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Title	Heterogeneous Catalysis for the Synthesis of Chemicals using Dehydrogenation/Hydrogenation Properties of Metal Nanoparticles and Hydrophobicity of Acidic Zeolites [an abstract of dissertation and a summary of dissertation review]
Author(s)	Poly, Sharmin Sultana
Degree Grantor	北海道大学
Degree Name	博士(工学)
Dissertation Number	甲第13813号
Issue Date	2019-09-25
Doc URL	<a href="https://hdl.handle.net/2115/75938">https://hdl.handle.net/2115/75938</a>
Rights(URL)	<a href="https://creativecommons.org/licenses/by/4.0/">https://creativecommons.org/licenses/by/4.0/</a>
Type	doctoral thesis
File Information	Sharmin_Sultana_Poly_review.pdf, 審査の要旨



# 学 位 論 文 審 査 の 要 旨

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## 学 位 論 文 題 名

Heterogeneous Catalysis for the Synthesis of Chemicals using  
Dehydrogenation/Hydrogenation Properties of Metal Nanoparticles and Hydrophobicity of  
Acidic Zeolites  
(金属ナノ粒子の脱水素化/水素化特性と酸性ゼオライトの疎水性を利用した化学品合成のための不均  
一触媒作用)

Acceptorless dehydrogenative coupling (ADC) reactions by homogeneous catalysts have been recently developed as clean synthetic methods of various classes of organic compounds from alcohols. Development of heterogeneous catalysts for ADC is a key to overcome the critical issues of this method, including difficulties in product/catalyst separation and catalyst reuse. Development of Bronsted acid catalysts for transformations of hydrophobic substrates in a polar environment is another important target in modern synthetic catalysis. The thesis will show two classes of heterogeneous catalysts for these two issues: supported Pt nanoparticles (NPs) for ADC reactions (Chapters 2,3) and high-silica beta zeolites for hydration of epoxides and alkynes in water and acetalization of glycerol to acetal (Chapters 4,5) in a batch reactor. Combining these methods, a new catalytic method for methylation of xylenes with CO<sub>2</sub>/H<sub>2</sub> is developed (Chapters 6). Studies on structure-activity relationship and reaction mechanism are also described in order to propose design concept of effective heterogeneous catalysis for clean organic synthesis.

Chapter 2 demonstrates the first example of the heterogeneous catalysis for the synthesis of 2,4,6-trisubstituted pyrimidines by ADC reaction of secondary and primary alcohols and amidines using a carbon-supported Pt catalyst (Pt/C) with KOtBu. Pt/C showed higher yield than Pt-loaded metal oxides ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>, MgO, zeolite, Nb<sub>2</sub>O<sub>5</sub>. Pt/C promotes a higher yielding reaction than do other transition metal NPs supported on carbon (Ir/C, Ni/C, Pd/C, Rh/C, Ru/C, Re/C, Cu/C, and Ag/C). The reaction takes place efficiently for a wide range of substrates (32 examples). The Pt/C catalyst that promotes this process is reusable and has a higher turnover number (TON) than previously methods using homogeneous catalysts. The results of mechanistic studies suggest that the process takes place through a pathway that begins with Pt-catalyzed acceptorless dehydrogenation of the alcohol, which is followed by sequential condensation, cyclization, and dehydrogenation. Measurements of the turnover frequency (TOF) combined with the results of density functional theory calculations on different metal surfaces suggest that the adsorption energy of H on the Pt surface is optimal for the acceptorless dehydrogenation process, which causes the higher catalytic activity of Pt over those of other metals.

Chapter 3 shows the first heterogeneous catalytic method for the synthesis of pyridine derivatives by ADC reaction of amino alcohols and secondary alcohols using the Pt/C catalyst. The reaction involves nucleophilic attack by the amine group of a  $\alpha$ -amino alcohol molecule on the ketone can produce an imine intermediate, followed by dehydrogenation of the resulting imine-alcohol intermediate and C-C bond formation by condensation under basic reaction

conditions, eventually leading to a dihydropyridine derivative which is further dehydrogenated to the desired pyridine.

