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Introduction

1,2-Diols, such as ethylene glycol (EG) and 1,2-propylene glycol (PG), are important raw materials of polyester resins, antifreezes, cosmetics, medicines, and other products.¹ Especially in recent years, the increasing consumption of polyester products has greatly promoted the demand for EG, which could be above 17 million tons per year by 2018. However, the current industrial production process for EG, the direct hydration of ethylene oxide (EO), is less competent in this task due to the huge consumption caused by a large excess use of water (22 molar ratio of H₂O to EO) and low EG yield (~89%)

Sterically controlling 2-carboxylated imidazolium salts for one-step efficient hydration of epoxides into 1,2-diols[†]

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In order to overcome the disadvantages of excessive water and many byproducts in the conventional process of epoxide hydration into 1,2-diols, 2-carboxylated imidazolium salts were first adopted as efficient catalysts for one-step hydration of epoxides into 1,2-diols. By regulating the cation chain lengths, different steric structures of 2-carboxylated imidazolium salts with chain lengths from C1 to C4 were prepared. The salt with the shortest substituent chain (DMIC) exhibited better thermal stability and catalytic performance for hydration, achieving nearly 100% ethylene oxide (EO) conversion and 100% ethylene glycol (EG) selectivity at 120 °C, 0.5 h with just 5 times molar ratio of H₂O to EO. Such a tendency is further confirmed and explained by both XPS analysis and DFT calculations. Compared with other salts with longer chains, DMIC has stronger interaction of CO_2^- anions and imidazolium cations, exhibiting a lower tendency to release CO_2^- and form $HO-CO_2^-$, which can nucleophilically attack and synergistically activate ring-opening of epoxides with imidazolium cations. The strong huge sterically dynamic structure ring-opening transition state slows down the side reaction, and both cations and anions stabilized the transition state imidazolium-EG-HO- CO_2^- , both of which could avoid excessive hydration into byproducts, explaining the high 1,2-diol yield. Based on this, the cation–anion synergistic mechanism is then proposed.

resulting from a large amount of byproducts (Scheme 1).² As one of the energy-intensive chemical processes, EG production has triggered great interest for technical innovation both in academia and industry, of which two-step transformation from CO_2 and EO is thought to be an alternative energy-saving process for EG production.^{3,4} A two-step process via first fixation of CO₂ into ethylene carbonate (EC) and then hydrolysis into EG provides an efficient way for high selectivity with a lower H₂O/EO molar ratio (<1.5) and realizes the efficient utilization of CO2.3,5 However, it needs excessive CO2 to completely convert EO and the recycling of the residual CO2-EO mixture makes the process more complex and unsafe.⁶ For simplicity, one-step catalytic hydration of EO with no introduction of CO₂ is an alternative route. To date, various acid or base catalysts have been developed for improving EG yield at a low H₂O/EO ratio,^{1,7-11} e.g. carboxylic acid-carboxylate composites, NY bimetallic salts,12 amines,13 supported metal



Scheme 1 Conventional direct hydration process of EO into EG.

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oxides,¹¹ cation- or anion-exchange resins,¹⁰ *etc.* Although significant progress has been made, unsatisfactory activity of heterogeneous catalysts and low selectivity of homogeneous catalysts, environmental problems, and a high H₂O/EO molar ratio (6–8) are still the disadvantages needed to be overcome.^{7,8} Thus, the development of an efficient and environmentally benign catalyst to produce 1,2-diols at a lower H₂O/epoxide molar ratio with both high activity and selectivity is still a huge challenge.

To combine the advantages of two-step transformation and avoid the disadvantages of direct hydration, inspired by the two-step process wherein CO_2 acts as an intermediate, from the perspective of atom-economy, the synthesis of EG might be simplified as one-step catalytic hydration of EO with a catalyst functioning as CO_2 (Scheme 2). 2-Carboxylated imidazolium salts are very appropriate choices in this catalyst design due to their adjustable cation and anion structures, and the environment-friendly properties.¹⁴ To the best of our knowledge, few research studies have been reported associated with 2-carboxylated imidazolium salts as catalysts for one-step hydration of epoxides.

