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A new catalyst for the solvent-free conversion of CO_2 and epoxides into cyclic carbonate under mild conditions

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ABSTRACT

A new Cu_6 cluster $[Cu_6(\mu_4\text{-}O)_2(SO_4)_4(DMA)_6]$ (**1**) with high density of active Lewis acid sites turns out to be a good catalyst for the chemical fixation of CO_2 into value-added cyclic carbonates without the use of any organic solvents under room temperature and atmospheric pressure. Above all, the preparation of **1** is very simple and rapid with low cost, which has important implications for industrial applications.

1. Introduction

Annually emitted into the atmosphere in large quantities, carbon dioxide (CO_2) has become the main contributor to global warming and a consequent series of environmental problems in recent decades [1]. In the past, great efforts have been made in CO_2 capture and sequestration (CCS), in which the chemical fixation of CO_2 reveals a cheerful prospect in applications [2]. The utilization of CO_2 as a feedstock for chemicals can not only settle the environmental problems caused by CO_2 but also provide high-value products such as methanol, benzoic acid, urea, propiolic acids and so on [3]. Given the 100% atom efficiency, the conversion of CO_2 with epoxide into cyclic carbonate has attracted a wide attention (Scheme 1). The resulting product, cyclic carbonate, is a very important material for biology, medicine and industry as degreaser, electrolytes in lithium ion batteries, raw materials for plastics, precursors for pharmaceutical intermediates, and eco-friendly nonprotic solvents [4].

The history of preparing cyclic carbonate with CO_2 is more than 50 years [5]. In industries, cyclic carbonate are prepared under high pressure (5 MPa), which requrie additional consumption of energy and may cause other environmental problems [5]. As a result, development of new catalysts for the coupling of CO_2 and epoxide at mild conditions is one of the essential challenge for the chemists. In recent years, different kinds of catalysts have been exploited [6,7]. Several sorts of heterogenous catalysts [6], such as metal oxides [8], zeolites [9], oxychlorides [10], titanosilicate [11], silica-supported salts [12], a microporous polymer [13], an organic network [14], and silica grafted imidazolium-based ionic liquids [15] have been employed in the lab. Though the heterogeneous catalysts are ease of purification and recycle, most of them perform poorly without rigorous temperatures, drastic CO_2 pressures or the use of co-solvent [8–15]. Recently, metal organic frameworks (MOFs), which feature a high density of active sites, high surface area and extraordinary chemical stability, have been reported to catalyze the reaction with high yields and mild conditions [16]. However, most of such functional MOFs strictly depends on several factors such as ligands, metal ions, and preparation conditions [16]. On the other hand, homogeneous catalysts [7] have been utilized as well in the coupling of epoxide and CO_2, such as salen complexes [17], for which harsh conditions are still necessary. Lately, Mashima's group has reported a series of tetranuclear clusters which can catalyze the reaction at ambient conditions and have a good tolerance of air and moisture, nevertheless, the synthesis of these clusters demand high temperature, evacuation and complicate operations with $M(OCOCF_3)_2$ as ingredient, which is environmentally unfavorite [18]. Herein, we report a new Cu_6 cluster $[Cu_6(\mu_4\text{—}O)_2(SO_4)_4(DMA)_6]$ (**1**) (Fig. 1a), which can effectively catalyze the coupling of CO_2 and epoxides at ambient conditions (25 °C, 1 atm) homogeneously. The synthesis of **1** is facile and less time-consuming with environmentally friendly stuffs and low cost in comparison with most of other catalysts, which indicates the great potential of **1** towards the application in industry and environment protection.

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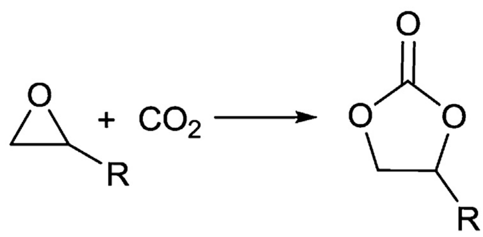

Scheme 1. Coupling of CO_2 and epoxides.

Single-crystal X-ray diffraction analysis exhibited a unique structure of **1**. In the cluster, six Cu(II) ions and two μ_4—O atoms form two $Cu_4(\mu_4—O)$ tetrahedra sharing a Cu-Cu edge. The four triangular Cu_3 faces which do not involve the shared edge are bridged by a μ_3-sulfato ligand each (Fig. 1b). The Cu(II) ions on the vertexes are apiece coordinated by one or two dimethylacetamide moleculars. As far as we know, this is the first observation of a Cu—O cluster with the Cu/SO_4^{2-} ratio other than 1:1. The PXRD patterns of the product are consistent with the patterns simulated from the single crystal X-ray diffraction data, which verify the phase purity of **1** (Fig. 2). **1** was also characterized and confirmed by X-ray photoelectron spectroscopy (XPS; Supporting Information, Figs. S1–S3). **1** owns four four-coordinate Cu(II) ions and two five-coordinate Cu(II) ions bridged by two μ_4-O atoms and capped by four sulfato ligands, which furnish considerable active sites.

