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Review Article

Nanocatalysts for chemical transformation of carbon dioxide

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ABSTRACT

This review deals with the applications of nanocatalysts in chemical transformation of CO_2, a field that has attracted great interest in the chemical, fuels, materials, and industrial communities. Literature has been surveyed from 2010 to 2017.

1. Introduction

Carbon dioxide (CO_2) is the major greenhouse gas responsible for global warming and climate change. Dry air contains 390 ppmv CO_2, and every year, human activity releases ~38 Gt of this gas into the atmosphere [1], hence there is an urgent need to reduce the accumulation of this greenhouse gas in the atmosphere. On the other hand, from the viewpoint of chemistry, CO_2 is considered as an abundant, nontoxic, nonflammable, and renewable C1 resource for the synthesis of useful chemicals [2–10]. However, this is a great challenge, owing to its inert nature and low reactivity. In fact, the most reactions involving CO_2 require use of stoichiometric amount of catalysts and drastic reaction conditions (high reaction temperature and/or high CO_2 pressure) [11]. Therefore, development of new and highly efficient catalytic systems for chemical transformation of CO_2 is a very attractive topic in modern organic synthesis. In the past decade, numerous homogeneous and heterogeneous catalysts have been developed to catalyze CO_2 conversion processes [11]. However, homogeneous catalysts suffer from the difficulty of their separation from the reaction medium. Furthermore, they can be easily destroyed during the course of the reaction. Alternatively, heterogeneous catalytic systems are developed and successfully employed to overcome these problems. Nanocatalysts as a kind of heterogeneous catalyst, attracts more and more attention in CO_2 conversion. Needless to say, nanomaterial-based catalysts due to their high surface area allow for rapid transformations under mild conditions. These catalysts can also be easily separated and be used several times without obvious loss in catalytic activity [12,13]. Considering the extensive attention on the employing nonocatalysts in chemical conversion of CO_2 in recent years, on the one hand and absence of a comprehensive review on the other hand, there is an urgent need for a detailed review article on this interesting field. In continuation of our works [14], in this review, we have classified these synthetic reactions based on the desired products (Fig. 1). It should be noted that we have not discussed synthesis of small molecules (such as methane, methanol, and formic acid), since they have recently been described in another publication [15].

2. Cyclic carbonates

Five-membered cyclic carbonates are important heterocyclic compounds used as excellent polar aprotic solvents and building blocks for different synthetic purposes [16–18]. The synthesis of these compounds from epoxides (or propargylic alcohols) and CO_2 is one of the most important methods for the utilization of CO_2 because this reaction has ideal atom economy (all the atoms present in the starting materials are present in the product) and cyclic carbonate products are useful molecules in chemistry [19]. Numerous homogeneous and heterogeneous catalytic systems have been developed to catalyze this transformation [20]. However, most of these catalysts require harsh reaction conditions and addition of hazardous organic solvent in the reaction mixture. To overpass this limitation, numerous nano-based catalytic systems have been developed in recent years. This section is focused on this subject.

