

# Reductive Amination of Carbonyl Compounds Catalyzed by Ruthenium Nanoparticles on Nb<sub>2</sub>O<sub>5</sub>

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**Abstract:** Ruthenium nanoparticles supported on Nb<sub>2</sub>O<sub>5</sub> exhibited high catalytic activity as heterogeneous and reusable catalyst for the reductive amination of various carbonyl compounds that contain reduction-sensitive functional groups such as heterocycles and halogens with NH<sub>3</sub> and H<sub>2</sub>, and prevents the formation of secondary amines and undesired hydrogenated byproducts. Mechanistic studies revealed that the selective catalysis of these materials is likely rationalized by the weak electron-donating capability of Ru particles on the Nb<sub>2</sub>O<sub>5</sub> surface.

**Keywords:** Reductive amination, Biomass, Heterogeneous catalyst.

## 1. Introduction

Primary amines are important and versatile building blocks in organic synthesis because they are widely utilized as intermediates for the production of polymers, drugs, dyes, and detergents.<sup>1</sup> Catalytic reductive amination of carbonyl compounds with NH<sub>3</sub> and H<sub>2</sub> is one of the most efficient and applicative reactions for synthesizing primary amines. Several catalytic systems have been reported for the reductive amination of carbonyl compounds with NH<sub>3</sub> and H<sub>2</sub> including enzymes, homogeneous and heterogeneous catalysts.<sup>2</sup> From the many advantages of heterogeneous catalysts, such as ease of recovery, reusability and stability, various systems based on zeolites, Ni, Cu, Pd, Ru, Rh, and Pt catalysts have been developed; however, selective formation of primary amines has been limited to the reductive amination of simple aryl and alkyl aldehydes due to the formation of secondary and tertiary amines and/or undesired over-hydrogenation of carbonyl groups and other substituents. We focused on electronic metal-support interactions which can influence to the intrinsic activity and selectivity, and developed Ru nanoparticles on Nb<sub>2</sub>O<sub>5</sub> exhibited high catalytic activity and selectivity toward reductive amination of various carbonyl compounds by controlling electron-donation from support to metal.<sup>3</sup>

## 2. Experimental

Supported metal catalysts were prepared by impregnation method. In the case of the Ru/Nb<sub>2</sub>O<sub>5</sub> (Ru: 1 wt%) catalyst, Nb<sub>2</sub>O<sub>5</sub> (2 g) was initially dispersed into aqueous Ru(NO)(NO<sub>3</sub>)<sub>3</sub> solution (50 mL, 4.0 mM, Aldrich) with stirring and kept overnight. The mixed solution was slowly evaporated at 333 K under 0.01 MPa and then dried at 373 K for 1 h under vacuum conditions. The corrected solid powder was pretreated under 5% H<sub>2</sub>/Ar flow (50 mL min<sup>-1</sup>) at 673 K for 2 h.

Catalytic tests for the reductive amination of carbonyl compounds were operated in an 18 mL Teflon high-pressure reactor covered by an external stainless steel cylinder with one gas injection port. The prepared catalyst (20 mg), substrate (0.5 mmol), and NH<sub>3</sub>/MeOH solution (Aldrich, 5 mL, 8 mmol NH<sub>3</sub>) were loaded into the reactor, and 4 MPa H<sub>2</sub> was then introduced. The reactor was set at 363 K under stirring. All products in the liquid phase were identified using GC (GC-17A), GC-MS (GCMS-QP2010 SE) and NMR. Chlorobenzene was utilized as an internal standard for calculation of the product yields.

### 3. Results and discussion

The support effects in the supported ruthenium catalysts was examined on reductive amination of furfural (**1**) with  $\text{NH}_3$  and  $\text{H}_2$  (Table 1). Among the catalyst tested,  $\text{Ru}/\text{Nb}_2\text{O}_5$  exhibited the highest catalytic activity to give furfuryl amine (**2**) in 89% yield (entry 1). The reaction almost quantitatively proceeded when gaseous  $\text{NH}_3$  was used instead of a methanol solution (entry 2).  $\text{Ru}/\text{SiO}_2$  and  $\text{Ru}/\text{TiO}_2$  gave **2** in good to moderate yield with the formation of dimer imine and over-reduction products (entries 3 and 4). In the case of amphoteric and basic oxide supports ( $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ , and  $\text{MgO}$ ), trimer was mainly formed without the production of **2** (entries 5-7). The present catalytic system was applicable to the various aldehydes and ketones, and had high functional group tolerance including halogen and heteroaromatics.