2-Carboxylated imidazolium salts, also called N-heterocyclic carbene CO₂ adducts (NHC–CO₂), have gained great attention in homogeneous catalysis which are generally synthesized by addition of imidazolium chlorides with CO₂ or one-step transformation from imidazole and dimethyl carbonates.^{15–17} In particular, the zwitterionic CO₂ adduct could be utilized as a convenient CO₂ carrier to accomplish CO₂ fixation through the nucleophilic incorporation of the O—C—O unit as proposed for various Lewis base catalyst systems, such as CO₂ cycloaddition with epoxides, in which CO₂ was thought to be added to the epoxide *via* nucleophilic attack of the carboxylate group on NHC–CO₂.^{18–20} Given this feature, it is promising to be used as a ring-opening catalyst for epoxides in a one-step hydration reaction, which has not been reported yet.

In this work, four kinds of 2-carboxylated imidazolium salts containing only clean element C/N/O/H with different chain lengths were prepared and first used for one-step hydration, namely 1,3-dimethyl-imidazolium-2-carboxylate (DMIC), 1-ethyl-3-methyl-2-carboxylate (EMIC), 1-propyl-3-methyl-2-carboxylate (PMIC), and 1-butyl-3-methyl-2-carboxylate (BMIC), respectively (Scheme 3). Firstly, the effect of different chain lengths on the properties and catalytic performance was suc-



Scheme 2 One-step catalytic hydration of epoxides into 1,2-diols by 2-carboxylated imidazolium salts functioning as CO_2 .



Scheme 3 2-Carboxylated imidazolium salts with chain length from C1 to C4.

cessively investigated. Then, reaction conditions were optimized and the suitability of the optimal catalyst for different epoxides was tested. The catalytic mechanism was finally proposed based on the XPS analysis and DFT calculation results. This work not only pioneers the catalytic hydration of epoxides by using 2-carboxylated imidazolium salts, but also provides a new idea in turning the multi-step reaction to one step by designing a catalyst similar to intermediates.

Results and discussion

Characterization of 2-carboxylated imidazolium salts

2-Carboxylated imidazolium salts with chain lengths from C1 to C4 were successively prepared according to the typical synthetic procedures.²¹ Both ¹H NMR and ¹³C NMR analyses were conducted for all the samples, as listed in the following experimental section. For all the samples, the NMR together with ESI-MS (Fig. S1[†]) showed consistent results with those reported previously, indicating that 2-carboxylated imidazolium salts with C1 to C4 chains were successfully synthesized. Elemental analysis results of all the prepared samples (DMIC, EMIC, PMIC, BMIC) are listed in Table S1.† As shown in Table S1,† the measured C/N molar ratio for these four samples was respectively 3.01, 3.53, 4.01, and 4.56, which was well consistent with that calculated from theoretical molecular weight. FT-IR spectra were obtained for confirmation of the chemical structure of the as-prepared samples. The spectra of all samples are displayed in Fig. 1. The characteristic peaks of C=O feature near 1625–1675 cm^{-1} ,^{22,23} and the peak representing C-C stretch (corresponding to the bond between the imidazolium carbon and the carboxylate carbon theoretically to occur around 1300 cm⁻¹) were observed in all the samples, which indicates the formation of the carboxylate $(O-C=O^{-})$. Thermogravimetric analysis (TGA) gave the decomposition temperatures of these four salts. All their thermal decomposition temperatures were labelled on the TGA curves in Fig. S2,† which were 225 °C, 190 °C, 170 °C and 160 °C, respectively, for DMIC, EMIC, PMIC and BMIC. As shown by the curves, the decomposition temperature exhibited a decreasing trend with the increasing chain length of alkyl substituents from C1 to C4. DMIC which has the shortest chain length and the best symmetry of the nitrogen substituents had



Fig. 1 FT-IR spectra of 2-carboxylated imidazolium salts with chain lengths from C1 to C4.

the highest thermal stability with the highest decomposition temperature.

