

論文 / 著書情報  
Article / Book Information

題目(和文)	
Title(English)	Study on Reductive Amination of Carbonyl Compounds over Supported Transition Metal Catalysts
著者(和文)	DengDian
Author(English)	Dian Deng
出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第11456号, 授与年月日:2020年3月26日, 学位の種別:課程博士, 審査員:原 亨和,鎌田 慶吾,北野 政明,野村 淳子,本倉 健
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第11456号, Conferred date:2020/3/26, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	要約
Type(English)	Outline

## Thesis Outline

Primary amines are indispensable parts of modern life due to their wide application in the pharmaceutical, agrochemical and fine chemical industries. One of the most useful tools for synthesis of these versatile compounds is the direct amination of abundant carbonyl compounds with ammonia (reductive amination). Although reductive amination reactions are widely utilized, achieving high levels of reactivity while maintaining excellent chemoselectivity and functional group compatibility under mild reaction conditions remains a challenging task.

The overarching aim of the current thesis focused on the development of highly efficient and selective supported transition metal catalysts to ensure amination proceed under mild conditions.

A further objective of this research was to study the effect of choice of metal oxide support on the performance of transition metal-based catalysts. Based on catalyst performance and catalyst characterization results, insights are gained into the structure-performance relationships governing the reaction, knowledge that can aid the further development of more superior catalysts for reductive amination.

Two catalytic systems have been developed during my PhD studies and investigated in detail.

They shared the same focal point, namely supported transition metal catalyzed reductive amination for forming primary amino groups, as indicated by the title.

A general introduction covering the importance of primary amines, along with a detailed summary of important amination methods. For primary amine synthesis, a more detailed overview of transition metal based catalytic systems for reductive amination with ammonia is described in Chapter 1.

It has been demonstrated in previous work that Ru nanoparticles supported acidic  $\text{Nb}_2\text{O}_5$  support resulted in excellent performance with respect to both the activity and selectivity toward primary amine. In order to investigate the influence of support acid sites on reductive amination, in Chapter 1, a series of  $\text{Ru}/\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  catalysts were prepared at different reduction temperatures for the reductive amination of furfural with ammonia, were investigated via various characterizations.

The temperature used for reduction of the catalyst had a significant influence on the low-temperature reductive amination over Ru-deposited  $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ . From the characterization results, it can be concluded that the catalyst prepared at a reduction temperature of 300 °C had the maximum catalytic activity for reductive amination. The high performance of the catalyst can be attributed to a high density of acid sites. Investigation into individual reaction step also indicating that larger amount of acid sites favors the adsorption of imine and highly reactive primary imine would react on the catalytic surface to form the primary amine. In addition,  $\text{Ru}/\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ -300 exhibited high catalytic performance for the reductive amination of other carbonyl compounds.

In both academic laboratories and industrial applications, platinum-group metals (including Pt, Ru, Rh, Ir, and Pd) have typically been used for the catalytic reductive amination. However, the limited availability, high cost, and toxicity of these precious

metals demand their substitutes with abundant, inexpensive, and nontoxic metals.

In the following chapter I turned my interest towards the development of more abundant first-row transition metals catalyzed reductive amination under mild conditions. In this context, Co-based catalysts with different metal oxide supports were prepared by impregnation method and subsequently tested for the reductive amination of aldehyde in the presence of ammonia and hydrogen. For a model reaction with furfural, Co/SiO<sub>2</sub> catalyst showed the distinctive catalytic performance, entirely comparable to the reported noble metal catalyst. In contrast, other supports gave substantially less active or even inactive catalysts.

After optimization of the reaction conditions, furfural could be converted to the corresponding primary amine in the presence of the Co/SiO<sub>2</sub> catalyst under extremely mild conditions. The yield and chemo-selectivity under mild conditions are exceptional in comparison with previous cobalt catalysts and even noble-metal catalysts.

Summary of the main results, as well as with some perspectives on potential future research covered in this PhD thesis are presented in Chapter 4.