2.3. Effects of Alkali on Ru activity with the same AM/Ru atomic ratio

Reaction rate (TOF), BE shift, Ru dispersion, CO-FTIR (Ru\(^0/\)Ru\(^{n+}\) ratio) and properties of the promoter cations are summarized in Table 4.3. The activities of promoted catalysts with the same AM/Ru atomic ratio (2.2:1) measured at 220°C are shown in the following order: 5Cs-220°C (TOF=0.69s\(^{-1}\)) > 2K-220°C (TOF=0.47s\(^{-1}\)) > 1Na-220°C (TOF=0.30s\(^{-1}\)). The catalyst activity increases with a decrease in the promoter electronegativity (charge/surface), Na\(^+\) (0.085) > K\(^+\) (0.045) > Cs\(^+\) (0.030), and also with an increase in the ion radii Na\(^+\) (98nm) < K\(^+\) (133nm) < Cs\(^+\) (165nm) and polarizability Na\(^+\) (0.03) < K\(^+\) (1.10) < Cs\(^+\) (2.90)\(^{132}\). Polarizability is defined as the measure of an ion’s ability to deform its electronic core to external electric fields. The effects of Ru BE shift, CO-FTIR (Ru\(^0/\)Ru\(^{n+}\) ratio), surface acidity of catalysts and Ru surface morphology will now be discussed individually.

Table 4.3 Summary of reaction rates, characterization data, and properties of promoter cations for promoted catalysts with the same (AM:Ru) atomic ratio (2.2:1) and unpromoted catalyst.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ru 3d5/2 BE shift (ev)</th>
<th>Ru(^0/)Ru(^{n+}) ratio</th>
<th>Ru dispersion (%)</th>
<th>TOF s(^{-1})</th>
<th>Ionic radius (nm)</th>
<th>Charge /Surface</th>
<th>Polarizibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>5Cs-220°C</td>
<td>0.66</td>
<td>5.3</td>
<td>47.6</td>
<td>0.69</td>
<td>165</td>
<td>0.030</td>
<td>2.90</td>
</tr>
<tr>
<td>2K-220°C</td>
<td>0.60</td>
<td>4.4</td>
<td>55.6</td>
<td>0.47</td>
<td>133</td>
<td>0.045</td>
<td>1.10</td>
</tr>
<tr>
<td>1Na-220°C</td>
<td>0.42</td>
<td>4.3</td>
<td>55.6</td>
<td>0.30</td>
<td>98</td>
<td>0.085</td>
<td>0.03</td>
</tr>
<tr>
<td>2RuAlSEA</td>
<td>0</td>
<td>3.4</td>
<td>62.5</td>
<td>0.08</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
4.3.2.4. Ru BE shift

To confirm the electronic effect, the BE shift of 5Cs-220°C, 2K-220°C and 1Na-220°C were observed after calibrating with C1s (284.6ev), which are presented in Table 4.3. The shift of the Ru 3d_{5/2} binding energy toward lower values is observed for the three promoted catalysts with respect to metallic Ru (280.1ev). The BE shift follows the order Cs^+ (0.66ev) > K^+ (0.60ev) > Na^+ (0.42ev), which has the same trend as TOF stated above. It has been reported that alkali metal can lower the binding energy of Ru 3d_{5/2} on Ru supported catalysts. Bukhtiyarov et. al 118 found a 1.2ev negative shift of Ru 3d_{5/2} relative to the bulk Ru metal (280.1ev) in Ru/MgO with the addition of Cs^+. The similar effect was observed by Mazhar 119, who reported the negative BE shift with addition of K to a Mn-Ru/Al_2O_3 catalyst. For example, the presence of 2.8% potassium causes the lower the binding energy of Ru 3d_{5/2} by 0.9ev. Finally, Hercules et. al 117 discussed how charging effects can cause BE shift for the insulating materials (SiO_2 support) in Na or K promoted Ru/SiO_2 catalyst system. If the Ru particles in the unpromoted and promoted catalysts had different average size, charging effect differences could occur because larger Ru particles may increase electronic conductivity. As a result, H_2 chemisorption shows a decrease of Ru dispersion with the addition of alkali dopants (Table 4.1). Average Ru particle sizes was determined by XRD (Figure 4.1), which indicates that the Ru particles remained small before and after doping potassium (less than 1.5nm), therefore, it is concluded that the BE shift of Ru 3d_{5/2} is due to the chemical nature, and not the charging effects.
4.3.2.5. CO-FTIR

Our previous study also suggests (based on peak fitting IR spectra of CO-adsorbed on Ru catalysts) - that the relative fraction of Ru$^0$/Ru$^{n+}$ has a positive impact on the Ru activity for LA hydrogenation \(^{23}\). Further, the relative fraction of Ru$^0$/Ru$^{n+}$ significantly increases with the addition of potassium. In the present study, similar experiments were performed to explore the role of alkali metal. A detailed curve-fitting procedure and the fitted spectra of the catalysts shown in Figure 4.4 are discussed and presented in Table B.1 (Appendix B). As shown in Table 4.3, the relative fraction of Ru$^0$/Ru$^{n+}$ in the three promoted catalysts follows the order Cs$^+$ (5.3) > K$^+$ (4.4) > Na$^+$ (4.3) and each of them is larger than that of the unpromoted catalyst 2RuAlSEA (3.4). Indeed, the relative fraction of Ru$^0$/Ru$^{n+}$ represents the degree of “metallic state of Ru”, CO-FTIR as an independent technique has a good agreement with BE shift obtained from XPS, which confirms the electronic effect.

4.3.2.5. Acidity effect

XPS and CO-FTIR data both suggest the role of alkali metal ascribed to the electronic effect on the enhanced activity, which belongs to modification of Ru metal as discussed in the introduction session. In order to further check the alkali effect on the modification of support, pyridine-FTIR experiments were also performed. Figure 4.11 displays the IR spectra of pyridine on the promoted catalysts and unpromoted catalyst, the acidity decreases following the order: Na$^+$ < K$^+$ < Cs$^+$. Roughly speaking, the acidity is inversely related to the electronegativities of the active chemical state of the alkalis (Cs$_2$O, K$_2$O and Na$_2$O) under our reaction conditions. Since the basicity and activity
follows the same order Na$^+$ < K$^+$ < Cs$^+$, this implies that basicity also plays an important role on the Ru activity.

![IR spectra of pyridine adsorbed](image)

Figure 4.11 IR spectra of pyridine adsorbed on (a) 2RuAlSEA, (b) 1Na, (c) 2K, and (d) 5Cs.

4.3.2.6. Ru Surface Morphology

The surface morphology is also an important factor on metal activity. Although ruthenium is believed to be affected by electronic configuration, such a structural factor should still be considered. In fact, it has been reported that the morphology of Ru may change in the presence of alkali or alkaline earth metal. Larichev et. al $^{118}$ found that a Cs-containing layer of disordered structure covered the surface of Ru particles and the areas of the support surface in the closest proximity to the Ru particles in a Cs doped Ru/MgO catalyst, where the Ru particle size is in the 5-10 nm range. It appears that the Ru particle shape changes from a sphere to a hexagram.
compared to the Cs-free Ru/MgO catalyst. Similarly, Jacobsen et. al $^{134}$ also reported that patches of Barium-containing phase are on several of the Ru crystal surfaces with 5.5wt%Ba- 4.1wt%Ru on Boron nitride, where particle size of Ru is about 3.5nm. However, in the present study, the Ru particle size is about 0.9nm. It is difficult to visualize how alkali metal affects the morphology of Ru because of its tiny size. Another limitations is, alkali metal is typically very mobile under electron beam irradiation, and alumina support degrades quickly too.

In summary, on the basis of discussion on electronic effect, it appears that successful promoters are large and highly polarizable ions under reaction conditions. In fact, the ionic radii and the values of the Pauling polarizabilities of Cs$^+$ is the largest of any of the naturally existing elements $^{132}$. Furthermore, higher basicity gives higher activity in those three promoted catalysts, indicating basicity has a positive effect on the Ru activity. Therefore, we ascribed the role of alkali metal to (1) electronic effect, such as push-pull type of electronic effect that could be envisioned to assist in the desorption step from Ru surface sites, (2) acidity effect, appropriate basicity helps the adsorption of the intermediate, but it has opposite effect when basicity is above that point.

4.3.2.7. Effect of Reduction Temperature (220°C VS 400°C)

It has been reported that the reduction temperature of alkali nitrates has an effect on metal activities by causing the changes of the chemical state and position of alkali metals. This effect on the Ru activity for Ammonia Synthesis was seen by Aika Ken-ichi et, al $^{135}$, who proposed how CsNO$_3$ is disproportionate on Ru Raney as well as Ru/Al$_2$O$_3$ catalyst. In this case, the reaction of CsNO$_3$ with H$_2$ takes place at a lower
temperature (200-270°C) shown in equation 4.2, while the decomposition of Cs₂O occurs
at a higher temperature (300-400°C) shown in equations 4.3 and 4.4. Lastly, Cs may react
easily with surface OH group from Al₂O₃ support to become CsOH (equation 4.5). King
et al.²⁴ also studied the chemical state of the alkali species after the reduction
pretreatment step by using TGA for KNO₃-Ru/SiO₂ catalyst (K:Ru atomic ratio about 2:1), TGA data shows that 42.6% of KNO₃ decomposed to K₂O at 607°C under 10% H₂/He
without Ru/SiO₂ catalyst, a similar treatment on the KNO₃-Ru/SiO₂ catalyst appears that
the decomposition of KNO₃ occurs at 207°C in presence of Ruthenium, indicating
Ruthenium may catalyze the decomposition of nitrate to K₂O at 220°C. Similarly, De
Paola et al.¹³⁶ reported that coadsorption of potassium and oxygen on Ru (001) surface
yielded stable K₂O and K₂O₂ compounds. On the basis of XPS data in their study, it is
also notable that both ruthenium and promoter precursors reduced simultaneously,
suggesting a synergistic effect. On alumina, K₂O may be turned to KOH by a reaction
with surface OH. A similar conclusion may be applied to other alkali metal systems. The
effects of reduction temperature on Ru activity, active chemical state and redistribution of
alkali metal will be discussed respectively.

\[
\begin{align*}
2\text{CsNO}_3 + 8\text{H}_2 & \rightarrow \text{Cs}_2\text{O} + 2\text{NH}_3 + 5\text{H}_2\text{O} \\
2\text{Cs}_2\text{O} & \rightarrow \text{Cs}_2\text{O}_2 + 2\text{Cs} \\
\text{Cs}_2\text{O}_2 + \text{H}_2 & \rightarrow 2\text{CsOH} \\
\text{Cs} + \text{OH} & \rightarrow \text{CsOH}
\end{align*}
\]

