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Effect of Different Ionic Liquids on 5-Hydroxymethylfurfural Preparation from Glucose in DMA over $AlCl_3$: Experimental and Theoretical Study

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In this work, effect of different ionic liquids (ILs) on 5-hydroxymethylfurfural (HMF) preparation from glucose in *N*,*N*-dimethylacetamide (DMA) over $AlCl_3$ was revealed by a combined experimental and computational study. ILs used as cocatalysts in this work included *N*-methyl-2-pyrrolidone hydrogen sulfate ([NMP]HSO_4), *N*-methyl-2-pyrrolidone methyl sulfate ([NMP]CH_3SO_3), *N*-methyl-2-pyrrolidone chlorine ([NMP]Cl) and *N*-methyl-2-pyrrolidone bromide ([NMP]Br) which were endowed with the same cation but different anions. According to the conclusion that fructose was intermediate product from glucose to HMF, we found fructose was transformed to more by-products by [NMP]HSO_4, making HMF yield decline significantly when glucose was treated as substrate. Neither glucose nor fructose could be converted by [NMP]CH_3SO_3 efficiently, leading to its no influence on glucose conversion to HMF. [NMP]Br had a higher selectivity for HMF from fructose than [NMP]Cl and $AlCl_3$. Besides, Al^{3+} preferred to combine with Br^-, slightly decreasing both the overall free energy barrier for glucose isomerization and activation barrier for H-shift at 393.15 K. So a high HMF yield of 57% was obtained from glucose catalyzed by $AlCl_3$ together with [NMP]Br under mild conditions.

Keywords anions, quantum chemistry, complex, glucose isomerization, H-shift

Introduction

With the increase in population, the rapid development of global economy and depletion of fossil fuels, the utilizing of renewable resources is becoming more and more urgent. Biomass is abundant, CO_2 neutral and can be treated as feedstock for the production of chemicals and fuels.[1-3] 5-Hydroxymethylfurfural (HMF) is listed as one of the top building-block chemicals obtained from biomass.[4] It is considered as an important intermediate for preparing fine chemicals, pharmaceuticals, plastic resins, liquid transportation fuels, *etc*.[5] Carbohydrates are major constituents of lignocellulosic biomass and their conversion to the platform chemicals has gained significant attention. Fructose has been widely studied as substrate for HMF preparation and high yield has been obtained over acids or ionic liquids (ILs).[6-9] While high price of fructose prevents HMF from large scale production. Glucose, monomer of cellulose,[10,11] seems to be more attractive as feedstock. Unfortunately, its conversion to HMF is still a challenge. So far various catalysts have been developed for the production of HMF from glucose, including Lewis acid catalysts,[12] ionic liquids (ILs),[13,14] zeolites,[15] chromium(0) nanoparticles,[16] Sn-Mont catalysts,[17] phosphate-immobilized anatase TiO_2[18] and so on. Among all catalytic systems, IL/Lewis acid system is the most efficient. Zhang and co-workers[19] demonstrated a significant HMF yield of 70% from the dehydration of glucose by $CrCl_2$ in 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) ionic liquid. Han *et al*.[12] reported that $SnCl_4$ in 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM]BF_4) enabled synthesis of HMF from glucose in good yield of 61%. What's more, $SnCl_4$ could show the best result only in IL with BF_4^- rather than Cl^-, Tf_2N^-, TFA^-, $Trif^-$, $Sacc^-$ as anion. In other words, anion of IL has a great influence on activity of metal chloride.

Molecular level insight into the structural and coordination properties of copper(II) and chromium(II) chlorides, their complexes with glucose in dialkylimidazolium chloride ([RMIM]Cl) ionic liquids and the mechanism of glucose dehydration in MCl_2/[EMIM]Cl (M＝Cr, Cu and Fe) system were researched by combination of kinetic experiments and density functional theory (DFT) calculations.[20-23] $[MCl_4]^{2-}$ complexes were demonstrated as the reactive species for glucose isomerization. Catalytic activities of MCl_3 (M＝W, Mo

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and Fe) in 1-butyl-3-methyl-imidazolium chloride ([BMIM]Cl) were also compared using DFT calculations.[24] However, current theoretical studies are mostly based on the systems which are not environmentally friendly or not effective for preparation of HMF. What's more, how different anions besides Cl^- affect glucose isomerization has been rarely studied.

