Development of Immobilized Molecular Catalysts for CO_2 Transformation Reactions

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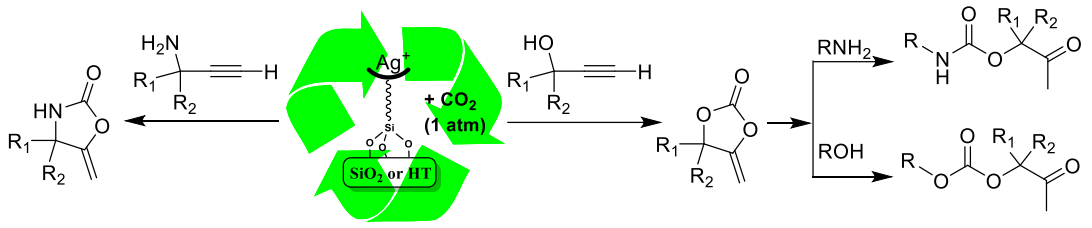
CO_2 emission has been one of the greatest problems in recent years because it is the most important cause of global warming. Great efforts have been implemented for developing the strategies to reduce CO_2 levels in the atmosphere. Conversely, this gas has been regarded as a nontoxic, abundant, nonflammable, and renewable one-carbon (C1) feedstock for the synthesis of a variety of value-added chemicals. On this aspect, chemical fixation is one of the attractive and effective way to utilize CO_2, however, only small amount of such an abundant material is utilized for its conversion into various value-added products through chemical synthesis because of its high thermodynamic stability and kinetic inertness.

There have been numerous advances on the metal-catalyzed synthesis of various organic compounds utilizing CO_2 as a C1 source where major challenges have been faced for designing, evaluating and finding more efficient catalyst for the chemical transformation of CO_2. The reactions of CO_2 with unsaturated alcohols and amines to afford carbonates and carbamates through carboxylative cyclization process is a promising green route to convert CO_2. These compounds have wide range of application in organic synthesis for being important building blocks and potential biological activity. Silver has the potential to activate alkynes and has been extensively studied for chemical transformation of CO_2. Most of the studies have concentrated on homogeneous catalysis using relatively large amounts of Ag based catalysts[1]. Compared to homogeneous systems, heterogeneous system is advantageous for development of green and sustainable society in terms of good activity and reusability. To date, very few heterogeneous catalysts for this transformation including Copper and Silver are reported. In this context, solid immobilized molecular catalysts with ligands supported on silica, metal oxide and polymers by covalent grafting could be an ideal choice

The solid materials such as Hydrotalcite (HT) and silica (SiO_2) are applied extensively in catalysis. The presence of hydroxyl groups makes them an active support for immobilization of various transition metals. The immobilization of catalyst on solid supports not only transfers the catalytic property of homogeneous catalyst to a heterogeneous catalyst, combining the advantages of both homogeneous and heterogeneous catalyst, but also is an important requirement of chemical industry for the ease of separation and recovery of a catalyst from the reaction mixture. Alkoxysilane linkage is one of the

easiest ways to link homogeneous or heterogonous catalyst on solid surface. Herein, we carry out the CO_2 transformation reactions with propargyl alcohols and amines using heterogeneous Silver catalyst on functionalized HT and silica. The active catalysts were synthesized or generated in situ which carry out the reaction under mild condition with good activity and reusability. The catalysts prepared were quite stable, versatile and could be stored without the need of protective atmosphere.



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