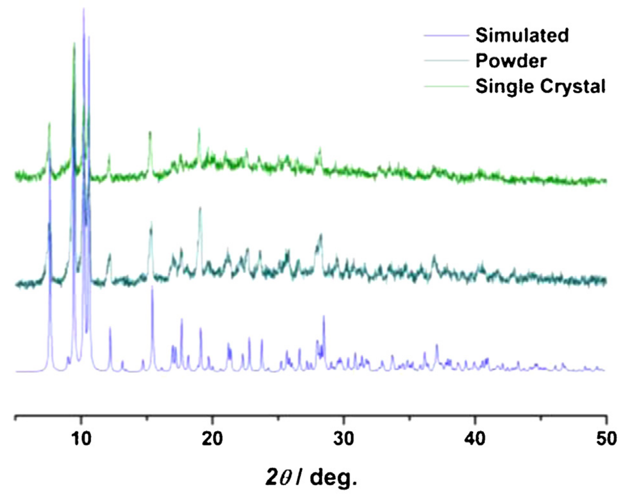

Fig. 2. Powder XRD patterns of $[Cu_6(\mu_4\text{-}O)_2(SO_4)_4(DMA)_6]$ single crytals and powders.

2. Results and discussion

Since **1** possesses a higher density of active sites in each molecular than most of known Cu (II) complexes [16], we inferred it may exhibit high activity for the conversion of CO_2. As shown in Table 1,**1** turns out to be a good Lewis acid catalyst for the coupling of epoxides and CO_2 into cyclic carbonates at ambient conditions with a yield of 98.2% in 24 h (Table 1, entry 1). Blank experiments were carried out without **1** (Table 1, entry 6) or without tetrabutylammonium bromide (TBAB) (Table 1, entry 7), but the yields are poor, which indicated **1** as a new efficient catalyst for the conversion of CO_2 into cyclic carbonates.

Then **1** was attempted to fix CO_2 with a wide variety of terminal epoxide substrates. Under the same conditions as entry 1, the reaction of CO_2 and 2-(chloromethyl)oxirane gave the corresponding cyclic carbonate with a yield of 78.2% at 25 °C and 1 atm pressure in 24 h (Table 1, entry 2), which also certified the superior catalytic ability of **1**. Styrene oxide and benzyl phenyl glycidyl ether were also used to synthesis the corresponding cyclic carbonates yielding in 53.2% (Table 1, entry 3) and 51.5% (Table 1, entry 4), respectively. The activity decrease of **1** could be attributed to the hindrance effect of the substrates preventing further interaction of epoxides [19]. Cyclohexene oxide was less reactive compared to the previous epoxides, which could be possibly ascribed to steric hindrance of the tertiary carbons (Table 1, entry 5) [19].

Upon combining some previous reports with our work [18–20], a conceivable mechanism is proposed for the CO_2 insertion into epoxide catalyzed by **1** in the presence of TBAB, as illustrated in Scheme 2: at first, the oxygen atom of the epoxide is coordinated by the the Lewis acidic site of **1**, and the epoxide is activated. At the same time, CO_2 is fixed and activated on **1** in a similar way. Then the nucleophilic bromide ion provided by TBAB selectively attacks the carbon atom which is less substituted and opens the epoxy ring. The halo-alkoxide intermediate generated by the ring-opening of the epoxide reacts with the activated CO_2 yielding an alkylcarbonate anion, which eventually turns into the corresponding cyclic carbonate through cycloaddition with regeneration of catalysts. We owes the high catalytic activity of **1** to its high density of active

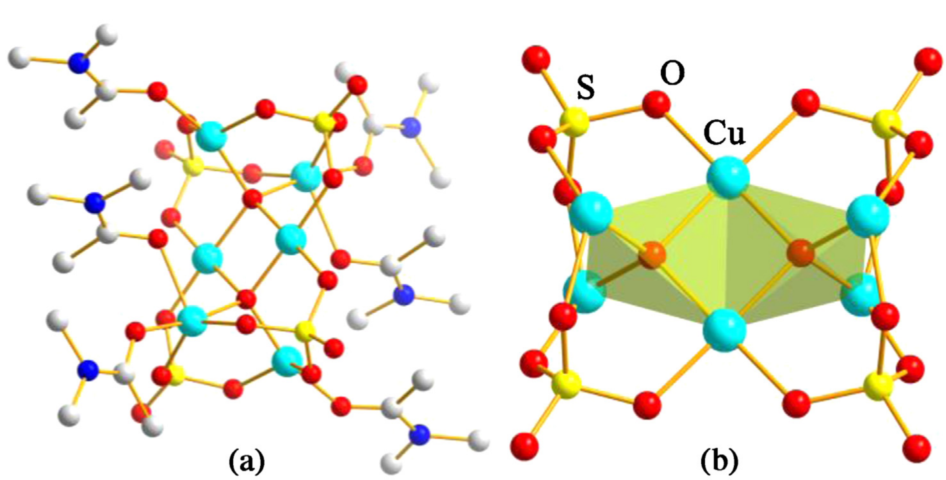

Fig. 1. (a) Structure of $[Cu_6(\mu_4\text{-}O)_2(SO_4)_4(DMA)_6]$ (**1**); (b) $[Cu_6(\mu_4\text{-}O)_2(SO_4)_4(DMA)_6]$ with the nonoxygen atoms of the DMA ligands removed for clarity. Colour code: Cu(II), light blue; O, red; N, blue; C, grey; S, yellow. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)