$AlCl_3$ is a cheap, nontoxic and abundant chemical. It showed high activity for conversion of glucose into HMF under microwave heating in a H_2O/THF solvent system.[25] So in this paper, $AlCl_3$ was chosen as catalyst and *N*-methyl-2-pyrrolidone hydrogen sulfate ([NMP]HSO_4), *N*-methyl-2-pyrrolidone methyl sulfate ([NMP]CH_3SO_3), *N*-methyl-2-pyrrolidone chlorine ([NMP]Cl), *N*-methyl-2-pyrrolidone bromide ([NMP]Br) were treated as cocatalyst, respectively. We mainly discussed effect of anions. The advantages of ILs that were used in this study are easy preparation and less dosage. Based on above green system, experimental and computational approaches were combined to unravel catalytic mechanism of different catalysts and how different anions of ILs affect glucose dehydration by $AlCl_3$ in *N*,*N*-dimethylacetamide (DMA).

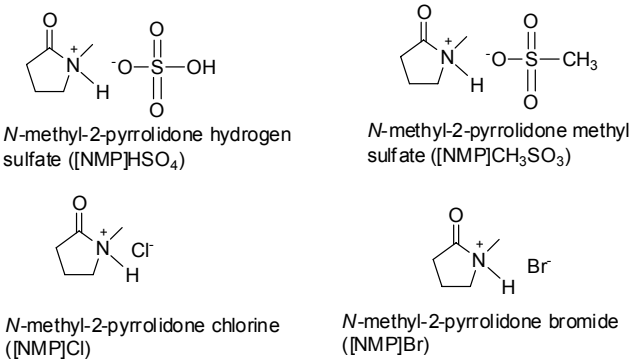

Figure 1 Structures of ILs prepared and used in this paper.

Experimental

Materials

D-Glucose (Glu, AR), anhydrous $AlCl_3$ (AR), *N*,*N*-dimethylacetamide (DMA, AR), *N*-methyl pyrrolidone and other chemicals (AR) were all commercial product from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). $AlCl_3$ was wax seal stored in a cool, dry and well-ventilated cupboard. Sulfuric acid (98%) and other chemicals (AR) are commercially available and used without further purification unless otherwise stated.

Synthesis of cocatalysts

[NMP]HSO_4 was prepared by dropping concentrated sulfuric acid (0.12 mol) slowly into *N*-methyl-2-pyrrolidone (0.1 mol) at 0—5 ℃ and stirring for 4 h at room temperature. The unreacted chemical reagents and other impurities were removed by vacuum distillation. The obtained product [NMP]HSO_4 was washed with ethyl acetate (10 mL×3) and dried at 60 ℃ in vacuum for 2 d.[26-30] ^{1}H NMR (D_2O, 400 MHz) δ: 2.01—2.09 (m, 2H), 2.46 (t, J=8.0 Hz, 2H), 2.84 (s, 3H), 3.52 (t, J=8.0 Hz, 2H). Synthetic processes of [NMP]CH_3SO_3, [NMP]Cl and [NMP]Br were similar to [NMP]HSO_4. [NMP]CH_3SO_3: ^{1}H NMR (D_2O, 400 MHz) δ: 2.0—2.08 (m, 2H), 2.44 (t, J=8.0 Hz, 2H), 2.80 (s, 3H), 2.83 (s, 3H), 3.51 (t, J=8.0 Hz, 2H).

Glucose dehydration test

The catalytic activity experiments were performed in 50 mL round bottom flask that was heated in the oil-bath with magnetic stirrer at 120 ℃. At different time intervals, 50 μL samples were extracted and quenched immediately with deionized water (×100) for analysis.

