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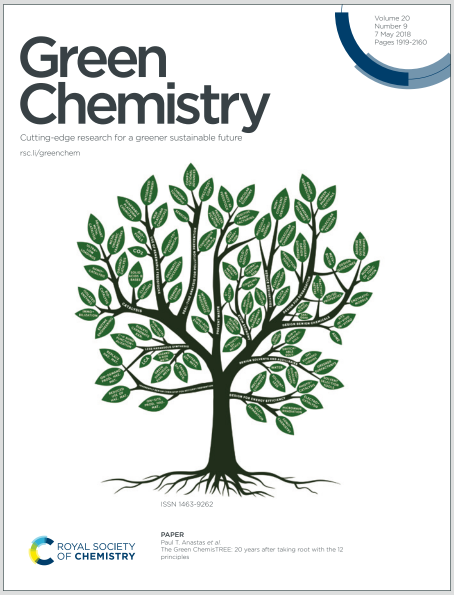

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Unraveling the Cation and Anion Effects and Kinetics for Ionic Liquid Catalyzed Direct Synthesis of Methyl Acrylate at Mild Condition

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The direct synthesis of methyl acrylate (MA) from methyl acetate and trioxane at 350-380^{o}C is regarded as a supplementary route for the industrial propylene oxidation process, however, it suffers rapid catalyst deactivation. Herein, a novel ionic liquid catalyzed mild liquid-phase system was developed for direct synthesis of MA from methyl acetate and trioxane, where the *N, O*-bis(trimethylsilyl) acetamide (BSA) was used as probase for *α*-deprotonation and enol silyl etherification of methyl acetate. The trioxane decomposition to formaldehyde and methyl acetate enolization to 1-methoxy-1-trimethylsilyloxyethene proceeded with the catalysis of [Cation]Cl/MCl$_x$ (M = Cu$^+$, Fe^{3+}, Zn^{2+} and Al^{3+}) and [Cation]F, respectively. The cation and anion were observed to have significant effects on yield and selectivity of MA, owing to the steric hindrance, acid site category and strength confirmed by pyridine probing FT-IR characterization.

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As a result, up to 60.2% yield with 94.6% selectivity of MA could be achieved when [N3,3,3,3]F and [N3,3,3,3]Cl/$AlCl_3$ with 67 mol.% $AlCl_3$ were used in the presence of BSA at 25^{o}C. The kinetic studies indicated the trioxane decomposition with activation barrier of 41.2 ± 0.3 kJ mol^{-1} was the rate-determining step.

Keywords: Methyl acrylate, Ionic liquid, Aldol condensation, Liquid-phase system, Kinetic

Introduction

Methyl acrylate (MA) as a very important chemical stock is widely used in the field of paints, polyacrylate materials and acrylic plastics production. [1-3] The industrial routes to MA are mainly based on two-step propylene oxidation, which includes selective oxidation to acrolein first on Mo-Bi and then to acrylic acid on Mo-V catalyst, and acrylonitrile hydrolysis. [4-7] However, the propylene oxidation process is recently restricted by the gradual depletion resource of fossil oil and increase of petroleum price. And the acrylonitrile hydrolysis technology needs large amounts of poisonous hydrogen cyanide as raw material, leading to the production of equivalent mole of ammonium sulfate wastes, which are relatively difficult to dispose. [8] In recent years, the coal-based chemicals and their downstream products, especially for formaldehyde, trioxane, methyl acetate and methanol, are faced with the challenging problems of overcapacity and commercial marketing. Hence, the development of new strategy for production of MA based on the utilization of these low-cost and well-sourced feedstock has stimulated researchers' interests.

