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FULL PAPER



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Synthesis of 2, 2, 4-trimethyl-1, 3-pentaerediol monoisobutyrate catalyzed by homogeneous catalysisliquid/liquid separation catalytic system based on Bibasic sites Ionic Liquids

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1 | INTRODUCTION

2, 2, 4-trimethyl-1, 3-pentaerediol monoisobutyrate (CS-12) is a major environmental friendly green filming aid for latex paint. However, preparation of CS-12 is mostly achieved through conventional basics-catalyzed reaction processes, presenting various disadvantages, such as heterogeneous reaction, poor recyclability, hardly separation

Herein a novel homogeneous catalysis-liquid/liquid separation catalytic system based on 1, 8-diazabicyclo-[5.4.0] undec-7-ene (DBU)-functionalized, 1, 1, 3, 3-tetramethyl guanidine-functionalized and imidazolium-functionalized bibasic sites ionic liquids (BSILs) ([HDBU]IM, [Aemim]IM, [TMG]IM, [Aemim] Pro, [Aemim]Gly, [HDBU]Pro and [HDBU]Gly) with a room temperature liquid/liquid phase transition characteristic were reported. And for the first time, this novel catalytic system was employed for the synthesis of 2, 2, 4-trimethyl-1, 3-pentaerediol monoisobutyrate (CS-12), achieving homogeneous catalysis, easy recycling and long service-life of the catalyst. Additionally, the mechanism of homogeneous catalysis-biphasic separation might be explained by the solubility of reactant and product in BSILs/H₂O catalytic system and the existence H-bonding between BSILs and H₂O. Bibasic sites were confirmed by two endothermic peaks on the TG-DCS curve of [Aemim]IMC (the CO₂ captured by [Aemim]IM).

K E Y W O R D S

catalyst recycling, CS-12, homogeneous catalysis, ionic liquids, separation

and corrosion for equipment.^[1,2] Therefore, it is hoped that a process, which is greener, could be explored.

In recent years, ionic liquids (ILs) have been the focus of significant amount of research owing to their "green" pedigree, negligible vapor pressure and tunability, also excellent separation ability, recyclability and simple reaction process.^[3–5] More recently, we reported a kind DBU-functionalized monbasic site ionic liquids (MSILs) with a room temperature ILs/H₂O-IBD phase transition

characteristic.^[6,7] The MSILs catalyst system can be recycled for 5 times, and the yield of CS-12 is 66.17%.^{[[8]} This has been touched on to provide potential insights for higher alkaline density and structural strength bibasic sites ionic liquid (BSILs) by modification of cations and anions to bind specific functional group.

In this study, BSILs (that is, [HDBU]IM, [Aemim]IM, [TMG]IM, [Aemim]Pro, [Aemim]Gly, [HDBU]Pro and [HDBU]Gly) with a room temperature liquid/liquid phase transition characteristics have been synthesized and have been applied in homogeneous catalysis-and liquid/liquid effective separation system. In this system, the catalytic reaction is performed in a homogeneous aqueous solution,^[9] and after reaction the produced CS-12 can be easily separated by a simple phase separation from BSILs/H₂O system. The separated BSILs/H₂O system possessed the recyclability at least 14 times with no obviously decrease of yield. The advantages of homogeneous and biphasic catalysis herein were combined perfectly with the high selectivity, easy separation and long service-life of catalyst. The results of related characterization show that BSILs synthesized have good thermal stability, high purity and strong alkalinity. Besides, DFT is applied to calculate electrostatic and covalent interaction of jons of BSILs.^[10] The calculated alkaline sequence is good consistent with the experimental results. [Aemim] IM, as the model catalyst for preparation of CS-12, appears yield of 72.2%. The miscibility with reaction substrates/products and solubility in various solvents were determined. Water as solution was mainly because of its relatively polar, strong ionic interactions and internal pressure effects (H-bonding) with BSILs.^[11-14] Bibasic sites were confirmed by two endothermic peaks on the TG-DCS curve of [Aemim]IMC.^[15-17]

2 | EXPERIMENTAL

2.1 | Monomer synthesis

Synthesis of 1-(1-aminoethyl)-3-methylimidazolium imidazolide ([Aemim]IM).

