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PAPER

Lactic acid production from glucose over polymer catalysts in aqueous alkaline solution under mild conditions

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Methods for the transformation of carbohydrates into lactic acid (LA), which is an versatile platform chemical, have been widely investigated. These methods typically employ harsh reaction conditions, especially when water is used as a solvent. In the present study, a one-pot route that uses polymerizates of imidazole and epichlorohydrin ([IMEP]Cl) as catalysts to convert glucose to LA in water was described.
10 The highest LA yield of 63% (mol %) was achieved with 99% glucose conversion at 100 ℃ in 50 mM NaOH solution. Compared to the previous reports, the process has lower reaction temperatures and lower concentration of alkaline. A possible reaction mechanism was proposed that the coordination between the weak Lewis acid centers of the polymer with the electronegative oxygens on the intermediates efficiently facilitated the rate determining step during the reaction. This route allows for facile catalyst recovery and
15 recycling while providing a new strategy for carbohydrate conversion.

1. Introduction

Because the dependence on fossil fuels for energy and chemicals has become unsustainable, the search for a sustainable supply of abundant and renewable fuels and chemicals is critical. Biomass
20 resources could meet these demands of the future.[1-3] Glucose is the monomer unit of cellulose in biomass and may serve as a sustainable resource in the future as biomass is increasing utilized for renewable fuels and chemicals.[4] Lactic acid (LA) is a high value product derived from glucose. LA is a versatile commodity
25 chemical with various applications, including those in the food, cosmetics and pharmaceutical industries. Most importantly, LA has recently received attention as a material used for preparing biodegradable polymers with a low environmental impact.[2, 5] Consequently, the efficient and environmentally responsible
30 production of LA from abundant and cheap glucose has recently received considerable attention.[6]

Presently, the major process used to produce lactic acid is the fermentation of glucose derived from starch or cellulose-containing material via hydrolysis by using genetically modified
35 enzymes.[1, 7] However, this biotechnological process has some disadvantages, such as a limited space-time yield, the need for control over the fermentation conditions in the reactor (temperature and pH), high waste production and population control regulations for the microorganisms. Therefore, novel
40 chemo-catalytic methods that directly convert sugars into LA have recently attracted additional attention. Utilizing environmentally benign solvents in chemical reactions is one of the most interesting areas in green chemistry.[8] Water is a desirable solvent for chemical reactions because it is abundant,
45 readily available, inexpensive, non-toxic and non-flammable; in addition, various organic reactions have demonstrated improved reactivity and selectivity in aqueous solutions.[9] Bicker et al.[10]

reported the catalytic effects of Ni⁻, Co⁻ and $ZnSO_4$ during the conversion of a 1 wt% glucose aqueous solution in subcritical
50 flowing water at 300 ℃ and 25 MPa, generating LA in an approximate 40% yield. A 23.6% yield of LA from glucose at 300 ℃ while using 0.75 M NaOH was obtained by Kishida et al.[11] Yan et al.[12, 13] studied the effect of alkali at 300 ℃ during the conversion of glucose in a batch reactor, observing a
55 maximum yield of 27% for the LA while using 2.5 M NaOH. Heeres et al.[14] studied the conversion of D-glucose in water under the action of various metal salts at 140 ℃ for 6 h, but LA yields were below 20% (for $AlCl_3$). Esposito et al.[15] reported the use of barium hydroxide as the base, affording LA in yields up to 57%
60 at 250 ℃ under hydrothermal conditions. Wang et al. used copper oxide combined with 1 M NaOH to convert glucose in a continuous flow reactor, achieving a selective production of LA with the highest yield of 59% and acetic acid with the highest yield of 32% at 188 ℃ in 0.15 min.[16] Almost all of these
65 hydrothermal methods involve either high reaction temperatures or concentration of alkaline, limiting potential industrial applications.

In order to overcome these challenges, new strategies have been proposed. Onda et al.[17] converted glucose to LA in less than
70 20% yield while using activated hydrotalcites in a NaOH solution. Subsequently, a one-pot reaction using supported metal catalysts in alkaline media resulting in 45% LA yield was reported by Onda and co-workers.[18] Epane et al. presented a microwave-assisted conversion of glucose into LA with an optimum yield of
75 75% using alumina supported potassium hydroxide in a solvent-free process.[19] Holm et al.[20] and de Clippel et al.[21] reported that Sn(IV)-beta and Sn(IV) grafted on a mesoporous carbon-silica composite could catalyze the conversion of carbohydrates into LA in water. However, zeolites and related materials suffer from

hydrothermal instability in aqueous systems. Recent reports have revealed that dilute lead(II) ions could catalyze the conversion of carbohydrates in water at 190 ℃, yielding 71% LA for the conversion of glucose.[22] Although this method seemed promising, waste water with lead(II) ions after reaction could be hazardous to the environment. Consequently, an efficient and economical system is urgently needed.