Aldol condensation as an effective and atom-economic reaction is widely used for

C-C and C=C construction. [9-12] Since Ai reported the gaseous one-step synthesis of MA from coal-based products of methyl acetate and formaldehyde (or trioxane) *via* aldol reaction at 350-380°C, it has been paid more attention to. [13-16] Up to now, series of VPO and Cs-P based acid-base bifunctional catalysts have been developed for this attractive process. Feng developed a kind of VPO catalyst with high fraction of δ-$VOPO_4$ entity and density of medium strong acid sites, which was fabricated by employing poly ethylene glycol additive, for conversion of methyl acetate and formaldehyde with the highest formation rate of 19.8 μmol g_{cat}^{-1} min^{-1} for desired acrylic acid and MA. [17] Guo conducted this reaction on VPO composite and found the P/V ratio had great influence on not only the physicochemical properties of catalyst, but also catalytic activity and selectivity, the highest yield of MA could reach 75.9 % at 370°C when the P/V ratio was 1.2. [18] Yang modified the VPO compound with zirconium element, which would be distributed in the surface adjacent layers and partially incorporated into VPO species, to enhance the fraction of β-$VOPO_4$ and distorted entity of $(VO)_2P_2O_7$, which could promote the formation rate of MA and inhibit the carbon deposition. [19, 20] While Zhao reported a VPO supported γ-Al_2O_3 catalyst and found the yield of MA could be enhanced from 35% to 42% when the γ-Al_2O_3 support was pre-treated with phosphoric acid. [21] Zuo performed the reaction on VPO catalyst in the oxygen atmosphere, which could efficiently inhibit carbon deposition and increase the yield and selectivity of MA. [22] Zhang observed the loading percentage of Cs and P elements would affect the acid-base properties of Cs-P/γ-Al_2O_3 catalyst and the highest yield of MA could climb to 46.2% at 380°C when the Cs and P element was loaded as 5 wt.% and 10 wt.%, respectively. [23] Jiang carried out the reaction on Cs-P/γ-Al_2O_3 catalyst with 5 wt.% Cs and 10 wt.% P loading in fluidized bed reactor, which solved the problems of rapid deactivation and regeneration of catalyst, and the yield of MA could still remain 39.5% after 1000 h of lifetime evaluation. [24] Zuo utilized ZSM-5 instead of γ-Al_2O_3 as support to modulate the acid-base properties of Cs-P catalyst and the maximum yield of MA could attain 43% at 370^{o}C. [25, 26] He prepared Cs supported silica catalyst for MA synthesis and conducted DFT calculation, revealing the appropriate amount of Cs was required since much higher loading would lead to excessive decomposition of methyl acetate and MA. [27, 28] Yan reported a Cs/SBA-15 catalyst with weak Lewis acid-base pairs loaded on the surface, the highest yield and selectivity of MA could reach 46.0% and 95.0%, respectively. [29]

Except for the VOP and Cs-P catalysts, Bao reported barium based catalysts including Ba/Al_2O_3, Ba/γ-Ti-Al_2O_3 and Ba-La/Al_2O_3 for MA production, and the yield could reach up to 45.1% with a selectivity of 90.2%. [30-32] Although it has achieved progress in vaporous one-step synthesis of MA from methyl acetate and trioxane (or formaldehyde) *via* heterogeneous catalysis, the problem of rapid catalyst deactivation and regeneration at high temperature still confuses the researchers. Very recently, our group developed the mild liquid-phase catalytic system for direct synthesis of MA from methyl acetate and trioxane (or methanol) with the highest 90.7% yield and 91.8% selectivity, and found the α-deprotonation of methyl acetate and trioxane decomposition (or methanol dehydrogenation to formaldehyde) were the crucial steps. [33-38] However, both of the trimethylsilyl trifluoromethanesulfonate and dibutylboryl trifluoromethanesulfonate for methyl acetate activation are not stable at lab condition and require the experimental operation under inert atmosphere. In addition, the generated silicon and boron wastes are difficult to recycle, and the effects of cation and anion of ionic liquid catalyst are still unknown.

It is reported that the decomposition of trioxane can proceed with catalysis of strong Lewis acid [33-36], and the α-deprotonation and enolization of ester will undergo with catalysis of fluoride ion in the presence of probase *N, O*-bis(trimethylsilyl) acetamide (BSA) [39, 40]. Stimulated by these discoveries, a novel and efficient ionic liquid catalyzed reaction system was developed for direct synthesis of MA from methyl acetate and trioxane in the presence of BSA at 25°C, which can be operated under lab atmosphere. The effects of cation and anion of ionic liquid on yield and selectivity of MA were investigated and demonstrated with pyridine probing FT-IR. The reaction pathway for MA production was proposed based on the mechanistic experiments and intermediates determined by GC-MS. Also, the kinetic studies were conducted to obtain the parameters and activation barriers, which will promote to have a better understanding on this new process. In addition, the ionic liquid catalyst can be recycled and the silicon compounds generated during reaction can be recovered for BSA preparation.

Experimental

Main materials

Methyl acetate (purity ≥ 99.0%), AgF (purity of 99.0%) and *N, O*-bis(trimethylsilyl) acetamide (BSA, purity ≥ 97.0%) were purchased from *J&K*

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Scientific Ltd., China. Dry dichloromethane (purity ≥ 99.5%) and trioxane (purity of 99.5%) were provided by Xilong Chemical Co., Ltd., China. Octane (purity ≥ 99.5%) was supported by Aladdin Industrial Co., China. All of the ionic liquids (purity ≥ 99.0%) were supplied by Linzhou Keneng Materials Technology Co. Ltd., China. It should be noted that the reactants used for synthesis reactions should be dehydrated by 5 Å zeolite.