100 ml flask was charged with 8.22 g (0.1 mol) 1-methylimidazole, 20.48 g (0.1 mol) 2-Bromoethylamine hydrobromide and 30 ml absolute ethanol under nitrogen atmosphere. The mixture was stirred at 78 °C for 24 hr and filtered. Then the filtrate was evaporated under reduced pressure to give a yellow viscous liquid 1-(1-aminoethyl)-3-methylimidazolium bromide ([Aemim]Br). 50 ml beaker was charged with 6.80 g (0.1 mol) imidazole, 4.00 g (0.1 mol) NaOH and 15 ml methanol under vigorous stirring at 25 °C for 0.5 hr to obtain a milky white liquid sodium imidazole (NaIM). Then 10.30 g (0.05 mol) ([Aemim]Br, 4.50 g (0.05 mol) imidazole sodium (NaIM) and 15 ml methanol were added into a 100 ml flask under vigorous at 25 $^{\circ}$ C for 20 hr and filtered. The filtrate was evaporated under reduced pressure to give the colorless and transparent liquid [Aemim]IM (Scheme 1).

2.2 | Synthesis of 8-hydrogen-1, 8-diazabicyclo-[5.4.0]-undec-7-enium imidazolide ([HDBU]IM)

6.80 g (0.1 mol) imidazole was divided into several parts and added into a mixture of 15.22 g (0.1 mol) DBU and 15 ml absolute ethanol in batches in a 100 ml flask under vigorous stirring at 25 °C for 24 hr and evaporated to give a dark yellow transparent liquid [HDBU]IM (Scheme 2)

The synthesis of 1-aminoethyl-3-methylimidazolium glycinate ([Aemim]Gly) (Scheme S1) and 1-aminoethyl-3-methylimidazolium prolinate ([Aemim]Pro) (Scheme S2) are the same as that of [Aemim]IM. 8-hydrogen-1,-8-diazabicyclo-[5,4,0]-undec-7-enium prolinate ([HDBU] Pro) (Scheme S3), 8-hydrogen-1,8-diazabicyclo-[5,4,0]-undec-7-enium glycinate ([HDBU]Gly) (Scheme S4) and 1, 1, 3, 3-tetramethylguanidine imidazolide ([TMG]IM) (Scheme S5) are synthesized as the same as [HDBU]IM. And, chemical structures of seven BSILs are listed in Figure 1.

3 | **RESULTS AND DISCUSSION**

3.1 | Chemical structures and thermal properties

FT-IR and TG spectra of BSILs were shown in Figure 2. From Figure 2A, B and C, there was an obvious peak around 1,431–1,481, 1,316–1,395 and 1,058 cm⁻¹; 1,434–1,495, 1,315–1,432 and 1,154 cm⁻¹; 1,412–1,472, 1,298–1,403 and 1,058 cm⁻¹ in the spectrum of all ILs due to typical characteristic peak of C=C, C=N and C-N species in Imidazole ring, respectively.^[18] Accordingly, the peak in the range of 2,809–3,161, 2,994–3,100 and



SCHEME 1 Synthesis process and molecular structure of [Aemim]IM



SCHEME 2 Synthesis process and molecular structure of [HDBU]IM and [TMG]IM

2,842–2,948 cm⁻¹ was attributed to the stretching vibration of saturated and unsaturated C-H respectively. There were some obvious peaks at 1575, 1625 and 1,589 cm⁻¹ (Figure 2(A)a, b and c). It was the typical characteristic peaks of C=N in imidazole, DBU and TMG units respectively. The peak absorption band at *ca*. 2149 cm⁻¹ (Figure 2(A)c) was the typical characteristic peak of C-N in TMG units. The broad peak absorption band at *ca*. 3425 and 3,419 cm⁻¹ (Figure 2(B)b, c and 2(C)a, c) proved the existence of carboxyl groups.^[19] There was an obvious peak around 1,610 cm⁻¹ in the spectrum of DBU cation group (Figure 2(C)), due to typical characteristic peak of C=N species in DBU ring.

