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# The formation of a series of carbonates from carbon dioxide: Capturing and utilisation



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#### ABSTRACT

An efficient approach for capturing and utilising high concentrations of  $CO_2$  from the atmosphere involves converting the  $CO_2$  into stable and valuable products, such as a series of carbonates. First, we review the reactions and thermodynamic conditions for the carbonate formation using  $CO_2$  and for the fast back reactions of pure  $CO_2$  releasing from the carbonates. The related reactor and process design for  $CO_2$  transformation into carbonates is also discussed. The metal carbonates that can decompose into metal oxides and  $CO_2$  at low temperature is mentioned briefly. Thermodynamic approaches can be applied to determine whether the reaction is favourable or unfavourable. Several parameters, namely the role of surface structure, moisture, pressure and temperature, are major factors that can influence the  $CO_2$ -adsorbent interactions. Theoretical data from molecular simulations, such as atomic charge and attraction energy, can aid in the understanding of  $CO_2$  adsorption. Over the last six years, highly active catalysts for the synthesis of cyclic and polycyclic carbonates from epoxides and  $CO_2$  have been developed. This reaction appears to be useful for  $CO_2$  utilisation programmes. The mechanisms behind the formation of carbonates can help to elucidate the reaction of  $CO_2$  and epoxides to form a series of cyclic carbonates.

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#### 1. Introduction

In recent years, international attention has been devoted to the abundant greenhouse gas carbon dioxide ( $CO_2$ ). Because  $CO_2$  presents the possibility of adverse effects with regard to the sustainability of ecosystems worldwide, many novel technologies have been considered to minimise their emissions into the atmosphere. As the main contributor to anthropogenic climate change, the volume of  $CO_2$  emissions has triggered a wide range of corrective initiatives to mitigate their impact. In addition to  $CO_2$  capture to address environmental concerns, the removal of  $CO_2$  from gas streams is also necessary in other applications, including air purification in confined spaces [1–4], separation from flue gases [5–9] and natural gas treatments [10,11].

The proposal for  $CO_2$  sequestration in the ocean and on land has generated considerable debate regarding the long-term effects. Zoback and Gorelick [12] claimed that carbon capture and sequestration (CCS) technologies would literally cost trillions of dollars and that these technologies are vulnerable to moderate-sized earthquakes. Surprisingly, even small-sized earthquakes would threaten the seal integrities of  $CO_2$  repositories. Therefore, industrial large-scale CCS is a risky and likely unsuccessful strategy for significant reductions in greenhouse gas emissions. Instead, the utilisation of  $CO_2$  and conversion into value-added products, such as hydrogen, methanol, acetic acid and a series of carbonates, is a better approach in terms of  $CO_2$  capture [13–18]. Similarly, many

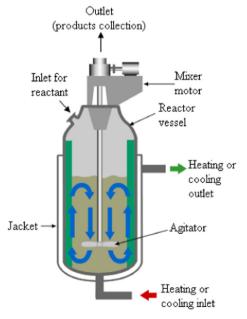


Fig. 1. Stirred-tank batch reactor [26].

countries in Asian focusing on low carbon economy which target to reduce  $CO_2$  emissions by using renewable energy source for power generation and green building development [19]. This strategy also capable to achieve the low carbon society by low  $CO_2$  emissions in atmosphere [20].

CO<sub>2</sub> molecules can attach to metal oxide surfaces in two ways, namely physisorption (an abbreviation of 'physical adsorption') and chemisorption (an abbreviation of 'chemical adsorption'). The predominant force in physisorption involves van der Waals interactions (for example, a dispersion or a dipolar interaction) between the adsorbate and the substrate. Van der Waals interactions are long-range interactions, but they are weak, and the energy released for a physisorbed particle is in the same order of magnitude as that of the enthalpy of condensation. In chemisorption, CO<sub>2</sub> molecules adhere to the surface by forming a chemical bond, predominantly a covalent bond, and they tend to find sites that maximise their coordination number with the substrate [21].

The chemisorption of CO<sub>2</sub> typically creates another substance, namely carbonates. Carbonates are very useful products in many fields, and the process of chemisorption can adsorb CO<sub>2</sub> in huge amounts compared to physisorption. Additionally, as a potential pathway for the effective chemical utilisation of carbon dioxide, the synthesis of cyclic carbonates via coupling carbon dioxide and epoxides has attracted much attention [22]. Currently, cyclic carbonates are used industrially as solvents in cleaning processes, as electrolytes in Li-ion accumulators or as substrates for the synthesis of other high value-added molecules [23]. Additionally, the selective cycloaddition of CO<sub>2</sub> to epoxides is a significant approach for both the chemical utilisation of CO<sub>2</sub> and the production of cyclic carbonates, which find wide application as raw materials in the synthesis of

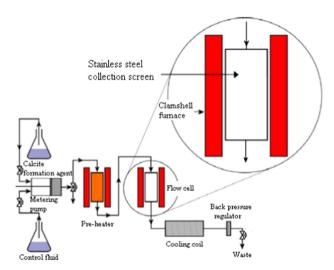


Fig. 2. Schematic drawing of the high-temperature/high-pressure reactor [32].

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