

# Recyclable Heterogeneous Catalyst

Lu Wang\*

Department of Sciences, Hokkaido University, China

## Introduction

Heterogeneous metal catalysts rather than homogeneous ones are recommended for industrial applications after considering their performance in activity, separation, and recycling [1]. The recycling of metal catalysts is important from economic and environmental points of view. When supported and bulk metal catalysts are used in liquid-phase organic reactions, there is a possibility that active metal species are leaching away into the liquid phases [2,3]. The metal leaching would make it difficult for the catalysts to maintain their desired initial performance for repeated batch reactions and during continuous ones. The metal leaching would also cause some undesired contamination of products by the metal species dissolved in the reaction mixture, and the separation of the metal contaminants would be required to purify the products. Therefore, various novel methods have been proposed so far to immobilize/stabilize the active metal species and to separate/collect/reuse the dissolved metal species [4]. In addition, knowledge on the heterogeneous and homogeneous natures of organic reactions using heterogeneous catalysts is important to discuss their reaction mechanisms and catalytically working active species.

This is interesting for original and review articles on such organic synthetic reactions as CO<sub>2</sub> conversion, biomass conversion, selective hydrogenation, C-C coupling, and reductive amination reactions. The design of magnetic catalysts is one of the most efficient strategies for the synthesis of durable and reusable catalysts, which can be easily recovered by magnetic forces and recycled. Reviews the design, preparation, recyclability of various nanostructured magnetic catalysts for, in particular, the reduction of nitro aromatic compounds. Promotional effect of SnO<sub>x</sub> on the catalytic performance of Ru/Al<sub>2</sub>O<sub>3</sub> catalysts in the selective hydrogenation of m-dinitrobenzene to m-nitroaniline [5]. They explain that electron transfer between active Ru species and SnO<sub>x</sub> additives modifies the adsorption of the nitro group of the substrate, influencing the product selectivity, and also improves the stability of the catalysts. Catalytic performance of phosphorus-doped Ni/Al<sub>2</sub>O<sub>3</sub> catalysts for the hydrogenolysis of a biomass-derived compound of glycerol. These are recyclable and selective catalysts for the production of 1, 2-propanediol. The relative amounts of Ni and NiO species, which depend on the presence of a phosphorous dopant, are significant in determining the catalytic performance; a slight loss in activity occurs due to the deposition of carbonaceous materials on the catalyst surface. Linear polystyrene-stabilized Pd nanoparticles are active and recyclable catalysts for a series of C-C coupling reactions in water. In these reactions, some Pd species leach and the dissolved Pd species are stabilized in the presence of tetrabutylammonium bromide and may participate in the catalytic processes [6]. These Pd species may redeposit onto the polystyrene support and are recyclable even though a slight increase in the size of supported Pd particles occurs during the reaction. Polymer supported triphenylphosphine-palladium acetate complex catalyst for the indirect reductive amination of aldehydes. The catalyst is highly selective to the formation of the desired

products and can be recovered and recycled without loss in the activity. Catalyst containing guanidine hydrochloride and ZnI<sub>2</sub> for the environmentally benign synthesis of cyclic carbonates under mild reaction conditions [7]. The catalyst gives a high yield of propylene carbonate and can be recycled, which is versatile for the cycloaddition of CO<sub>2</sub> to other epoxides.

Heterogeneous catalysis is widely used in the synthesis of bulk and fine chemicals. In a general, small scale batch reaction, the catalyst, reactants, and solvent are stirred together until completion of the reaction, after which the bulk liquid is separated by filtration. The catalyst can then be collected for either recycling or disposal [8]. In a continuous process, the catalyst can be fixed in space and the reaction mixture allowed to flow over it. The reaction and separation are thus combined in a single step, and the catalyst remains in the reactor for easy recycling. Beyond facilitating separation, the catalyst may have improved lifetime due to decreased exposure to the environment, and reaction rates and turnover numbers can be enhanced through the use of high concentrations of a catalyst with continuous recycling. The benefits of flow are seemingly obvious, yet it has only recently become a widely adopted method for bench-scale synthesis [9]. The most common application of continuous heterogeneous catalysis is in hydrogenation reactions,<sup>2</sup> where the handling and separation of solid precious metal catalysts is not only tedious but hazardous under batch conditions. Moreover, the mixing between the three phases in a hydrogenation is generally quite poor. The use of a flow reactor gives a higher interfacial area between phases and thus more efficient reactions. For example, Ley and co-workers found that the hydrogenation of alkene 1 to 2 was challenging in batch, requiring multiple days at 80 bar of H<sub>2</sub> (Scheme 1).<sup>3</sup> Using a commercially available H-Cube<sup>®</sup> reactor, the reaction time was shortened to 4 hours, the pressure reduced to 60 bar, and manual separation and recycling of the catalyst from the reaction was unnecessary. The increased efficiency is due to a combination of improved mixing of the three phases, as well as the continuous recycling and high local concentration of the catalyst. The H-Cube offers a further safety advantage because it generates hydrogen gas on demand from water, obviating the need for a high pressure H<sub>2</sub> tank [10].

## Acknowledgment

None

## Conflict of Interest

Author declares there is no conflict of interest

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\*Address for Correspondence: Lu Wang, Department of Sciences, Hokkaido University, China, Email: kevinlwang@nitech.edu.cn

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