On the basis of FT-IR and ¹H NMR results (Figure S1), it could be found that BSILs were synthesized successfully.

Thermal behavior of BSILs was studied using TG methods. Figure 2D, E and F show [HDBU]IM, [Aemim] Pro, [HDBU]Pro exhibit excellent thermal stability. Correspondingly, the onset temperature is 95, 103 and 104 $^{\circ}$ C, respectively. Structural change could lead to

change in thermal stability, which is related to the interaction between heteroatom-carbon atoms and heteroatom-hydrogen-bonding.^[20] The sequence of thermal stability of cations and anions is as follows: $[HDBU]^+ > [Aemim]^+ > [TMG]^+$ and $Pro^- > im^- > Gly^-$.

3.2 | Alkalinity

The value of pK_b can be calculated by using *Equation* 1. pOH = 14-pH and C₀ is the concentration of ILs solution.^[21]

$$pK_{b} = lg \left[\frac{C_{0} - 10^{-pOH}}{\left(10^{-pOH} \right)^{2}} \right]$$
(1)

The value of pK_{b} is inversely proportional to alkalinity. Table 1 illustrates that BSILs possess strong alkalinity. The basic strength of three categories BSILs was in the sequence as follows: [HDBU]IM > [TMG] IM > [Aemim]IM, [HDBU]Pro> [HDBU]Gly > [HDBU] IM and [Aemim]Pro> [Aemim]Gly > [Aemim]IM. When the anions are the same, [HDBU]IM shows the highest alkalinity. This is attributed to the larger volume of the cation, which weakens the Coulomb force between anion and cation. When the cations are the same, [Aemim]Pro and [Aemim]Gly exhibit highest alkalinity. Because aliphatic compounds are more alkaline than aromatic compounds.^[22] So the Im⁻, Pro⁻ and Gly⁻ anion moiety of the synthesized ILs are easy to disperse in aqueous.



FIGURE 1 3D structures of BSILs:
(a) [Aemim]IM, (b) [HDBU]IM,
(c) [TMG]IM, (d) [HDBU]Gly,
(e) [HDBU]Pro, (f) [Aemim]Pro,
(g) [Aemim]Gly (Blue, gray, white, red atom represented nitrogen, carbon, hydrogen and oxygen, respectively).b



FIGURE 2 FT-IR and TG curves of BSILs: ((A), (D)) imidazole anion group, ((B), (E)) imidazole cation group and ((C), (F)) DBU cation group

3.3 | Density functional theory (DFT) calculations

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Energy calculations and structural optimization of BSILs were calculated by density functional theory (DFT) in the Gaussian 09 program. All-electron basis of Pople was 6-31G (++, d, p).^[23] Pyrrole, as a probe molecule, was an amphoteric substance, which can interact with Lewis base center. As a proton receptor, the base center can directly interact with hydrogen on Pyrrole N-H bond. At the microscopic level, electrostatic interaction and covalent interactions are the key factors in analysis of alkalinity between BSILs and pyrrole, an effective guide to explain and predict the electrostatic reaction ability (electron transfer ability) of molecules is the most-negative-surface electrostatic potential (Vs, min) and the lowest surface average local ionization energy (Is, _{min}) of the investigated molecule.

The simulation results of V_{s, min} and I_{s, min} of BSILs are shown in the Figure 3 and Figure S2, S3, S4, S5, S6 and S7. The V_{s, min} and I_{s, min} value are cleanly exhibited in Table 2.