Product analysis

The products were analyzed by high performance liquid chromatography (HPLC) on an Agilent Alliance 1100 series chromatograph equipped with refractive index detector and Shodex SURGER SP-0810 columns (300 mm×8.0 mm). The mobile phase was ultrapure water at a flow rate of 0.7 mL•min^{-1} and the column temperature was 70 ℃. The concentrations of products were calculated based on the standard curve that was obtained with known concentrations of the standard substance.

Confirmation of initial form of $AlCl_3$ in DMA

A certain amount of anhydrous $AlCl_3$ was mixed with moderate DMA and stirred at 120 ℃ for 2 h. The mixed solution was analyzed by electron spray ionization mass spectrometry (ESI-MS) under negative ion mode.

Density functional theory calculations

The geometries of all structures, including glucose, $AlCl_4^-$, DMA, the four anions (HSO_4^-, $CH_3SO_3^-$, Cl^- and Br^-) and various complexes were optimized using density functional theory (DFT) with hybrid Becke 3-Lee-Yang-Parr (B3LYP)[31,32] exchange-correlation functional using Gaussian 03 program.[33] The 6-311G(d,p) basis set was used for C, H, O, N, Al, Cl and S atoms, while the Br atom was treated with the LanL2DZ basis set.[34] In order to be consistent with experiment condition, all of the compounds were optimized using the polarizable continuum model (PCM) for DMA. Vibrational frequency calculations, from which the zero-point energies (ZPEs) were derived had been performed for each optimized structure at the same level to verify that the computed structures corresponded to energy minima. Various initial geometries of glucose were optimized and the most stable one was used for subsequent research. As for the study of reaction mechanism, DFT calculations were carried out to obtain energy barriers for reactants, intermediates (IMs), transition states (TSs) and products by the same method which was described above. Minima in potential energy

surfaces that corresponded to stable molecular species and saddle points that corresponded to transition states were obtained at the same time. The intrinsic reaction coordinate (IRC) pathways have been traced in order to verify that the saddle point links two desired minima.

Results and Discussion

Examination of various catalytic systems

A set of glucose dehydration experiments were performed in DMA at 120 ℃ for different times. The results are summarized in Figure 2. From Figure 2a, we can see glucose is converted to HMF in moderate yield (39%) by $AlCl_3$. Decreased yield (*ca.* 20%) can be obtained by the addition of $[NMP]HSO_4$ (7 mol% to glucose) while other ILs have no effect on the yield. After increasing the dosage of ILs (Figure 2b), there is still no change in HMF yield for [NMP]Cl and $[NMP]CH_3SO_3$. While to our surprise, generation rate of HMF and the maximum yield increase significantly (57%) after addition of [NMP]Br.

In order to reveal this phenomenon, supplementary experiments were carried out based on the conclusion that HMF was obtained by glucose isomerization to fructose and fructose dehydration (Table 1). As can be seen from Table 1, HMF can not be obtained from glucose just over ILs. But ILs except $[NMP]CH_3SO_3$ can promote fructose dehydration to HMF. In another word, $[NMP]CH_3SO_3$ has neither positive nor negative effect on the reaction. However, $[NMP]HSO_4$ shows so low selectivity for HMF. That may be one of the reasons why addition of $[NMP]HSO_4$ suppresses HMF formation. Large amounts of [NMP]Br shows higher HMF selectivity than [NMP]Cl,[35] increasing the yield of HMF. All of the above tells us ionic liquids except $[NMP]CH_3SO_3$ are mainly responsible for fructose dehydration in DMA. That corresponds to previous report.[36]

But Raines and Binder speculated that the halide additives may also serve as ligands for metal and bromide potentially offered the optimal balance of nucleophilicity and coordinating ability, enabling unparalleled transformation of glucose into HMF.[35] $[MCl_4]^{2-}$ complexes were demonstrated as the reactive species for glucose isomerization.[21] In order to reveal whether [NMP]Br acts as ligand of $AlCl_3$ and how it affects the activity of $AlCl_3$ for glucose isomerization in DMA at the molecular level, the action mechanism was explored with quantitative method.