Polymerizates of imidazole and epichlorohydrin (referred as [IMEP]Cl hereafter) have very good solubility in water and have become one of the benchmarks for current developments in chemistry regarding leveler additives in the industrial copper damascene process.[23] [IMEP]Cl possess many cationic imidazole groups that can behave as weak Lewis acid sites, according to Howarth et al.;[24] the presence of Lewis acid sites is important during the production of LA when chemical methods are used.[21] [IMEP]Cl have been used catalytically during the conversion of glucose to LA under the alkaline condition in the present study. The effects of varying the bases, anions, NaOH concentrations, [IMEP]Cl loading, temperature and atmosphere were investigated in detail. In addition, a possible reaction mechanism for the conversion of glucose to LA has been proposed. Finally, several kinetic parameters for the reaction were obtained.

2. Experimental section

2.1. Materials

Imidazole (99%), epichlorohydrin (99.5+%), ethanol (99.8+%), pyruvic aldehyde (32%), lithium perchlorate (95+%), potassium acetate (99+%) and sodium benzoate (99%) were purchased from Aladdin Chemistry Reagent Company (Shanghai, China). Sodium hydroxide (AR), potassium hydroxide (AR), acetone (99%), sodium hexafluorophosphate (98%), sodium tetrafluoroborate (98%), 1,3-dihydroxyacetone (DHA, 98%), D-glucose, D-fructose, D-mannose, D-galactose and D-xylose were purchased from J&K Scientific Ltd. (Beijing, China). A 1.0 N standardized LA solution (Alfa Aesar Company) was used during the quantitative analysis of LA. All reagents were used as received.

2.2. Catalysts preparation

[IMEP]Cl have been synthesized using a procedure similar to that provided by Eckles & Starinshak[25] and Rogers & Woehst[26] (see Scheme 1). In a typical procedure, a 1 L flame-dried round bottom flask equipped with a Teflon coated magnetic stir bar, reflux condenser and glass stopper was charged with 1 mol of imidazole and 300 mL ethanol. While stirring vigorously under room temperature, 1 mol of epichlorohydrin was added to the solution dropwise. Then, the mixture was heated up step wisely to 85 ℃ and refluxed for at least one week. The resultant precipitate was isolated by vacuum filtration and subjected to at least three ethanol wash/filtration cycles. After drying under vacuum, [IMEP]Cl were obtained as a white powder. A prolonged synthesis time (one week) enabled the polymer to form a longer chain with a high molecular weight of 6.611×10^6 g mol^{-1} (PD =1.002). ^{1}H NMR (D$_2$O, 600 MHz) δ: 4.23 (t, J=10.2 Hz, 2H), 4.36 (s, 1H), 4.53 (d, J=13.8 Hz, 2H), 7.56 (s, 2H); ^{13}C NMR (D$_2$O, 150MHz) δ: 50.78, 68.56, 121.98, 146.15; IR (KBr) ν: 3414, 3143, 3104, 2947, 2856, 1564, 1445 cm^{-1}. TGA (see Figure S1 of the supporting information): The polymer is thermally stable at temperatures up to 300℃.
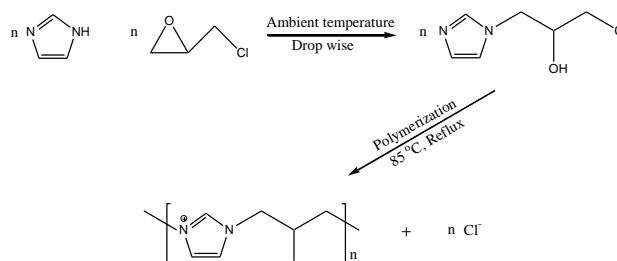
Scheme 1 Reaction scheme indicating the synthesis of [IMEP]Cl