Equation 4.2
Equation 4.3
Equation 4.4
Equation 4.5
4.3.2.7.1. The effect of Reduction Temperature on Ru activity: 220°C versus 400°C

As discussed above, higher reduction temperature may lead to the changes of chemical state and redistribution of alkali metal, and will result in the change of Ru dispersion and surface acidity of the catalyst. With the aim of investigating the reduction temperature effect on Ru activity, two potassium promoted catalyst sets (KNO₃ and KOH) were selected as representatives. Reduction temperatures of 220°C and 400°C were used to compare the reactivity of the promoted catalysts. KOH was used as the precursor for comparison purposes in order to determine the active chemical state of potassium. As shown in Table 4.1, the higher temperature (400°C) does not cause significant Ru particle sintering in the case of potassium nitrate set. For higher potassium loadings (3%, 4% and 5%), the Ru dispersion is about 50% for both reduction temperatures. On the other hand, the potassium hydroxide set, the potassium hydroxide set displays varying results. With loadings of 1% and 3%, the dispersion remains constant at 62.5%, however, the 5% sample exhibits an increase in dispersion from 47.6% to 52.6% with an increase in temperature. From the TOF plots in Figure 4.12, there is an obvious enhancement for all potassium loadings pretreated at higher temperature (400°C) for the potassium nitrate set, but not potassium hydroxide set. For example, the TOF of the optimum potassium loading at 3% increases by 14% from 0.57 s⁻¹ to 0.65 s⁻¹. For a higher potassium loading of 5%, the TOF increases by about 50% from 0.29 s⁻¹ to 0.45 s⁻¹ in the potassium nitrate set. However, the same TOFs were obtained at 220°C for the potassium hydroxide set, which is not surprising since a higher temperature will only result in a change of chemical state and redistribution of potassium, but KOH already exists as its active chemical state.
4.3.2.7.2. Chemical State of Alkali metal

Ozaki et al.\textsuperscript{106} proposed the possible active chemical state of K when the nitrate salt was used as the precursor. The data suggested KOH was the active state and would form when potassium nitrate is reduced at 400°C, but only form K$_2$O at 200°C. To explore the active chemical state of K, KOH was employed as the precursor to achieve various potassium loading (1%, 3% and 5%) to compare with KNO$_3$ doped catalysts. H$_2$ chemisorption data in Table 4.1 shows the KOH has higher Ru dispersion (62.5%) than KNO$_3$ (50% dispersion) with the optimum potassium loading (3%), even at a higher reduction temperature (400°C). However, the same Ru dispersion (50%) was seen by both potassium precursors. In Figure 4.12, a similar volcano-shape appears,

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4_12.png}
\caption{TOF versus wt loading of potassium for KNO$_3$ and KOH sets, solid square represents KNO$_3$ samples treated at 220°C, open square represents KNO$_3$ samples treated at 400°C, open triangle represents KOH samples treated at 220°C, and cross represents KOH samples treated at 400°C.}
\end{figure}
where the maximum activity occurs at 3%. Comparing with the TOFs, 3KOH-220°C (TOF=0.69 s\(^{-1}\)) shows a higher activity than 3K-220°C (TOF=0.57 s\(^{-1}\)), but a similar TOF was obtained as 3K-400°C (0.65 s\(^{-1}\)), that strongly suggests that the active chemical state of potassium is KOH. Since the relative fraction of Ru\(^0/Ru^{n+}\) has a positive relationship to the Ru activity, and 3KOH-220°C (0.67 s\(^{-1}\)) gives the same TOF as 3K-400°C, it is worth comparing the Ru\(^0/Ru^{n+}\) ratio for 1K-400°C, 3K-400°C, 5K-400°C and 3KOH-220°C samples. This plot is shown in Figure 4.13, where the ratio of Ru\(^0/Ru^{n+}\) for 3KOH-220°C and 3KNO\(_3\)-400°C are 8.0 and 7.9 respectively, which is almost identical. In addition, the ratio of Ru\(^0/Ru^{n+}\) increases with the increase of the potassium loading, 5K-400°C (9.8) > 3K-400°C (7.9) > 1K-400°C (4.8) >2RuAlSEA (3.4), which is in good agreement with TOF versus BE shift plot shown in Figure 4.9. This further confirms the electronic effect from the addition of alkali metal.

![Figure 4.13](image-url)  
Figure 4.13 Filled circles represent TOF of 1K-400°C, 3K-400°C and 5K-400°C, open squares represent the TOF of 3KOH-220°C and Ru\(^0/Ru^{n+}\) (open) versus potassium loading.
4.3.2.7.3. Redistribution of alkali metal by treating at higher temperature

We measured the XPS spectra of 3K, which was pretreated in-situ at 220°C and 400°C. The results are shown in Figure 4.6 and surface compositions are summarized in Table 4.2. XPS data clearly shows that higher reduction temperature (400°C) is able to lower the binding energy of Ru3d_{5/2} by 0.3ev. It is not surprising that the TOF increased by 14% from 0.65 s^{-1} to 0.57 s^{-1} when a higher reduction temperature was used, because KOH would form, which is the active chemical state of potassium. On the other hand, the increase of surface composition of potassium suggests that the higher reduction temperature causes redistribution of potassium. Combing the pyridine-FTIR data shown in Figure 4.7, lower acidity was obtained at a higher temperature (400°C), indicating that potassium does not migrate from the support to the Ru surface, rather the potassium wets the surface of Ru. In fact, Compton et al.\textsuperscript{137} has observed a change in CO adsorption states on potassium doped Rh/SiO\textsubscript{2} surfaces at a higher temperature for the reduction step, which suggested that higher reduction temperatures helped redistribute the promoter on the metal surface.

Note: Alkaline earth metal promoted catalysts were evaluated and characterized with similar experiments as alkali metal discussed in this manuscript; all information for alkaline earth metal promoted catalysts is presented in the supplementary materials.
4.4. CONCLUSION

Strong promotional effects were observed for alkali and alkaline earth promoted catalysts. With the same ratio of dopant to Ru, the reaction rate follows the order: \( \text{Na}^+ < \text{K}^+ < \text{Cs}^+ \) for alkali metal and \( \text{Ba}^{2+} < \text{Mg}^{2+} < \text{Ca}^{2+} \) for alkaline earth metal (shown in Appendix B). Several trends were revealed by this parallel study. First, the role of alkali metal is ascribed to the combination of modification of Ru metal by electronic effect, modification of alumina support by acidity effect. The role of alkaline earth metal appears to acidity effect (shown in Appendix B). Second, alkali dopant catalysts suggest a successful promoter should be large with high polarizability. Finally, higher reduction temperature (400°C) may form a more active chemical state (alkali hydroxide) and redistribute alkali metals, leading to higher TOF.
CHAPTER 5
SYNTHESIS, CHARACTERIZATION AND EVALUATION OF BIMETALLIC RUTHENIUM-RHENIUM CATALYSTS BY STRONG ELECTROSTATIC ADSORPTION FOR HYDROGENATION OF LEVULINIC ACID TO GAMMA-VALEROLACTONE

5.1. INTRODUCTION

The conversion of lignocellulosic biomass into sustainable chemicals and fuels is of a great interest as the worldwide fossil fuel and petroleum resources dwindle \(^1,2\). Many catalysts have been screened for biomass conversion, but the major challenge is the stability of catalysts over time, ability to regenerate and selectivity to the desired product. These problems have been magnified in real industrial processes by the presence of many impurities and by-products. Catalyst optimization could be an effective way to minimize this issue by using different combinations of metals, supports and promoters. Bimetallic catalysts offer the possibility of enabling lignocellulosic processing to become a larger part of the biofuels and renewable chemicals industry. The interaction between metals can modify the surface properties of the catalysts, which enables the increase of stability of catalysts and the selectivity to the desired product \(^97\).

Levulinic Acid (LA) can be obtained inexpensively in high yields by acid hydrolysis of cellulosic materials. Because of that, LA has the potential to be used as a platform molecule for the production of a wide range of value-added compounds such as monomers for plastics, fuel additives and chemicals \(^6, 97\). GVL also has attracted
considerable attention as it is renewable, safe to store and could be used in many
applications, such as green solvents, food additives and an intermediate in the synthesis
of many value-added chemicals. Therefore, the hydrogenation of LA to GVL is a
key reaction in the development of economically viable and carbon-efficient
biorenewable routes to chemicals, and liquid transportation fuels. To date, Ru-based
catalysts have been shown to exhibit the highest GVL productivities, notably, Ru/C
catalyst gives high activity and selectivity for hydrogenation of LA. A
search of the literature to assess the application of supported bimetallic catalysts on the
conversion of LA to GVL is discussed here. Dumesic et al. reported that RuRe/C catalyst
with 3 to 4 Ru:Re atomic ratio shows significantly higher activity than a traditional Ru/C
catalyst with reaction streams comprised of LA, FA and H$_2$SO$_4$. The addition of Re
improves the stability of catalysts in the presence of sulfuric acid. Under the same
reaction condition, Wettstein et al. also reported that the addition of Sn improves the
stability of Ru/C in RuSn/C system and selectivity towards to GVL. However, the
addition of Sn caused the lower activity for bimetallic RuSn than monometallic Ru/C
catalyst. Shimizu et al. tested a series of base metal (Ni, Co, Cu, and Fe) and metal
oxides (Mo, V and W oxides) co-loaded carbon, Ni-MoOx/C showed 300 times higher
rate than previously reported Noble- metal-free catalysts. Recently, Luo et. al studied
bimetallic of Pd/TiO$_2$ and found that the addition of Au (AuPd/TiO$_2$) yields 27 fold
higher activity than its monometallic counterparts. They also found that the addition of
Ru (RuPd/TiO$_2$) gives excellent selectivity of GVL. However, Lange et al. observed
that PtRe and PtRu did not enhance activity comparing with a monometallic Pt catalyst.
The synthesis of bimetallic catalysts is often employed by either simultaneous co-impregnation of both metal precursors onto the catalyst support or by successive steps of metal precursors addition. For either of these preparative methods, it may form not only bimetallic particles but also separated metallic particles of both metals, which makes it more difficult to correlate catalyst activity with bimetallic catalyst composition. Recently, our group reported on a simple and precise synthesis methodology for the synthesis of bimetallic catalysts with very narrow particle size distribution and homogeneous, alloyed nanoparticles by electrostatic adsorption of mixed metal precursors (co-SEA) \(^{63}\).

