論文 / 著書情報
Article / Book Information

題目(和文)	
Title(English)	Mesoporous Silica Supported Pd Complex with Designed Surface for Concerted Catalysis
著者(和文)	DINGSiming
Author(English)	Siming Ding
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12425号, 授与年月日:2023年3月26日, 学位の種別:課程博士, 審査員:冨田 育義,多湖 輝興,山中 一郎,横井 俊之,和田 裕之,本倉 健,眞中 雄一
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第12425号, Conferred date:2023/3/26, 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

Mesoporous Silica Supported Pd Complex with Designed Surface for Concerted Catalysis

DING Siming

Department of Chemical Science and Engineering

School of Materials and Chemical Technology

Tokyo Institute of Technology

In this dissertation, the thinking of surface design for immobilized heterogeneous catalyst was implemented for better activity and reaction conditions for allylation. Results revealed that the Tsuji-Trost allylation was enhanced by the precisely designed functionalized heterogeneous surface.

A brief review for the design of catalyst and the closely related reports were introduced in Chapter I. The design for catalytic reaction aimed a well-known synthetic strategy for the C-C bond formation, Tsuji-Trost allylation, which passed through a π-allylpalladium intermediate involved mechanism. Various immobilization method and supporting materials were concluded to tell the wide range of choice in heterogeneous catalysis. Catalyst design concept of this thesis was also demonstrated.

Chapter II focused on the protection of Pd complex in water by co-immobilizing organic group R on the surface of mesoporous silica. The designed catalysts were well studied their catalytic abilities with respect to their TON in versatile solvents and solvent free conditions. In aqueous environments, the Tsuji-Trost allylation reaction between ethyl acetoacetate and allyl methyl carbonate was successfully catalyzed by a Pd complex

surrounded by phenyl groups. Higher grafting amount of phenyl groups led to higher hydrophobicity, and meanwhile, higher catalytic reactivity. Moreover, the aqueous solution showed better reactivity than neat, which has higher concentration of substrates. Around 1300 TON of the Pd-based allylation were produced. With respect to the synthesized library, an improved catalytic performance was made possible by the support's 3.1 nm pore size and Pd/phenyl = 1/15 group. The robust catalyst can afford 5 times of reuse while maintaining the reactivity with the first cycle and caused only 0.4mol% of leached Pd. As a comparison, catalysts without phenyl co-immobilized dropped the reactivity after reuses. The grafting hydrophobic organic groups explored strategy of design for water endurable heterogeneous catalysts.

As a conclusion for this chapter, to create the heterogeneous aqueous transition metal catalysis, a number of Pd complex catalysts co-immobilized with organic R groups on MS supports were devised and created. The TON of the synthesized catalysts was studied in a variety of solvents and solvent-free environments. The Tsuji-Trost allylation reaction involving ethyl acetoacetate and allyl methyl carbonate in aqueous medium was catalyzed by a Pd complex that was surrounded by phenyl groups grafted onto MS almost quantitatively. Higher grafting amount of phenyl groups led to higher hydrophobicity, and meanwhile, higher catalytic reactivity. Moreover, the aqueous solution showed better reactivity than neat, which has higher concentration of substrates. Around 1300 TON of the Pd-based allylation were produced. In comparison to the synthesized library, the MS(C18) supported catalyst had increased catalytic performance thanks to its 3.1 nm pore size and Pd/phenyl group. The robust catalyst can afford 5 times of reuse while maintaining the reactivity with the first cycle and caused only 0.4mol% of leached Pd. As a comparison, catalysts without phenyl co-immobilized dropped the reactivity after reuses.

The grafting hydrophobic organic groups exploited strategy of design for water endurable heterogeneous catalysts.