Preparation of ionic liquid catalysts

The fluoride-type ionic liquids ([Cation]F) were synthesized from the corresponding chloride-type ionic liquids ([Cation]Cl) and AgF, and the general procedure was described as follows. The aqueous AgF (1.02 eq.) solution was dropwise added into the ethanol solution of [Cation]Cl (1 eq.) at room temperature under vigorous stirring. Then the generated precipitates were filtered off and the filtrate was placed under high vacuum at 40^oC to remove the solvent. After that, the obtained crude [Cation]F ionic liquid was dissolved in ethanol and then filtered off again to remove the remaining AgF. Afterwards, the filtrate was placed under high vacuum at 40^oC again, giving the needed [Cation]F ionic liquid with required purity confirmed by ^{19}F-NMR (**Table S1**, **ESI**).

The Lewis acid-type ionic liquids ([Cation]Cl/MCl_x, M = Cu^+, Fe^{3+}, Zn^{2+} and Al^{3+}) were prepared from metal chloride and corresponding [Cation]Cl ionic liquids according to the following procedures. In a glove box, the suitable amount of metal chloride was charged into a flask, then the flask was sealed and kept in the alcohol bath under -20^oC. Afterwards, the [Cation]Cl ionic liquid, which had been dried under high vacuum at 90^oC for 24 h, in a needed molar ratio was added dropwise into the flask

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under vigorous stirring and kept it for 4 h.

Synthesis reaction

The synthesis reactions for catalytic evaluation were carried out in a 50 mL round-bottomed flask equipped with condenser and magnetic stirrer under atmospheric pressure. The air and moisture inside it should be purged out by charging N_2 before adding the reagents and the reaction mixture was kept in a temperature-controlled water bath. A typical reaction solution was consisted of methyl acetate, BSA, ionic liquid catalyst ([Cation]F and [Cation]Cl/MCl_x) and octane which was used as the internal standard for quantitative analysis. To keep the concentrations consistent, solutions for synthesis reactions with other reagents were prepared to have the same concentration as that of methyl acetate (0.1 mol L^{-1}). The methyl acetate in a needed molar ratio to trioxane, octane and 5 wt.% ionic liquid catalyst were mixed in the solvent of CH_2Cl_2 prior to being charged into the flask. Then BSA with the needed ratio to methyl acetate was added dropwise into the solution under the suitable stirring speed. The product samples collected periodically were qualitatively and quantitatively analyzed on MS and GC part of GC-MS. The yield and selectivity of MA were defined as equations (1) and (2).

$$\text{Yield of MA} = \frac{C_{\text{methyl acetate}, o} - C_{\text{methyl acetate}, t}}{C_{\text{methyl acetate}, o}} \times 100\% \qquad (1)$$

$$\text{Selectivity of MA} = \frac{C_{\text{MA}, t}}{C_{\text{methyl acetate}, o} - C_{\text{methyl acetate}, t}} \times 100\% \qquad (2)$$

Where the $C_{\text{methyl acetate}, o}$ is the initial concentration of methyl acetate before reaction, $C_{\text{methyl acetate}, t}$ and $C_{\text{MA}, t}$ is respect to the concentration of methyl acetate and

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MA after reaction.

For the understanding of reaction pathway, the synthesis reaction in the absence of [Cation]Cl/MCl$_x$ and the treatment of methyl acetate with BSA and [Cation]F in the medium of CH_2Cl_2 were also performed under similar condition. The decomposition of trioxane (0.1 mol/L) without methyl acetate catalyzed by [N3,3,3,3]Cl/MCl$_x$ (5 wt.%) in the solvent of CH_2Cl_2 was conducted at 25°C. While the synthesis of MA from 1-methoxy-1-trimethylsilyloxyethene (0.1 mol/L) and trioxane (0.1 mol/L) with catalysis of [N3,3,3,3]Cl/MCl$_x$ (5 wt.%) in the solvent of CH_2Cl_2 was conducted at 25°C.