In the present paper, we investigate the effect of adding Re to the Ru/C catalyst system by comparing the reaction rate and stability of Ru\(_x\)Re\(_y\) (where x and y are varied to obtain a range of Ru:Re atomic ratio) nanoparticles supported on carbon and alumina supports. Furthermore, various characterization techniques, such as TPR-H\(_2\), STEM/EDXS, XPS, and CO-FTIR were employed in order to study the geometric and electronic effect on catalytic activity \(^{141-143}\). Finally, we report XRD data of fresh and spent catalysts to provide insights into the nature of the active catalyst and possible sources of catalyst deactivation. Importantly, the catalysts synthesized by co-SEA show greater stability than ones synthesized by conventional method, co-DI. We demonstrate the impact of synthesis method on the stability of catalyst.
5.2. EXPERIMENTAL METHODS

5.2.1. Materials

Hexaammineruthenium(III) chloride (Ru(NH₃)₆Cl₃), Potassium hexacyanoruthenate(II) hydrate K₄Ru(CN)₆, Potassium Perrhenate KReO₄, Ammonium perhenate NH₄ReO₄, EDTA, Levulinic acid (98%) and 1,4-Dioxane(99.8%) were purchased from Sigma-Aldrich. Vulcan XC-72R carbon (VXC72R, surface area of 184m²/g) and SBA-200-gamma-Alumina (γ-Al₂O₃, surface area of 189m²/g) supports were obtained from Cabot and Aerosil, respectively.

5.2.2. Ruthenium Rhenium bimetallic catalyst preparation

Since there are only anionic Re (KReO₄ and NH₄ReO₄) and Ru (K₄Ru(CN)₆) salts available on the market, high point zero charge (PZC) of supports will be required for the co-SEA method. The PZC determination of VXC72R and and γ-Al₂O₃ supports, uptake survey experiments and details of Ru anionic precursor synthesis (RuEDTA⁻) supports are given in the Supporting Information for Chapter 5 (Appendix C). The UV-vis spectra of H₂EDTA and Ru(NH₃)₆Cl₃ solutions are also shown Figure C.1 (Appendix C).

Once the pH of strongest electrostatic adsorption was determined (described in Appendix C), a large amount of catalyst was synthesized at this condition by scaling up the volume. 5g of 0.8%Ru0.8%Re/VXC 72R catalyst was prepared with 100ppm RuEDTA⁻ and 100ppm ReO₄⁻ at a surface loading (SL) of 500m²/l at optimal initial pH of 1.51. Then 5g of 0.7%Ru0.6%Re/Al₂O₃ catalyst was prepared with 70ppm Ru(CN)₆⁴⁻ and 280ppm ReO₄⁻ at surface loading SL=2000m²/l at optimal initial pH of 2.31. Prior to reduction, the catalysts were dried in room temperature for 48h, and then at 100°C overnight. For comparison, catalysts with the same Ru and Re metal loading catalysts
were prepared by DI. In order to avoid introducing potassium to the catalyst \(^{23}\), \(\text{NH}_4\text{ReO}_4\) was used rather than KReO\(_4\) as potassium was found to significantly improve the Ru activity in our previous study. Finally, to study the effect of RuRe composition on the catalytic activity in hydrogenation of LA to GVL, bimetallic RuRe catalysts with various RuRe atomic ratios were prepared on both supports in the same manner. A summary of catalysts is given in Table 5.1.

5.2.3. Catalyst characterization

Temperature programmed reduction (TPR) with a CHEMBET-3000 station (Quantachrome Instruments) was employed for all prepared Ru catalysts. A thermal conductivity detector was used to monitor the H\(_2\) concentration in the flow as a function of temperature and the data were recorded using the TPRWin software. TPR was also used to further determine optimal H\(_2\) titration temperatures of O-precovered surfaces and the subsequent extent of Ru-Re interactions for the bimetallic catalysts. All catalysts were reduced in flowing H\(_2\) for 3 h at 450\(^\circ\)C and then purged with flowing N\(_2\) for 30 min at 450\(^\circ\)C before cooling to 40\(^\circ\)C in N\(_2\). A gas stream of O\(_2\) was then passed for 30 min to form O-precovered Ru and Re surface species. After purging with N\(_2\) for 30 min to remove residual gas and weakly adsorbed O\(_2\), 10\% H\(_2\)/balance N\(_2\) was passed over the sample while heating from 40\(^\circ\)C to 400\(^\circ\)C at 10\(^\circ\)/min ramp rate.

X-ray Photoelectron Spectroscopy (XPS) measurements were conducted with a Kratos AXIS Ultra DLD XPS system equipped with a monochromatic Al K source operated at 15 keV and 120 W. A catalyst pretreatment cell attached to the UHV system permitted samples to be pretreated at 220\(^\circ\)C in H\(_2\) before being analyzed by XPS. The
samples were analyzed under identical conditions and the resulting spectra were fitted by applying a Shirley-type background subtraction and a charging correction with reference to carbon 1s at 284.6 eV.

Powder X-ray diffraction (XRD) analysis was performed using a Rigaku MiniFlex II system equipped with a silicon strip (D/teX Ultra) detector. The radiation source used was Cu Kα (λ=1.5405Å) with a tube voltage of 30kV and a current of 15 mA. All spectra were taken at a scan rate of 0.5°/min and a sampling width of 0.02°. The XRD patterns were compared to JCPDS reference spectra using JADE software.

About 0.050g of ground sample was pressed into pellets with a diameter of 0.5 in. and a thickness of approximately 20mg/cm² for Fourier transform infrared (FTIR) spectroscopic studies of adsorbed CO. Transmission FTIR spectra were collected in the single beam mode, with a resolution of 2 cm⁻¹, using a Thermo Electron model 4700 spectrometer with a liquid nitrogen-cooled MCT detector. All experiments were performed in a stainless steel cylindrical sample cell, which can be heated externally and cooled by flowing water. A gas flow rate of 70ml/min entered the cell in front of the pellet and exited behind the pellet. Briefly, prior to each experiment, the samples were reduced in H₂ for 2h at 220°C, held in He for 0.5h at 220°C, cooled to RT in He, exposed to 1% CO/He, and then flushed with pure He. The initial background spectra were taken before CO exposure until no further changes were observed. Finally, spectra were collected after purging He to remove physisorbed and gas phase CO.

The high angle annular dark Field (HAADF) images of the reduced co-SEA prepared RuRe bimetallic catalysts were obtained by scanning transmission electron microscopy (STEM) using a JEOL JEM-ARM200CF 200kV electron microscope with
field emission electron gun source, 200kV electron microscope, the JEOL JEM-ARM200CF. The microscope has an imaging resolution below 0.08nm and an energy resolution of 0.35ev. Microanalyses of the catalysts were done using x-Ray energy dispersive spectroscopy (XEDS) to generate elemental maps of Ru and Re. The XEDS maps were acquired through an Oxford Instruments XMax100TLE SDD detector also fitted to the JEM-ARM200CF. Ru\textsubscript{2}Re\textsubscript{1}/C (0.8%Ru-0.8%Re) and Ru\textsubscript{2}Re\textsubscript{1}/Al (0.7%Ru-0.6%Re) synthesized by co-SEA and co-DI were selected for STEM imaging and XEDS in order to obtain the best possible imaging contrast and spectroscopic signal, respectively.

X-ray fluorescence (XRF) (Model XDAL) was used to determine the RuRe weight ratio for all bimetallic catalysts at operating conditions of x-ray tube voltage of 50kvp and a current of 1mA.

5.2.4. Reactivity evaluation

The hydrogenation of LA was performed in a stainless steel EZE-Seal batch reactor with 100 ml capacity from Autoclave Engineers. Reactions were run for 4h at 200psi H\textsubscript{2} and 220°C in 1,4 Dioxane solvent. The operation of the reactions is as described in detail in our previous work \cite{23}. Each catalyst reported here was evaluated at least two times. The only product observed in all runs was GVL (i.e., selectively was 100%).
5.3. RESULTS AND DISCUSSION

5.3.1. Uptake surveys of single and mixed metal precursors (co-SEA)

Trends in the metal uptake of individual metal complexes versus pH over carbon and alumina are shown in Figure 5.1, all displaying typical SEA volcano shape characteristics. The maximum adsorption densities achieved by RuEDTA$^-$ and Ru(CN)$_6^{4-}$, over a positively charged carbon or alumina surface, is about 0.71 $\mu$mol/m$^2$ on carbon and 1.37 $\mu$mol/m$^2$ on alumina. The uptake of ReO$_4^-$ on alumina at 0.67 is higher than that over carbon, 0.43 $\mu$mol/m$^2$.

Figure 5.1 Adsorption survey for single metal over (a) VXC72R carbon support (b) alumina support.

The uptake onto carbon and alumina of metals from a solution containing both Ru and Re anionic precursors is shown in Figure 5.2 (a) and (b). The surface density of Ru and Re anions adsorbing over the carbon has an optimal final pH value near 1.51, which corresponds to an initial pH value of 1.51 of the ReO$_4^-$ and RuEDTA$^-$ containing
solution. The maximum Ru and Re surface density of 0.47 and 0.33 $\mu$mol/m$^2$ respectively corresponds to a Ru and Re weight loading of about 0.9wt% and 1.0wt%. Maximum total metal adsorption density over carbon is 0.81$\mu$mol/m$^2$, which is higher than the density achieved by either single metal. The higher total adsorption density may arise from the sharing of hydration sheaths between the two metal complexes. For the alumina support shown in Figure 5.2 (b), the maximum Ru and Re surface densities are 0.31 and 0.12 $\mu$mol/m$^2$ respectively which corresponds to 0.7wt% Ru and 0.6wt% Re. It is evident that Ru anion dominates Re anion because of the more negative charge. The maximum total adsorption is 0.43$\mu$mol/m$^2$ which occurs at a final pH of 4.29. This total uptake is lower than either metal adsorption, which suggests that the mixed monolayer metal anion precursors pack less efficiently than the single metal species. Similar results were also observed in Pd (NH$_3$)$_4$Cl$_2$ and Pt (NH$_3$)$_4$Cl$_2$ uptake on alumina and carbon system $^{63}$. 

\[
\begin{align*}
\text{Final pH} & \quad 0 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 \\
\gamma (\mu\text{mole/m}^2) & \quad 0 & 0.1 & 0.2 & 0.3 & 0.4 & 0.5 \\
\end{align*}
\]
Figure 5.2 Adsorption survey for metal uptakes via co-SEA over (a) VXC72R carbon support (b) alumina support.

