Catalytic Performance of Metal-containing Ionic Liquids for Synthesis of cyclic carbonate by Ring-coupling reaction of CO_2

Dongwoo Kim, Hyeongook Kim and Deughee Cho*
Center for Chemical Industry Development, Korea Research Institute of Chemical Technology Ulsan, Republic of Korea

*E-mail: dhcho@krict.re.kr

The increasing levels of carbon dioxide in the atmosphere have widely been considered detrimental to the carbon balance of the biosphere, a major effect being global warming. However, CO_2 holds the tag for one of the most non-toxic, non-flammable and nearly inexhaustible source of C1 for the production of a range of compounds such as dimethyl carbonate, N,N′-disubstituted ureas, cyclic carbonates, cyclic urethanes, and formic acid.[1]

Ionic liquids are well known as environmentally benign media for catalytic processes and chemical extraction because of their outstanding properties, which include negligible vapor pressure, excellent thermal stability, and other special characteristics that distinguish them from conventional organic and inorganic solvents.[2] Ionic liquids have recently been successfully applied as immobilizing reagents for transition-metal catalysts, combining the advantages of both homogeneous and heterogeneous catalysis and leading to improved process performance.[3] With the purpose of turning the acidic character, ionic liquids containing metals have recently received increased research attention.[4] Beyond their application as mere reaction media, imidazolium based metal-containing ionic liquids possessing a weak base as the anion have been successfully used as catalysts themselves, e.g. in Friedel-Crafts alkylation and glycerolysis.[5] Only few reports exits that discuss the utilization of metal containing ionic liquids as promising catalysts towards CO_2 fixation.

In this study, the imidazolium-based metal-containing ionic liquid $(RIm)_2MX_2$ (where R is methyl (Me), ethyl (Et), or butyl (Bu); M is Fe, Cu, or Zn; and X is Cl, Br, or I), which is a bifunctional catalyst in which the metal ions serve as the acidic center and the anion as nucleophile, is prepared by a metal insertion reaction. The catalytic performances of $(RIm)_2MX_2$ catalysts for the synthesis of cyclic carbonate from CO_2 and epoxide under solvent free conditions are investigated. We have attempted to compare the reactivity of three different metal-containing (Fe, Cu, and Zn) ionic liquid catalysts using quantum mechanical calculations (i.e., DFT) for synthesis of cyclic carbonate by cycloaddition of CO_2 to epoxide.

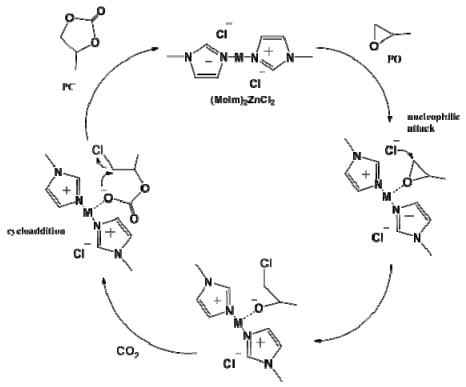

Fig.1 Proposed mechanism for cycloaddition of CO_2 using $(MeIm)_2ZnCl_2$ catalysts.

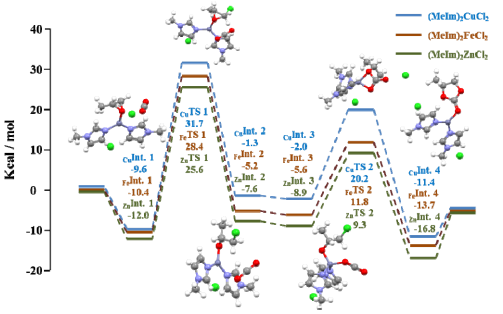

Fig. 2 Energetics profile for cycloaddition of CO_2 using $(MeIm)_2MCl_2$ catalysts.

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