TABLE 1 pK_b value of BSILs

BSILs	concentration	pН	pK _b
[Aemim]IM	0.01	12.03	2.18
[HDBU]IM	0.01	12.20	1.43
[TMG]IM	0.01	12.15	1.53
[HDBU]Pro	0.01	12.49	1.17
[HDBU]Gly	0.01	12.31	1.29
[Aemim]Pro	0.01	12.25	1.36
[Aemim]Gly	0.01	12.17	1.49

Generally, three categories BSILs of imidazolium anionbased, imidazolium cation-based and DBU cation-based composed of various anions are good consistent with the expectation. It can be seen that the alkalinity of three kinds of BSILs are very strong, and the order of absolute values of $V_{s, \min}$ as well as $I_{s, \min}$ is $[HDBU]^+ > [TMG]^+ > [Aemim]^+$, $[Pro]^- > [Gly]^- > [Im]^-$, respectively.

3.4 | Purity

The ILs were analyzed by element analyzer, and the elemental analysis measured values are shown in Table 3. The result shows that the elemental analysis measured values are in close proximity to the calculated values, illustrating high purity of BSILs.

3.5 | Solubility

Solubilities of BSILs in various solvents of different polarity were studied and listed in Table 4. The results adhere to the principle of similar compatibility.^[24] By comparing the yields of different BSILs in diverse solvents under the same conditions, water is selected as the reaction solvent.

3.6 | Cloud point

The cloud point of BSILs was clarified in Table 5. That is when they reach a certain temperature, stratification occurs, which proves that BSILs are thermoregulated.^[25]



FIGURE 3 The optimized geometries with corresponding electrostatic potential at the isodensity contour (0.004 electrons/bohr3) surface of the reactants, and in color ranges of -158 (red) through 0.0 (green) to157 (blue) (unit: kJ/mol) and -5.82 (red) through 0.0 (green) to 5.82 (blue) (unit: eV) respectively. a cyan hemisphere was used to denoted The position of Vs,min and Is, min for an imidazole anion group. The Vs, min and Is, min value for [Aemim] + and IM- is demonstrated in the column graph, in kJ/mol and eV

 $\textbf{TABLE 2} \quad V_{s, \ min} \ and \ I_{s, \ min} \ of \ various \ cation \ and \ anion \ of \ BSILs \ with \ pyrrole$

Ions	[Aemim] ⁺	[HDBU] ⁺	[TMG] ⁺	IM ⁻	Gly ⁻	Pro ⁻
V _{s, min}	604	642	573	433	491	606
I _{s, min}	6.26	6.45	5.93	4.49	5.09	6.28

TABLE 3 Elemental analysis data of BSILs

		Measured value (calculated value)/%		
BSILs	Molecular formula	с	Н	N
[Aemim]IM	$C_9H_{15}N_5$	55.96(55.83)	7.77(7.61)	36.27(36.13)
[HDBU]IM	$C_{12}H_{19}N_4$	65.75(65.57)	8.68(8.59)	25.57(25.41)
[TMG]IM	$C_8H_{16}N_5$	52.75(52.58)	8.79(8.60)	38.46(38.32)
[HDBU]Pro	$C_{14}H_{24}N_3O_2$	63.16(63.08)	9.02(8.96)	15.79(15.60)
[HDBU]Gly	$C_{11}H_{20}N_3O_2$	58.41(58.29)	8.85(8.74)	18.58(18.42)
[Aemim]Pro	$C_{11}H_{20}N_4O_2$	55.00(54.82)	8.33(8.21)	23.33(23.21)
[Aemim]Gly	$C_8H_{16}N_4O_2$	48.00(47.88)	8.00(7.89)	28.00(27.93)