The summary of the synthesis systems for bimetallic and monometallic catalysts on carbon and alumina supports and catalytic activities is presented in Table 5.1. The metal weight loading was determined by ICP and AAS and further confirmed with XRF. Catalytic activity (rate) is expressed as reacted moles of LA per gram of metal per second. For simplicity, bimetallic RuRe with atomic ratio x:y on carbon and alumina by co-SEA will be expressed as Ru\textsubscript{x}Re\textsubscript{y}/C/co-SEA and Ru\textsubscript{x}Re\textsubscript{y}/Al/co-SEA, respectively. As an example of naming the monometallic catalysts, 1.4Ru/C represents 1.4%Ru/VXC72R by SEA.
Table 5.1 Summary of bimetallic RuRe and Re catalysts on Carbon and Alumina with various RuRe compositions (Note: Rate*10^3 (mol LA)/(g metal*s) )

<table>
<thead>
<tr>
<th>System: VXC72R carbon</th>
<th>x:y Ru/Re atomic ratio</th>
<th>Ru wt%+ Re wt%</th>
<th>Rate*10^3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface loading: 500m²/L at pH_i=1.51, pH_f=1.51</td>
<td>Nominal</td>
<td>ICP&amp;AAS</td>
<td>XRF</td>
</tr>
<tr>
<td>9.5ppm RuEDTA &amp;100ppm (ReO₄)⁻ by co-SEA</td>
<td>0.25:1</td>
<td>0.28:1</td>
<td>0.35:1</td>
</tr>
<tr>
<td>19ppm RuEDTA⁻ &amp;100ppm (ReO₄)⁻ by co-SEA</td>
<td>0.5:1</td>
<td>0.5:1</td>
<td>0.55:1</td>
</tr>
<tr>
<td>37.5ppm RuEDTA &amp;100ppm (ReO₄)⁻ by co-SEA</td>
<td>1:1</td>
<td>0.9:1</td>
<td>1.1:1</td>
</tr>
<tr>
<td>100ppm RuEDTA⁻ &amp;100ppm (ReO₄)⁻ by co-SEA</td>
<td>1.5:1</td>
<td>1.5:1</td>
<td>1.5:1</td>
</tr>
<tr>
<td>150ppm RuEDTA &amp;100ppm (ReO₄)⁻ by co-SEA</td>
<td>2:1</td>
<td>1.8:1</td>
<td>1.8:1</td>
</tr>
<tr>
<td>300ppm RuEDTA⁻ &amp;100ppm (ReO₄)⁻ by co-SEA</td>
<td>4:1</td>
<td>3.9:1</td>
<td>2.8:1</td>
</tr>
<tr>
<td>Ru(NH₃)₆Cl₃ &amp; NH₄ReO₄ on VXC 72 by co-DI</td>
<td>2:1</td>
<td>----</td>
<td>1.9:1</td>
</tr>
<tr>
<td>Ru(NH₃)₆Cl₃ &amp; NH₄ReO₄ on VXC 72 by co-DI</td>
<td>1.5:1</td>
<td>----</td>
<td>1.3</td>
</tr>
<tr>
<td>Concentration</td>
<td>Reactant 1</td>
<td>Reactant 2</td>
<td>Ru/Re Atomic Ratio</td>
</tr>
<tr>
<td>---------------</td>
<td>------------</td>
<td>------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>100ppm RuEDTA by SEA</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>200ppm KReO$_4$ by SEA</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Alumina</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>System: $\gamma$-Al$_2$O$_3$</td>
<td>Ru/Re atomic ratio</td>
<td>Ru wt% + Re wt%</td>
<td>Rate $^{10^3}$</td>
</tr>
<tr>
<td></td>
<td>Nominal</td>
<td>ICP&amp;AAS</td>
<td>XRF</td>
</tr>
<tr>
<td>9ppm (Ru(CN)$_6$)$^{3+}$ &amp; 280ppm (ReO$_4$)$^-\text{by co-SEA}$</td>
<td>0.25:1</td>
<td>0.27:1</td>
<td>0.35:1</td>
</tr>
<tr>
<td>18ppm(Ru(CN)$_6$)$^{3+}$ &amp; 280ppm (ReO$_4$)$^-\text{by co-SEA}$</td>
<td>0.5:1</td>
<td>0.45:1</td>
<td>0.52:1</td>
</tr>
<tr>
<td>35ppm(Ru(CN)$_6$)$^{3+}$ &amp; 280ppm (ReO$_4$)$^-\text{by co-SEA}$</td>
<td>1:1</td>
<td>1.15:1</td>
<td>1.04:1</td>
</tr>
<tr>
<td>70ppm(Ru(CN)$_6$)$^{3+}$ &amp; 280ppm (ReO$_4$)$^-\text{by co-SEA}$</td>
<td>2:1</td>
<td>2.15:1</td>
<td>1.70:1</td>
</tr>
<tr>
<td>70ppm(Ru(CN)$_6$)$^{3+}$ &amp; 140ppm (ReO$_4$)$^-\text{by co-SEA}$</td>
<td>4:1</td>
<td>4.5:1</td>
<td>4.5:1</td>
</tr>
<tr>
<td>Ru(NH$_3$)$_3$Cl$_3$ &amp; NH$_4$ReO$_4$ on $\gamma$-Al$_2$O$_3$ by co-DI</td>
<td>2:1</td>
<td>----</td>
<td>2.7:1</td>
</tr>
<tr>
<td>Ru(NH$_3$)$_3$Cl$_3$ &amp; NH$_4$ReO$_4$ on $\gamma$-Al$_2$O$_3$ by co-DI</td>
<td>0.5:1</td>
<td>----</td>
<td>0.6:1</td>
</tr>
<tr>
<td>Ru(NH$_3$)$_3$Cl$_3$ &amp; NH$_4$ReO$_4$ on $\gamma$-Al$_2$O$_3$ by co-DI</td>
<td>1:1</td>
<td>----</td>
<td>1.3:1</td>
</tr>
<tr>
<td>100ppm K$_4$Ru(CN)$_6$ by SEA</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>200ppm KReO$_4$ by SEA</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
</tbody>
</table>
5.3.2. Catalysis synthesis and characterization

Once the optimal conditions for co-SEA were determined, the adsorption experiment was simply scaled up to yield enough catalyst for characterization and testing. In response to the TPR data of the selected catalysts shown in the Figure C.2 (Appendix C), bimetallic catalysts and monometallic Ru catalyst supported on carbon were reduced in flowing H\(_2\) at 450°C for 1h, but at 520°C for 1h with the alumina support. Re catalysts were reduced for 1h at 320°C for carbon and 400°C for alumina before further characterization by XRD, STEM/EDXS, FTIR and XPS.

Figure 5.3 (a) and (b) show the XRD patterns of Ru catalysts supported on VXC72R carbon and \(\gamma\)-Al\(_2\)O\(_3\), respectively, with the patterns of the pure supports for comparison. In Fig.3a, the diffraction peaks of metallic Ru phase (2\(\theta\)=38.4\(^\circ\), 42.2\(^\circ\), 44.0\(^\circ\), 58.3\(^\circ\) and 69.4\(^\circ\))\(^{23,144}\) only appeared for co-DI sample. Neither Ru nor Re display any crystal peaks for both SEA and co-SEA samples. This indicates that Ru, Re and bimetallic RuRe particles are less than the detection of limit of the instrument, which is about 1.5nm. Figure 5.3 (b) does not display Ru or Re peaks for any of the alumina supported catalysts, indicating the particle size are all smaller than 1.5nm.
Figure 5.3 (a) XRD patterns of monometallic and bimetallic catalysts on carbon after reduction treatment (1) VXC72R (2) 1.4Ru/C (3) 1.5Re/C (4) Ru0.25Re1/C/co-SEA (5) Ru0.5Re1/C/co-SEA (6) Ru1Re1/C/co-SEA (7) Ru1.5Re1/C/co-SEA (8) Ru2Re1/C/co-SEA (9) Ru2Re1/C/co-DI (10) Ru4Re1/C/co-SEA (b) XRD patterns of monometallic and bimetallic catalysts on alumina after reduction treatment (1) γ-Al2O3 (2) 2.0RuAl (3) 1.0ReAl (4) Ru0.25Re1/Al/co-SEA (5) Ru0.5Re1/Al/co-SEA (6) Ru1Re1/Al/co-SEA (7) Ru1.5Re1/Al/co-SEA (8) Ru2Re1/Al/co-SEA (9) Ru4Re1/Al/co-SEA.

Representative STEM images for bimetallic Ru2Re1 catalysts synthesized by co-SEA and co-DI on both supports are provided in Figure 5.4. The particle sizes calculated from STEM images (number average Ru particle size)23,53 matched with ones observed from XRD (<1.5nm). The mean particle size of the carbon supported metal nanoparticles in the co-SEA catalyst was 1.3nm (Figure 5.4 (a)) with a tight size distribution (0.4nm); co-DI also produced particles with a small mean size of 1.6 nm, however, the size distribution is much broader (1nm). The larger particles may explain the sharper peaks shown in the XRD pattern (Figure 5.3 (9)). On the other hand, the alumina supported
catalysts, produced small nanoparticles using both either by co-SEA (0.82nm) or co-DI (1.2nm) method with very narrow distributions of 0.2 and 0.3nm respectively. The reason why both methods yield small particles is most likely due the high mobility of Re. These results are in good agreement with Miniajlik et al’s work\textsuperscript{145}, where the small mean metal particle size (varying from 0.9nm to 1.3nm by changing the Ru/Re atomic ratio from 50:50 to 90:10) was obtained using co-wet impregnation. However, Pt-Pd system reported by Regalbuto et al. where they found that co-SEA produces a smaller mean particle size than co-DI due to a much stronger interaction between Pt and Pd\textsuperscript{63}. EDXS elemental maps were generated for the selected catalysts in order to obtain some insight into the bimetallic morphology of the Ru-Re particles. However, the majority of the particles are either single atoms or the clusters of atoms, less than 1nm, therefore, only representative maps of relatively large particles on carbon only are shown in Figure 5.4. These EDXS maps suggest that there is a bimetallic alloyed RuRe structure present along with some well dispersed separated Re particles (bright spot). This is evidenced by overlapping the maps of the individual metals and noticing the extra Re particles.
<table>
<thead>
<tr>
<th>STEM Images</th>
<th>Mapping of Ru &amp; Re</th>
<th>Particle size distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) co-SEA on carbon</td>
<td>Ru-red Re-yellow</td>
<td>![Histogram of particle size distribution]</td>
</tr>
<tr>
<td>b) co-DI on carbon</td>
<td>Ru-red Re-yellow</td>
<td>![Histogram of particle size distribution]</td>
</tr>
<tr>
<td>c) co-SEA on alumina</td>
<td></td>
<td>![Histogram of particle size distribution]</td>
</tr>
<tr>
<td>d) co-DI on alumina</td>
<td></td>
<td>![Histogram of particle size distribution]</td>
</tr>
</tbody>
</table>

