

Study on Catalytic Carbon Dioxide Fixation under Mild Conditions by Homogeneous and Heterogeneous Catalysts

モハメド サダム ホセイン

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氏 名 : Md. Saddam Hossain (モハメド サダム ホセイン)

論 文 名 : Study on Catalytic Carbon Dioxide Fixation under Mild Conditions by Homogeneous and Heterogeneous Catalysts (均一系および不均一系触媒による温和な条件下での二酸化炭素固定化反応に関する研究)

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論 文 内 容 の 要 旨

In chapter 1, The development of an efficient and sustainable catalytic system is crucial for CO₂ transformation to high-value chemicals or intermediates on the aspect of global carbon management. Among various transformation of CO₂, cycloaddition of CO₂ with epoxides is an 100% atom-economical reaction to afford cyclic carbonates which has a great potential in the perspective of green and sustainable chemistry. In this work, several transformations of CO₂ have been described briefly. In introduction, cyclic carbonates and different synthesis routes of cyclic carbonates have been described concisely. Different catalysts like homogeneous, heterogeneous for the synthesis of cyclic carbonates have been described from the previous literature. In addition, a few examples of coupling of CO₂ with epoxides under mild condition have been shown. Some photocatalytic systems for the synthesis of cyclic carbonates have also been reviewed. However, a suitable catalytic system for the present reaction under atmospheric condition is an urgent issue as well as challenging. Moreover, the photocatalytic synthesis mechanism of cyclic carbonate is still not clear. Therefore, to develop new catalytic system for the fixation of CO₂ to epoxides is attractive and the mechanistic study of photocatalytic system is expected in this field.

In chapter 2, a homogeneous catalytic system based on a crown ether-linked Schiff base in combination with alkali halides has been investigated for the transformation of CO₂ into cyclic carbonates from CO₂ and epoxide. The system exhibits high-performance as well as good recyclability. The designed catalyst features multiple active sites, including a Lewis acidic alkali ion center and a nucleophilic iodide source, enabling the efficient activation of epoxides under solvent-free conditions under atmospheric pressure. Effects of cations and calcium salts have been explored to evaluate the cause of enhancing catalytic performance. Several substrates with different functions groups have been performed by the present catalytic system. The reaction was also performed using simulated post-combustion exhaust gas (CO₂: 7.5 %, N₂: 92.5 %, relative humidity: 90 %) which was concentrated to 97 %. Furthermore, the catalyst was easily recovered and reused for multiple cycles. This study provides a practical and environmentally-friendly approach for CO₂ utilization, contributing to the advancement of sustainable catalytic processes.

In chapter 3, a heterogenous photocatalytic system based on M^{n+}/TiO_2 with TBABr have been developed for the synthesis of cyclic carbonates from the coupling of epoxides with CO_2 under visible light irradiation and mild reaction conditions. The synthesis procedure of the catalyst from commercially available TiO_2 and metal source was described. Effect of metal ions for the modification of TiO_2 has been evaluated. Solar energy was performed for the present system to convert CO_2 to high value-added carbonates. Furthermore, a wide range of epoxides have been explored by the present protocol (Mg^{2+}/TiO_2 with TBABr) to synthesis the corresponding cyclic carbonates. Additionally, recycle experiment of Mg^{2+}/TiO_2 photocatalyst was performed, as well as the large-scale synthesis of styrene carbonate by the present catalytic system (Mg^{2+}/TiO_2 with TBABr) was performed. Detailed studies for the dependence of CO_2 pressure on the catalytic cycle was carried out and the use of simulated post-combustion exhaust gas containing 8% CO_2 for the catalytic reaction was investigated. The visible light boosted the catalytic performance of M^{n+}/TiO_2 and TBABr system affords a new path for the CO_2 cycloaddition to epoxide which was supported by DFT investigation. This study represents a cost-effective and efficient method for performing the CO_2 cycloaddition reaction under mild conditions and hence should be considered as a promising process. We believe that the present work will create new opportunities for the chemical conversion of CO_2 into valuable chemicals sustainably using solar light.

In chapter 4, the summary of this work and perspective of the future work have been depicted. Such catalytic systems i) crown ether-linked Schiff base and alkali halides and ii) Mn^{n+}/TiO_2 with TBABr were first explored for the cycloaddition of CO_2 with epoxides to afford cyclic carbonates. A new photocatalytic reaction mechanism path for this reaction was proposed. However, there are several queries remain still unclear that should be a future research plan on this area for the sustainable development of the environment.