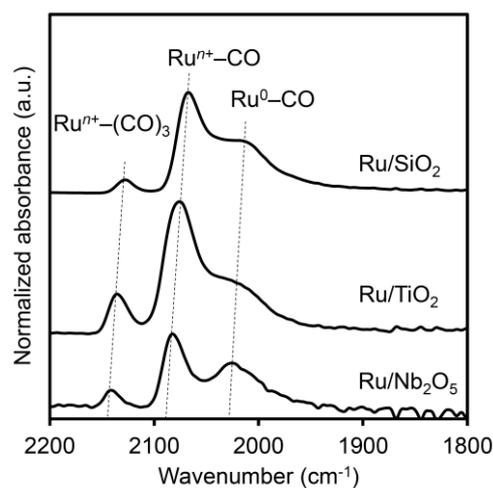
Time course studies using some effective catalysts revealed that **2** was gradually decreased with reaction progress except for  $\text{Ru}/\text{Nb}_2\text{O}_5$ . To disclose the high selectivity of the present catalytic system, the electronic state of Ru nanoparticles on  $\text{Nb}_2\text{O}_5$ ,  $\text{TiO}_2$  and  $\text{SiO}_2$  was investigated using CO-adsorbed Fourier transform infrared spectroscopy measurements. Figure 1 shows FT-IR spectra of CO-adsorbed  $\text{Ru}/\text{Nb}_2\text{O}_5$ ,  $\text{Ru}/\text{TiO}_2$ , and  $\text{Ru}/\text{SiO}_2$ . The bands assignable to the stretching vibration of linearly adsorbed CO on  $\text{Ru}/\text{Nb}_2\text{O}_5$  and  $\text{Ru}/\text{TiO}_2$  are blue-shifted compared with that on  $\text{Ru}/\text{SiO}_2$ , indicating that Ru on  $\text{Nb}_2\text{O}_5$  and  $\text{TiO}_2$  has weaker electron-donating capacity than Ru particles on  $\text{SiO}_2$ . Such a blue shift of the CO stretching vibration was observed by doping early transition metal to Pt catalyst and Mo-doping had positive effects to suppress the ring-hydrogenation of toluene.<sup>4</sup> Thus, the electronic state of  $\text{Ru}/\text{Nb}_2\text{O}_5$  probably affects the adsorption of furan rings and/or activity of adsorbed hydrogen atoms, which results in the highly selective reductive amination of **1** to **2**.

**Table 1.** Support Effects<sup>a</sup>

entry	catalyst	yield (%)	
		<b>2</b>	others
1	$\text{Ru}/\text{Nb}_2\text{O}_5$	89	4
2 <sup>b</sup>	$\text{Ru}/\text{Nb}_2\text{O}_5$	99	1
3	$\text{Ru}/\text{SiO}_2$	84	8
4	$\text{Ru}/\text{TiO}_2$	72	14
5	$\text{Ru}/\text{Al}_2\text{O}_3$	< 1	31
6	$\text{Ru}/\text{ZrO}_2$	< 1	24
7	$\text{Ru}/\text{MgO}$	< 1	30

<sup>a</sup> Reaction conditions: catalyst (20 mg), **1** (0.5 mmol), MeOH (5 mL),  $\text{NH}_3$  (8 mmol),  $\text{H}_2$  (4 MPa), 90 °C, 4 h.

<sup>b</sup>  $\text{NH}_3$  (0.1 MPa)



**Figure 1** CO-adsorbed FT-IR spectra

### 4. Conclusions

$\text{Ru}/\text{Nb}_2\text{O}_5$  acted as a highly active and durable heterogeneous catalyst for the reductive amination of various carbonyl compounds containing reduction-sensitive functional groups to the corresponding primary amines. Low electron density in Ru on  $\text{Nb}_2\text{O}_5$  surfaces with positive charges largely contributes to the selective catalysts.

### References

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