Figure 5.4 STEM images and EDXS of (a) Ru$_2$Re$_1$/C/co-SEA (b) Ru$_2$Re$_1$/C/co-DI (c) Ru$_2$Re$_1$/Al/co-DI (d) Ru$_2$Re$_1$/Al/co-DI. Elemental mapping colors are red for Ru and yellow for Re.
To better understand the interaction between the two metals, temperature programmed reduction (TPR) of O pre-covered, selected bimetallic RuRe catalysts was conducted from 40 to 500°C. The results are presented in Figure 5.5 (a) and (b) for monometallic and bimetallic catalysts supported on carbon and alumina, respectively. In Figure 5.5 (a), the reduction of oxygen pre-covered 1.4Ru/C occurs with maximum peak at 130°C and a small shoulder at 230°C. This is similar to the TPR pattern of 5%Ru/C reported in Dumesic’s work. The TPR pattern of 1.5Re/C presents multiple peaks at 295°C, 310°C and 350°C due to the various oxidation state of Re. For bimetallic RuRe catalysts, the apparent Re-O reduction peak was shifted to a lower temperature from 310°C to 160°C for both co-SEA and co-DI samples. TPR profiles of representative catalysts supported on alumina are shown in Figure 5.5 (b). The 1Re/Al reduction profile shows a maximum at 260°C and a very broad, subtle feature at 390°C that may correspond to the segregated rhenium species that have a strong interaction with the alumina surface. These observations are consistent with the report by Miniajlu et al., who indicated that the peak maximum reduction temperature varies between 275 and 600°C depending on the Re content and type of support. The profile of the 2RuAl catalyst shows a broad reduction peak, with a maximum at 120°C and a small shoulder at 200°C. This shoulder may explain the strong interaction between the ruthenium particles and the alumina surface. The addition of Re (Ru_x:Re_y=2:1) in the co-SEA sample resulted in a shift of the Ru reduction peaks from 120°C to 90°C and from 200°C to 140°C, as well as the Re reduction peaks from 260°C to 200°C. In contrast, for co-DI sample, a shift from 260°C to 200°C was observed for the Re-O peaks, but none for the Ru-O peak. It is notable that the peaks located at 390°C remained in the same position even in the
presence of Ru in both co-SEA and co-DI. This is attributed to segregated Re species, which could migrate to the Ru surface and help to reduce Ru-O in the co-SEA case. However, the peak at 390°C did not appear in the carbon samples because the mobility of Re oxide increases with support hydration, which means highly dehydrated alumina strongly interact with Re oxide species. This leads to the formation of highly dispersed Re oxide which disrupts alloy formation\textsuperscript{146}. The TPR results evidently show that the presence of Ru significantly lowers the Re-O reduction which can be explained by the catalytic effect of Ru on the reduction of Re species.

![Graph showing H2 consumption vs. Temperature (°C)](image)
To explore the nature of the bimetallic interaction, XPS was employed to determine possible electronic interaction between Ru and Re. The XPS spectra of the Ru 3d<sub>5/2</sub> and Re 4f<sub>7/2</sub> regions for bimetallic RuRe supported on carbon are presented in Figure 5.6 (a) and (b) as they are the most intensive peak, respectively. The BE positions have been referenced to the C 1s peak (284.6ev) of the carbon support for all comparisons. The peak binding energy of Ru 3d<sub>5/2</sub> in the bimetallic Ru<sub>0.25</sub>Re<sub>1</sub> catalyst appears at 280.64ev, which corresponds to Ru<sup>2+</sup> and/or Ru<sup>4+</sup> (280.70ev) <sup>23</sup>, <sup>80</sup>. However, increasing the amount of Ru species to Ru<sub>0.5</sub>Re<sub>1</sub> and beyond, lowers the BE of Ru 3d<sub>5/2</sub> to 280.5ev. This suggests more Re species covering the Ru surface at Ru<sub>0.25</sub>Re<sub>1</sub> since Re is dominant compared to Ru<sub>3</sub>Re<sub>1</sub>. XPS data also reveal the presence of RuO<sub>x</sub> (metallic Ru (280.1ev) <sup>23</sup>, <sup>79</sup> on the surface in the bimetallic catalysts as synthesized after reduction at
220°C. This indicates electron transfer from surface Ru to surface Re atoms as a result of Ru (1.9) being less electronegative than Re (2.2)\(^{147}\). The Re 4f\(_{7/2}\) peaks of the bimetallic catalysts were shown in Figure 5.6 (b), where the XPS spectrum of NH\(_4\)ReO\(_4\) was taken as the control experiment for Re oxidation state. The most intense peaks of Re 4f\(_{7/2}\) in the bimetallic catalysts, 41.5ev, 43.2ev and 45.2ev, are attributed to Re\(^{4+}\), Re\(^{5+}\), and Re\(^{6+}/\text{Re}^{7+}\) respectively, which confirms the three peaks observed from the TPR data in Figure 5.5 (a) (4). However, there is a 0.7ev difference between the published value of Re\(^{4+}\), Re\(^{5+}\), and Re\(^{6+}/\text{Re}^{7+}\) (42.2ev, 43.9ev and 45.9ev) and the actual values noted here\(^{148}, \, 149\), indicating a high level of electron transfer to the oxidized Re sites from Ru. Furthermore, the oxidation state of Re in NH\(_4\)ReO\(_4\) is Re\(^{7+}\), the binding energy of Re 4f\(_{7/2}\) appears at 45.9ev, which has a good agreement with the published valve mentioned above. It is also showing highly dispersed and positively charged Re on the surface of the bimetallic catalysts. Finally, the peaks of metallic Re 4f\(_{7/2}\) (39.4ev)\(^{149}\) were observed in the Ru\(_2\)Re\(_1\) bimetallic catalysts prepared by co-SEA, even for co-DI sample. It is not surprising that ReO\(_x\) alloyed with Ru atoms indicating from XPS and EDXS/map data as Re particles are small, well dispersed and easily to be oxidized by air.
Figure 5.6 (a) and (b) XPS spectra for Ru 3d and Re 4f regions of bimetallic RuRe catalysts supported on carbon with various RuRe atomic ratio (1) Ru\textsubscript{4}Re\textsubscript{1}/C/co-SEA (2) Ru\textsubscript{2}Re\textsubscript{1}/C/co-DI (3) Ru\textsubscript{2}Re\textsubscript{1}/C/co-SEA (4) Ru\textsubscript{0.5}Re\textsubscript{1}/C/co-SEA (5) Ru\textsubscript{0.25}Re\textsubscript{1}/C/co-SEA, inset of peak fitting of Re, with permission.
Figure 5.7 shows IR spectra of CO adsorbed on the bimetallic RuRe supported on alumina, along with analogous data for the monometallic Re catalyst. No evident peaks appear in the 1ReAl catalyst spectrum, indicating ReO$_x$ is mainly present on the surface since CO cannot adsorb on ReO$_x$. With the addition of the Ru species, three distinct peaks at 2000 cm$^{-1}$, 2075 cm$^{-1}$ and 2141 cm$^{-1}$ were observed in all of the bimetallic catalysts, which can be assigned to linearly CO adsorbed on high energy defects sites and/or isolated Ru species surrounded by partially oxidized Ru, dicarbonyl species and tricarbonyl CO species on Ru$^{n+}$, respectively. This indicates the existence of isolated Ru particles by Re species 23, 150. Furthermore, FTIR and XPS both suggest the oxidation state of Ru is Ru$^{n+}$. A notable new feature which appears in the bimetallic Ru$_2$Re$_1$/Al/co-SEA spectrum is the peak at 2040 cm$^{-1}$, assigned to CO linearly adsorbed on Re and Ru 150, 151, indicating the formation of metallic Re with the assist of Ru, which agrees well with XPS data (see Figure 5.6 (b)), but, somehow, only Ru$_2$Re$_1$ shows this different type of site perhaps due to a special geometric arrangement. An additional reason for the formation of metallic Re under our reaction condition (220°C) may be caused by H spillover from Ru to Re as the reduction of Re-O shift from 310°C to 160°C for carbon support and 260°C to 200°C for alumina support when the atomic ratio of Ru Re is 2:1 (see Figure 5.5). A similar spectrum was observed for the Ru$_2$Re$_1$/Al/co-DI catalyst but with peaks of lower intensity, indicating the numbers of available metal surface sites in co-DI are less than ones in co-SEA. This is in good agreement with STEM and XRD data. The bimetallic Ru$_2$Re$_1$ catalysts show a predominantly geometric effect due to the formation of CO linearly adsorbed on Re. Notably, much less CO is adsorbed on the Ru-Re catalyst than on 2RuAl, as can be seen from the intensity in the FTIR spectra in Figure
5.7 which gives further insight into the bimetallic catalytic performance. First, Ru shows a good interaction with Re atoms, indicated by the Ru-Re alloy seen by EDXS mapping. Second, a weakened interaction between Ru and alumina support in the bimetallic sample and also the strong electronic interaction between Ru and Re, seen by XPS, this being where the presence of Re species on the surface dilutes and isolates the active Ru sites.

Figure 5.7 FTIR spectra of catalysts on alumina with various RuRe atomic ratio from top to bottom 2RuAl, Ru$_2$Re$_1$/Al/ co-SEA, Ru$_2$Re$_1$/Al/ co-DI, Ru$_4$Re$_1$/Al/ co-SEA, Ru$_1$Re$_1$/Al/ co-SEA, Ru$_{0.5}$Re$_1$/Al/ co-SEA, Ru$_{0.25}$Re$_1$/Al/ co-SEA, Re/Al/SEA and inset of FTIR spectra of the 2RuAl sample.

5.3.3. Activity and stability of bimetallic catalysts

Hydrogenation of LA to GVL was evaluated over all bimetallic RuRe and monometallic Ru and Re catalysts on both supports to determine the effects of RuRe atomic ratio and support type (carbon or alumina). The details of reaction experiments could be found in our previous study and the kinetic study under the current condition have been reported without external and internal mass transfer limitations $^{23}$. In Table
5.1, catalytic activity is reported in terms of rates based on mass of metal, which were obtained at the times corresponding to 10% LA conversion. The further analysis of this data will be discussed in the next session.