TABLE 4 Solu	ubility of in common	organic solvents
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BSILs	H ₂ O	МеОН	EtOH	$C_{6}H_{12}$	C ₇ H ₈	$\mathrm{CH}_2\mathrm{Cl}_2$
[Aemim]IM	\checkmark	\checkmark	\checkmark	×	×	
[HDBU]IM	\checkmark	\checkmark	\checkmark	×	×	\checkmark
[TMG]IM	\checkmark	\checkmark	\checkmark	×	×	\checkmark
[HDBU]Pro	\checkmark	\checkmark	\checkmark	×	×	\checkmark
[HDBU]Gly	\checkmark	\checkmark	\checkmark	×	×	\checkmark
[Aemim] Pro	\checkmark	\checkmark	\checkmark	×	×	\checkmark
[Aemim] Gly	\checkmark	\checkmark	\checkmark	×	×	\checkmark

 $\sqrt{}$: mutual dissolution. \times : immiscible.

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3.7 | Catalytic performances

Table 6 and Figure 4 show the effect of different BSILs on the synthesis of CS-12. [Aemim]IM is selected as the catalyst model due to its highest yield of 72.2%. The selectivity is approximately 12% higher that of ILs with monobasic site.

3.8 | Bibasic sites

The morphology of [Aemim]IM before and after CO_2 absorption was shown in Figure S8. The stability of [Aemim]IM and [Aemim]IMC was studied by TG-DSC.

As shown in Figure 5, the endothermic peak begins at a very low temperature, which could be attributed to the absorption of some moisture by carbamate during the experiment. The endothermic peaks at around 80 and 100 °C attributed to the decomposition of [Aemim]IMC with CO_2 liberation, indicating that BSILs has two basic sites. The last two endothermic peaks show that volatilization of [Aemim]IM appears at around 125 and 190 °C.

On the basis of previous reports and observed experimental data, a tentative mechanism of CO_2 -[Aemim]IM systems (Figure 6) was established. CO_2 could be trapped into the BSILs by reaction with aqueous to produce bicarbonate species.^[26–28] The anion/cation-CO₂ interaction can be described as a Lewis acid–base reaction, correspondingly. As the basicity of anion/cation increases, the interaction becomes stronger.^[29–32]

3.9 | Thermoregulated phase-transfer mechanism

[Aemim]IM was selected as a model catalyst for studying the density and concentration of [Aemim]IM, H₂O and {[Aemim]IM (1) + H₂O (2)} system (Table S1). Thereby, the physical parameters (*e.g.*, viscosity deviation $\Delta \eta$,

TABLE 5 Cloud point of BSILs in aqueous solution

BSILs	Solvent	RT	MT/°C
[Aemim]IM	H_2O	Homogeneous phase	33
[HDBU]IM	H_2O	Homogeneous phase	37
[TMG]IM	H_2O	Homogeneous phase	36
[HDBU]Pro	H_2O	Homogeneous phase	45
[HDBU]Gly	H_2O	Homogeneous phase	42
[Aemim]Pro	H_2O	Homogeneous phase	39
[Aemim]Gly	H_2O	Homogeneous phase	35

(RT: room temperature, MT: miscibility temperature, 1.0 g BSILs, $10 \text{ ml H}_2\text{O}$)

TABLE 6 Effect of BSILs on conversion, selectivity and yield

BSILs	Conversion rate /%	Selectivity/ %	Yield/ %
[Aemim]IM	83.8	86.2	72.2
[HDBU]IM	80.8	82.1	66.3
[TMG]IM	80.2	81.4	65.4
[HDBU]Pro	81.4	82.7	67.3
[HDBU]Gly	78.8	79.3	62.5
[Aemim] Pro	79.1	82.2	65.0
[Aemim] Gly	78.1	81.3	63.5

(60 °C, 500 r/min, 10.0 g IBD, 1.0 g BSILs, 10 ml H_2O)

excess molar volume V^E , excess Gibbs energy ΔG^{*E} and Gibbs energy ΔG^*) of {[Aemim]IM (1) + H₂O (2)} system were calculated (Table S2). These parameters could reflect the structural differences and intermolecular forces between the actual liquid mixture and the ideal liquid mixture. The existence and strength of hydrogen bonds could be explained. The specific calculation method is as follows.