Chapter III gave an improving method of activity for the Tsuji-Trost allylation with unactivated allylic alcohol and its derivatives. Al-doped mesoporous silica supported Pd complex, MS-Al/PP-Pd, afforded high yield for the allylation with allylic alcohol under neat conditions. The reaction was studied concerted effect mechanism including the activation of allylic alcohol by forming hydrogen bonds with silanol groups on the supporting materials and Lewis acid also helped the activation. Increasing the surface acidity of supporting mesoporous silica raised the reactivity, and substituted derivatives raised greater. FT-IR analysis of pyridine adsorbed catalysts revealed that the Pd complex immobilized on the Brönsted acid site, which is close to the surface Lewis acidic Al site. This Pd complex-Lewis acid combination should accelerate the concerted activation of allylic alcohols. The novelty focused on the concerted catalysis on surface. The work contributes to not only highly efficient organic synthesis but also precise design of multifunctional solid surface. Moreover, SBA-15 was found a supporting material with higher performance in this catalysis system. A version with higher Lewis acidity was observed in a Zr dopant. A wide sight of view in designing the catalyst is exploited and expected expanding to other well-applied reactions.

In this chapter, a series of Pd complex catalysts supported by aluminium doped mesoporous silica, MS-Al/PP-Pd were synthesized and characterized. The immobilized catalysts were examined their catalytic activation toward the Tsuji-Trost type allylation of 2-phenylpropionaldehyde and achieved a yield up to 92% with allylic alcohol, the most efficient and green leaving group under neat condition. A coordinated effect, involving the activation of allylic alcohol through the formation of hydrogen bonds with silanol

groups on the supporting materials and the assistance of Lewis acid, catalyzed the reaction. Increasing the surface acidity of supporting mesoporous silica raised the reactivity. Compared with normal allylic alcohol, substituted allylic alcohols can be activated by surface acid sites to a greater extent. FT-IR analysis of pyridine adsorbed catalysts revealed the immobilization of Pd complex on the Brönsted acid site, resulting the presence of Pd complex close to the surface Lewis acidic Al site. This Pd complex-Lewis acid combination should accelerate the concerted activation of allylic alcohols. The novelty focused on the concerted catalysis on surface. The work contributes to not only highly efficient organic synthesis but also precise design of multifunctional solid surface. To our study, SBA-15, which showed higher reactivity in this catalysis system, was tried with higher Lewis acidity by a zirconia dopant. A wide sight of view in designing the catalyst is exploited and expected expanding to other well-applied reactions.

Chapter IV cut into a unique factor of reactivity for the supported heterogeneous concerted catalysis, the distance between active sites, metal complex and surface acid sites. A model compound [Pt(2-aminopyridine)(2-phenylpyridine)Cl] was prepared and characterized its structure by ^{1}H NMR and single-crystal XRD, which is similar to its analogue with Bpin attached for immobilization. The design is believed to afford us a series of catalysts with different distance between concerted activation sites and the inspiration for the design of heterogeneous catalyst with much higher reactivity.

In this chapter, a design route for concerted heterogeneous catalysts with fixed distance, which is an important factor for catalytic activity, between active metal center and surface acidic sites was introduced. Prior to the synthesis, a model compound **[Pt(2apy)]** was achieved and studied its structure by ^{1}H NMR and single-crystal XRD. The simple mix of **[Pt(2apy)]** with MS(C12)-Al-15 showed the ability to form hydrogen

bonding N---H-O between bridging ligand 2-aminopyridine and surface silanol groups or acidic sites. The Bpin attached analogue was also synthesized and characterized. Although the final product was not achieved, we are reasonable to believe that the following steps can afford us the many desired catalysts for this type.

Chapter V gave the brief conclusion for the development and future sight of view. Different from the homogeneous metal complex catalysts, which made great efforts on tuning their ligands, prospective for future of heterogeneous material supported metal complex catalysts is more spacious by the simple co-immobilization of functional groups or the works on supporting materials. Especially for the expensive Pd complexes, these strategies are very useful for balancing the high reactivity and wide usage of Pd complex with cheap and easy work-up costs, which is expected to be useful for industrial application in the near future.