Different types of IMEP-based catalysts were synthesized using ion-exchange process analogous to that provided by Smith et al.[27] In a typical procedure, 5 mL of a ethanol containing 1.60 mmol of [IMEP]Cl was added to a centrifuge tube, to which a 4 M excess of a ethanol solution of a perchlorate, acetate, hexafluorophosphate or benzoate salt was added. The solution was shaken vigorously. The precipitate was isolated by centrifugation and subjected to at least three ethanol wash/centrifugation cycles prior to drying in a vacuum drying oven. **[IMEP]ClO$_4$.** ^{1}H NMR (600 MHz, D$_2$O) δ: 4.21 (t, J= 10.55 Hz, 2H), 4.33 (s, 1H), 4.49 (d, J=14.1 Hz, 2H), 7.53 (s, 2H); ^{13}C NMR (151MHz, D$_2$O) δ: 52.10, 68.09, 123.18, 138.24; IR (ATR) ν: 3464, 3154, 3121, 2973, 2895, 1565, 1447 cm^{-1}. **[IMEP]Ac.** ^{1}H NMR (600 MHz, D$_2$O) δ: 4.27 (t, J=9.94 Hz, 2H), 4.40 (s, 1H), 4.58 (d, J=14.1 Hz, 2H), 7.61 (s, 2H); ^{13}C NMR (151MHz, D$_2$O) δ: 52.18, 68.17, 123.25, 136.72; IR (KBr) ν: 3442, 3148, 3112, 2862, 2747, 1564, 1412 cm^{-1}. **[IMEP]PF$_6$.** ^{1}H NMR (600 MHz, D$_2$O) δ: 4.22 (t, J=11.4 Hz, 2H), 4.34 (s, 1H), 4.50 (d, J=15.2 Hz, 2H), 7.56 (s, 2H); ^{13}C NMR (151MHz, D$_2$O) δ: 51.62, 68.50, 122.53, 136.14; IR (KBr) ν: 3427, 3156, 3104, 2958, 2851, 1564, 1446 cm^{-1}. **[IMEP]PhCOO.** ^{1}H NMR (600 MHz, D$_2$O) δ: 4.01 (t, J=8.3 Hz, 2H), 4.15 (s, 1H), 4.30 (d, J=14.3 Hz, 2H), 7.35 (s, 2H); ^{13}C NMR (151MHz, D$_2$O) δ: 51.99, 67.91, 123.02, 136.27; IR (KBr) ν: 3424, 3143, 3087, 2863, 2740, 1552, 1410 cm^{-1}. [IMEP]BF$_4$ were synthesized according to Branco et al.[28] [IMEP]Cl (3.20 g, 0.02 mol) were transferred to a 100 mL flask. Acetone (30 mL) was added followed by NaBF$_4$ (2.46 g, 0.022 mol). This mixture was stirred at room temperature for 24 h. The resulting solid precipitate was collected by vacuum filtration and washed with acetone (3×50 mL). The product was then dried in a vacuum drying oven at 50 ℃ overnight. **[IMEP]BF$_4$.** ^{1}H NMR (600 MHz, D$_2$O) δ 4.27 (t, J=9.47Hz, 2H), 4.40 (s, 1H), 4.57 (d, J=13.56 Hz, 2H), 7.62 (s, 2H); ^{13}C NMR (151 MHz, D$_2$O) δ: 52.14, 68.18, 123.26, 137.02; IR (KBr) ν: 3426, 3143, 3104, 2952, 2858, 1564, 1446 cm^{-1}.

2.3. General procedure for the conversion of glucose to LA

Glucose was converted into LA in a 25 mL micro-autoclave. A mixture of glucose and catalyst was dissolved in water, followed by the addition of NaOH. To remove any air, the autoclave was slowly flushed with argon three times before adding nitrogen. The system was stirred at 600 rpm throughout the reaction procedure. The reactor was positioned in a copper heating block, and the temperature was monitored using a thermocouple inside the vessel. After the desired interval, the autoclave was put into a cold-water bath to quench the reaction. The liquid samples were diluted with ultra-pure water, acidified with sulfuric acid and

filtered through a 0.22 μm membrane. Salts were transformed into their free acid forms through this procedure.

The liquid fraction were analyzed by HPLC (Varian Prostar 310, UV detector) using a Bio-Rad Aminex HPX-87H column at 60 ℃ with H_2SO_4 (5 mM) as eluent at a flow rate of 0.6 mL/min. The concentration of carbohydrates was analyzed by HPLC (Agilent 1200, USA) using a Bio-Rad Aminex HPX-87C column at 35 ℃ with ultra-pure water as eluent at a flow rate of 0.2 mL/min. A Refractive Index Detector was employed.

The conversion of glucose and the yield of LA were determined based on carbon.[16] The experiments were replicated at least three times and were reported as the mean values. The error was below 5%.

