The Second Green and Sustainable Chemistry Award Awarded by the Minister of Education, Culture, Sports, Science and Technology

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Highly Efficient Organic Syntheses Using Environmentally Benign Catalysts

To promote atom efficiency in synthesis and to avoid the generation of environmental waste, the use of stoichiometric amounts of condensing reagents or excess substrates should be avoided. In esterification, excess amounts of either carboxylic acids or alcohols are normally needed. Dr. Ishihara has found that hafnium(IV) or zirconium(IV) salts are highly effective as catalysts for the direct condensation of equimolar amounts of carboxylic acids and alcohols. This catalytic system can be applied to the direct polyesterification, the selective esterification of primary alcohols with carboxylic acids in the presence of secondary alcohols or aromatic alcohols, and may be suitable for large-scale operations.

On the basis of the same concept, he has found that 3,4,5-trifluorophenylboronic acid is a highly effective catalyst for the amide condensation of amines and carboxylic acids. Arylboronic acids bearing electron-withdrawing substituents at the aryl group behave as water-, acid-, and base-tolerant thermally stable Lewis acids, and can be easily handled in air. He has succeeded in applying this catalytic system to a direct thermal amide polycondensation to form not only aliphatic polyamides but also aromatic polyamides and polyimides. Furthermore, he has developed 3,5-bis (perfluorodecyl) phenylboronic acid which serves as a highly active and reusable catalyst by virtue of the electron-withdrawing effect and the immobility in the fluorous recyclable phase of the perfluorodecyl group. It is noteworthy that this fluorous catalyst is simply recovered by filtration without using any fluorous solvents. Simplification of product workup, separation, and isolation as well as reuse of solid catalysts can lead to an economical system. He has found that perrhenic acid is an extremely active catalyst for dehydration of not only primary amides but also aldoximes to the corresponding nitriles. The reaction proceeds under essentially neutral conditions, and the catalyst is recoverable and reusable. He has succeeded in preparing polystyrene-bound super Brønsted acid which is effectively swollen by both polar and nonpolar organic solvents, and its catalytic activity for various organic reactions is superior to that of Nafion®-H. The resin-bound catalyst can be repeatedly reused in a batch system, and have been applied to a flow reaction system to avoid physical degradation of the resin beads. In addition, they have developed a fluorous super Brønsted acid catalyst, 4-(1*H*,1*H*-perfluorotetradecan-oxy)-2,3,5,6-tetrafluorophenyl-bis(trifluoromethanesulfonyl)methane, which can be recycled by using liquid/solid phase separation without fluorous solvents.

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