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学位論文内容の要旨

博士 (環境科学)

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学位論文題名

Precise control of the environment around active sites toward efficient cooperative catalysis
(効率的に協奏触媒作用を引き出すための活性サイト周辺環境の精密制御)

The marked development of chemical industry has greatly improved our quality of life, but at the same time caused various environmental issues. Since catalysis is useful chemical phenomenon to increase productivity of chemical processes and reduce waste generation, catalytic science has been steadily grown with the development of the chemical industry, and various concepts have been proposed to develop highly active, selective, and durable catalysts. A concept is “bifunctional catalyst”, which is the catalyst having more than two functional groups with different properties. In the bifunctional catalysts, the functional groups cooperatively work as a catalyst, which is called “cooperative catalysis”. By this, the bifunctional catalysts show unexpectedly high catalytic performances comparing to those with single functional group and can proceed difficult and unattainable reactions. A pair of acid and base is the most common functional groups in the cooperative catalysis, which has been widely used to develop acid-base bifunctional catalysts. However, precise and rational design of the acid-base pair sites on heterogeneous catalysts was still not achieved.

The catalytic performance is primarily determined by the properties of active center itself. Thus far, catalysis over the acid-base bifunctional catalysts has been understood basically in terms of three fundamental properties, including types, strengths, and amounts of acid and base sites. Recently, control of the environment around the active sites has been investigated for the acid-base bifunctional catalysts, for which active functional groups including sulfo, carboxyl, and amino groups are grafted on siliceous materials. The control of the environment around the active functional group would be considered as an additional property important for the design and development of the acid-base bifunctional catalysts. Thus, this thesis aimed to develop a robust approach for precise control of the environment around active sites to achieve high catalytic performance in heterogeneous catalysis. The background, motivation, and objectives of this thesis mentioned above are described in Chapter 1.

Chapter 2 describes a novel method to definitely create adjacent acid-base pair sites on SiO₂ through hydrolysis of secondary amide grafted in advance on SiO₂. This method enables to create the pair sites with close proximity between acid and base sites, which are carboxyl and amino groups, respectively, by hydrolysis of amide. This method is further applicable to create acid-base pair sites with precisely controlled distance by hydrolysis of amide having appropriate linker moiety.

In Chapter 3, it was demonstrated that the distance between carboxyl and amino groups on SiO₂ had a significant effect on the catalytic performance. The catalyst with the adjacent carboxyl and amino groups showed

excellent catalytic performance for aldol condensation of 4-nitrobenzaldehyde with acetone, overwhelming the catalyst having only amino group and an acid-base catalyst prepared in a conventional manner. This cooperative effect was strongly dependent on the distance between amino and carboxyl groups.

Chapter 4 describes octyl and propylsulfonic acid co-fixed $\text{Fe}_3\text{O}_4@\text{SiO}_2$ as a magnetically separable and highly active solid acid catalyst for hydrolysis of ethyl acetate in water. The catalyst showed activity twice as high as that of the catalyst without octyl modification. In addition to the high catalytic activity, the modification with octyl groups improved the catalyst stability over repeated use in hydrolysis of ethyl acetate in water. High hydrophobicity over the surface and around the acid sites by the octyl group was responsible for the high catalytic activity and high stability in water.

In Chapter 5, the findings of each chapter are summarized, and general conclusions and future considerations are described.

Based on the results throughout the thesis, it can be concluded that the control of the environment around active sites is an effective approach to significantly improve the catalytic performance of heterogeneous catalysts owing to cooperative action between the active site and functional group located close to it. In addition, the approach developed in this thesis is considered to give a robust solution for precise control of the environment around active sites toward efficient cooperative catalysis. The next challenge in this approach is certainly to derive the cooperative effect of multiple functional groups on the surface, which would result in more uniform pairings and spacing of them. Due to their limitless application and design, the control of the environment around active sites will continue to be a topic of much research for years to come.