Analysis of active groups

To further figure out main active sites of catalysts, the effect of different substituent chain lengths on the binding energy was investigated by XPS analysis. Typically, two extremes with C1 and C4 chain length (DMIC and BMIC) were chosen for O 1s XPS analysis. As illustrated in Fig. 2, those peaks in O 1s spectra representing C-O and C=O were found respectively at 530.00-530.13 eV and 529.28-529.70 eV. Compared with DMIC, all the peaks of BMIC (530.00 eV and 529.28 eV) shifted to higher binding energies (530.13 eV and 529.70 eV), suggesting the stronger interior interaction of C-O and C=O, which might lead to weaker binding interaction with the imidazolium ring.²⁴ Such a tendency was consistent with the thermal stability obtained from TGA. Furthermore, the strength in the interaction with the imidazole ring reflects the ability of the $O=C-O^{-}(CO_{2}^{-})$ group to react with other molecules. Thus, CO₂⁻ might be the main active group.

Catalyst screening

With EO as a model reactant, the hydration reaction was conducted under identical conditions by using the prepared samples as catalysts. In order to ensure the efficient conversion of EO, it is necessary to keep EO in the liquid phase system by giving certain external pressure to prevent EO from gasification in the reaction process. To avoid the influence of the atmosphere on the reaction, inert gas N_2 is used for pressurization during the hydration reaction. First of all, all the catalysts were tested under modest conditions (120 °C, 2.0 MPa N_2 , 0.5 h) with equal molar quantity. The results listed in Table 1 show an increase in EO conversion but a decrease in EG selectivity as the chain length grows. By comparing the results in Table 1, DMIC and EMIC with a shorter chain are found to have higher selectivity for EG (~87.0%) than others



Fig. 2 XPS spectra of 2-carboxylated imidazolium salts with chain lengths of C1 and C4.

Table 1 Catalyst screening for the EO hydration reaction

Entry ^a	Catalyst	EO conv. (%)	EG selec. (%)	
1	Blk-N ₂	72.2	77.8	
2^{b}	Blk-CO ₂	97.5	83.3	
3	DMC	79.1	70.9	
4	N-Methyl imidazole	99.1	40.1	
5	<i>N</i> -Ethyl imidazole	98.7	33.8	
6	N-Propyl imidazole	99.0	33.7	
7	N-Butyl imidazole	99.6	22.6	
8	Na_2CO_3	99.9	69.5	
9	NaHCO ₃	99.9	82.2	
10	DMIC	75.2	86.8	
11	EMIC	77.8	87.4	
12	PMIC	85.2	85.0	
13	BMIC	89.1	83.1	

Reaction conditions: EO: 1.0 mL, 120 °C, 0.5 h, $H_2O/EO = 5:1$, and Cat: 2.1 mol% of EO. ^{*a*} 2.0 MPa N_2 . ^{*b*} 2.0 MPa CO₂. All yields and selectivities were determined by GC.

(entries 10 and 11), which is much higher than that of $Blk-N_2$ without any catalyst, together with conventional hydration catalysts Na_2CO_3 (entry 8) and $NaHCO_3$ (entry 9). Furthermore, to explore the function of DMIC, the $Blk-CO_2$ with no catalyst under a CO_2 atmosphere instead of the inert N_2 was tested. It