Based on the composition dependence of density, V^E could be calculated by the following formula:

$$V^{E} = \frac{x_{1}M_{1} + x_{2}M_{2}}{\rho} - \left(\frac{x_{1}M_{1}}{\rho_{1}} + \frac{x_{2}M_{2}}{\rho_{2}}\right)$$

 x_1 and x_2 are the mole fractions of components 1 and 2; The M_1 and M_2 are the molar mass of components 1 and 2; ρ_1 , ρ_2 and ρ are the densities of pure components 1, 2, and their mixtures, respectively.

 $\Delta \eta$ of binary mixtures could be calculated by the following formula from the experimental viscosity:

 η_1 , η_2 and η are the viscosity of pure components 1, 2, and their mixtures, respectively.

According to the theory of absolute reaction rate, $\triangle G^*$ and $\triangle G^{*E}$ could be calculated by the following equations:^[33]

$$\Delta G^* = RT\Pi\left(\frac{\eta V}{hN_A}\right) \bigtriangleup G^{*E} = RT\left[\Pi\left(\frac{\eta V}{V_2^0 \eta_2}\right) - x_1\Pi\left(\frac{\eta_1 V_1^0}{\eta_2 V_2^0}\right)\right]$$

V is the molar volume of the binary mixture; h, R, and N_A are the Plank's constant, gas constant and Avogadro's number, respectively. V0 1 and V0 2 are the molar volume of pure components 1 and 2, respectively.







FIGURE 5 The DSC curve of [Aemim]IM and [Aemim]IMC

The V^E values of studied system indicate negative deviation in the whole mole fraction range seen in Figure 7(a), due to the strong H-bonding interactions between BSILs and aqueous. Generally, the H-bonding decreases with the increase of temperature, which leads to the V^E values of the mixture being less negative. Also, it can be seen that the η values of researched system increase firstly and then decrease and reach maximum value at $x_1 = 0.4$, demonstrating that BSILs and aqueous are apt to form H-bonding interactions (Figure S9).^[34] Besides, $\Delta \eta$ values show that the H-bonding interactions between BSILs and aqueous are dominated (Figure 7(b)). Theoretically, the entropy which reflected by viscosity is related to the liquid's structure. Thus, the change at value of $\Delta \eta$ can be explained by the competition between Hbonding and Vander Waals interactions in mixtures containing a molecular solvent and an ionic species. And, the formation of the H-bonding interactions between the BSILs and aqueous was indicated by the positive ΔG^{*E} values in the entire composition (Figure 7(c) and 7(d)). All data indicate that H-bonding exist between [Aemim] IM and H₂O.

3.10 | Separation and recycling

Excellently, thermoregulated phase-transfer were achieved by utilizing the characteristic of H-bonding controlled BSILs/H₂O separation of BSILs (Figure 8).^[35] Thermoregulated performance and miscibility with reaction and products were shown in Figure S10. The immiscibility at room temperature could ensure that the product CS-12 could be separated naturally from the BSILs/H₂O. The separation mechanism of catalyst is the same as that of aqueous/catalyst-organic biphasic catalysis systems, such as aqueous/nanometer Rhodium-1-butanol and aqueous/ $(p-C_6H_4(C_2H_4)_5OH)_3$ -styrene.^[36] Homogeneous catalysis-liquid/liquid separation catalytic system is the reverse temperature-aqueous solubility property of the nonionic surfactant (cloud point), which is the breaking and recovery of H-bonding by temperature change.^[37-39] The cations and anions provided both