3. Results and discussion

3.1. Effect of the composition of the reaction medium on glucose conversion and LA yield

Reaction systems containing different bases and catalysts were employed to produce LA from glucose. The glucose conversion obtained while using different systems varied from 94.6% to 99.2%; however, the yields and selectivities for LA varied remarkably. Hydroxide salts with monovalent and divalent cations were selected for the reaction medium. Under the same concentration of hydroxide ions, the most efficient conversion of glucose into LA was obtained when using KOH and NaOH, followed by $Ba(OH)_2$ and $Ca(OH)_2$. When ammonium hydroxide was used at 50 mM, LA was obtained in only 7% yield (Table 1, entry 2) because the solubility of ammonia decreased as the temperature increased. According to previous studies, the presence of divalent cations was crucial for improving the yield of LA.[15] However, in the present study, KOH demonstrated the highest catalytic activity, indicating that the solubility of the hydroxides might affect the conversion of glucose to LA with [IMEP]Cl.[29] Considering the possible economic cost, NaOH was used to verify the effect of [IMEP]Cl on the conversion of glucose to lactic acid in alkaline solution. In combination with [IMEP]Cl, a 63% yield of LA, which was among the few most promising yields of LA produced from carbohydrates via chemical methods, was obtained when using 50 mM NaOH, indicating that using [IMEP]Cl could drastically decrease both the concentration of NaOH and the reaction temperature compared to former reports, as mentioned above (see Table 1, entry 1).

Furthermore, [IMEP]Cl samples modified with different types of anions were also employed as catalysts during the production of LA from glucose (see Table 1, entries 1 and 5-9). IMEP with chloride anions provided the highest yield and selectivity for LA (63% and 63.5%, respectively), and a comparable yield of LA (58.1%) could be obtained when using the BF_4-modified IMEP. However, the yields of LA catalyzed by ClO_4^-, Ac^- and $PhCOO^-$ modified IMEP were relatively low, which were 50.1%, 44.8% and 33.2%, respectively. The lowest yield of LA (9.5%) was obtained when using [IMEP]PF_6, which proceeded with a 94.6% conversion of glucose. These results appears to be explicable in terms of the effective positive charge density of the active sites of IMEP. With chloride as a counter anion, the IMEP is expected to dissociate completely in aqueous solutions, thereby the positive charge density at the cationic imidazolium parts is regarded as

high, while hexafluorophosphate anion is assumed to form a tight ion-pair in aqueous solutions, resulting in reduced charge density at the active sites. According to the proposed reaction mechanism in Scheme 2, both the electronegative oxygen of substrates and hydroxyl ions are negatively charged; thus, adsorption onto the catalyst is strongly affected by the effective positive charge density of the cationic species. As a consequence, IMEP with chloride as a counter anion is expectedly more active than others which are inclined to form tight ion-pairs in aqueous solutions. The results are consistent with that of the effects of counter anion on the antibacterial activity of polymeric phosphonium salts observed by Kanazawa et al.[30] Therefore, [IMEP]Cl was the best catalyst among the six types of IMEP-based catalysts. Consequently, [IMEP]Cl was chosen for the further study in aqueous NaOH solution.

Table 1 Conversion of glucose to LA in various systems at 100 ℃ over 30 min with 25 mM of glucose, 50 mM of OH^- and 100 mM of catalyst under nitrogen.

Entry	Base	Catalyst	Conversion (%)	Yield (%)	Selectivity (%)
1	NaOH	[IMEP]Cl	99.2	63	63.5
2	KOH	[IMEP]Cl	98.9	65.5	66.2
3	NH_4OH	[IMEP]Cl	97.9	7	7.2
4	$Ca(OH)_2$	[IMEP]Cl	95.8	21	21.9
5	$Ba(OH)_2$	[IMEP]Cl	98.3	26	26.4
6	NaOH	[IMEP]BF_4	97.5	58.1	59.6
7	NaOH	[IMEP]ClO_4	98.1	50.1	51
8	NaOH	[IMEP]Ac	96.2	44.8	46.6
9	NaOH	[IMEP]PF_6	94.6	9.5	10
10	NaOH	[IMEP]PhCOO	95.3	33.2	34.8