Chapter 4 is the catalytic study for the hydration of hydrophobic epoxides and alkynes in water using proton-exchanged \*BEA zeolite (Hbeta). Among 24 types of heterogeneous and homogeneous catalysts tested, Hbeta zeolite with a relatively high Si/Al ratio (Si/Al = 75), Hbeta-75, is an effective catalyst for both of the reactions in water. Hbeta-75 showed wide substrate scope, good reusability, and applicability in gram-scale synthesis for both types of reactions. The effects of hydrophobicity, acidity, and the size of zeolite pores were also comprehensively studied through the hydration of hydrophilic and hydrophobic epoxides and alkynes with different molecular sizes using two types of zeolite (Hbeta and HZSM5). Hydrophobicity and acidity of different zeolites were studied by various characterization methods, including TPD, adsorption experiments in water, and IR spectroscopy. It is concluded that the high catalytic activity of Hbeta-75 are attributed to the three important factors: 1) hydrophobic interaction between zeolite pores with the substrates; 2) large pore size; 3) Brønsted acidity. The larger pore size of Hbeta-75 compared to HZSM5-75 played an important role in achieving high yields. The higher Si/Al ratio results in the higher TOF, which is caused by larger adsorption capacity of hydrophobic substrate in water.

Chapter 5 shows that Hbeta-75 is effective for the acetalization of glycerol with carbonyl compounds. This catalyst system was amenable to a wide substrate scope and exhibited good reusability. The TOF, based on Bronsted acid site concentration, increased as a function of Si/Al ratio, monotonically increases with increasing Si/Al ratio, which is similar to the dependency of hydrophobicity on the Si/Al ratio. The results indicate that hydrophobic nature of the Hbeta catalysts accelerate the acetalization reaction. On the hydrophobic inner pore surface, the generated H<sub>2</sub>O molecule, as a co-product, easily desorbs, thus accelerating the acetalization reaction. The results in Chapters 4,5 show that Hbeta-75, having the Bronsted acid sites at the hydrophobic inner surface of large pore zeolite, is general and versatile catalyst for organic reactions in water or in the presence of water as a byproduct.

Chapter 6 shows development of new catalytic reaction, methylation of xylenes with CO<sub>2</sub>/H<sub>2</sub>, by combining the two catalytic materials studied in this thesis: supported metal nanoparticles and hydrophobic zeolites. Screening study showed that TiO<sub>2</sub>-supported Re (Re/TiO<sub>2</sub>) with Hbeta-20 (Si/Al=20) is the best combination for achieving high activity for this reaction. Under the optimized reaction conditions (PCO<sub>2</sub> = 1 MPa; PH<sub>2</sub> = 5 MPa; T = 513 K), this catalytic system achieved high performance for the synthesis of polymethyl benzenes with high yield. Re metal NPs catalyze a hydrogenation step, while the Hbeta-20 zeolite catalyzes alkylation step.

Chapter 7 is the general summary. Chapters 2,3 show the first examples of heterogeneous catalysis for the synthesis of heterocycles via ADC reactions of alcohols based on dehydrogenation-condensation and cyclization-dehydrogenation steps with elimination of water and liberation of H<sub>2</sub> as byproduct. Pt metal NPs play an important role in the dehydrogenation step. Chapters 4,5 conclude that Hbeta-75, having the Brønsted acid sites at the hydrophobic inner surface of large pore zeolite, is general and versatile catalyst for organic reactions in water or in the presence of water as a byproduct. Chapter 6 shows development of a new catalytic reaction for methylation of xylenes with CO<sub>2</sub>/H<sub>2</sub> combination of metal NPs catalysts and acidic zeolites. The developed catalyst (Re/TiO<sub>2</sub> with Hbeta-20) gave polymethyl benzenes in high yield. Re metal NPs catalyze the hydrogenation step, while the Hbeta-20 zeolite catalyzes alkylation step. These three types of heterogeneous catalytic methods will be useful in sustainable synthesis of chemicals. Conceptual conclusions from structure-activity relationship and mechanistic studies will be useful for designing more effective heterogeneous catalysts.

Considering these research achievements, we conclude that the author is eligible to have a Doctor degree of engineering.