Product analysis and quantification

The product samples were quantitatively analyzed on GC part of GC-MS (QP 2020, Shimadzu) equipped with an Rtx-5MS column (30 m × 0.32 mm × 0.25 μm) by using octane as internal standard. Each component in reaction mixture was identified by comparison with the standards and MS information. The initial temperature of oven was 40°C and hold for 2 min, then increased to 300°C at the rate of 15°C min^{-1} and kept for 5 min. The injector and detector temperature was 300°C and 250°C. The relative mass correction factor of each component to octane was obtained from the standard mixture samples. For other compounds without the standard sample, it was estimated with effective carbon number method. [41, 42]

Characterization methods

The ^{19}F-NMR analysis was conducted on a Bruker AVANCE instrument (600 MHz) and the spectra were recorded at ambient temperature. All of the pyridine probing FT-IR spectra were obtained from a Nicolet Fourier transform infrared spectrophotometer at room temperature and the samples were prepared by mixing pyridine, which was firstly dried with KOH and distilled over 4 Å zeolite, with ionic liquid catalyst in the volume ratio of 1:5 under inert atmosphere.

Results and discussion

Catalytic system evaluation

First of all, the ionic liquid catalyzed system for direct synthesis of MA from methyl acetate and trioxane in liquid-phase at 25°C was constructed and evaluated, and the results were shown in **Table 1**. Without probase BSA (Entry 1, 2 and 3), no product of MA can be detected even if [N3,3,3,3]F is used in combination with [N3,3,3,3]Cl/$AlCl_3$ ionic liquid. In the presence of BSA, there's still no MA is recorded on GC-MS when [N3,3,3,3]F (Entry 4) or [N3,3,3,3]Cl/$AlCl_3$ (Entry 5) ionic liquid is used alone. Only if the [N3,3,3,3]F is utilized with [N3,3,3,3]Cl/$AlCl_3$ ionic liquid in the existence of BSA (Entry 6), 60.2% yield of MA is achieved with a selectivity of 94.6%, which is comparable to the bulk VPO catalytic system [17-20] and much higher than that obtained under the catalysis of Cs-P supported materials at 350-380°C [23-29].

As reported in literatures, the trioxane should be decomposed into formaldehyde monomer, which then undergoes aldol condensation with the enolate of methyl acetate for MA production, and the fluoride ion can catalyze the cleavage of Si-O in BSA to generate the strong onium amide base, which is very efficient for *α*-deprotonation and enol silyl etherification of ester. [33, 40] When the reactions were conducted in the absence of BSA (Entry 1, 2 and 3), the onium amide base would not generate for *α*-deprotonation and enol silyl etherification of methyl acetate, so the aldol condensation

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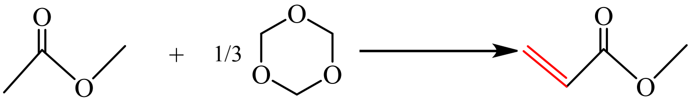
between formaldehyde and the enolate of methyl acetate for production of MA could not proceed. Very similarly, the onium amide base will not produce without catalysis of [N3,3,3,3]F (Entry 5), despite the BSA exists in the reaction system and formaldehyde monomer will generate with catalysis of [N3,3,3,3]Cl/$AlCl_3$. Although the strong onium base will form with the catalysis of [N3,3,3,3]F for α-deprotonation and enol silyl etherification of methyl acetate (Entry 4), the trioxane unit can't undergo aldol condensation with the enolate of methyl acetate. Therefore, the [N3,3,3,3]F must be used in combination with [N3,3,3,3]Cl/$AlCl_3$ ionic liquid in the presence of BSA for production of MA.

Table 1. Catalytic system evaluation for MA synthesis from methyl acetate and trioxane [a]



Entry	Ionic liquid catalyst [b]	probase	Yield of MA /%	Selectivity of MA /%
1	[N3,3,3,3]F	-	0	-
2	[N3,3,3,3]Cl/$AlCl_3$	-	0	-
3	[N3,3,3,3]F and [N3,3,3,3]Cl/$AlCl_3$	-	0	-
4	[N3,3,3,3]F	BSA	0	-
5	[N3,3,3,3]Cl/$AlCl_3$	BSA	0	-
6	[N3,3,3,3]F and [N3,3,3,3]Cl/$AlCl_3$	BSA	60.2	94.6

[a] Reaction condition: 0.1 mol/L trioxane, methyl acetate and BSA ($n_{trioxane} : n_{methyl\ acetate} : n_{BSA} = 1:1:1$) in 20 mL CH_2Cl_2 with 5 mol.% of catalyst at 25°C for 3 h.

[b] The fraction of $AlCl_3$ in [Cation]Cl/$AlCl_3$ ionic liquid is 67 mol.%.