3.2. Effect of the NaOH and [IMEP]Cl concentrations on the conversion of glucose to LA
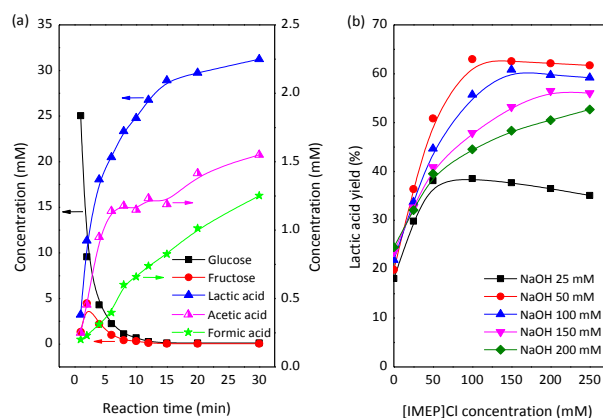
Figure 1 Yield of LA with [IMEP]Cl in alkaline solution. (a) Concentration of the reactant and major products during glucose conversion. (b) LA yield while varying the NaOH and [IMEP]Cl concentrations (Conditions: 25 mM glucose, 100 ℃; 0.1 MPa N2, 30 min).

When prolonging the reaction, the concentration of glucose declined rapidly as a transient amount of fructose appeared,

indicating the isomerization of glucose at the beginning of the conversion process. Both formic acid and acetic acid were observed during the reaction in trace amounts. As shown in Figure 1a, the LA yield plateaued at approximately 30 minutes and remained nearly constant at longer reaction times. Therefore, a reaction time of 30 minutes was chosen for further study.

The effect of the NaOH concentration on the yield of LA with different loadings of [IMEP]Cl was investigated when the feed glucose concentration was 25 mM at 100 ℃. When no catalyst was added, the yield of LA was generally below 25% (shown in Figure 1b). Adding [IMEP]Cl efficiently increased the yields of LA in the studied range of NaOH concentrations: 25 mM to 200 mM.

At a fixed amount of [IMEP]Cl, the LA yield increased when increasing the concentration of NaOH ($\leq$ 50 mM). However, increasing the amount of NaOH decreased the LA yield slightly, indicating that overloading the system with NaOH greatly weakened the impact of [IMEP]Cl on the reaction. However, a positive effect of [IMEP]Cl on the conversion of glucose was confirmed. The optimal concentration of NaOH (50 mM) was twice that of glucose (25 mM), indicating that the optimal molar ratio NaOH/glucose was 2.

For a specific concentration of NaOH, e.g., 50 mM, the yield of LA increased from 19% to 63% as the [IMEP]Cl concentration increased from 0 to 100 mM. Moreover, this value remained almost constant when increasing the catalyst concentration further. The same tendency was observed for the other NaOH concentrations, indicating that increasing the amount of [IMEP]Cl favored the conversion of glucose. However, adding additional catalyst did not necessarily improve the reaction. An optimal molar ratio [IMEP]Cl/OH⁻ of 2 was obtained, suggesting that only half of the cationic sites were coordinated. Therefore, these empty sites were also vital for the catalytic conversion of glucose along with NaOH. The NaOH concentration presently used was much lower than that reported by Yan et al.[12] and Onda et al.[18]

### 3.3. Effect of varying temperatures on the production of LA
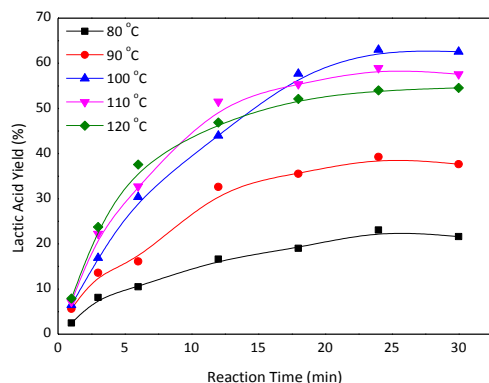
Figure 2 Effect of varying the temperature and reaction time on the conversion of glucose to LA with catalytic [IMEP]Cl (Conditions: 25 mM glucose, 50 mM NaOH, 100 mM [IMEP]Cl, 0.1 MPa N2).

Figure 2 shows the LA yields as a function of the reaction time at different temperatures with [IMEP]Cl as the catalyst. Obviously, the reaction temperature significantly affected the LA yield. The yield of LA increased significantly along with the increase of temperature when it was below 100 ℃, from 23% to 63%. However, slightly lower final yields of LA (59% for 110 ℃, and 55% for 120 ℃) were obtained when increasing the reaction temperature above 100 ℃, possibly due to a series of side and degradation reactions at elevated temperatures.[13, 29] An increasing amount of formic acid and acetic acid could be analyzed by HPLC when increasing the temperature (data not shown). Moreover, the color of the reaction solution changed from yellow to dark brown when increasing the temperature, especially after long reactions. This change might be caused by the polymerization and cross-polymerization of intermediates at higher temperatures. From these observations, the most appropriate temperature should be 100 ℃, indicating that obviously gentle conditions were obtained in contrast to sub- and supercritical water.