turns out that even 2.0 MPa CO_2 (0.02 mol according to the formula "n = PV/RT" which is almost 50 times DMIC) is used, and no obvious advantages in improving EG selectivity were found compared with DMIC (0.0004 mol). This concluded that DMIC functioned more than CO2 itself. In addition, other catalysts with similar function in ring-opening of epoxides were also tested for EO hydration under identical conditions (EO: 1.0 mL, 120 °C, 0.5 h, H₂O/EO = 15 : 1, cat: 5.4 mol% of EO). A higher H₂O/EO ratio of 15:1 was used to fully stimulate the catalyst performance. As displayed in Fig. 3, these common catalysts with a ring-opening function, such as 1-ethyl-3methylimidazolium bromide (EmimBr) and 1-butyl-3-methylimidazolium bromide (BmimBr), exhibited almost the same catalytic activity for EO conversion (99.9%) and EG selectivity (84.8%). Among all the evaluated catalysts, DMIC and EMIC exhibited the best catalytic activity at a value of 99.9% in both EO conversion and EG selectivity, higher than conventional carboxylic imidazolium ionic liquids (EmimAc, BmimAc, and N(Et)₄Ac). In comparison with Blk-CO₂ which achieved only 99.1% in EO conversion and 94.1% in EG selectivity, DMIC and EMIC were further confirmed to be a catalyst functioning better than only the CO₂ bulk phase. Considering the better stability than that of EMIC, DMIC was preferred for this reaction and used for further investigation.

With DMIC as the catalyst and EO as the model substrate, the reaction conditions including temperature, N_2 pressure, time, H_2O/EO molar ratio and catalyst amount were optimized successively. All the results are displayed in Fig. S3.[†] For this EO hydration reaction, the by-products (DEG, TEG, *etc.*) were generated from the condensation of EO with the glycol product in the last step. Thus, once the product is generated and accumulates to a certain concentration, the next step reaction is about to start. To obtain both high EO conversion and EG selectivity, the reaction rate must be controlled in an appropriate stage by adjusting the reaction conditions. From the



Fig. 3 Comparison of DMIC and EMIC with common catalysts for ringopening.

curves shown in Fig. S3,† 2.0 MPa of N₂ pressure is optimal for good EO conversion. According to the EO saturated pressure at different temperatures calculated from the Aspen Plus TM software (Table S1^{\dagger}), lower N₂ pressure than 2.0 MPa is not enough to keep EO in the liquid phase, explaining the worse EO conversion therein. However, higher N₂ pressure is also not good for EO transformation which might be due to mass transfer resistance caused by high gas solubility in the liquid phase. To give consideration of EO conversion and EG selectivity, 30 min, 120 °C, and H₂O/EO ratio of 5 are chosen for further investigations based on the results in Fig. S3.† When the catalyst quantity reaches over 500 mg, namely 18.0 mol% of EO, both the EO conversion and EG selectivity will be nearly up to 100%. Therefore, the optimal conditions for EO hydration are 18.0 mol% DMIC of EO at a H₂O/EO ratio of 5 at 120 °C, 2.0 MPa N₂, 0.5 h.

The catalytic suitability of various epoxide substrates was then tested with DMIC as the catalyst under the optimal conditions. All the catalytic results are listed in Table 2, DMIC could catalyze these epoxides with high 1,2-diol selectivity, most of which reached nearly 100%. For small-molecule reactants, such as EO and propylene oxide (PO), high conversion was also obtained, which might be due to the easier mass transfer of reactant molecules to active sites. Hence, DMIC could be widely used in the production of many kinds of 1,2diols from various epoxides.

Confirmation of active sites

To confirm the possible active sites, the density functional theory (DFT) calculations were carried out to analyze the Natural Population Analysis (NPA) charge and bond energy of the structures with different substituent chain lengths (C1 to C4). All calculations were carried out using the Gaussian 09 program. The B3LYP/6-311++G(d,p) method has been used for structure optimizations, and subsequent frequency calculations at the same level verify the optimized structures to be

able 2	Catalytic suitability test for different epoxides

Entry	Time (h)	Substrate	Product	EO conv. (%)	EG selec. (%)
1	0.5	\wedge	но он	99.9	99.9
2	0.5	ß	но он	94.6	94.3
3	0.5	Å	ОНОН	41.5	99.9
4	0.5	CI-	он сіон	85.6	99.9
5	2.0	$\bigcirc \circ$	ОН	57.2	99.9
6	2.0	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	ОН	63.7	99.9
		$\langle \rangle$			

Reaction conditions: EO: 1.0 mL, 120 °C, 2 MPa $\rm N_2,~H_2O/EO$ = 5 : 1, and cat: 18.0 mol% of EO.



