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論文名	「Investigations on Heterogeneous Catalysis of Mesoporous Materials Decorated with Organometallic Complexes and Metal Nanoparticles (有機金属錯体および金属ナノ粒子で修飾したメソ多孔性材料の不均一系触媒作用に関する研究)」
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論文要旨

Nowadays, catalysts play an important role not only in the development of synthetic processes for chemical reagents but also in the establishment of sustainable chemical processes which contribute to save energy consumption and reduce the undesirable by-product formation. Metal nanoparticles (NPs) and organometallic complexes are known to show efficient catalytic activities in numerous organic and pharmaceutical chemical syntheses. Most of them have been used as homogeneous catalysts, which possess well-defined active sites for promoting reactions effectively, while their recyclability is limited by difficulties in the handling of the spent catalysts. In this line, heterogeneous catalysts, which can be easily separated from reaction mixture and reused, have emerged as key materials in modern chemistry to realize green processes. Since one of the most important goals in this area is to develop heterogeneous catalysts having well-defined active sites in analogy with homogeneous catalysts, so far many researches have been devoted to the immobilization of homogeneous catalysts onto various kinds of solid

supports such as mixed metal oxides, zeolites and mesoporous materials.

This thesis concerns the development of effective heterogeneous catalysts that are composed of mesoporous materials decorated with organometallic complex or metal NPs. Mesoporous materials are one of the most promising support materials to immobilize catalytically active species owing to their highly-ordered porous structures and large specific surface areas. These structural properties facilitate the uniform immobilization of such active species while keeping their original characteristics and also provide enhanced catalytic activity by increasing the local concentration of reaction substrates around the catalytically active sites. Post-synthetic modifications are promising methods which enable the unique catalyst design combining modified mesoporous materials and immobilized active species. In this sense, organometallic complex and metal NPs were immobilized within mesoporous materials and applied to heterogeneous catalysts for various useful organic synthesis reactions.

Chapter 1 summarized the research background of the present study, which also consists of purpose of the research work and the outline of this study.

In Chapter 2, a cyclopentadienyl ruthenium(II) complex (CpRuBz: Cp = cyclopentadienyl and Bz = benzene) was immobilized on MCM-41 modified with aminopropyl groups through an amide bond formation reaction ([MCM-41-NHCOCpRuBz]PF₆). FT-IR, UV-vis, and XAFS measurements showed successful immobilization of the cyclopentadienyl ruthenium complex onto the mesoporous silica surface by utilizing the amino group as a connector. The hydrosilylation of 1-hexyne with triethylsilane in acetonitrile proceeded efficiently on [MCM-41-NHCOCpRuBz]PF₆ under UV-light irradiation at room temperature with high α -selectivity ($\alpha/\beta = 9/1$). It was found that the reaction proceeds through in-situ

generation of the corresponding acetonitrile complex, $[\text{MCM-41-NHCOCpRu}(\text{CH}_3\text{CN})_3]\text{PF}_6$, as catalytically active species via ligand exchange reaction. Besides, the catalyst was able to be reused for the hydrosilylation reaction, showing its effectiveness as a recyclable heterogeneous catalyst.

Chapter 3 deals with the construction of an organoruthenium complex catalyst within a carbon-coated mesoporous silica (C-MCM-41) and its application to a heterogeneous catalyst for hydrosilylation reaction. C-MCM-41 was synthesized by carbonization of 2,3-dihydroxynaphthalene adsorbed on the surface of mesoporous silica, then the ligand exchange reaction between $[(\text{CH}_3\text{CN})_3\text{RuCp}]\text{PF}_6$ and six-membered carbon ring at the surface of C-MCM-41 as a framework ligand was carried out to yield $[\text{C-MCM-41-RuCp}]\text{PF}_6$. XAFS study demonstrated that the structure of the constructed ruthenium complex is closely similar to that of a molecular $[\text{BzRuCp}]\text{PF}_6$ complex. $[\text{C-MCM-41-RuCp}]\text{PF}_6$ was found to act as a heterogeneous ruthenium complex catalyst and promoted hydrosilylation of 1-hexyne by triethylsilane at 473 K to give α -vinylsilane as a major product.