3.4. Effect of atmosphere on the conversion of glucose to LA

To better understand the influence of the gas on the reaction, further studies were carried out at 100 ℃ under air and oxygen atmospheres with a constant pressure of 0.1 MPa (shown in Figure 3). Obviously, different types of atmosphere notably influenced the yields of LA. The maximum LA yield (63%) was obtained at a nitrogen atmosphere; however, reaction systems under air or pure oxygen led to low yields of LA, 39% and 18%, respectively, because the oxygenated system affects the alkaline degradation of glucose and facilitates the oxidation reactions.[18, 31] Consequently, utilizing the [IMEP]Cl under an anaerobic atmosphere was more effective during the reaction. Interestingly, in the presence of oxygen, less [IMEP]Cl was needed to maximize the LA yield.
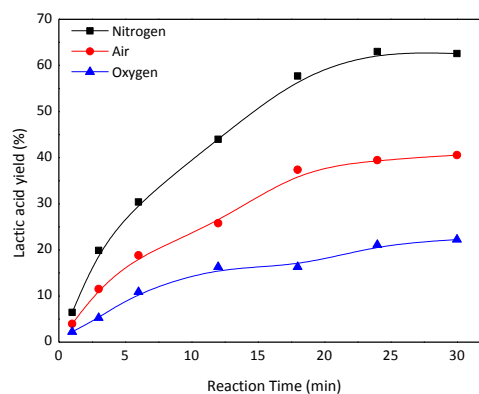
Figure 3 Effect of atmosphere on the conversion of glucose to LA (Conditions: 25 mM glucose, 50 mM NaOH, 100 mM [IMEP]Cl, 100 ℃).

3.5. Varying the initial concentrations of glucose

Glucose concentrations ranging from 25 mM to 200 mM were also investigated while studying the conversion of glucose, as well as the yields of formic acid, acetic acid and LA. As shown in Figure 4, the glucose converted rapidly, reaching approximately 90% conversion at concentrations below 50 mM within 5 minutes; after 30 minutes, near-complete conversion was achieved, leading

to a LA yield above 50%.

However, the conversion of glucose fell below 80% after increasing the glucose concentration from 100 mM to 200 mM; a near plateau glucose conversion was reached within 5 minutes.
[5] Unfortunately, a dramatically lowered yield of LA, which was below 30%, was obtained for two reasons. First, the solution after the reaction had a nearly neutral pH, indicating that the organic acids were neutralized by hydroxyl ions, greatly reducing the concentration of NaOH. Second, the formation of humins,
[10] possibly via the condensation of carbohydrate intermediates, was more effective in more concentrated glucose solutions, consuming excess reactants or occupying the active sites of the catalyst.
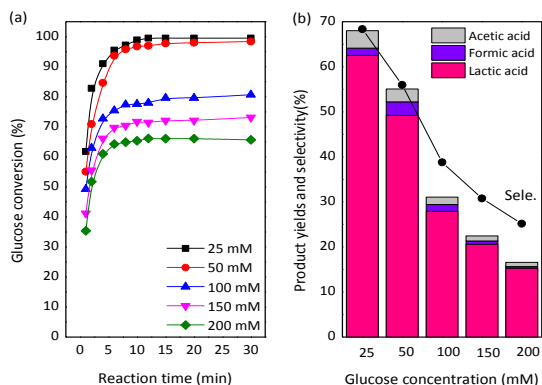
Figure 4 Glucose conversion and product yields when varying
[15] the initial concentrations of glucose (a) Glucose conversion. (b) Product yields and selectivities. Sele., selectivity (Conditions: 50 mM NaOH, 100 mM [IMEP]Cl, 100 °C, 0.1 MPa N2, 30 min).

The yield of acetic acid followed the same trend as LA, but the maximum yield of formic acid was obtained when using 50 mM
[20] glucose. The GC/MS analysis of silylated aqueous phase products was shown in Figure S2. Although the total selectivity of the three quantified organic acids decreased dramatically from 68% to 25%, this method remains a viable new strategy to the conversion of carbohydrates.