Fig. 4 Optimized structure with different chain lengths from C1 to C4.

ground states without imaginary frequencies (NImag = 0) (Fig. 4).

The NPA charge distributions by Natural Bond Orbital (NBO) calculations of two O atoms in C-O and C=O on different structures are depicted in Table 3. A decreasing trend in bond energy of the imidazole ring and carbonate anion (IMC_2-C) was observed from C1 to C4, while fewer changes were examined for NPA charge of O both in C-O and C=O. As shown in Table 3, the IMC₂-C bond energy decreases from 191.4 to 189.2 with the increase of the chain length. The NPA analysis of O shows that with the increase of the chain length, the charge density increases slightly from -0.701 to -0.703. The increase of negative charge density of O atoms might contribute to the increase of the binding interaction of CO_2^{-} , as obtained from XPS analysis. Therein, the IMC2-C bond was more sensitive to changes of substituent chain lengths than others, which might lead to different thermal stabilities and even the catalytic activities.²⁰ Therefore, CO₂⁻ may be the main active site in the reaction process. The highest EG selectivity for DMIC might be attributed to the strongest IMC2-C bond energy, wherein the active site CO_2^- is strongly bound with the imidazole ring, slowing down the rate of the whole reaction, especially the next side reaction. The lower bond energy of IMC₂-C from C1 to C4 leads to easier activation of its adjacent CO2⁻, hence higher EO conversion was obtained and continuous side reaction was ineluctable, explaining the lower EG selectivity from C1 to C4.

Proposed catalytic mechanism

Considering the good activity and selectivity of DMIC, the reaction process was further investigated by using DMIC as the catalyst. At first, the possible intermediate was detected by ESI-MS. As shown in the spectra in Fig. S4,† two kinds of intermediates were obtained as I and II. Based on the intermediates, four possible reaction routes were proposed based on XPS and DFT results. The routes were respectively displayed as A, B, C and D in Scheme 4.

For Route A and Route C with I as the intermediate, DMIC first reacts with the H⁻ in H₂O to form DMICH with OH⁻ as anions,² and the OH⁻ nucleophilically attacks C-O bonds to induce ring-opening of EO together with a hydrogen-bonding effect from IMC₂-COOH of the cation. The whole process is a strong alkali catalytic process, which is less possible to occur because of low stability of strong base OH⁻ from weak base CO_2^{-} . According to previous research, there exists a reversible transformation between CO₂⁻ and HO-CO₂⁻ (II) in water solution (Route B and Route D). Considering the steric hindrance caused by the imidazole skeleton, HO-CO₂⁻ free from the cation connection effect was thought to be the main site for activating reactant molecules, which could attack C-O bonds to induce ring-opening of EO together with a hydrogenbonding effect from IMC2-H of the cation. Thus, the following discussion is mainly focused on Route B and Route D.

For Route B and Route D with II as the intermediate, DMIC first interacts with H_2O to form DMIHC with $HO-CO_2^-$ as the anion,^{25,26} and the $HO-CO_2^-$ nucleophilically attacks C-O bonds to induce ring-opening of EO and meanwhile the IMC₂-H from the cation could synergistically stabilize the transition state *via* the hydrogen-bonding effect. The whole process is a weak alkali catalytic process. Considering the nearly neutral reaction system, Route B and Route D are more reasonable.

Table 3 NPA charge distributions and the bond energy of C-C bonds (Kcal mol⁻¹) for different structures

Parameters	C1	C2	C3	C4
NPA charge of O in C–O and C==O	-0.701/-0.701	-0.701/-0.702	-0.702/-0.703	-0.702/-0.703
IMC2–C bond energy	191.4	190.1	189.5	189.2



Scheme 4 Possible routes for EO activation by DMIC.



