## Bifunctional heterogeneous silica—supported imidazolium salt and silver catalyst for efficient chemical fixation of carbondioxide

(¹Tokushima University, ²National Institute for Materials Science (NIMS), ³The University of Tokyo) ○Sangita Karanjit¹, Emiko Tanaka¹, Masaya kashihara¹, Lok Kumar Shrestha², Atsushi Nakayama¹, Katsuhiko Ariga².³, Kosuke Namba¹

Keywords: heterogeneous catalyst, carbondioxide conversion, Silver catalyst

Carbondioxide (CO<sub>2</sub>) has attracted considerable attention in recent years due to the environmental degradation and global warming caused by its emission. Great efforts have been implemented to reduce CO<sub>2</sub> levels in the atmosphere. Conversely, this gas has been regarded as a nontoxic, abundant, nonflammable, and renewable one-carbon (C1) feedstock for the synthesis of a variety of value-added chemicals. The reactions of CO<sub>2</sub> with unsaturated alcohols and amines to afford carbonates and carbamates through carboxylative cyclization process is one of the most promising green routes to convert CO<sub>2</sub>. Silver has the potential to activate alkynes and has been extensively studied for chemical transformation of CO<sub>2</sub>. Most of the studies have concentrated on homogeneous catalysis using relatively large amounts of Ag-based catalysts<sup>1</sup>. However, in general, harsh reaction condition and sophisticated process for catalyst preparation are required for these reactions.

Compared to homogeneous systems, heterogeneous system is advantageous for the development of green and sustainable society in terms of good activity and reusability. To date, very few heterogeneous catalysts for this transformation including Cu and Ag are reported. In this context, solid catalysis with ammonium salts by covalent grafting (supported ionic liquids, SILs) could be an ideal choice because of the fact that in SILs, ammonium salts are used in small amounts, while their efficiencies are similar or sometimes even much better than non-supported ones. In this work, we prepared a silica-supported bifunctional heterogeneous catalytic system based on imidazolinium salt where the Im<sup>+</sup>Cl<sup>-</sup>@SiO<sub>2</sub> activated both Ag-catalyst and substrate for carboxylative cyclization reaction of propargyl alcohols by efficient utilization of CO<sub>2</sub> with excellent yields of the corresponding carbonates and carbamates under mild reaction condition. We also confirmed the reusability of catalyst up to five cycles.

$$\begin{array}{c} XH \\ R_1 \\ R_2 \end{array} H + \begin{array}{c} CO_2 \\ (1 \text{ atm}) \end{array} \begin{array}{c} Ag\text{-catalyst} \\ X = O, \, NH \end{array} \end{array}$$

1) S. Kikuchi, S. Yoshida, Y. Sugawara, W. Yamada, H.-M. Cheng, K. Fukui, K. Sekine, I. Iwakura, T. Ikeno, T. Yamada, *Bull. Chem. Soc. Jpn.* **2011**, *84*, 698–717.