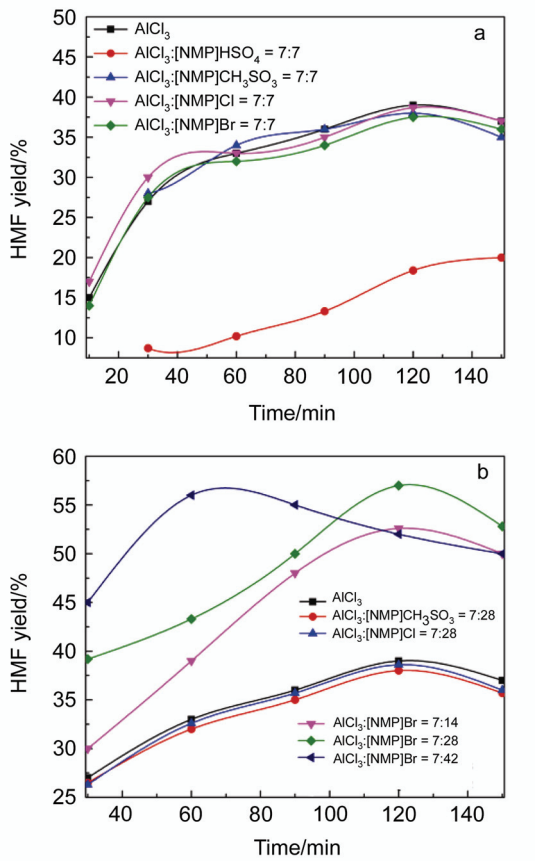

Figure 2 Glucose conversion to HMF in DMA for various reaction times using $AlCl_3$ and $AlCl_3$+IL as catalysts. Reaction conditions: 5 mL DMA, 1 mmol glucose, $AlCl_3$ (7 mol% to glucose), T=120 ℃.

Table 1 Dehydration of glucose and fructose in DMA[a]

Substrate	Catalyst (Dosage/mol%)	t/min	Conversion/%	HMF yield/%
Glucose	$[NMP]HSO_4$ (7)	60	48.7	0
Glucose	$[NMP]CH_3SO_3$ (7)	60	0	0
Glucose	[NMP]Cl (7)	60	37.7	0
Glucose	[NMP]Br (7)	60	54.1	0
Fructose	$[NMP]HSO_4$ (7)	60	86.0	41.4
Fructose	$[NMP]CH_3SO_3$ (7)	60	55.8	0
Fructose	[NMP]Cl (7)	60	93.6	70.2
Fructose	[NMP]Br (7)	60	91.6	72.1
Fructose	[NMP]Cl (28)	5	97.0	60.3
Fructose	[NMP]Br (28)	5	98.7	80.3

[a] Reaction conditions: 5 mL DMA, 1 mmol glucose or fructose, catalyst (7 or 28 mol% to substrate), T=120 ℃.

The form of anhydrous $AlCl_3$ in DMA

Due to the structure characteristics of anhydrous $AlCl_3$, it is necessary to discuss the initial form of $AlCl_3$ before getting a better understanding of the catalytic reaction process. ESI-MS of $AlCl_3$ in DMA (Figure 3) explains that form of $AlCl_3$ before addition of glucose and ILs is mainly $AlCl_4^-$ and this structure is used for the next research.

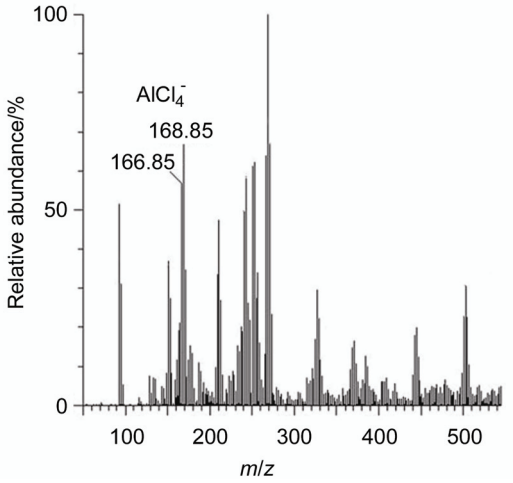

Figure 3 ESI-MS of $AlCl_3$ in DMA.