Fig. 5 Potential energy surface profiles of the DMIC-catalyzed process according to Route B (Mechanism B) and Route D (Mechanism D), and the optimized geometries for the intermediates and transition states.

To compare the relative energy of Route B and Route D and screen the most reasonable route, the quantum chemistry calculations were conducted. The reactants, products, intermediates, and transition state equilibrium geometries were optimized using the B3LYP method and 6-31+G(d,p) basis set (B3LYP/6-31+G(d,p)). The vibrational frequency calculations were carried out at the same level to confirm the nature of the extreme points of the potential energy surface. Vibrational frequency with only one imaginary frequency stands for the transition state. Then, the intrinsic reaction coordinate theory was employed to construct the minimum-energy path (MEP). All the above calculations were performed using the Gaussian 09 program.

The mechanisms of the DMIC-catalyzed process according to Route B (Mechanism B) and Route D (Mechanism D) were respectively analyzed by calculation (Fig. 5). The main difference between Mechanism B and Mechanism D is the source of the hydrogen donor. For Mechanism B, H₂O acts as a hydrogen donor while for D it is the IMC₂-H. From the calculation results in Fig. 5, it is found that different donors cause different relative energies for transition states. For Mechanism B with H₂O as the donor, the relative energy of transition state TS-FG is 17.7 kcal mol⁻¹, and for Mechanism D with IMC₂-H as the donor, the relative energy of TS-AB is 29.8 kcal mol^{-1} . Thus, the initially activated step of Mechanism B occurred more easily than Mechanism D. Meanwhile, a more stable ending state J was obtained according to Mechanism B $(-30.4 \text{ kcal mol}^{-1})$ rather than that E in Mechanism D $(-26.5 \text{ kcal mol}^{-1})$. Therefore, the main reaction step from EO to EG during the hydration process without the DMIC cation effect occurs more easily than that with the DMIC cation effect. This tendency is in accordance with the above catalytic test results where NaHCO3 exhibited higher EO conversion than DMIC, which indicates that HO-CO₂⁻ functions more for the main reaction. However, the faster reaction rate leads to uncontrollable EG selectivity because of the quick side reaction in the presence of $HO-CO_2^-$. For DMIC, due to the steric interaction of imidazolium cations, the stable transition state TS-AB and reactant H_2O could form a relatively stable intermediate which would not easily be broken for further side reaction. This might explain the higher EG selectivity catalyzed by DMIC than NaHCO₃, which attributes to the DMIC cation inhibition. Furthermore, there exists a balance between DMIC and DMIHC with HO-CO₂⁻ to be main active sites for EO activation. The difficulty in shifting the balance to DMIHC slows down the speed for the reaction. Compared with other 2-carboxylated imidazolium salts with longer chain lengths, DMIC has higher interior binding energy which is more difficult in bonding with H₂O molecules, therein the dragging effect inhibits the side reaction and leads to higher EG selectivity.

To further understand the side reaction process for two different mechanisms, the charges of different transition states, I in Mechanism B and D in Mechanism D, were obtained and analyzed. As shown in Fig. 6, for I, the H of the H_2O molecule swayed between itself and EG, causing a relatively high charge (-0.930) of the O compared to the charge (-0.823) of O in D. The exposed O of EG tended to attack the C atom of another EG, leading to a side reaction and formed the byproduct condensed glycol. Thus, considering the cation effect in catalytic performance, the Mechanism D is more reasonable to explain the DMIC-catalyzed process.

Above all, with EO hydration taken as an example, the possible reaction mechanism for the DMIC-catalyzed process is depicted as follows (Scheme 5). The CO_2^- in DMIC first transforms into HO- CO_2^- in the aqueous phase. With the synergistic effect of hydrogen bonding from IMC₂-H and nucleophilic



Fig. 6 The charge distribution of different transition states I and D in Mechanism B and Mechanism D.



