

**【Grant-in-Aid for Scientific Research(S)】**  
**Science and Engineering (Chemistry)**



**Title of Project : The New World of Organic Chemistry Using Water as a Solvent**

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Research Area : Chemistry

Keyword : Organic reaction, water solvent

**【Purpose and Background of the Research】**

Current organic chemistry is based on the common sense that organic reactions are performed in organic solvents. Generally, organic compounds are soluble only in organic solvents and homogeneous reaction systems are thought to be essential for efficient reactions. As a result, various kinds of organic solvents have been developed. However, organic solvents are often harmful and in many cases, flammable. We have been investigating the use of water as a solvent for organic reactions. Water is a main component in human body, animals and plants. Furthermore, water is safe, nonflammable, and inexpensive; it is abundant in nature. Therefore, it is ideal if water can be used instead of organic solvents. We are planning to construct "New world of organic chemistry using water as a solvent".

**【Research Methods】**

Main topics are as follows:

1) Regioselective reactions in aqueous media

We have already found unique regioselectivity in allylation reactions in aqueous media using zinc or copper catalysts. The selectivities are apparently different from those in organic solvents. The reaction mechanism will be clarified and application to other reactions will be investigated.

2) Zero-valent metal catalysis in water

Recently we have found zero-valent indium metal accelerates allylation reactions in water. The effect of zero-valent metals in water is promising. In this project, we will investigate the effect of indium metal on other reactions and use of various zero-valent metals.

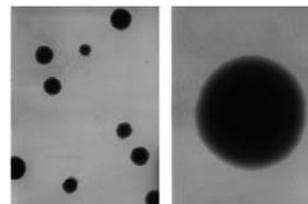
3) The use of water-soluble molecules

Very recently, we have developed selective primary amine synthesis from ammonia in aqueous media in the presence of palladium catalyst. The result is promising since selective reactions using small and water-soluble molecules such as ammonia are difficult. We will investigate selective organic reactions in aqueous media using such small and water-soluble molecules.

**【Expected Research Achievements and Scientific Significance】**

All these topics are based on our original findings concerning organic reactions in water. It is expected that new world of organic chemistry in water which is different from that in organic solvent system will be constructed. This will have a significant impact on whole organic chemistry.

**Figure:** reaction environments (colloidal particles) formed in water (TEM analysis)



**【Publications Relevant to the Project】**

- Zn-Catalyzed Asymmetric Allylation for the Synthesis of Optically Active Allylglycine Derivatives. Regio- and Stereoselective Formal  $\alpha$ -Addition of Allylboronates to Hydrazono Esters, M. Fujita, T. Nagano, U. Schneider, T. Hamada, C. Ogawa, S. Kobayashi, *J. Am. Chem. Soc.*, **130**, 2914-2915 (2008).
- Lewis Acid Catalysis in Water with a Hydrophilic Substrate : Scandium-Catalyzed Hydroxymethylation with Aqueous Formaldehyde in Water, M. Kokubo, C. Ogawa, S. Kobayashi, *Angew. Chem. Int. Ed.*, **47**, 6909-6911(2008).

**【Term of Project】** FY2009-2013

**【Budget Allocation】** 166,000 Thousand Yen

**【Homepage Address and Other Contact Information】**

[http://www.chem.s.u-tokyo.ac.jp/users/synorg/index\\_E.html](http://www.chem.s.u-tokyo.ac.jp/users/synorg/index_E.html)