Effects of cation of [Cation]F and [Cation]Cl/$AlCl_3$ ionic liquids

The studies on fluoride ion catalyzed probase method for α-deprotonation of ester

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conducted by Teng and Kondo revealed the cation in generated onium amide base would affect the yield and selectivity of product. [39, 43] Thus, the effects of cation in fluoride and Lewis acid-type ionic liquids were investigated and the cation in these two kinds of ionic liquids were kept the same to ensure the unambiguous result analysis. In this part of work, three types of cation including *N, N*-disubstituted imidazolium, *N*-substituted pyridine and quaternary ammonium were selected for this catalytic system and the results were shown in **Fig. 1**.

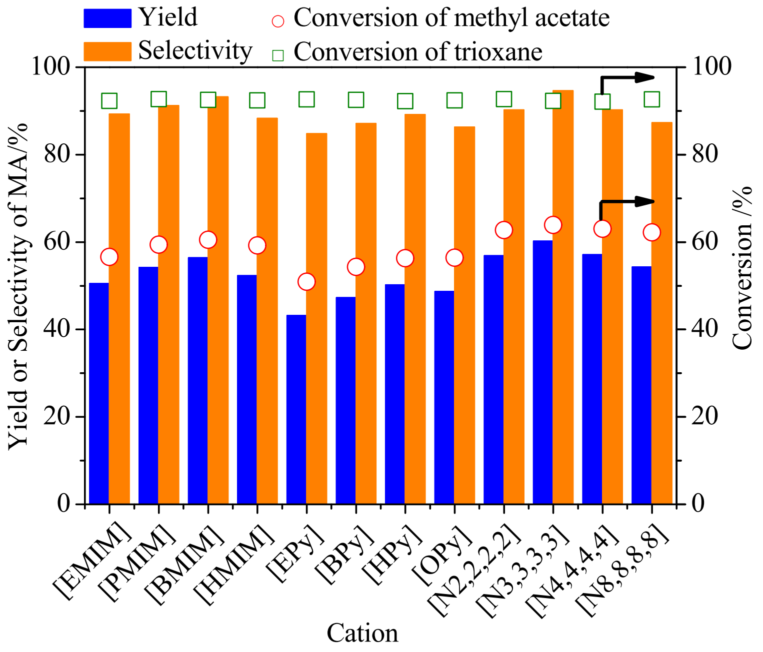

Fig. 1. Effects of cation of [Cation]F and [Cation]Cl/$AlCl_3$ ionic liquids on catalytic performance at the reaction condition of 0.1 mol/L trioxane, methyl acetate and BSA ($n_{trioxane}$: $n_{methyl\ acetate}$: n_{BSA} = 1:1:1) in 20 mL CH_2Cl_2, 5 mol.% of [Cation]F and [Cation]Cl/$AlCl_3$ (with 67 mol.% $AlCl_3$) ionic liquids, 25°C, 3 h. The full names of cation abbreviated in the figure are as follows: [EMIM] (1-Ethyl-3-methylimidazolium), [PMIM] (1-Propyl-3-methylimidazolium), [BMIM] (1-Butyl-3-methylimidazolium), [HMIM] (1-Hexyl-3-methylimidazolium), [EPY] (*N*-ethylpyridinium), [BPY] (*N*-butylpyridinium), [HPY] (*N*-hexylpyridinium), [OPY] (*N*-octylpyridinium), [N2,2,2,2] (Tetraethyl ammonium), [N3,3,3,3] (Tetrapropyl ammonium), [N4,4,4,4] (Tetrabutyl ammonium), [N8,8,8,8] (Tetraoctyl ammonium)

As it can be seen that the cation of [Cation]F and [Cation]Cl/$AlCl_3$ ionic liquids has significant influence on the yield and selectivity of MA. And it also reveals a very interesting phenomenon that the yield and selectivity of MA and the conversion of methyl acetate increase first to the maximum value and then decrease with the extension of substituted alkyl chain length. The catalytic performance of these cation series on MA production follow the order of *N*-substituted pyridine < *N, N*-disubstituted imidazolium < quaternary ammonium. Among the cation tested, the [N3,3,3,3] exhibited the highest performance with the 60.2% yield and 94.6% selectivity towards MA. However, the conversion of trioxane is not affected by the cation, indicating the trioxane decomposition is determined by the anion of [Cation]Cl/$AlCl_3$ that exhibits strong Lewis acidity.

