Insight into the role of weak interaction played in the fixation of CO$_2$ catalyzed by the amino-functionalized imidazolium-based ionic liquids

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ABSTRACT

The mechanism of coupling reaction of CO$_2$ with propylene oxide (PO) catalyzed by the amino-functionalized imidazolium-based ionic liquid is theoretically investigated by the density functional theory (DFT). Although the mechanisms of the fixation of CO$_2$ catalyzed by various room-temperature ionic liquids or functionalized ionic liquids have been theoretically elucidated in previous literatures, it is not totally suitable for the amino-functionalized ionic liquid. First, the 1-(3-aminopropyl)-3-methylimidazolium chloride ([APmim]Cl) would react with CO$_2$ to produce the 1-(3-carbamic acid propyl)-3-methylimidazolium chloride ([CAPmim]Cl). Then, [APmim]Cl, [CAPmim]Cl, and combination of them would be employed as the catalyst leading to nine possible routes. Different from the previous work, this work allows a better comprehension of the mechanism by means of a new model that the cooperative effect of two same or different components is considered. Both the interaction between catalyst and reactant and the influence between different catalytic components are considered. Besides the nucleophilic attack of the Cl$^-$ anion, the [CAPmim]$^+$ cation is taken as the main component to activate the O atom of PO directly leading to the ring-opening. The [APmim]$^+$ cation is utilized to stabilize the [CAPmim]$^+$, which is the most favorable route. The noncovalent interactions (NCI) plot is employed as a tool to analyze the reason of the higher catalytic efficiency of top three favorable routes. The hydrogen bond and dispersive attractive interaction is confirmed to play a determining role in the catalytic activity.

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1. Introduction

There is a global demand to search for the alternative carbon sources because of the continuous decline of nature fossil fuels and the increasing demand for energy day by day as well as the serious environmental issues [1,2]. Carbon dioxide (CO$_2$) is regarded as a potential renewable C1 source, which is nontoxic, inexpensive, and abundant [3,4]. The utilization of CO$_2$ would be beneficial for not only reducing the CO$_2$ emitted into the atmosphere but also generating thousands of valuable compounds. The conversion of CO$_2$ to useful chemicals is taken as one of the most promising strategies for the fixation of CO$_2$. Although there are various pathways to convert CO$_2$ into chemicals, few of them have been applied in industrial scale due to the thermodynamic stability and kinetic inertness of CO$_2$. The coupling reaction of CO$_2$ with propylene oxide (PO) to propylene carbonate (PC) is one of the promising utilizations, which has attracted lots of research endeavors to complete it in a benign condition [5,6]. In recent years, a large number of catalysts have been developed, such as metal oxides [7], transition metal complexes [8,9], metal-organic frameworks [10–12], organometallic compounds [13,14], quaternary ammonium, phosphonium salts [15,16], and ionic liquids (ILs) [17–19]. Among them, ionic liquids have attracted particular attention owing to their unique properties including negligible vapor pressure, excellent thermal stability, nonflammability, and tunable structure. Besides the room temperature ILs, the task-specified ILs have also been developed and showed better catalytic activity with no co-catalyst or additional organic solvent, such as hydroxyl-functionalized [20], amino-functionalized [17], and

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carboxyl-functionalized ILs [21]. Although some progresses have been made, there are lots of spaces to be improved to develop single-component catalyst with high efficiency in a more benign condition.

Besides the experimental studies, tremendous theoretical researches have been focused on the development of new ILs. Elucidating the mechanism from the molecular level is helpful to design the novel catalysts with the desired properties. As early as 2007, the detailed mechanism of CO_2 and PO catalyzed by alkylmethylimidazolium chlorine ([$C_n$mim]Cl) IL has been clarified by Zhang et al. [22]. Three-step mechanism was confirmed to be the most favorable route, i.e., ring-opening, insertion of CO_2, and ring-closure. The same three-step mechanism is also testified to be suitable for functionalized ILs including hydroxyl-functionalized, carboxyl-functionalized, and sulfonic acid-functionalized ILs [23–26]. If the same three-step mechanism is applied to the amino-functionalized guanidinium-based ILs [27], the rate-determining barrier height is as high as 22.90 kcal/mol that is higher than those of carboxyl-functionalized and hydroxyl-functionalized guanidinium-based ILs, which is contradictory with the experimental result [28] that amino-functionalized guanidinium-based IL has the better activity than other two task-specified guanidinium-based ILs. Considering that the carbamic acid is detected in experiment, a four-step mechanism was proposed by us [27]. Initially, two amino-functionalized guanidinium-based ILs would firstly react with one CO_2 molecule to produce the carbamic acid-functionalized ILs. Then, the carbamic acid-functionalized IL is taken as essential catalyst to promote the coupling reaction following the three-step mechanism (See Fig. S1). The rate-determining barrier height is decreased greatly to a reasonable level. In previous work [27], only carbamic acid-functionalized IL is considered in the following three-step catalytic cycle. The amino-functionalized IL is thought to transfer into carbamic acid-functionalized IL totally, which is not involved in the catalytic process of activating the PO. Recently, Xiao et al. [29] have

synthesized a series of amino-functionalized imidazolium-based ILs, which are effective catalysts for the synthesis of PC by PO and CO_2. Moreover, they proposed that amino-functionalized and carbamic acid-functionalized imidazolium-based ILs would catalyze the reaction cooperatively, which promotes us to consider the mechanism catalyzed by amino-functionalized ILs again. In almost all reported theoretical studies [30–32], the model including single catalyst and single reactant is employed. The interactions among catalysts are omitted, which has been testified to play a vital role in determining the relative activity sequence [33] although the mechanism would not be varied.