Possible combinations of $AlCl_4^-$ and DMA or [NMP]Br

Raines *et al*.[35] proposed that in DMA-LiCl solvent, lithium ions could associate with DMA to form DMA-Li^+ macrocations, resulting in a high concentration of weakly ion-paired chloride ions. Lin *et al*.[37] inferred that in CPL-LiCl, lithium ions associated with CPL to form CPL•Li^+ macrocations. So we speculated that weak interaction existed between Al^{3+} and solvent molecules (DMA) or cocatalyst (IL). The species of Al^{3+} in DMA/glucose/$AlCl_3$ and DMA/glucose/$AlCl_3$/[NMP]Br systems were speculated by theoretical calculation (Table 2).

The smaller the value of ΔE or ΔG is, the more easily the corresponding complex forms. Data in Table 2 show that four-coordinated complexes are more stable. In DMA/glucose/$AlCl_3$ system (Entries 1－5), complexes of $AlCl_4^-$ and solvent molecules are formed more easily than that of $AlCl_4^-$ and glucose. In DMA/glucose/$AlCl_3$/[NMP]Br system, $AlCl_4^-$ can hardly bind with cation of IL (Entry 6), just as what was discussed in previous literature,[21] cations provide an efficient charge-compensating environment for the anionic metal chloride complexes. Complexes of $AlCl_4^-$ and Br^- are formed facilely. Taking value of ΔE, $\Delta G_{298.15K}$, $\Delta G_{393.15K}$ and steric hindrance into account, $AlCl_3$-DMA; $AlCl_2$-2Br, AlCl-3Br and Al-4Br were chosen as reactive species in DMA/glucose/$AlCl_3$ and DMA/glucose/$AlCl_3$/[NMP]Br system, respectively. The corresponding configurations are shown in S2 of Supporting Information. In order to simplify the simulation, cation of every IL was not considered during the later mechanism research.

Mechanism of glucose isomerization with different complexes as active species

According to previous literature,[23,38] the mechanism of Al^{3+} complex-catalyzed isomerization of glucose to fructose is proposed as Scheme 1. The reaction is initiated by the direct coordination of glucose with the Lewis acidic Al^{3+} center and deprotonation of O(1)H moiety of the carbohydrate by free Cl^- (intermediate **2**). The subsequent protonation of O(5) opens the glucopyranose ring and O(2)H is deprotonated at the same time (intermidate **4**). What happens next is H-shift from C(2) to C(1) which is a rate-determing step and also the focus of our discussion (TS-H-shift). Fructose is formed by protonation of intermidate **5** at the anionic O(1) site and closure of the furanose ring. In an attempt to explain the effect of Br^- on activity of Al^{3+}, mechanism of glucose isomerization with different active species

Table 2 Possible combinations of Al^{3+} and DMA or [NMP]Br before glucose transformation[a]

Entry	Solvent	Ligand	Species of Al^{3+}	ΔE^c/(kJ•mol^{-1})	$\Delta G_{298.15K}$/(kJ•mol^{-1})	$\Delta G_{393.15K}$/(kJ•mol^{-1})
1	DMA	DMA	$AlCl_3$-DMA＋Cl^b	–9.15	6.42	17.58
2	DMA	DMA	$AlCl_2$-2DMA＋2Cl^-	–11.06	23.02	50.39
3	DMA	DMA	AlCl-3DMA＋3Cl^-	–2.78	222.31	88.64
4	DMA	DMA	$AlCl_4$-DMA	0.09	48.13	67.32
5	DMA	glucose	$AlCl_3$-glucose＋Cl	74.42	91.24	108.30
6	DMA	NMP[d]	$AlCl_3$-NMP＋Cl^-	120.48	267.45	70.69
7	DMA	Br^-	$AlCl_3$-Br＋Cl^-	–4.55	–4.54	–4.03
8	DMA	Br^-	$AlCl_2$-2Br＋2Cl^-	–8.67	–8.67	–8.73
9	DMA	Br^-	AlCl-3Br＋3Cl^-	–12.34	–12.29	–11.64
10	DMA	Br^-	Al-4Br＋4Cl^-	–15.48	–9.27	–7.81
11	DMA	Br^-	$AlCl_4$-Br	31.85	57.62	72.31