It has been confirmed the activation and breakage of Si-O bond in BSA undergoes with the catalysis of [Cation]F, generating the acetamide anion which interacts with the cation to form onium amide base. Although the catalytic activity of [Cation]F derives from the fluoride ion, the steric hindrance and molecular voidage of cation will increase with the extension of substituted alkyl chain length, [44-46] which will enhance the capacity of BSA molecules in ionic liquid clusters and promote the interaction with catalytic centers. As a result, the transformation of BSA into onium amide base can be accelerated, contributing to the α-deprotonation and enol silyl etherification of methyl acetate. However, the further extension of alkyl chain length will increase the steric hindrance of onium amide base, leading to the inhibition of α-deprotonation of methyl acetate to enolate for the followed aldol reaction between the enolate of methyl acetate and formaldehyde. This explanation is consistent with the experimental fact that the yield of 1-methoxy-1-trimethylsilyloxyethene produced from the enol silyl etherification of methyl acetate is affected by the steric hindrance of cation in [Cation]F

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ionic liquid (**Table S2**, **ESI**). So it can be concluded that the cation with suitable steric hindrance can not only conduce to the generation of onium amide base from BSA, but also promote the enol silyl etherification of methyl acetate.

Effects of metal ion in [N3,3,3,3]Cl/MCl$_x$ ionic liquid

It has been believed that when [Cation]Cl ionic liquid was mixed with metal chloride, the [Cation]Cl/MCl$_x$ shows Lewis acidity, however, the strength will be affected by the metal ion. [40] Herein, series of [N3,3,3,3]Cl/MCl$_x$ (M = Cu^+, Fe^{3+}, Zn^{2+} and Al^{3+}) ionic liquid with 67 mol.% metal chloride was used in combination with [N3,3,3,3]F for catalytic synthesis of MA from methyl acetate and trioxane, and the results were shown in **Fig. 2**. Also, the decomposition of trioxane to formaldehyde catalyzed by these four ionic liquids without methyl acetate were conducted and the results were summarized in **Table S3** (**ESI**). The catalytic performance of these ionic liquid series on both trioxane decomposition and MA production can be ranked as [N3,3,3,3]Cl/CuCl < [N3,3,3,3]Cl/$FeCl_3$ < [N3,3,3,3]Cl/$ZnCl_2$ < [N3,3,3,3]Cl/$AlCl_3$. In addition, the catalytic activity of these ionic liquids on synthesis of MA from 1-methoxy-1-trimethylsilyloxyethene, which is the enolate of methyl acetate, and trioxane follows the same trend, which is shown in **Table S4** (**ESI**).

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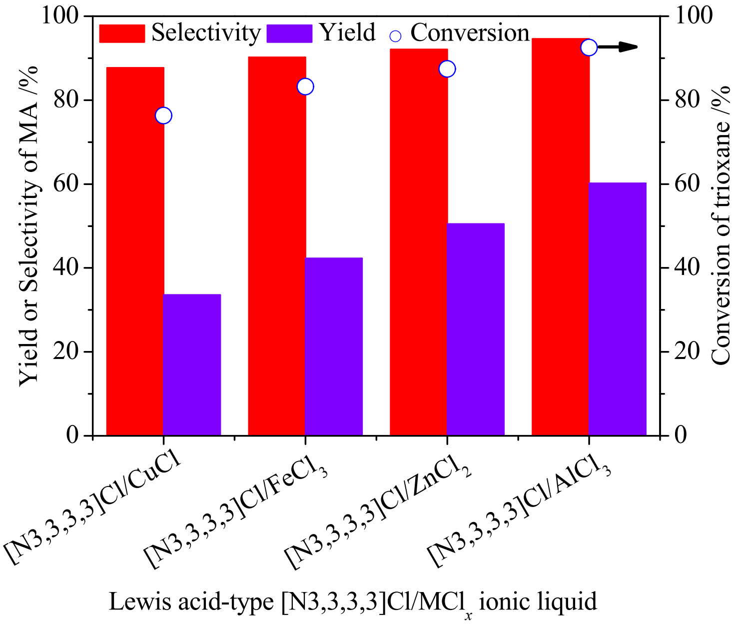

Fig. 2. Effects of metal ion in [N3,3,3,3]Cl/MCl*x* on catalytic performance at the reaction condition of 0.1 mol/L trioxane, methyl acetate and BSA in 20 mL CH_2Cl_2, 5 mol.% of [N3,3,3,3]F and [N3,3,3,3]Cl/MCl_x with 67 mol.% MCl_x, 25°C, 3 h.