Scheme 5 Proposed mechanism for EO hydration catalyzed by DMIC.

action from the $HO-CO_2^-$, the EO ring could be opened (TS-AB). The strong binding effect of interior DMIC causes the slower ion transforming step, which slows down the subsequent $HO-CO_2^-$ formation, C-O activation and hydration, which might exist temporarily as an interacted steric dynamic structure. Meanwhile, the IMC_2 -H and $HO-CO_2^-$ could stabilize the formed EG as a stabilizing structure of imidazolium-EG-HO- CO_2^- by a hydrogen-bonding effect (TS-CD), which also prevented the pre-formed EG molecule from contacting EO for excessive hydration into byproduct, so that the formed intermediate could go through an intramolecular condensation to produce EG and in the meantime released $HO-CO_2^-$. The $HO-CO_2^-$ then dehydrated to restore DMIC.

The whole reaction process was further confirmed by *in situ* FT-IR (500–3000 cm⁻¹), with propylene oxide (PO) as the model reactant. As shown in Fig. 7, the characteristic peaks of C–O, –OH, C=C, C=N and C=O were detected. The C–O peak and –OH peak might be respectively attributed to reactant PO and product propylene glycol (PG), which respectively showed a decreasing trend and increasing trend as the reaction proceeded. The C=C and C=N peaks might be attributed to imidazole of the catalyst DMIC, of which the peak intensity remains almost constant in the whole process. The C=O peak might be attributed to the CO₂⁻ of DMIC and the HO–CO₂⁻ of the catalyst intermediate DMIHC, of which the peak intensity



Fig. 7 In situ FT-IR spectra for PO hydration catalyzed by DMIC.

increases initially and then remains constant, together with ESI-MS (Fig. S4†) this explains the transformation process from CO_2^- to $HO-CO_2^-$.

Conclusions

Four kinds of 2-carboxylated imidazolium salts with different substituent chain lengths (C1-C4) were prepared. 1,3-Dimethylimidazolium-2-carbonate (DMIC) with the shortest substituent chain length was found to be the most efficient catalyst both in activity and selectivity. Both XPS analysis and DFT calculations proved that CO_2^- is the active site for EO activation and higher binding energy of its adjacent C-C bond of DMIC contributes to higher thermal stability and catalytic selectivity for EG. The catalytic mechanism was finally proposed that CO_2^{-} functions as the nucleophilic agent by reversibly forming HO-CO₂⁻ with water, which induced ring-opening of EO synergistically with a hydrogen-bonding effect from IMC₂-H. The high EG selectivity resulted from the huge steric dynamic structure and the stabilizing structure of imidazolium-EG-HO-CO2⁻, both of which avoid excessive hydration into byproducts. This work provides a new approach for EG selectivity improvement, which might be a good reference for effective product yield in the reaction involving intermediates.

Experimental section

Preparation of 2-carboxylated imidazolium salts

First of all, 5 g of *N*-methylimidazole and certain amounts of dimethyl carbonates (1.7 molar ratios of *N*-methylimidazole) were successively added to a 50 mL stainless-steel reactor. The reactor was sealed and stirred at 120 °C for 24 h. Thereafter, the reactor was cooled to room temperature and the mixture in the reactor was filtered. The filter cake was transferred into a beaker with methanol solution in the refrigerator below 0 °C. DMIC was obtained after drying the recrystallized white solid at 50 °C in the vacuum oven overnight. According to the above similar steps, a series of 2-carboxylated imidazolium salts with different chain lengths (DMIC, EMIC, PMIC, BMIC) were obtained (see ESI-MS in Fig. S1[†]).

1,3-Dimethylimidazolium-2-carboxylate (DMIC)

Synthesized by the reaction of 1-methylimidazole and dimethyl carbonate. ¹H NMR (600 MHz, D₂O) δ (ppm): 3.92 (s, 6H, N–CH₃), 7.63 (s, 2H, imidazole). ¹³C NMR (600 MHz, D₂O) δ (ppm): 35.68 (d, *N*-CH₃), 123.23 (dm, C4 and C5), 138.14 (s, C2), 163.42 (s, COO⁻).