[a] Optimizations and frequencies were calculated at the B3LYP/6-311G(d,p) level using the polarizable continuum model (PCM) for DMA. [b] $AlCl_4^-$ combined with one solvent molecules and released one Cl^-: $AlCl_4^-$＋DMA; $AlCl_3$-DMA＋Cl^-. [c] $\Delta E = E_{complex} + nCl^- - E_{AlCl4} - nE_{DMA\ or\ anion}$ (n＝1, 2, 3, 4), the similar method for $\Delta G_{298.15K}$ and $\Delta G_{393.15K}$. [d] Cation of IL.

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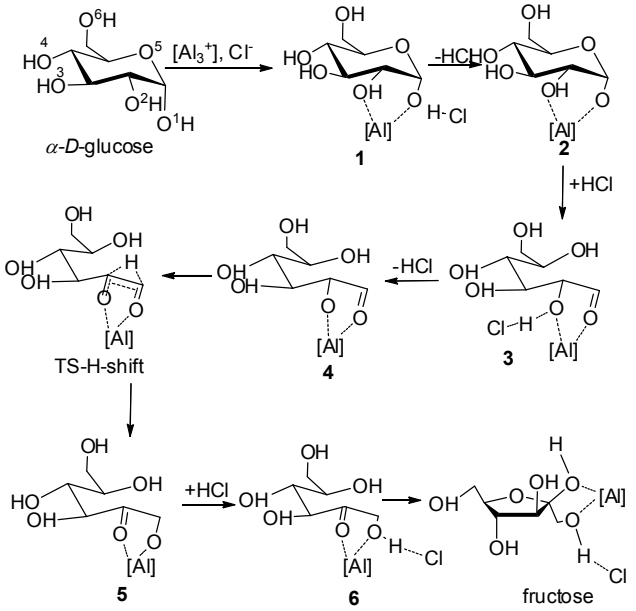
($AlCl_3$-DMA, $AlCl_2$-2Br, AlCl-3Br, Al-4Br,) was studied by theoretical calculation. $AlCl_3$-DMA presents DMA/glucose/$AlCl_3$ system and $AlCl_2$-2Br, AlCl-3Br, Al-4Br present DMA/glucose/ $AlCl_3$/[NMP]Br system.

Scheme 1 Mechanism of glucose isomerization to fructose catalyzed by Al^{3+} complex in DMA ([Al^{3+}] represents different complexes of Al^{3+} and anions or DMA.)



Optimized structures of reaction intermediates and transition-state during glucose isomerization to fructose over different complexes in DMA were obtained (see section S3 of Supporting Information). The corresponding free energy diagrams are shown in Figure 4. The overall barrier decreases when Br^- combines with Al^{3+} center. What's more, the barrier decreases as more and more Br^- coordinating with Al^{3+}. In addition, glucose isomerization can be accelerated by the lower activation barrier for H shift that is a rate-controlling step.[20] From Figure 4 we can also see that the activation free energy barriers for H-shift decrease in the order $AlCl_3$-DMA (71.2 kJ/mol) > $AlCl_2$-2Br (43.3 kJ/mol) > AlCl-3Br (38.5kJ/mol) > Al-4Br (34.4 kJ/mol). Configurations (b), (c) and (d) in Figure 5 reveal that Br^- is released completely by Al^{3+} to interact with H during H-shift, which may facilitate migration of the H. That is in agreement with the experimental results that addition of [NMP]Br accelerates HMF generation and the yield rises with increasing of IL dosage. What's more, in report of Xu *et al*.[39] $AlBr_3$ showed higher selectivity for HMF than $AlCl_3$ in DMA. So we conjectured that Br^- not only promoted selective conversion of fructose but also strengthened activity of Al^{3+} for glucose isomerization slightly by serving as ligand.

