

Decomposition of Ethylene carbonate on imidazolium ionic liquid-zinc halide composite catalysts: Active site and mechanism

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Highlights

- Effects of halogen and imidazolium on the decomposition of EC were explored.
- The essential active site of the composite catalyst was identified.
- Decomposition and polymerization reactions were distinguished.
- Mechanism was proposed by using combined molecular dynamics and DFT calculation.

1. Introduction

Conversion of CO₂ with epoxides to cyclic carbonates such as ethylene carbonate (EC) is considered as one of the most efficient methods for the industrial utilizations of CO₂.¹ Among all the studied catalysts for the synthesis of EC, imidazole based ionic liquid exhibits outstanding activity and stability, thus displaying great industrial application prospects.^{2,3} Generally, a vacuum distillation system follows the high-pressure reactor system to acquire the product EC with the catalyst separation and recirculation under a temperature of 130-150 °C, which often brings about by-products by the side reactions of EC decomposition with a negative effect on the purity of the final product. This phenomenon is rarely addressed in the open literatures so far.⁴ It is known that, EC is prone to reversibly decompose into CO₂ and EO or polymerize into polycarbonates, which not only affect energy consumption and product purity, but also arise the safety risk of industrial production.⁵ In this work, we explored the catalytic decomposition reactions of EC on the composite ionic liquid catalysts systematically, with the active center and catalytic performance were revealed by molecular dynamics and density functional theory calculations.

2. Methods

Experiments were performed in a 50 mL graduated glass tube equipped with a condenser and vacuum pump. The reaction solution was kept at a reduced pressure (3~30 kPa absolute pressure) for the removal of gaseous products. After reaching the set temperature, the reaction solution is refluxed for 1 h, with the decomposition rate being measured by the weight loss of the product. ¹H NMR spectrums were collected with a Bruker AVANCE III HD 400 spectrometer and referenced with residual non-deuterated solvent shifts ($\delta_{\text{CHCl}_3} = 7.26$ ppm). The molecular interactions between imidazolium cations and zinc halide anions dissolved in EC were investigated using commercial software suite of Accelrys Materials Studio 2019 software. Density functional theory (DFT) calculations were performed using the B3PW91 functional with the 6-311+G(d, p) basis set as implemented in Gaussian 16 program package. The DFT empirical dispersion correction (DFT-D3) was utilized to improve the accuracy of relative energies along the mechanisms.

3. Results and discussion

The overall decomposition reaction results depicted in Fig. 1(a), which shows inconsistent activity order with DFT calculated one when it only includes the reversible reaction of EC synthesis. Thus, the polymerization correction was performed by NMR test (Fig. 1c), which is verified by the DFT calculations. Furthermore, the results indicated that Br⁻ has a higher activity for EC decomposition, while Cl⁻ promotes the polymerization side reaction of EC, and the imidazolium cation has little effect on the decomposition of EC (Fig. 1b).

Molecular dynamics (MD) simulations were used to further analyze the interactions of different catalytic compounds in EC solvent. From the radical distribution of hydrogen-1 atoms to bromine ions shown in Fig. 2(a), Over 70% of imidazole salt molecules display an increase of Br-H1 distance indicating the tendency of dissociation. Moreover, typical composite catalyst systems were tested and PES scan was established as shown in Fig. 2(b). As a result, the active center of one imidazolium cation attached with zinc tetracoordinate complex were established. The catalytic mechanism was also studied by DFT calculation, which identified the ring opening of EC as the rate-determining step, with an activity order of $\text{ZnBr}_2/[\text{Emim}]\text{Br} > \text{ZnCl}_2/[\text{Emim}]\text{Br} > \text{ZnBr}_2/[\text{Emim}]\text{Cl} > \text{ZnCl}_2/[\text{Emim}]\text{Cl}$. In addition, $^1\text{H-NMR}$ tests were carried out to quantitatively analyze the polymerization reaction, as shown in Fig. 2(c).

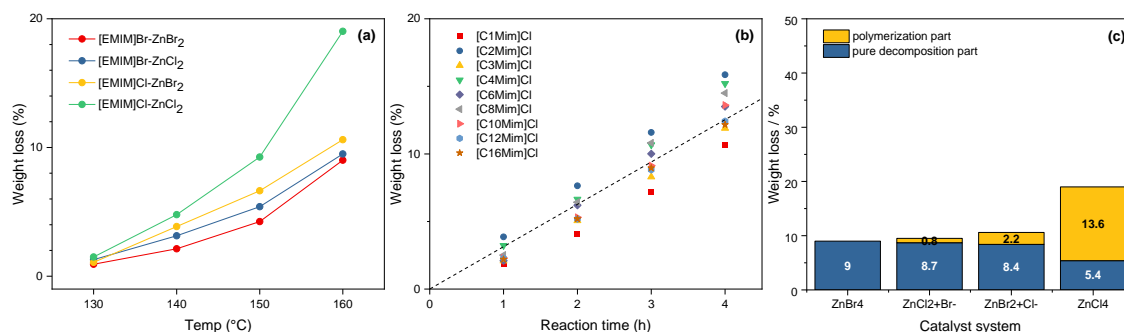


Figure 1. EC decomposition performance: (a) catalyzed by $[\text{Emim}]\text{X-ZnY}_2$ ($\text{X}, \text{Y}=\text{Cl}, \text{Br}$) in 1 hour; (b) with different imidazole cations under $140\text{ }^\circ\text{C}$; (c) The correction of weight loss [1 h, $160\text{ }^\circ\text{C}$].

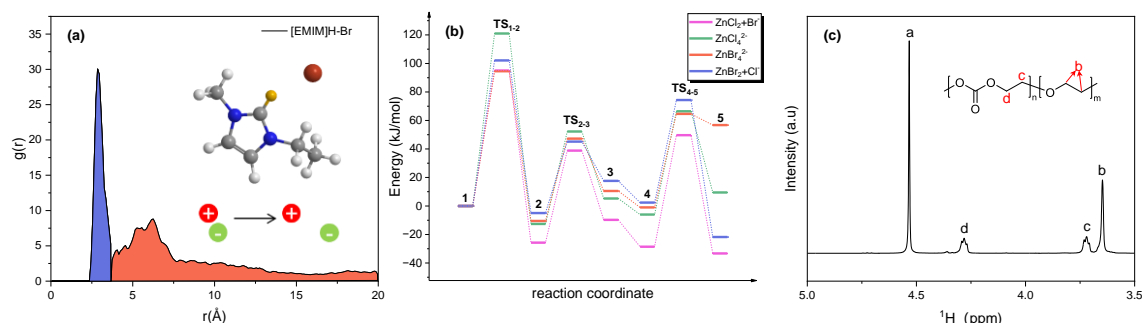


Figure 2. Simulation and characterization results: (a) Radial distribution function (RDF) for Br-H1 distance while selected hydrogen atom was shown in yellow; (b) Potential energy profile for the decomposition process of EC; (c) $^1\text{H-NMR}$ spectrum of reaction mixture catalyzed by $\text{ZnCl}_2/[\text{Emim}]\text{Cl}$ system, chemical shift from 3.5 to 5 ppm.

4. Conclusions

The chain length of imidazole salts had no effect on the activity of EC decomposition. Molecular simulation results showed that the four coordinated zinc ions could be the essential catalytic active center. Combining decomposition experiments and DFT calculations, the real activity of different imidazole salt composite catalysts is investigated. Br^- has a higher activity for EC decomposition, while Cl^- enhances the polymerization side reaction of EC.

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Keywords

CO_2 utilization; Cyclic carbonate; Ionic liquid; DFT calculation.