In Chapter 4, a periodic mesoporous ethylenesilica (PME)-based heterogeneous catalyst containing PdNPs and alkyl phosphine groups (Pd@PME-PPh_2) was developed for Tsuji-Trost reaction without using any external additives, such as base and ligands. XPS measurements revealed the successful introduction of alkyl phosphine groups to bridging ethylene moieties of PME through bromination and following nucleophilic substitution with KPh_2 . Moreover, it was found from TEM observations that the immobilized PdNPs are uniform in size and exist in a highly dispersed state. The results of catalytic tests showed that Pd@PME-PPh_2 is an effective catalyst for the Tsuji-Trost reaction and can produce allylation

product in a high yield. The comparison of catalytic performance of Pd@PME-PPh₂ with PME-PPh₂ and Pd-loaded PME suggested that both PdNPs and alkyl phosphine groups are indispensable for the promotion of the reaction. Additionally, the Pd@PME-PPh₂ catalyst was able to be reused at least three times without significant loss of catalytic activity.

Chapter 5 described the development of a bifunctional catalyst comprising Au-loaded PME modified with ethylenediamine (Au/PME-ED) and its application for a one-pot tandem reaction. The successful introduction of diamine moieties to bridging ethylene moieties of PME by epoxidation reaction and following nucleophilic addition was confirmed by FT-IR measurements. Besides, a strong band assigned to C=O derived from polyvinylpyrrolidone covering Au NPs was able to be observed after Au NPs loading. Knoevenagel condensation reaction between benzaldehyde and various active methylene compounds to assess base properties of PME-ED demonstrated that a proton can be abstracted from diethyl malonate (pKa: 16.4) but not be abstracted from benzyl cyanide (pKa: 21.9) on PME-ED. Moreover, Au/PME-ED was found to promote a one-pot tandem reaction consisting of alcohol oxidation and Knoevenagel condensation, suggesting its bifunctional catalysis associated with Au NPs and diamine moieties.

Finally, the results and conclusions of the core topics of chapter 2 to 5 were summarized in the final chapter 6. This chapter also presented several topics for further studies.

審査結果の要旨

本論文は、メソ多孔性担体上に有機金属錯体および金属ナノ粒子を固定化した新規不均一系触媒の調製法の開拓と、その上で誘起される高選択的な触媒反応の探索を行うとともに、触媒

活性点構造および反応機構の詳細を各種分光法により解明することを目的として行った研究をまとめたものであり、次のような成果を得ている。

- (1) アミノ基修飾したメソポーラスシリカ上にアミド結合を介して有機ルテニウム錯体 $((\text{CH}_3\text{CN})_3\text{Ru}+\text{Cp})$ を固定化することに成功した。また、同錯体が固液系における不均一系触媒の活性種として作用し 1-ヘキシンのヒドロシリル化反応を促進するとともに、生成物として α -ビニルシランを選択的に与えることを明らかにした。
- (2) 有機化合物の炭化反応により表面をカーボン被覆したメソポーラスシリカ上に、配位子交換反応を用いてシクロペンタジエニルルテニウム錯体を安定に固定化することに成功した。本触媒は 473 K において固気相系での 1-ヘキシンのヒドロシリル化反応を促進し、 α -ビニルシランを選択的に与えることを明らかにした。
- (3) アルキルホスフィンで修飾したメソポーラス有機シリカ中に固定化した Pd ナノ粒子が外部からの塩基や配位子の添加なしに Tsuji-Trost 反応を触媒することを見出した。本触媒系は複数種の求核試薬に対しても適用可能であり、優れた触媒再利用性を示すことを明らかにした。
- (4) 架橋エチレン部位をエチレンジアミンで修飾したメソポーラス有機シリカが固体塩基触媒として Knoevenagel 縮合反応を促進することを見出した。さらに、同固体塩基触媒に Au ナノ粒子を担持することで、アルコール酸化反応と Knoevenael 縮合反応を逐次的に行う One-pot 反応を進行させることが可能な二元機能触媒の開発に成功した。

以上の成果は、メソ多孔体を担体とする新規な不均一系触媒の創製、およびその高選択的な触媒反応への応用とその作用機構の解明に貢献すること大である。また、申請者が自立して研究活動を行うに十分な能力と学識を有することを証したものである。