Seven catalysts were selected for a durability study: Ru\textsubscript{1.5}Re\textsubscript{1}/C/co-SEA, Ru\textsubscript{1.5}Re\textsubscript{1}/C/co-DI, Ru\textsubscript{2}Re\textsubscript{1}/C/co-DI, Ru\textsubscript{2}Re\textsubscript{1}/Al/co-SEA, Ru\textsubscript{2}Re\textsubscript{1}/Al/co-DI, Ru\textsubscript{0.5}Re\textsubscript{1}/Al/co-DI and Ru\textsubscript{1}Re\textsubscript{1}/Al/co-DI Catalysts were aged at reaction conditions for 6h, then recovered by filtration and dried overnight at 120\textdegree C. XRD was employed for post-aging characterization. XRD patterns of all used catalysts except Ru\textsubscript{2}Re\textsubscript{1}/Al/co-DI, Ru\textsubscript{1}Re\textsubscript{1}/Al/co-DI and Ru\textsubscript{0.5}Re\textsubscript{1}/Al/co-DI catalysts were virtually indistinguishable from those of the fresh catalysts, which implies that at least no significant particle sintering occurs in those bimetallic catalysts. As for Ru\textsubscript{2}Re\textsubscript{1}/Al/co-DI shown in the enlarged inset Figure, several new peaks were observed at 27.9\textdegree, 33.7\textdegree, 40.0\textdegree and 53.0\textdegree, which are assigned to RuO\textsubscript{2}\textsubscript{152-154}, while 38.4\textdegree, 41.5\textdegree and 42.5\textdegree are assigned to Re\textsuperscript{153}, and 21.4\textdegree is assigned to RuO\textsubscript{3}\textsuperscript{153} along with some unknown peaks were observed, indicating that sintering occurs. The same trends were also observed for Ru\textsubscript{1}Re\textsubscript{1}/Al/co-DI and Ru\textsubscript{0.5}Re\textsubscript{1}/Al/co-DI catalysts. Importantly, after aging Ru and Re particles became separated in the alumina supported catalysts prepared by co-DI method due to the lesser interaction between the two metals than the co-SEA preparations.
Figure 5.8 XRD patterns of spent bimetallic catalysts (a) supported on carbon, Ru$_{1.5}$Re$_1$/C/co-SEA before and after reaction (1) and (2), Ru$_2$Re$_1$/C/co-DI before and after reaction (3) and (4), Ru$_{1.5}$Re$_1$/C/co-DI before and after reaction (5) and (6) (b) supported on alumina, Ru$_2$Re$_1$/Al/co-SEA before and after reaction (1) and (2), Ru$_2$Re$_1$/Al/co-DI before and after reaction (3) and (4), Ru$_1$Re$_1$/Al/co-DI before and after reaction (5) and (6), Ru$_{0.5}$Re$_1$/Al/co-DI before and after reaction (7) and (8), inset of enlarged Figure b (4).
5.3.4. Activity of bimetallic catalysts, optimal RuRe atomic ratio, geometric, electronic and bifunctional effects, and support effect

The catalytic activities of the bimetallic and monometallic catalysts are summarized in Table 5.1. The rate of LA hydrogenation was calculated based on the mass of metal, when the conversion of LA reached 10%. Plotting the carbon- and alumina-supported bimetallic catalyst rate versus the atomic ratio of RuRe (x:y), there appears to be a volcano shape for both supports as shown in Figure 5.9. For carbon supported catalysts, compared to the rate observed for monometallic 1.4RuC-SEA (2.4 mol/(g*s)/10^3), the addition of Re to Ru/C by co-SEA method initially decreases the rate of hydrogenation of LA, then increases to a maximum (3.3 mol/(g*s)/10^3) at a ratio of 2:1. The rate then decreases as the ratio further increases to 4:1. In contrast, the activities of all bimetallic catalysts are higher than the monometallic 1.5ReC-SEA catalyst (0.35mol/(g*s)/10^3). A similar trend was observed for the alumina-supported catalysts in Fig. 8, where bimetallic Ru_2Re_1 (0.8 mol/(g*s)/10^3) gives higher rate than either 2RuAl (0.48mol/(g*s)/10^3) or 1ReAl (0.16mol/(g*s)/10^3). Changes in surface reactivity of bimetallic catalysts are usually considered to be a consequence of a combination of electronic and geometric effects. The effects of geometry, electron and support will now be discussed individually.
5.3.4.1. Support effect

A support effect was observed in our previous study\textsuperscript{23}, where oxidized carbon showed better activity than alumina. In this study, it is notable that VXC72R was used as the support rather than oxidized carbon. The same trend was observed in Figure 5.9; carbon supported catalysts show higher activity than alumina supported catalysts. The acidity of support follows the order of VXC72R < oxidized VXC 72 ∼ $\gamma$-Al$_2$O$_3$. Three catalysts with similar particle size were selected to explore the support effect, 1.4%Ru/VXC72R (Ru particle size 1.3nm) (STEM image in Fig S.4), 1.5%Ru oxidized VXC72 (Ru particle size 1.3nm shown in our previous study), and 2%Ru $\gamma$-Al$_2$O$_3$-
calcined 100°C (Ru particle size 1.1nm shown in our previous study). The activity follows this order, VXC72R (2.4mol/(g*s)/10^3) > (1.7mol/(g*s)/10^3) ~ 1.8mol/(g*s)/10^3), indicating the activity increased as overall acidity decreased. This could be caused by the strong interaction between metal and support. Since XPS and FTIR data both show that ReOx is on the surface, which may introduce acidity to the catalyst, leading to the decrease of rate.

5.3.4.2. Geometric, Electronic, and Bifunctional effects

Volcano-shape plots of catalytic activity versus metal atomic ratio is typically attributed to geometric, electronic and/or bifunctional effects in bimetallic systems. Volcano-shaped activity trends have been seen in many cases. For example, Song et al. reported that the selectivity for aromatics reaches the maximum at Fe/Pd=0.7 in bimetallic FePd catalyst supported on ordered mesoporous carbon for catalytic decomposition of phenethyl phenyl ether to aromatics. Prati et al. also reports the increase of activity reached a maximum value when Au/Pd was 6:4 and then decreased in bimetallic AuPd supported on carbon catalysts for D-sorbitol oxidation. Finally, volcano-like activity was also observed and the maximum activity appears at Au:Pd=10:1 in bimetallic AuPd nanoparticles for selective oxidation of alcohols. According to our previous study, XPS (negative BE shift of Ru) and CO-FTIR (the ratio of Ru^0 to Ru^n+) both suggest that the degree of metallic Ru has a positive correlation on the rate of LA hydrogenation. This was also indicated by studying the alkali interaction with Ru (Chapter 4), as alkali metal could shift electron density to Ru.
In this study, the partial positive charge on Re as seen in XPS, the Ru/Re structure in the EDXS map, and the evidence obtained from CO-FTIR for Ru covered by Re species, all suggest a bimetallic alloyed Ru/ReOₓ structure. Trends with Ru:Re ratio were parallel for both supports, with the carbon supports exhibiting relatively higher activity at any particular Ru:Re ratio (Figure 5.9). Initially, for the low Ru:Re ratios the high concentration of Re dilutes the critical ensemble size of Ru atoms essential for the hydrogenation. Furthermore, it was seen in XPS that Ru showed a partial positive charge as Ru transferred electrons to Re, which means there is less degree of metallic Ru on the surface. With less reactive Ru, and less Ru sites (Ru loading is low compared to the Ru-only catalyst), it is not surprising that the activity went down relative to the pure Ru catalyst. When the Ru:Re ratio increased to 2:1, however, the activity surpassed that of the Ru-only catalysts, despite the Ru loading in the case of carbon (0.8 wt%) being only 60% that of the Ru-only catalyst (1.4 wt%). This can only be attributed to an overwhelming bifunctional effect, as the electronic and geometric effects of support have negative impacts on the hydrogenation rate. XPS (Figure 5.6) and CO-FTIR data (Figure 5.7) both suggest the presence of metallic Re in Ru₂Re₁ sample. It is well known that Re is active for C-OH activation ¹⁵⁸, thus we propose that Re may activate C-OH in 4-hydroxypentanoic acid (HPA) to promote the dehydration step, which was found to be the slowest step as its apparent activation energy (70 kJ/mol) is larger than that of the hydrogenation step (48 kJ/mol) ¹⁵.

However, with further decreases of Re to Ru:Re = 4:1, the activity went down again over both supports. The carbon supported catalyst contains more Ru (1.6 wt%) than the Ru-only carbon catalyst (1.4 wt%). Perhaps the most critical observation is that
CO-FTIR does not give evidence of 2040 cm\(^{-1}\) peak, indicative of metallic Re, for the 4:1 ratio. This appears only for the 2:1 Ru:Re ratio both for the co-SEA and the co-DI samples. The reason why only the 2:1 ratio is able to generate metallic Re cannot be hypothesized at present. The lower activity of the co-DI samples can be attributed to larger particle size and overall lower numbers of active sites.

5.4. CONCLUSION

XPS, CO-FTIR and EDXS/Map suggest the presence of a bimetallic alloyed RuRe structure along with segregated ReOx species in the bimetallic catalysts. The catalytic properties of Ru/C were modified significantly by the addition of Re as seen by a volcano shape in activity versus atomic with a maximum at Ru:Re (2:1). This is ascribed to the presence of metallic Re at the 2:1 Ru:Re ratio, giving rise to a bifunctional effect that overcomes negative geometric and electronic effects. Ru\(_2\)Re\(_1\) on both supports give higher activity than monometallic Ru catalysts respectively. Co-SEA method yields better interaction between the two metals, a smaller mean metal particle with a tighter distribution, and more stability than the co-DI method, which demonstrates a simple and precise way to rationally synthesize bimetallic catalysts.
6.1. CONCLUSION

In summary, the results shown in my dissertation demonstrate the effects of Ru particle size, support, alkali and alkaline earth dopants, the addition of Re and solvent on the Ru activity for hydrogenation of LA to GVL by rational synthesis of Ru-based catalysts, which provides an insight into the commercialized this reaction by optimizing catalysts through studying synthesis-structure-function relationships.

Firstly, well dispersed Ru particles were achieved by applying the SEA method to oxidized carbon and γ-Al₂O₃ supports. The surface of oxidized carbon in the solution above its PZC (4.0), becomes deprotonated and negatively charged and is able to absorb cationic [Ru(NH₃)₆]³⁺. On the other hand, the surface of γ-Al₂O₃ in solution at pHs below its PZC (8.1), becomes protonated and positively charged and able to absorb anionic [Ru(CN)₆]⁴⁻. The maximum uptake of [Ru(NH₃)₆]³⁺ on oxidized carbon occurs at the final pH of 9.9 and of [Ru(CN)₆]⁴⁻ on γ-Al₂O₃ occurs at the final pH 2.1. The maximum surface densities over the respective supports correspond to Ru metal loadings of 1.5 wt% for Ru/C and 2.0wt% for Ru/γ-Al₂O₃. The Ru (number) particle size after reductions were 1.30 nm for Ru/C and 0.92 nm for Ru/Al₂O₃ as observed with STEM. The high dispersion of these Ru nanoparticles on carbon and their promotion by potassium on
carbon and alumina has led to the highest reported activity (per g Ru, per g catalyst, and TOF) of Ru catalysts for LA hydrogenation to GVL. Aging in the reaction medium for 24 h led to significant deactivation; up to 18% for the undoped catalysts due to nanoparticle sintering, and up to 58% for the K-doped alumina and carbon catalysts due to both sintering and K loss.