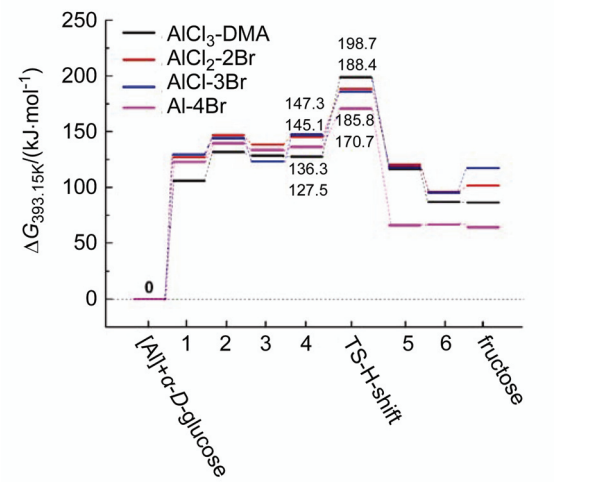


Figure 4 The DFT-computed free energy diagrams of $AlCl_3$-DMA, $AlCl_2$-2Br, AlCl-3Br and Al-4Br catalyzed process. All of the compounds were optimized using the polarizable continuum model (PCM) for DMA at 393.15 K. [Al] presents complex of Al^{3+}.

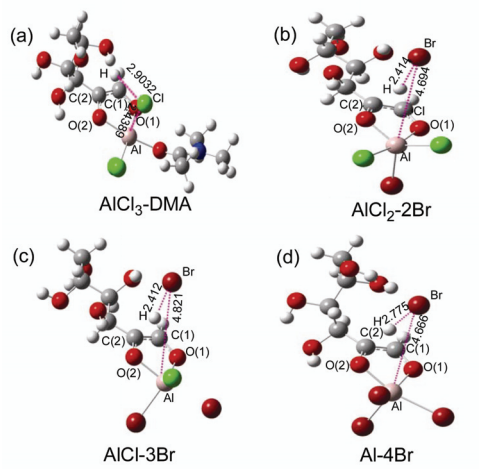


Figure 5 Optimized structures of transition-state during H-shift over (a) $AlCl_3$-DMA, (b) $AlCl_2$-2Br, (c) AlCl-3Br and (d) Al-4Br. Selected bond lengths are given in Å.

Conclusions

How different anions of ILs (Brönsted acids) affect HMF preparation from glucose in DMA over $AlCl_3$ was researched with experimental and theoretical methods. Brönsted acids except [NMP]CH_3SO_3 are mainly responsible for fructose dehydration. HSO_4^- can debase the selectivity of HMF from fructose. Compared with HSO_4^- and Cl^-, Br^- can promote selective conversion of fructose. On the other hand, Br^- can combine with Al^{3+}, forming different complexes and slightly lowering the overall free energy barrier. Process of H-shift is considered as a rate-controlling step. Optimized structures of transition-state during H-shift over these complexes show that Br^- is released completely by Al^{3+}, interacting with H which is transferring from C(2) to C(1). As a result, this decreases the activation free energy barriers for rate-controlling step. So we speculate [NMP]Br may also promote glucose isomerization. In general, because of favourable nucleophilicity and coordinating ability for Br^-, it acts as two roles: facilitat-

ing conversion of fructose and serving as ligand for aluminium. All of the above reveal positive or negative effect of acidic ILs on HMF preparation from glucose. It can help us choose cocatalysts for metal chloride, realizing selective conversion of cellulosic biomass conversion.

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