[25] **3.6. The conversion of other monosaccharides**

The performance of [IMEP]Cl for different substrates during the production of LA was also investigated when utilizing the optimal molar ratio of substrates:NaOH:[IMEP]Cl (1:2:4) at 100 °C for 30 min. The generally accepted reaction mechanism
[30] involves an isomerization from aldose to ketose; the conversion of fructose tends to be easier (Scheme S1).[21] In fact, fructose was analyzed during the reaction of glucose, as shown in Figure 1a. Through this approach, the reaction of a representative aldose, specifically glucose, generated a comparable LA yield compared
[35] to that of a typical ketose, such as fructose or mannose; the yields were 63%, 65% and 50%, respectively. In addition, galactose and xylose, which were considered unfavorable for alkaline degradation compared with glucose, fructose and mannose,[17] generated relatively high yields: 53% and 47%, respectively.
[40] Therefore, the present system is suitable for converting monosaccharides to LA. The conversion of disaccharides or polysaccharides, such as cellulose, lignin and starch, remain under further investigation.

3.7. Proposed mechanism

[45] The [IMEP]Cl polymer efficiently facilitates the reaction due to its pure interfacial anion/cation-pairing mode action, which generates a high local concentration of hydroxyl anions around the polymer chains, enabling the efficient conversion of glucose at low NaOH concentrations.[23] This anion/cation-pairing on poly-
[50] cationic catalysts typically occurs through electrostatic coupling to the chemisorbed hydroxyl anions readily available in the reaction media under the experimental conditions. The poly cationic material behaves as weak Lewis acid centers, driving the conversion of glucose into LA.[20]
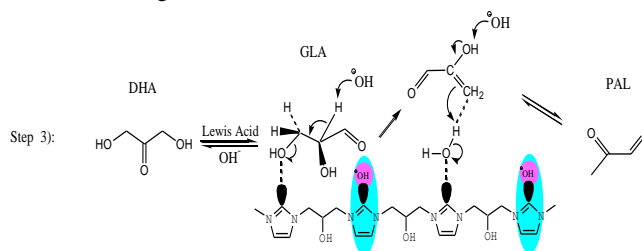

[55] **Scheme 2** Proposed reaction mechanism for the conversion of glucose to LA in the present system

In general, 4 steps are required to form LA from glucose: 1) the isomerization of glucose to fructose; 2) a retro-aldol reaction that splits the fructose into two triose, dihydroxyacetone (DHA)
[60] and glyceraldehyde (GLA); 3) the dehydration of DHA or GLA to form pyruvic aldehyde (PAL); 4) hydration of PAL followed by a 1,2-hydride shift to form the LA. A detailed reaction route alongside the exact type of catalyst needed for each step is depicted in Scheme S1. Step 3 was rate-determining, as
[65] confirmed both theoretically and experimentally by Rasrendra et al.[32] and de Clippel et al.[21] The yields of LA from both glucose and fructose were comparable, indicating that the catalyst [IMEP]Cl had limited impact on the isomerization of glucose to fructose in alkaline solutions. However, the direct reaction of
[70] DHA, which is an important intermediate during the formation of LA from the conversion of glucose, afforded LA in a 72% yield under the optimized conditions, while the non-[IMEP]Cl catalyzed reaction produced only a 56% yield of LA. Therefore, in the present approach, the added [IMEP]Cl might improve the
[75] conversion of trioses to LA, especially during the rate determining step that converts the trioses to PAL during step 3. One possible explanation is that the active hydrogens on the imidazole rings can behave as weak Lewis acid centers, and their coordination with the electronegative oxygens on the trioses or
[80] other intermediates might facilitate the dehydration/hydration or 1,2-hydride shift processes necessary to form the LA through keto-enol tautomerism (Scheme 2). Furthermore, experiments with pyruvic aldehyde showed that the yields of LA with and without the addition of [IMEP]Cl were 78% and 65%,
[85] respectively, indicating an increase of 20% using the polymer catalyst.

3.8. Recycling the catalyst and solvent

One of the most important factors in a catalytic process is long-term stability. After the reaction, the solution was acidified with
[90] dilute HCl and extracted with n-butanol, according to Chen et al.[33] The raffinate was reused for further reactions without further