To interpret this observed experimental phenomenon, the pyridine probing FT-IR characterization was conducted to measure the acid properties of these ionic liquid series and the results were presented in **Fig. 3**. It can be found that [N3,3,3,3]Cl/$AlCl_3$ and [N3,3,3,3]Cl/CuCl have both Brønsted and Lewis acid sites, however, [N3,3,3,3]Cl/$FeCl_3$ and [N3,3,3,3]Cl/$ZnCl_2$ have only Lewis acid sites. By comparing the Lewis acid site densities of these four ionic liquids, it follows the order of [N3,3,3,3]Cl/CuCl < [N3,3,3,3]Cl/$FeCl_3$ < [N3,3,3,3]Cl/$ZnCl_2$ < [N3,3,3,3]Cl/$AlCl_3$, which agrees with the trend of catalytic performance. Although the Brønsted acid sites in [N3,3,3,3]Cl/$AlCl_3$ and [N3,3,3,3]Cl/CuCl ionic liquids are also effective for the decomposition of trioxane into formaldehyde, it has no catalytic activity on condensation of 1-methoxy-1-trimethylsilyloxyethene with formaldehyde to produce MA. Similar results were also obtained in the aldol condensation between methyl acetate and benzaldehyde. [40] Thus, it can be concluded that the Lewis acid-type

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$[N3,3,3,3]Cl/MCl_x$ ionic liquid can catalyze not only the decomposition of trioxane into formaldehyde, but also the condensation between the enolate of methyl acetate (1-methoxy-1-trimethylsilyloxyethene) and formaldehyde to produce MA. And the metal ion in $[N3,3,3,3]Cl/MCl_x$ will affect the Lewis acid site density, which is required for this catalytic system.

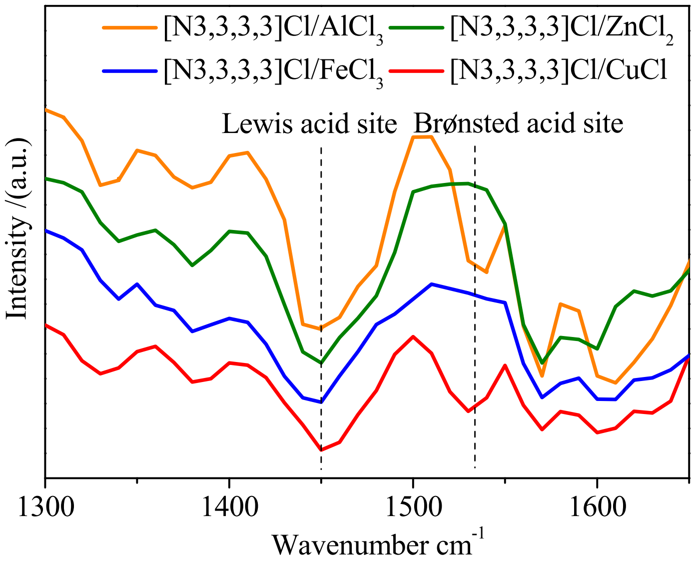

Fig. 3. Pyridine probing FT-IR spectra of $[N3,3,3,3]Cl/MCl_x$ ionic liquid with 67 mol.% of MCl_x ($M = Cu^+$, Fe^{3+}, Zn^{2+} and Al^{3+})

Effects of anion species in $[N3,3,3,3]Cl/AlCl_3$ ionic liquid

As reported by Kou that the anion species existing in $[Bmim]Cl/AlCl_3$ ionic liquid and the Lewis acid strength would be affected by the molar fraction of $AlCl_3$, changing from $AlCl_4^-$ to $Al_2Cl_7^-$ with the molar fraction increasing from 50% to 67%. [47] To investigate the effects of anion species on catalytic activity, the $[N3,3,3,3]Cl/AlCl_3$ ionic liquid with 50 mol.%, 55 mol.%, 60 mol.% and 67 mol.% of $AlCl_3$ were prepared for catalytic synthesis of MA from methyl acetate and trioxane. It can be seen from **Fig. 4** that both of the trioxane decomposition and MA production can be promoted by increasing the molar fraction of $AlCl_3$ from 50% to 67%, revealing the anion species of

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$Al_2Cl_7^-$ shows much higher activity than that of $AlCl_4^-$.

