

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)	審査の要旨
Type(English)	Exam Summary

論文審査の要旨及び審査員

報告番号	甲第		号	学位申請者氏名		Deng Dian	
論文審査 審査員		氏名		職名		氏名	職名
	主査	原 亨和		教授	審査員	本倉 健	准教授
	審査員	鎌田 慶吾		准教授			
		野村 淳子		准教授			
北野 政明			准教授				

論文審査の要旨 (2000 字程度)

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 in the presence of molecular hydrogen (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. As such, 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. Such knowledge can aid the further development of more superior catalysts for reductive amination.

The thesis comprises four chapters: 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. Chapter 2 describes reductive amination over Ru/Nb₂O₅·nH₂O catalyst. It has been demonstrated in previous work that Ru nanoparticles supported acidic Nb₂O₅ 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, a series of Ru/Nb₂O₅·nH₂O 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 Nb₂O₅·nH₂O. 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, Ru/Nb₂O₅·nH₂O-300 exhibited high catalytic performance for the reductive amination of other carbonyl compounds. Chapter 3 reports the catalytic application of Co-based catalysts for reductive amination with ammonia. 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 this context, the author turned her interest towards the development of more abundant first-row transition metals catalyzed reductive amination under mild conditions. In the preliminary study, 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/SiO₂ catalyst showed the distinctive catalytic performance under extremely mild conditions, entirely comparable to the reported noble metal catalyst. The chemoselectivity of Co/SiO₂ are exceptional in comparison with previous cobalt catalysts and even noble-metal catalysts. In Chapter 4, a summary of the notable results and their significance are presented. A perspective on potential future research concludes this thesis.

To sum up, Deng Dian's PhD thesis contains original and valuable scientific results of supported transition metal catalyzed reductive amination for the synthesis of primary amines, which is an important contribution to catalyst development. The level of the results is highlighted by the fact that part of them was published in scientific journal. This thesis is certainly meet the requirements laid down for the degree of Ph.D. in engineering.

注意：「論文審査の要旨及び審査員」は、東工大リサーチリポジトリ(T2R2)にてインターネット公表されますので、公表可能な範囲の内容で作成してください。