1-Ethyl-3-methylimidazolium-2-carboxylate (EMIC)

Synthesized by the reaction of 1-ethylimidazole and dimethyl carbonate. ¹H NMR (600 MHz, D₂O) δ (ppm): 1.38 (t, 3H, CH₃), 3.775 (s, 3H, N–CH₃), 4.110 (m, 2H, N–CH₂), 7.30 (d, 1H, imidazole), 7.37 (d, 1H, imidazole). ¹³C NMR (600 MHz, D₂O) δ (ppm): 14.24, 35.61, 44.91, 124.78, 126.53, 134.26, 163.57.

1-Propyl-3-methylimidazolium-2-carboxylate (PMIC)

Synthesized by the reaction of 1-propylimidazole and dimethyl carbonate. ¹H NMR (600 MHz, D₂O) δ (ppm): 0.82 (t, 3H, CH₃), 1.80 (m, 2H, N–CH₂), 3.805 (s, 3H, N–CH₃), 4.06 (t, 2H, N–CH₂⁻), 7.34 (d, 1H, imidazole), 7.38 (d, 1H, imidazole). ¹³C NMR (600 MHz, D₂O) δ (ppm): 9.76, 22.78, 35.52, 51.01, 122.11, 123.40, 135.60, 163.50.

1-Butyl-3-methylimidazolium-2-carboxylate (BMIC)

Synthesized by the reaction of 1-butylimidazole and dimethyl carbonate. ¹H NMR (600 MHz, D₂O) δ (ppm): 0.82 (m, 3H, CH₃), 1.20 (m, 2H, CH₂), 1.72 (m, 2H, CH₂), 3.88 (s, 3H, N-CH₃), 4.31 (t, 2H, N-CH₂), 7.30 (d, 1H, imidazole), 7.35 (d, 1H, imidazole). ¹³C NMR (600 MHz, D₂O) δ (ppm): 12.60 (s, C-CH₃), 18.76 (s, CH₂), 31.83 (s, CH₂) 36.39 (s, *N*-CH₃), 49.30 (s, N-CH₂⁻), 121.71 (s, C4), 123.07 (s, C5), 139.96 (s, C2), 158.48 (s, COO⁻).

Characterization of all 2-carboxylated imidazolium salts

The chemical structures of the materials were analyzed by Fourier transform infrared (FTIR) spectroscopy (Thermo Nicolet 380) with anhydrous KBr as the standard. Elemental analysis (C/H/N) was conducted on a Vario EL Cube elemental analyzer. The analysis of active groups was performed on an X-ray photoelectron spectroscope (ESCALAB250Xi). ¹³C and ¹H NMR spectra were recorded on a Bruker Advance III HD 600 M NMR instrument. TG-DTA measurements were conducted on a DTG-60H thermal analyzer (Shimadzu, Japan) at a heating rate of 10 °C min⁻¹ under a N₂ atmosphere using an empty crucible as the reference. The molecular weight of the synthesized samples was verified using electrospray ionization mass spectrometry (ESI-MS, micrOTOF-Q II, Bruker, Germany). All reactant conversion and product selectivity were recorded and analyzed via a GC (Agilent 6820) with a TCD detector. The composition of the products was identified by using GC-MS (GCMS-QP2020).

Catalytic test of 2-carboxylated imidazolium salts

With EO as the model reactant, the hydration reaction was conducted under identical conditions using 2-carboxylated imidazolium salts as catalysts. The hydration reaction of EO and H_2O was carried out in a 25 ml stainless steel reactor equipped with a magnetic stirrer and an automatic temperature control system. First the reactor was filled with 1 mL of EO and certain amounts of catalysts at room temperature, and then charged with N_2 to target pressure from a high-pressure reservoir tank before being heated. After that, the reactor was heated to the target temperature and maintained at this constant pressure for a desired period. When the reaction was over, the reactor was cooled down to room temperature and the N_2 was released slowly. The organic products were analyzed by GC-MS and GC.

Conflicts of interest

There are no conflicts to declare.

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