Inspired by it, a reaction model catalyzed by two catalysts is employed to consider the weak interaction between them besides the single catalyst. In this work, the mechanism of CO_2 with PO catalyzed by both the single [APmim]Cl or [CAPmim]Cl and the binary [APmim]Cl/[APmim]Cl, [CAPmim]Cl/[CAPmim]Cl, and [APmim]Cl/[CAPmim]Cl catalysts are investigated by the density functional theory (DFT). Various possible catalyzed routes are evaluated to determine the most favorable one. The central goals are to elucidate the mechanism catalyzed by amino-functionalized imidazolium-based ILs, to confirm the essential catalytic species, and to evaluate the influence of weak interactions between catalytic components or between catalyst and reactant on the activity.

2. Computational details

The geometries of reactants, intermediates, transition states, and product were calculated at the B3PW91 [34,35] level with the basis set of 6-31G(d,p) [36]. At the same level, the vibrational frequencies were carried out to determine the property of a critical point. The minimum and transition state correspond to all positive frequencies and only one imaginary frequency, respectively. Starting from the transition state, the minimum-energy path (MEP) was constructed by the intrinsic reaction coordinate (IRC)
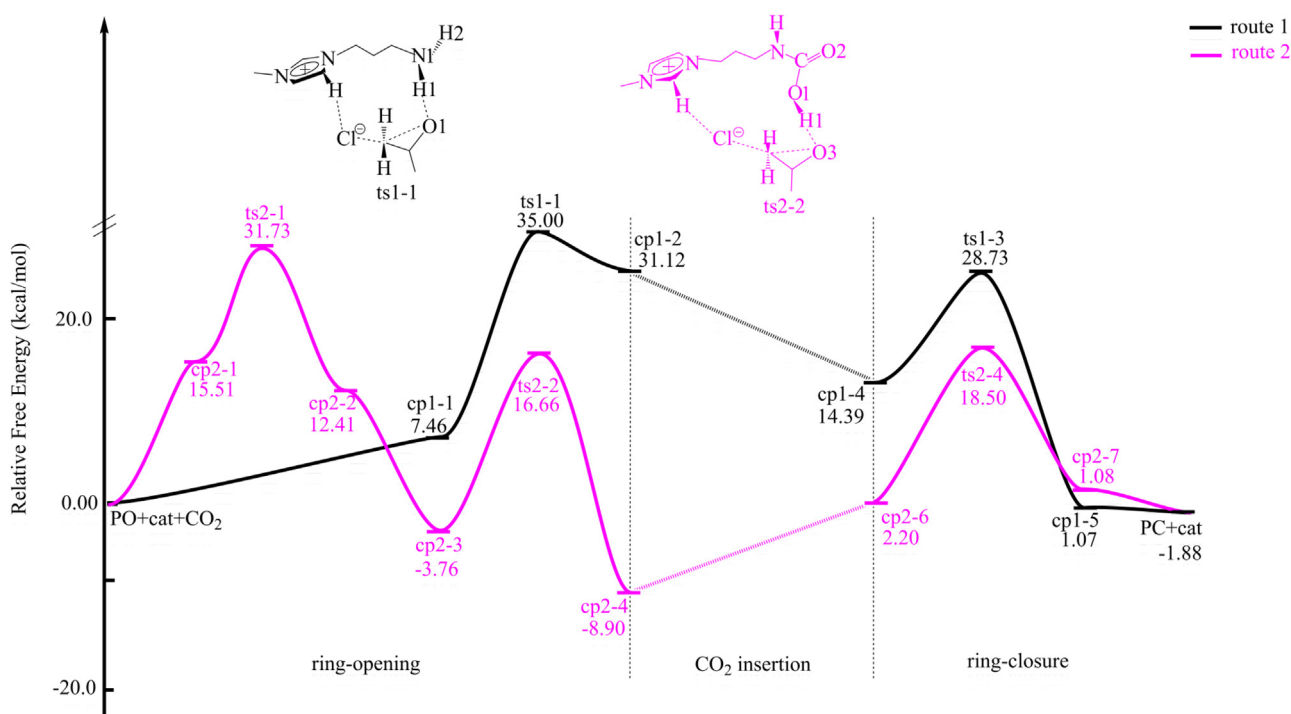

Fig. 1. Free energy profiles for the cycloaddition reaction along routes 1–2 calculated at the M06/6-311 + G(2d,2p)//B3PW91/6-31G(d,p) (PCM) level in Et₂O solvent.