Several other trends were revealed by this rational synthesis of Ru nanoparticles in 1,4 Dioxane. First, carbon supported catalysts were generally more active than alumina catalysts because of more formation of metallic Ru in carbon than alumina. Second, the presence of potassium significantly enhances the activity over either support, due to a significant decrease in the electron binding energy of Ru in the presence of K⁺. Finally, LA hydrogenation is structure sensitive and depends on Ru particle size, with a maximum in activity at about 1.5 nm, such particle size effect also was observed by Luo et al and Corma et al. However, strong solvent effect on Ru activity was observed in our further study in water as the rate was much faster than 1,4 Dioxane, Ru particle size and support effects were masked by the solvent effect.

Secondly, strong promotional effects were observed for alkali and alkaline earth promoted catalysts. With the same ratio of dopant to Ru, the reaction rate follows this order: Na⁺ < K⁺ < Cs⁺ for alkali metal and Ba²⁺ < Mg²⁺ < Ca²⁺ for alkaline earth metal. Several trends were revealed by this parallel study. First, the role of alkali metal is ascribed to the combination of modification of Ru metal by electronic effect, modification of alumina support by acidity effect. The role of alkaline earth metal appears to stem from acidity effect. Second, alkali dopant catalysts suggest a successful promoter for this reaction should be large with high polarizability. Finally, higher
reduction temperature (400°C) may form a more active chemical state (alkali hydroxide) and redistribute alkali metals, leading to higher TOF.

Lastly, XPS, co-FTIR and EDXS/Map suggest the bimetallic alloyed RuRe structure along with segregated ReOx species in the bimetallic catalysts. The catalytic properties of Ru/C were modified significantly by the addition of Re, a volcano plot appears at the maximum occurs at Ru:Re (2:1), in comparable to the monometallic Ru catalyst, which is ascribed to the combination of geometry, electronic and overall surface acidity of catalysts. Ru$_2$Re$_1$ on both supports give a better activity than monometallic Ru catalysts respectively, indicating the geometric effect plays an important role. Co-SEA method gives better interaction between two metals, less mean metal particle with tighter size distribution, more stable than co-DI method, which demonstrates a simple and precise way to synthesize rationally bimetallic catalysts.

6.2. PROPOSED FUTURE WORK

Future investigation for the hydrogenation of LA should focus on the design and development of the robust catalysts and that also can be scaled up for commercial purposes under the real biomass feedstock solution. A detailed understanding of the reaction mechanism is critical to achieve this goal. Experimentally, Isotopic labeling experiments could be studied. Computationally, Density Function Theory may help to derive reaction networks and the rate determining step also could be determined.

Furthermore, the strong promotion effects of alkali and alkaline earth metal on Ru activity were observed for LA to GVL. Post reaction catalysts were characterized by CO-FTIR. The data suggests (Table B.4) Cs leached after reaction even through Cs gives
highest activity compared to K and Na. However, K shows the best stability. Thus, K is a good candidate to commercialize this process. Now the question is how to stabilize the alkali metal on the Ru/support to reduce the leaching in the severe condition, especially when water is used as solvent. Since the support effect was found for this reaction in 1,4 Dioxane, TiO$_2$ support shows a promising alternative in terms of good stability under reaction and regeneration conditions. It may be a good option by modification of support. Atomic Layer Deposition, a potential technique, could be used to deposit alkali selectively on TiO$_2$ support.

Lastly, this dissertation also demonstrates a simple, scalable and reproducible way to synthesize monometallic (SEA) and bimetallic catalysts (co-SEA), bimetallic RuSn, RuNi, have shown the better activity and stability than monometallic Ru catalyst for hydrogenation of LA in the literature. However, the synthesis method (IWI) gives poor interactions between two metals and metal dispersion. As many impurities and byproducts are present in real feedstock solutions biomass, and also LA conversion processes are often under harsh conditions, such as highly polar, hydrothermal, corrosive conditions. It is possible to achieve better metal-metal interactions by applying co-SEA or even sequential-SEA so that ensuring high activity, high selectivity and yields, of course, good stability then having effective purification steps.

Further studies on the design and development of are recommended to conduct. Once, a suitable catalyst with good stability and high activity and selectivity was found, the next step is to evaluate it in the real biomass feedstock solution, which will be a big breakthrough for the commercialization of biomass conversion into liquid transportation fuels.
REFERENCES


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APPENDIX A: SUPPLEMENTARY INFORMATION FOR CHAPTER 3

Additional details of catalyst preparation by SEA

Ruthenium based catalyst preparation

Oxidized carbon synthesis

A commercial carbon (Vulcan XC72) was used as the starting material for oxidized VX72. 10g of VX72 mixed with concentrated nitric acid (>70%) was heated for 3h at 90-95°C and then cooled to room temperature. Subsequently, the mixture was washed with deionized water until the pH of the washing solutions reached 5, and was dried overnight at room temperature. The oxidized Vulcan 72 Carbon is labeled as Cox.

Determination of the optimal adsorption pH

In order to determine the pH at which maximum metal uptake could be achieved, adsorption experiments were conducted at a specific range of pH values (selected based on the PZC of the support). At first stock solution of metal precursor solution (e.g., Ru(NH3)6Cl3) of specific concentration was prepared and aged for 1 hour. After that a series of 50-ml pH adjusted (using HCl or NaOH) solution with desired metal concentration was prepared from the stock and then placed in 60-ml polypropylene bottles. For cationic precursors adsorption was studied within the pH range range of 9-13 whereas for anionic the range was 1-6 where electrostatic attraction is dominant. After final pH measurements 5-ml from each solution was filtered using 0.2 micro syringe filters for ICP measurement
to determine the final metal concentration. Additionally, prior to adding support 5-ml from each solution was also extracted and stored separately for ICP analysis to determine the initial metal concentration (before support addition). Difference between initial and final metal concentration for each pH sample solution is referred to as the adsorbed metal at that pH all of which were then plotted against the final pH values. From this plot the final pH value at which maximum uptake was observed was noted as the optimum pH. The reproducibility of ICP measurements is ±5%.

Synthesis of Ru based catalysts

2.0g of 1.5% Ru/Cox and 2.0% Ru Al₂O₃ catalysts were prepared with 100 ppm Ru (NH₃)₆Cl₃ at SL=1000 m²/l at optimal initial pH ~ 11.6 and 100ppm K₄Ru(CN)₆ at SL = 500 m²/l at optimal initial PH ~ 1.95, respectively. 4.4% Ru Cox catalysts were also prepared by performing sequential SEA 3 times at the same condition as 1.5% Ru Cox SEA catalyst. Afterwards, the catalysts were dried in room temperature for 48h, and then at 100°C overnight. For comparison, the same amounts of Ru metal loading catalysts were prepared by dry impregnation (DI). The amount of liquid used for DI was equal to the pore volume of the support and was not pH-adjusted. The concentrations of Ru solution were adjusted to obtain desired weight of metal. Dry impregnation was also used to dope the same amount of potassium (KNO₃) in 2.0% Ru γ-Al₂O₃ prepared by DI and into 1.5% Ru Cox and 2.0% Ru γ-Al₂O₃ both prepared by SEA.
Effect of agitation speed

To find the impeller speed at which external mass transfer limitations in the solid-gas-liquid system (solid catalyst, hydrogen gas and organic phase) were eliminated, agitation speed was varied from 200 to 1600 rpm, while keeping all other variables constant. The conversion of LA as a function of the speed is given in Figure A.1, which shows conversion slowly increased as stirring speed increased from 200-1000 rpm and did not change thereafter. These results indicate conversion is independent of the stirring rate at or above 1000 rpm. Catalytic experiments were performed at agitation speed of 1000 rpm.

![Diagram showing conversion percentage vs. agitation speed]

Figure A.1 The effect of agitation speed on the hydrogenation of LA
Activation Energy Measurement

The 5.0RuC-com catalyst was used to determine the rate constant at different temperatures at constant hydrogen pressure (200psi). The resulting Arrhenius plot is given in Figure A.2, the slope of this line gives an activation energy of 35 kJ/mol.

Figure A.2 Arrhenius plot for 5.0RuC-com catalyst

FTIR spectra peak fitting

Spectra deconvolution and fitting was performed by using peaks with an array of different shapes (i.e., Gaussian, Lorentzian, log-normal, etc.). In general, Gaussian peaks were used for weaker bonds at lower wavenumbers (i.e., 1700-1900 cm\(^{-1}\)), the bands exhibiting visible asymmetric tailing were fitted using log-normal peaks, and all other bands were fitted with peaks of a mixed Gaussian-Lorentzian type. Curve-fitting for all
sets of spectra keep the same position, peak width, fwhm, and percent of Lorentzian. All of the IR spectra shown in this paper are taken twice and deconvoluted, the data shows the correlation factors above 0.9999 and standard errors below 0.002.

Table A.1 Characteristic Frequencies and Peak Areas of Spectral Features Observed Following Room Temperature Adsorption of CO on Different Ru Particle Sizes on γ-Al₂O₃ and K-promoted sample

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<th>Sample</th>
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<th>3°</th>
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a Bridge-bonded CO, Bridge-bonded CO [Ru₂-CO]. b Dicarbonyl CO species on Ru⁰ [Ru⁰(CO)₂]. c Dicarbonyl CO species on Ru²⁺ [Ru²⁺(CO)₂]. d Linearly adsorbed CO on high energy defects sites and/or isolated Ru⁰ species surrounded by partially oxidized Ru, [Ru⁰-CO]. e Linearly adsorbed CO on Ru⁰ [Ru⁰-CO]. f Linearly adsorbed CO Ruⁿ⁺ [Ruⁿ⁺-CO]. g Tricarbonyl CO species on Ruⁿ⁺ [Ruⁿ⁺(CO)₃, n=1-3]
STEM images of the catalysts shown in Table 3.2

Mean particle size

A

1.08 ± 0.24nm

B

1.63 ± 0.56nm
Mean particle size:

- **C**: 1.70 ± 0.53 nm
- **D**: 1.80 ± 0.86 nm
- **E**: 1.62 ± 0.30 nm
I. Number of particles
Particle size (nm)
Mean particle size
0.92 ± 0.22 nm

J. Number of particles
Particle size (nm)
Mean particle size
1.30 ± 0.55 nm

K. Number of particles
Particle size (nm)
Mean particle size
1.10 ± 0.40 nm
Figure A. 3 STEM images and size distribution for A. 1.2RuC-SEA B. 1.5RuC-SEA-6h C. 1.5RuC-SEA-24h D. 2.0RuAl-SEA-24h E. 4.4RuC-SEA-6h F. 4.4RuC-SEA-24h G. 3K-1.5RuC-SEA-24h H. 3K-2.0RuAl-SEA-24h I. 3K-2.0RuAl-SEA-6h J. 3K-1.5RuC-SEA-6h K. 2RuAl-SEA-C100 L. 2RuAl-SEA-C200 M. 2RuAl-SEA-C300 N. 2RuAl-SEA-R520-24.
APPENDIX B: SUPPLEMENTARY INFORMATION FOR CHAPTER 4

FTIR spectra peak fitting

Spectra deconvolution and fitting was performed by using peaks with an array of different shapes (i.e., Gaussian, Lorentzian, log-normal, etc.). In general, Gaussian peaks were used for weaker bonds at lower wavenumbers (i.e., 1700-1900 cm⁻¹), the bands exhibiting visible asymmetric tailing were fitted using log-normal peaks, and all other bands were fitted with peaks of a mixed Gaussian-Lorentzian type. Curve-fitting for all sets of spectra keep the same position, peak width, fwhm, and percent of Lorentzian. All of the IR spectra shown in this paper are taken twice and deconvoluted, the data shows the correlation factors above 0.9999 and standard errors below 0.002.

