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Review

Catalytic developments in the direct dimethyl carbonate synthesis from carbon dioxide and methanol

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HIGHLIGHTS

- DMC are commonly used as fuel additive, in electrochemistry and organic synthesis.
- This study presents an overview of advances in direct DMC synthesis from CO_2 and methanol.
- It also summarizes the challenges such as necessity of dehydrating agents.
- And the uses of various catalysts to address challenges like low yield and thermodynamic limitations.

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ABSTRACT

The present review compiles the recently published literature for the single step dimethyl carbonate (DMC) synthesis from carbon dioxide (CO_2) and methanol. The various routes of DMC synthesis are also discussed in short with their advantages and disadvantages in order to distinguish the merits of direct DMC synthesis route. Next, the major applications of DMC such as in electrochemistry, as fuels additive, as solvent and building block in organic synthesis are described. The major problems in the direct DMC synthesis route such as low yield, reaction rate, thermodynamic limitations and hydrolysis of produced DMC are also pointed out. Furthermore, the significance of fabricating an effective dehydrating agent for the removal of water from the reaction is narrated for the enhancement of DMC yield. The type of catalyst materials based on their nature i.e. metal carbonates, tin-based catalysts, metal oxides, organic catalysts and polymer based materials, etc. used for title reaction are separately discussed in details. The varieties of dehydrating agents and their role in DMC production is explained with the help of most recent reported literature.

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1. Introduction

Increasing flue gasses in the open environment attributed to climate change in the form of global warming with the annual global emission of CO_2 escalated considerably during 1970 to 2004 which becomes a burgeoning issue for our age. The prime reason behind the occurrence of these harsh changes could be over dependence on fossil fuel for energy consumption. Conversely, CO_2 has considered as naturally abundant, cheap, recyclable and non-toxic carbon source and it can replace toxic chemicals such as phosgene, isocyanates or carbon monoxide [1–4]. From this perspective, CO_2 capture or chemical fixation becomes more and more important from the ecological and economic point of view. Various organizations all over the world including national and international governments, industries and a number of high-profile collaborative programs have been established to tackle CO_2 issue. These groups pointed out the urgent need in the development of new methodologies for CO_2 capture and storage (CCS) [5–7]. From this regards, several research groups all over the world have been paying significant attention toward designing suitable material for effective CO_2 capture and fixation into valuable chemicals. Fig. 1 reveals the possible uses of CO_2 in organic synthesis and other fields. More specifically, it is demonstrated that CO_2 is the best carbon feedstock and promising candidate as reagent or carbon building block in organic synthesis and energy applications. There are some review articles focusing on different aspects and applications of CO_2 for DMC synthesis are reported [8,9]. However, as per our best knowledge no review available which summarizes the catalysts used for direct DMC synthesis based on their compositions. Here we report a comprehensive review on the advancement of catalysts system in recent years for direct DMC synthesis from CO_2 and methanol. Various DMC synthesis routes and applications such as fuel additive, organic solvent, in Li ion battery, as organic feedstock and in polycarbonate synthesis, etc. are systematically described. The important challenges such as role of dehydrating agent and major developing directions are also highlighted.

1.1. Organic carbonates

In the organic family, organic carbonates are very important compounds which are capable to replace hazardous reagents in some organic processes by selectively and more efficiently. Organic carbonates are known for their simple structure, high polarity, low viscosity, low toxicity and easy degradability [10]. These remark-

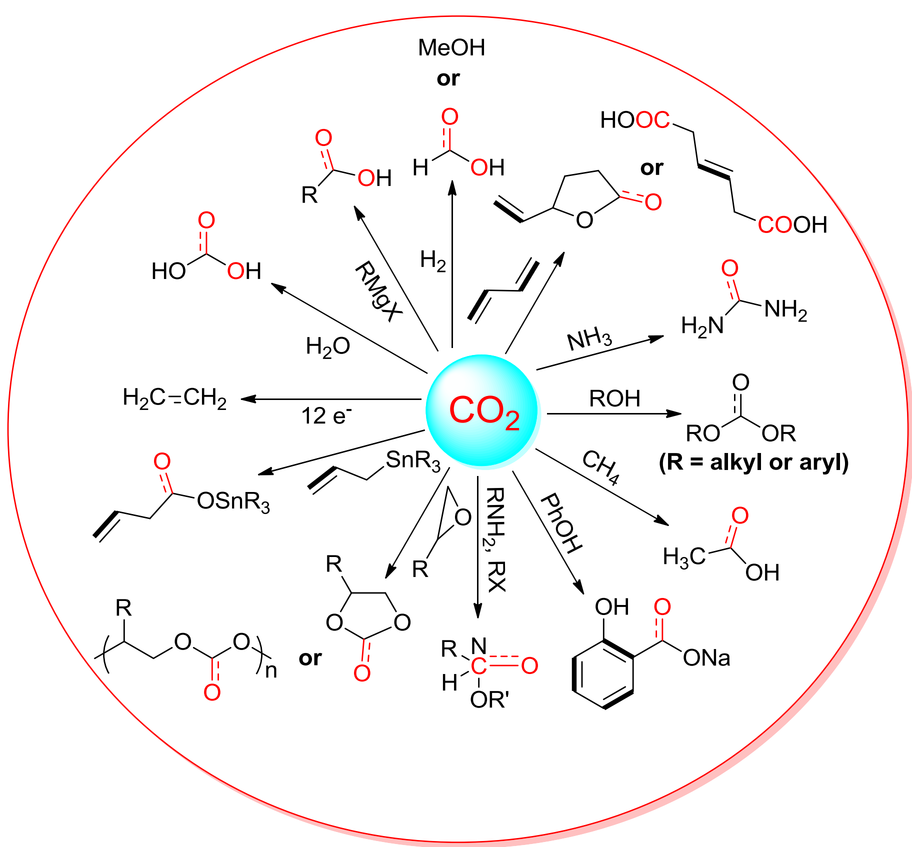

Fig. 1. The schematic of possible uses of CO_2 in organic synthesis.

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