



Title	Highly Efficient Ni-Based Catalysts as Noble-Metal-Alternative for (De)Hydrogenation Reactions [an abstract of dissertation and a summary of dissertation review]
Author(s)	Simanullang, Wiyanti Fransisca
Degree Grantor	北海道大学
Degree Name	博士(工学)
Dissertation Number	甲第14470号
Issue Date	2021-03-25
Doc URL	https://hdl.handle.net/2115/81300
Rights(URL)	https://creativecommons.org/licenses/by/4.0/
Type	doctoral thesis
File Information	Wiyanti_Fransisca_Simanullang_abstract.pdf, 論文内容の要旨



学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称 博士（工学） 氏名 ウィヤンティ フランシスカ シマヌラン

学 位 論 文 題 名

Highly efficient Ni-based catalysts as noble-metal-alternative for (de)hydrogenation reactions

水素化脱水素に有効な貴金属代替Ni触媒の開発

The use of noble metal i.e., Pd, Pt, Au etc, catalysts has been well-researched in various chemical reactions and industry. However, the cost of the catalyst is incredibly expensive. In order to develop cost effective production, non-noble metal catalysts should be applied. This thesis focused on the development of novel catalyst design concept for Ni-based noble-metal-alternative materials for efficient hydrogenation and dehydrogenation of hydrocarbons, where alloying of and/or chemical modification to Ni were applied. (1) First, Ni was alloyed with Si to form intermetallic Ni_3Si phase, which exhibited higher catalytic activity than pure Ni in hydrogenation of unsaturated hydrocarbons such as acetylene, ethylene, benzene, and toluene. (2) Second, the surface of intermetallic NiSi_2 powder was dealloyed by the treatment with a diluted aqueous solution of hydrofluoric acid. The resulting materials had a very unique surface structure, where small Ni clusters embedded in SiO_2 matrix were formed on the bulk NiSi_2 structure. This material showed very high catalytic activity in hydrogenation of unsaturated hydrocarbons, where 20-times higher activity than pure Ni or even greater activity than Pd was obtained in benzene hydrogenation. (3) Third, the unique system of Ni modified with SiO_2 was expanded to supported Ni nanoparticles. A conventional Ni/ SiO_2 catalyst was impregnated by ethanol solution of tetraethoxysilane ($\text{Si}(\text{OEt})_4$), followed by calcination and reduction, which gave SiO_x -decorated Ni nanoparticles on SiO_2 support. The silica-decoration changed the morphology of Ni nanoparticles from spherical to rough and step-abundant; therefore, the number of highly active step sites and the resulting catalytic activity significantly increased. The optimized Si-Ni/ SiO_2 catalyst exhibited 50 and 17 times higher TOF than Ni/ SiO_2 in methylcyclohexane dehydrogenation and toluene hydrogenation, respectively, thus achieving a highly active noble-metal-alternative catalyst for (de)hydrogenation. This result also provides the answer why the activity was enhanced by the hydrofluoric acid treatment to bulk NiSi_2 : similarly, step-abundant Ni nanoclusters were likely to be formed by surrounding the silica matrix. (4) Finally, the silica-modification methodology was applied also for NiZn alloy system for acetylene semihydrogenation, in which the concert of silica-modification effect (activity enhancement) and alloying effect (selectivity enhancement) was expected. The silica-modified NiZn catalyst, Si-NiZn/ SiO_2 , showed high ethylene selectivity (ca. 90%) at high acetylene conversion (95%), whereas unmodified NiZn/ SiO_2 gave low acetylene conversion (40%) with similar selectivity, demonstrating that the silica-modification methodology is compatible with the catalyst modification by alloying. In summary, this thesis discovered a novel catalyst design concept with silica-modification, which allows to develop a new class of noble-metal-alternative catalyst using base metals.