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学 位 論 文 審 査 の 要 旨

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学 位 論 文 題 名

Phase-Separation Aided Heterogeneous Catalysis for Selective Hydrogenation of Nitriles to Primary Amine and Its Derivatives
（ニトリル類の一級アミンおよびその誘導体への選択的水素化のための相分離型不均一系触媒作用）

Selectivity control is one of the most important goals in catalysis. For selective hydrogenation of nitriles as an example, selective production of primary amines is difficult, because high reactivity of primary amines results in their further reaction to secondary and tertially amines. The use of multiphase reaction media such as non-polar solvent /CO2/water can improve the selectivity if the products once formed are removed to the other phase containing no catalyst. CO2 dissolved in the aqueous phase can strongly interact with basic functional groups of substrates, intermediates, or products and then alter their reactivity or solvility in in the aqueous phase. The use of both CO2 and water can be also beneficial for the easy separation of products and catalysts and solvents in multiphase catalytic reactions. In addition to the physical (phase) separation shown above, we can control the selectivity by using chemical separation such as effective transformation of unstable intermediate (primary amine) by its reaction with another reagent. The present work demonstrates the usefulness of these two methodologies, (1) physical separation using n-hexane/CO2/water and (2) chemical separation using condensation of reactive intermediate (primary amine) with keto acids, in selective reductive transformation of nitriles by supported noble metal catalysts. First, I show that the concept (1) is effective for the Pd-catalyzed selective hydrogenation of nitriles to primary amines. I compare different multiphase systems such as (a) organic solvent, (b) organic solvent-CO2, (c) organic solvent-H2O and (d) organic solvent-CO2-H2O. Combined with in situ FTIR observation of the substrates (products) interacted with CO2 and water, I show a straregy for increasing the selectivity of primary amines. Next, I show the concept (2), chemical separation, for Pt-catalyzed selective synthesis of lactams by reductive conversion of keto acids with nitriles and H2.

Chapter 1 summarizes the research work included in Chapter 2-5 and introduces about the properties and usefulness of CO2 and water in multiphase reaction media. It presents general introduction on multiphase catalytic reaction media under pressurized CO2 and both pressurized CO2-water. Important literature references are discussed to generate an overview on the green components of CO2 and water in multiphase reaction media for various organic synthetic reactions using homogeneous and heterogeneous catalysts. The previous works offer attractive potentialities of multiphase reactions using dense phase CO2 and H2O. The CO2-H2O medium may improve the rate of reaction and/or the selectivity to the desired product. It would be interesting to carry out multiphase hydrogenation reactions of nitriles using organic solvent-water-CO2 medium.

In chapter 2, selective hydrogenation of benzyl cyanide (BC) to 2-phenylethylamine (PEA) was investigated with a commercial Pd/Al2O3 catalyst in different multiphase reaction media

including n-hexane, water and/or CO2. In neat n-hexane, the hydrogenation of BC occurred at a large rate but no PEA was formed and the secondary amine of N,N-bis(2-phenylethyl)amine (BPEA) was mainly produced. The pressurization of n-hexane with CO2 decreased the rate of hydrogenation and BPEA was still the main product. In this n-hexane – CO2 medium, the catalyst lost its activity during the reaction. When a similar volume of water was added to n-hexane, the rate of hydrogenation did not change so much but a small amount of the primary amine was detected to form in addition to the main product of BPEA. In contrast to these reaction media, a high PEA selectivity of > 90
In chapter 3, the applicability of the multiphase medium including CO2 and water was studied for the selective hydrogenation of various nitriles such as 2-phenylethyl cyanide (PEC), cinnamonitrile (CN), n-hexanenitrile (HN), and 4-cyanobiphenyl (CBP) with the same Pd/Al2O3 catalyst. The effectiveness of the multiphase reaction medium was different from one nitrile to another. The selective production of primary amine was achieved with PEC and HN, similar to BC, but not with the other nitriles. The rate of nitrile conversion in this multiphase medium is smaller than that in a neat organic solvent. This should result from the dilution of reacting species in the liquid phase by the dissolution of CO2, the change of reaction locus from the organic phase to the organic - aqueous interfacial layer, and the decreased reactivity of nitrile group via interactions with CO2 molecules.

In chapter 4, the usefulness of the multiphase reaction medium including both CO2 and water was further investigated with another commercial Pd/C catalyst different in the surface properties from Pd/Al2O3 using two substrates of BC and HN. In contrast to the results with the latter catalyst, no primary amines were formed with the former. That is, the coexistence of CO2 and water had no synergistic effects in the target selective hydrogenation with Pd/C. It was assumed that the difference in the product selectivity was ascribed to that in the hydrophilicity/hydrophobicity between the two Pd catalysts. Possible reasons were discussed to explain differences in the rate of reaction and catalyst deactivation between the two catalysts.

Chapter 5, shows the first general and reusable catalytic system for one-pot synthesis of lactams by reductive conversion of keto acids with nitriles and H2 using Pt-MoOx/TiO2 catalyst. High selectivity to lactams (low selectivity to side product, secondary amine) is due to removal of the primary amine by its fast reaction with keto acids.

Chapter 6 is a general summary. In conclusion, this work clarifies the usefulness of two concepts, (1) physical (phase) separation using n-hexane/CO2/water solvent and (2) chemical separation using condensation of reactive intermediate (primary amine) with keto acids, in selective reductive transformation of nitriles by supported noble metal catalysts.
Considering these research achievements, we conclude that the author is eligible to have a Doctor degree of engineering.