purification. The polymer cannot be extracted. [IMEP]Cl and solvent (water) were recycled six times without significant loss of activity, because the yield of LA was still 53.6% after six cycles (Figure 5). The slight decrease in yield could be ascribed to the cleavage of [IMEP]Cl during the reaction; a molecular weight of 6.143×10^6 g mol^{-1} was observed after six cycles, and the corresponding cleavage rate of [IMEP]Cl was 7.08%. Moreover, the intensive formation of humins during the reaction might partially deactivate the catalyst. This outcome demonstrates the recyclability of [IMEP]Cl and its potential for use during the conversion of carbohydrates.
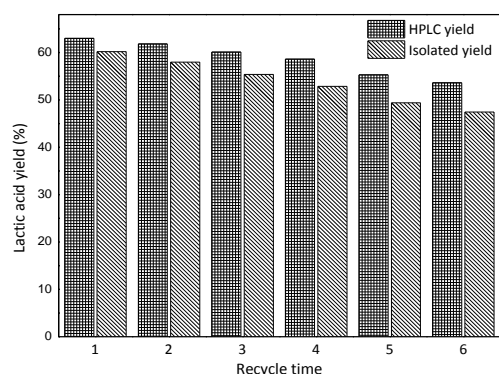
Figure 5 Recycling the [IMEP]Cl and solvent (Conditions: 25 mM glucose, 50 mM NaOH, 100 mM [IMEP]Cl, 100 °C, 0.1 MPa N2, 30 min).

3.9. Kinetic model

A kinetic analysis of the glucose conversion, as catalyzed by [IMEP]Cl in an alkaline solution, was performed. With regard to the glucose concentration, the alkaline degradation was previously identified as a first order reaction.[34]

Table 2 Reaction rate constants (k) of glucose conversion at different reaction temperatures using [IMEP]Cl (Conditions: 25 mM glucose, 50 mM NaOH, 100 mM [IMEP]Cl, 0.1 MPa N2, 30 min)

Entry	Temp. (K)	k (min^{-1})	Correlation coefficient
1	353	0.0826 ± 0.00296	0.9923
2	363	0.1633 ± 0.01035	0.98412
3	373	0.3317 ± 0.00928	0.9945
4	383	0.5164 ± 0.00994	0.9982
5	393	0.6924 ± 0.04078	0.9863

Table 3 Kinetic parameters of the glucose conversion using [IMEP]Cl

Parameter	Value
reaction order, n	1
activation energy, Ea (kJ mol^{-1})	62.66
pre-exponential factor, A (min^{-1})	1.7×10^8
correlation coefficient	0.9751

The values of ln(1-X) (where X is the conversion of glucose) were plotted against the reaction time (t) to obtain the pseudo-first-order rate constant (k). Table 2 shows that the value of k increases when increasing the temperature, indicating that a higher reaction temperature accelerates the glucose conversion reaction rate, as observed in Figure 2. An Arrhenius plot was generating using the rate constants. The kinetic parameters for the [IMEP]Cl-catalyzed conversion of glucose to LA are summarized in Table 3. The apparent activation energy is 62.66 kJ mol^{-1}, which is lower than that reported by Qu (99.2 kJ mol^{-1}) while using 1-butyl-3-methylimidazolium hydroxide as catalyst for dehydrating fructose to form 5-hydroxymethylfurfural.[35] The low activation energy of the [IMEP]Cl-catalyzed reaction allows the conversion to occur at moderate temperatures, minimizing the energy consumption and undesirable sugar degradation pathways.

Conclusions

An efficient synthesis of LA from glucose has been achieved while using [IMEP]Cl as catalysts in an alkaline solution. Several factors including the alkalinity, [IMEP]Cl loading, temperature and atmosphere influenced the yield. The optimal LA yield was 63%. Meanwhile, good activity was exhibited during the conversion of other monosaccharides. A possible reaction mechanism for the conversion of glucose was proposed. The activation energy of the glucose conversion was 62.66 kJ mol^{-1} with a pre-exponential factor of 1.7×10^8 min^{-1}. The excellent performance of [IMEP]Cl suggests that it might be used as catalysts for carbohydrate conversion.
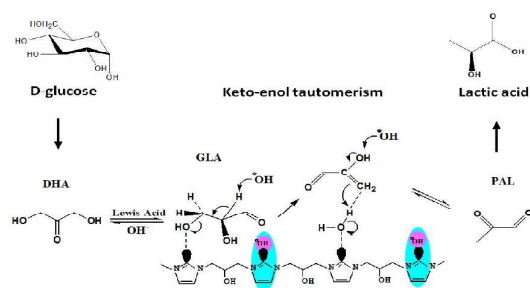
Acknowledgements

Notes and references

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† Electronic Supplementary Information (ESI) available: [The GC/MS spectra and detailed reaction mechanism for converting glucose to LA]. See DOI: 10.1039/b000000x/

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Polymerizates of imidazole and epichlorohydrin ([IMEP]Cl) were used to convert simple sugars to lactic acid in water at low temperatures.