Study of ruthenium particle size effect on hydrogenation of levulinic acid (LA) to ɣ-valerolactone (GVL)

John R Regalbuto [1*], Shuo Cao[1]
[1]*University of South Carolina, Columbia, SC 29208USA*
**corresponding author:regalbuj@cec.sc.edu*

Introduction

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[1]. To date the literature on the hydrogenation of LA to GVL has focused more on the process and less on the catalyst.

The goal of this work is 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 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.

Materials and Methods

Ru catalysts were prepared using strong electrostatic adsorption method [2] as well as dry impregnation method for comparison. (Nomenclature of carbon and alumina-supported catalysts synthesized are given in **Table 1**) The experiments were run in stainless steel batch reactor with 100ml capacity from Autoclave Engineers. In a typical reaction, the reactor was loaded 54g solvent (1-4 Dioxane), 6g reactant (LA), and 0.02mg catalyst. The reaction was performed at 220°C and 200psi H_2 for 6h period with a rate of 1000 rpm for impeller speed to eliminate external mass transfer limitations. Aging was used to make different particle size sets with the same condition as reaction's, aged catalysts were filtrated and dried for future evaluation. Each reaction was run twice at least to ensure the reproducibility and accuracy of data.

Table 1. Nomenclature of carbon and alumina-supported catalysts synthesized

catalyst	support	precursor	Method, pretreatment
carbon			
1.5RuC-SEA	oxidized Vulcan XC72 (Cabot)	$Ru(NH_3)_6Cl_3$	SEA, 250°C reduc.
1.5RuC-DI			DI, 300°C reduc.
4.4RuC-SEA			3X: SEA, 250°C reduc.
alumina			
2.0RuAl-SEA	SBA-200 g-alumina	$K_4Ru(CN)_6$	SEA, 520°C reduc.

Results and Discussion

Ru particle size was measured by X-ray Diffraction (XRD) and STEM. Catalytic activity was compared by rate and TOF.

Table 2. Summary of Ru particle size and catalytic activity.

Catalyst	Particle size (nm)		Rate*10^3 (mol LA)/ (g Ru*s)	Rate*10^5 (mol LA)/ (g cat*s)	TOF/ s^{-1}
	XRD	STEM			
Carbon					
1.5RuC-SEA	<1.50	1.30	1.70	2.50	0.220
1.5RuC-SEA aged 24h	<1.50	1.70	1.40	2.10	0.230
4.4RuC-SEA	<1.50	1.50	3.10	14.0	0.470
4.4RuC-SEA aged 6h	<1.50	1.62	2.50	11.0	0.410
4.4RuC-SEA aged 24h	<1.50	1.65	2.10	9.20	0.350
1.5RuC-DI	3.20	2.10	0.430	0.650	0.0900
Alumina					
2.0RuAl-SEA	<1.50	0.900	0.490	0.960	0.0500
2.0RuAl-SEA aged 24h	<1.50	1.80	0.430	0.910	0.0780

Note: Blank runs with carbon and γ-Al_2O_3 exhibited negligible activity.

Table 2 shows the method of strong electrostatic adsorption (SEA) yields well dispersed, homogeneously distributed Ru particles with tight particle size distributions over both types of supports and different particle size sets successfully were prepared by aging.

Figure 1 shows both the carbon and alumnina supported catalyst TOFs versus nanoparticle size, there appears to be a sharp and volcano-shaped, maximum in the activity of the carbon supported catalysts at 1.5 nm, which indicates that hydrogenation of LA is very structure sensitive on Ru particle size.

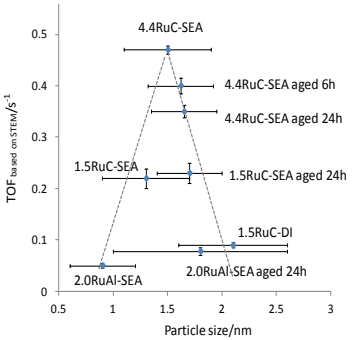

Figure 1 *TOF versus particle size estimated from STEM.*

Significance

This work described the way how to prepare different Ru particle size sets on Carbon and Alumina supports. Reaction data shows hydrogenation of LA is very structure sensitive on Ru particle size. Activity as a function of particle size appears to go through a maximum at about 1.5 nm.

References

1. Alonso, D. M.; Bond, J. Q.; Dumesic, J. A., *Green Chem.,* 2010**, *12***, 1493-1513..
2. Jiao, L.; Regalbuto, J. R., *Journal of Catalysis,* 2008**, *260***, 329-341.