Table B.1. Characteristic Frequencies and Peak Areas of Spectral Features Observed Following Room Temperature Adsorption of CO on alkali and alkaline earth promoted on Ruthenium/γ-Al₂O₃ samples.

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Information for alkaline earth metal dopant catalysts

Table B.2. Nomenclature, Ru dispersion and TOF of Alkaline earth (AEM) promoted catalysts as synthesized.

a Bridge-bonded CO, Bridge-bonded CO [Ru₂-CO]. b Dicarbonyl CO species on Ru⁰ [Ru⁰-(CO)₂]. c Dicarbonyl CO species on Ru²⁺ [Ru²⁺-(CO)₂]. d Linearly adsorbed CO on high energy defects sites and/or isolated Ru⁰ species surrounded by partially oxidized Ru, [Ru⁰-CO]. e Linearly adsorbed CO on Ru⁰ [Ru⁰-CO]. f Linearly adsorbed CO Ruⁿ⁺ [Ruⁿ⁺-CO]. g Tricarbonyl CO species on Ruⁿ⁺ [Ruⁿ⁺-(CO)₃, n=1-3].
**XRD**

![XRD Patterns](image)

Figure B.1. XRD patterns of gamma-alumina, 1Mg-220°C and 2Ca-220°C.

**XPS survey scan**

![XPS Survey Scan](image)

Figure B.2. XPS survey scan spectra for 3Mg-220°C, 5Ca-220°C and 5Ba-220°C.
Plot of Activity and BE shift versus wt% loading of alkaline earth metal

Figure B.3. TOF measured at 220°C versus wt% loading of alkaline earth metal (a) Mg series, (b) Ca series, and (c) Ba series.
Figure B.4. FTIR spectra (I left side) and the results of peak fitting (II right side) of alkaline earth promoted catalyst with the similar AEM/Ru atomic ratio about 2.2 and unpromoted catalyst pretreated at 400°C in-situ (a) 5Ba (b) 2Ca, (c) 1Mg, and (d) 2RuAlSEA.

Table B.3. Summary of reaction rates and characterization data for promoted catalysts with the same (AEM:Ru) atomic ratio (2.2:1) and unpromoted catalyst.

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</tbody>
</table>
Figure B.5. IR spectra of pyridine adsorbed on (a) 2RuAlSEA, (b) 1Mg, (c) 2Ca, and (d) 5Ba.

Note: The similar conclusions are made for alkaline earth metal promoted catalysts as the alkali metal promoted catalysts discussed in the manuscript except electronic effect. Notably, as suggested by the relative fraction of Ru\(^0\)/Ru\(^{n+}\) obtained from CO-FTIR (fraction is similar as unpromoed 2RuAl catalyst about 3.4) and XPS (BE shifts are 0 ev for Mg and Ca catalysts sets, BE shift is 0.3ev for Ba catalysts set) for alkaline earth metal promoted catalysts presented in Table S. 3, electronic effect is not a key factor on the effect of Ru activity for alkaline earth metal promoted catalysts. CO-FTIR and XPS data agree well with each other, once again it proves that the peaks fitting for CO-FTIR spectra as independent technique is reliable to study the electronic effect. Finally, Pyridine-FTIR data indicates that the basicity follows the order \(2\text{Ca}^{2+} > 1\text{Mg}^{2+} > 5\text{Ba}^{2+}\), which is the same order as the activity. Therefore, we conclude the role of alkaline earth
metal on the improving Ru activity for LA hydrogenation is by acidity effect and the change of Ru surface morphology, which is limited by the same reasons as discussed for alkali promoted catalysts in the manuscript.

Post-reaction catalysts characterization by CO-FTIR

![CO-FTIR spectra](image)

Figure B.6 CO-FTIR spectra of promoted catalysts post-reaction (2h) (a) 1wt%Na (b) 2wt%K (c) 5wt%Cs.
Table B.4 Summary of Ru$^0$/Ru$^{n+}$ ratio for post-reaction catalysts (2h).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ru$^0$/Ru$^{n+}$</th>
<th>Ru$^0$/Ru$^{n+}$ (after aged 2h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5wt%Cs</td>
<td>5.3</td>
<td>3.9</td>
</tr>
<tr>
<td>2wt%K</td>
<td>4.4</td>
<td>4.5</td>
</tr>
<tr>
<td>1wt%Na</td>
<td>4.3</td>
<td>6.0</td>
</tr>
<tr>
<td>2RuAl-SEA</td>
<td>3.4</td>
<td>----</td>
</tr>
</tbody>
</table>
APPENDIX C: SUPPLEMENTARY INFORMATION FOR CHAPTER 5

Additional details of bimetallic catalyst preparation by co-SEA

**Point Zero Charge (PZC) Measurement of VXC72R carbon and alumina supports**

The Point Zero Charge (PZC) of VXC72R is determined by single point measurement. This experiment was carried out to fill the pore volume of VXC72R by deionized (DI) water until carbon powder turn to a solid ball, followed by measuring the pH of solid ball, the pH value shows 8.2-8.5, which corresponds to the PZC of VXC72R. The PZC of γ-Al₂O₃ is about 8.3, which was determined by the method of Park and Regalbuto (equilibrium pH at high loading, EpHL).

**Anionic Ru precursor synthesis**

Anionic Ru precursor, K₄Ru(CN)₆, was employed for the uptake survey on VXC72R carbon and γ-Al₂O₃ supports with high PZC. Interestingly, the maximum uptake of Ru only gives 0.4wt% Ru on VXC72R carbon. To our knowledge, EDTA’s complexes have a high affinity for metal cations because of its high denticity, which may provide a way to synthesize an anionic Ru salt to achieve decent Ru uptake on VXC72R carbon support. Ru(NH₃)₆Cl₃ was used to synthesize RuEDTA⁻ by the following reaction formula:
\[
\text{Ru}(\text{NH}_3)_6^{3+} + \text{H}_4\text{EDTA} \leftrightarrow \text{RuEDTA}^- + 4\text{H}^+ + 6\text{NH}_3 \quad \text{equation C. 1}
\]

where molar ratio of \(\text{Ru}(\text{NH}_3)_6^{3+}: \text{H}_4\text{EDTA}\) is 1:3 to ensure \(\text{Ru}(\text{NH}_3)_6^{3+}\) completely react with \(\text{H}_4\text{EDTA}\). In order to prepare 400ml of 500ppm RuEDTA solution, 200ml of 1000ppm \(\text{Ru}(\text{NH}_3)_6^{3+}\) was mixed with 200ml \(\text{H}_4\text{EDTA}\) aqueous solution to place in a 500ml round bottom flask, put in an oil bath at 120°C for 3h with reflux, then cooled down to room temperature. Subsequently, this solution was analyzed by Ultraviolet – visible (UV-vis).

**Adsorption surveys**

Adsorption surveys of single metal complexes or mixture of metals were conducted over a range of pH as has been done previously. A series of 50-ml pH-adjusted solutions by using HCl or NaOH with desired metal concentrations were prepared from the stock, and then each was placed in a 60-ml polypropylene bottle. For VXC72R carbon support, 50ml of 100ppm \(\text{RuEDTA}^-\) and 100ppm \(\text{ReO}_4^-\) contacted with the amount of support leading to the surface loading (SL) is 500m²/l. The initial pH of metal solution about 1-6 were used. After aging 1h, the support was added into 60-ml bottle and then shaken for 1h, after which 5-ml portions were filtered for ICP and AAS measurement to determine the final concentration of Ru and Re in the solution. Following this, the final pH also was measured. On the other hand, in the case of alunia support, 50ml of 70ppm \(\text{Ru(CN)}_6^{4-}\) and 280ppm \(\text{ReO}_4^-\) were used to contact with the amount of support leading to the surface loading (SL) is 2000m²/l,

where \(\text{SL}(\text{m}^2/\text{L}) = \text{mass of solid (g) } \times \text{surface area (m}^2/\text{g})/\text{volume of solution (L)}\)

Adsorption data is plotted the final pH as surface density \(\Upsilon (\mu\text{mol metal }/\text{m}^2)\),

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\[ T (\text{\(\mu\text{mol metal /m}^2\)}) = \frac{\text{Concentration initial} - \text{Concentration final}}{\text{surface loading} \times \text{MW of metal}}. \]

**Anionic Ru precursor (RuEDTA\(^-\)) synthesis**

The UV-Vis spectra of the mixed solution with various reaction times under reflux at 120°C for 1.5h are shown in Figure C.1, the mix solution only contains Ru(NH\(_3\))\(_6\)Cl\(_3\) at zero min, a peak appears at 275nm, which is assigned to RuEDTA\(^-\), become evident after 30min, the spectrum remains same even treated for a longer time at 360mins, which indicates complexation is completed after 30mins.

![UV-vis spectra of mix solution with various reaction times under reflux at 120°C for 1.5h](image)

Figure C.1 UV-vis spectra of mix solution with various reaction times under reflux at 120°C for 1.5h.
Figure C.2. H$_2$-TPR patterns of catalysts (a) supported on carbon (1) $1.5\text{ReC}$ (2) Ru$_{1.5}\text{Re}_1/C/\text{co-SEA}$ (0.9Ru1Re) (3) $1.4\text{RuC}$ SEA (b) supported on alumina (1) $1\text{ReAl}$ (2) Ru$_2\text{Re}_1\text{Al}/\text{co-SEA}$ (0.7Ru0.6Al) (3) $1.2\text{RuAl}$.
Figure C.3 Representative STEM image of 1.4RuC catalyst.