FIGURE 6 Mechanistic picture of CO2-[Aemim]IM systems

FIGURE 7 Process simulation of synthesis of alcohol 12 in BSILs catalytic system



the basic site responsible for the high activity in the synthesis of CS-12 and the static interaction with H_2O lead to temperature responsive characteristics, which was responsible for the BSILs-organic phase transformation and separation. Once the anion is in the organic phase, it has very little hydration or solvation associated with it. The reaction process was indicated in Figure 9a. At the beginning of the reaction, IBD and [Aemim]IM/H₂O are heterogeneous (Figure S11a). At reaction temperature, IBD was dissolved in the [Aemim]IM, [Aemim]IM and IBD formed a homogeneous system (Figure S11b). With the temperature decreased, the produced CS-12 was on the top of the resulting mixture, and the [Aemim] IM/H_2O gradually sank to the bottom (Figure S11c). Immediately, a simple phase separation is sufficient for isolating CS-12 from BSILs/H₂O.^[39,40] There are almost no any significant decrease in yield for introducing IBD into the separated [Aemim]IM/H₂O for recycling up to



FIGURE 10 Proposed mechanism of synthesis of CS-12 catalyzed by [Aemim]IM

14 times (Figure 9b). 9 cycles times of ILs with monobasic site, and the IR spectrum for the recycled catalyst was well consistent with the fresh catalyst (Figure S12), demonstrate that BSILs have good stability.

4 | PRODUCT ANALYSIS AND THE MECHANISM

4.1 | Product analysis

Mass spectrometric analysis was performed on the obtained CS-12 without purification. According to peak time, the product CS-12 and minor by-products are shown in Figure S13 respectively. The by-products can be

purified and used for other industrial purposes. The characteristic peak of CS-12 is completely consistent with the standard spectrum. Its molecular formula is $C_{12}H_{24}O_3$ and molecular mass is 216,^[41] confirming the successful synthesis of CS-12. Products can be further purified by vacuum distillation.

4.2 | The mechanism for synthesis of CS-12

It takes aldol condensation, cannizzaro reaction and esterification three steps on synthesis of CS-12.^[42] The proposed mechanism of synthesis of CS-12 catalyzed by [Aemim]IM is demonstrated in Figure 10. As an organic

catalyst, imidazole anion involves the corresponding intermediate changes of imide salt receptors. Besides, the double basic site of the cation with amino group interacts with imidazole anion under the basic condition. Firstly, when imidazole anion contacts with active methylene, carbon anion intermediate is formed, and the condensation product is obtained by nucleophilic addition reaction. Then, the electrophilic addition reaction between imidazole anion and aldehyde group yielded Canizalo intermediate, and the redox reaction with condensation product under the action of alkali yielded Canizalo product. Finally, Canizalo product was esterified to produce CS-12.^[43] Particularly, BSILs can not only be recycled in each step of the reaction, but also act as both basic catalyst and phase-transfer catalyst.

5 | CONCLUSION

For the first time, a series of the functionalized thermoregulated phase-transfer bibasic sites ionic liquids catalysts (e.g., [HDBU]IM, [Aemim]IM, [TMG]IM, [Aemim]Pro, [Aemim]Gly, [HDBU]Pro and [HDBU]Gly) were synthesized successfully and applied in the synthesis of CS-12 at homogeneous catalysis-liquid/liquid separation system (BSILs/H2O-IBD). Remarkably, after simple phase separation, the separated BSILs/H₂O catalytic system was used in next catalytic reaction for at least 14 times without noticeable drop in yield. [Aemim]IM, selected as the model catalyst, exhibited high yield of 72.2%. Bibasic sites in BSILs were explicated by two endothermic peaks on the TG-DCS curve of [Aemim]IMC. The H-bonding between [Aemim]IM and water, the immiscibility at room temperature could thus assist the synthesize CS-12 reaction to ensure "low temperature phase separation, high temperature homogeneity". The strategy conceived in this work opens the avenue to achieve recycling of catalyst systems and highly efficient separation of products and catalysis.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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