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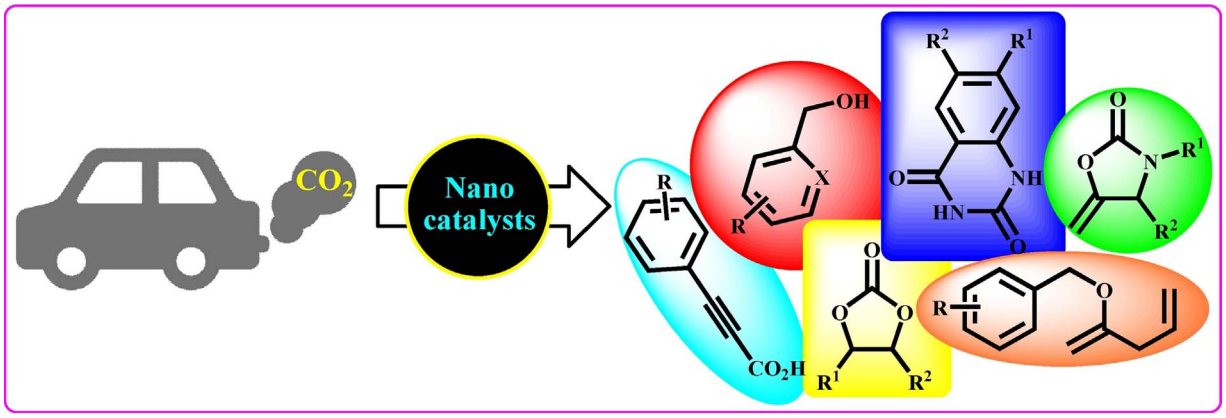
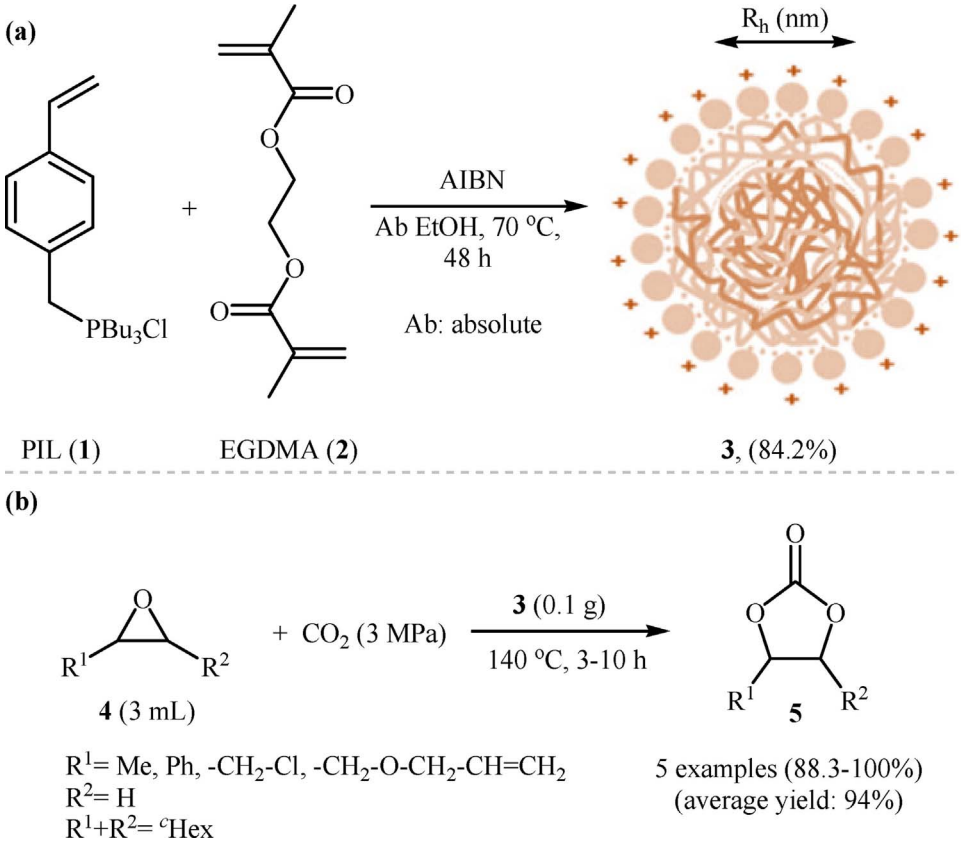


Fig. 1. Nanocatalysts for chemical transformation of carbon dioxide.

2.1. From epoxides

Alongside the first report on the nanoparticles (NPs) catalyzed fixation of CO_2 to epoxides, the group of Xiong introduced ionic liquid-based cross-linked polymeric nanoparticles **3** as catalytically active species. These NPs were synthesized by conventional radical copolymerization of the cross-linker, ethylene glycol dimethacrylate (EGDMA), and ionic liquid monomer, 4-vinylbenzyl-tributylphosphorous chloride (PIL), using AIBN (azobisisobutyronitrile) as the initiator (Scheme 1a). Among the various solvents like MeOH, EtOH, ^{i}PrOH, and Me_2O; ethanol was the most efficient for the copolymerization. In the presence of **3**, the corresponding cyclic carbonates **5** could be obtained in high to quantitative yields *via* the treatment of epoxides **4** with CO_2 (3 MPa) at 140 °C under solvent-free conditions (Scheme 1b). The result showed that catalyst was recyclable for six cycles with less than 1.5% loss of catalytic activity [21,22].

Subsequently, the same authors have developed novel imidazole-based highly cross-linked polymeric nanoparticles **6** (Scheme 2a) for the fixation of CO_2 with same set of epoxides **4**. The reaction was run under solvent-free conditions at 160 °C under 5 MPa of CO_2 pressure and gave expected carbonates in high to excellent yields. However, the need for elevated temperatures and high CO_2 pressure limits the synthetic utility of this reaction [23]. Inspired by these works, Adam and Batagarawa found that tetramethylguanidine–silica nanoparticles **7** (Scheme 2b) can efficiently catalyze the addition of CO_2 to epoxides [24]. However, required harsh reaction conditions (130 °C, 5 MPa) hindered this system from being sustainable. In 2015, the Coskun laboratory developed a class of nanoporous polymer incorporating sterically-confined N-heterocyclic carbenes **8** (NP-NHCs) that could catalyze conversion of CO_2 into cyclic carbonates at atmospheric pressure with excellent yields (Scheme 2c). It is noted that this nanoporous organocatalyst exhibited an exceptional CO_2 capture fixation



Scheme 1. (a) Synthesis of ionic liquid-based cross-linked polymeric nanoparticles **3**; (b) Xiong's synthesis of carbonates **5**.