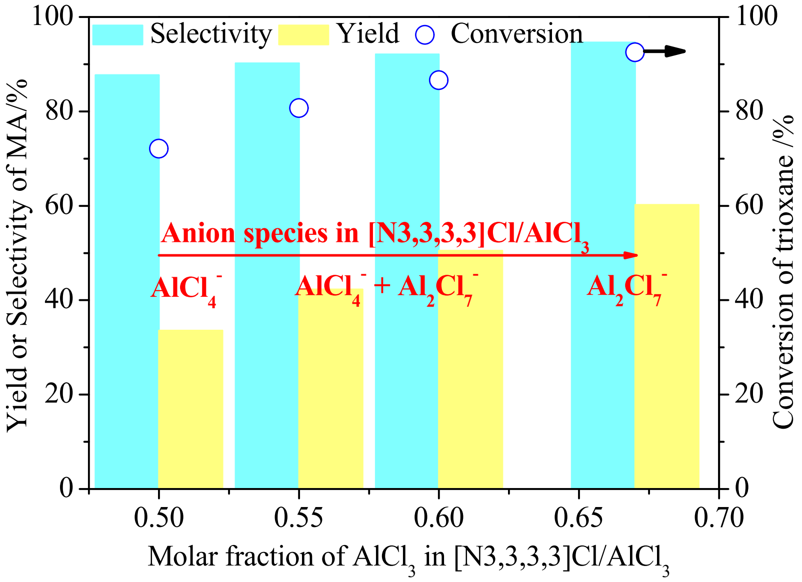

Fig. 4. Effects of molar fraction of $AlCl_3$ in [N3,3,3,3]Cl/$AlCl_3$ on catalytic performance at the reaction condition of 0.1 mol/L trioxane, methyl acetate and BSA in 20 mL CH_2Cl_2, 5 mol.% of [N3,3,3,3]F and [N3,3,3,3]Cl/$AlCl_3$, 25°C, 3 h.

Then the pyridine probing FT-IR characterization for these [N3,3,3,3]Cl/$AlCl_3$ ionic liquids with different molar fraction of $AlCl_3$ were performed and the results were presented in **Fig. 5**. It unravels that with the increasing molar fraction of $AlCl_3$, the peak for the coordination of pyridine at the position of Lewis acid sites shifts to higher wavenumber, suggesting their interaction becomes more intense at higher molar fraction, namely the Lewis acidity of $Al_2Cl_7^-$ is much stronger than that of $AlCl_4^-$. Therefore, it can be considered that the predominant anion species in [N3,3,3,3]Cl/$AlCl_3$ affected by the molar fraction of $AlCl_3$ has significant effects on both trioxane decomposition and MA production, owing to the change in strength of Lewis acidity. And the anion species of $Al_2Cl_7^-$, which exhibits stronger Lewis acidity, shows higher catalytic performance. Similar phenomenon can be observed by comparing the reported results of silyl enol ether with boron enol ether reaction system.

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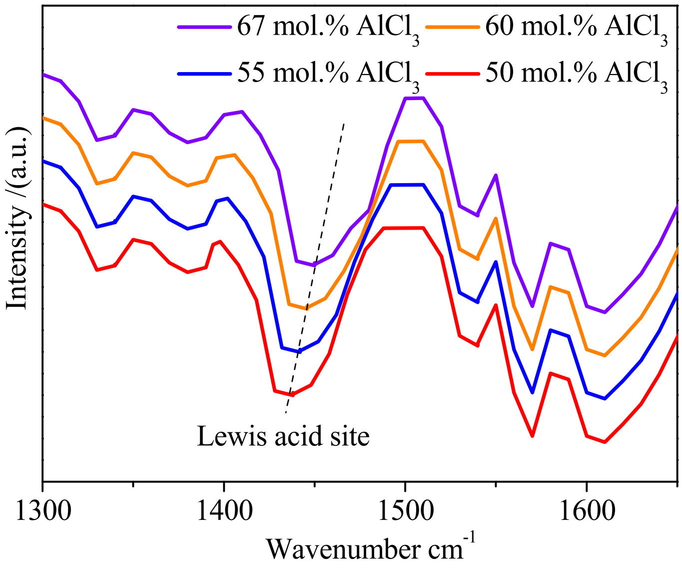

Fig. 5. Pyridine probing FT-IR spectra of [N3,3,3,3]Cl/AlCl$_3$ with different molar fraction of AlCl$_3$

Reaction pathways

As mentioned above, the trioxane should be decomposed into formaldehyde monomer before proceeding condensation with the enolate of methyl acetate to form MA. When the reaction was conducted with the catalysis of [Cation]F, no formaldehyde and MA were detected, but the 1-methoxy-1-trimethylsilyloxyethene as enolate of methyl acetate and *N*-trimethylsilyl acetamide were recorded on GC-MS (MS information are provided in **ESI**). Only [Cation]F was used in combination with [Cation]Cl/MCl$_x$, the formaldehyde and MA generated. Actually, the [Cation]Cl/MCl$_x$ with Lewis acidity is also effective for trioxane decomposition except for protonic acid (**Table S3**). In addition, the reaction between 1-methoxy-1-trimethylsilyloxyethene and trioxane with catalysis of [N3,3,3,3]Cl/MCl$_x$ in the medium of CH_2Cl_2 can also gave the product of MA with almost 100% selectivity after 2.5 h (**Table S4**). The GC-MS analysis for the components in the terminal reaction mixture showed the reaction

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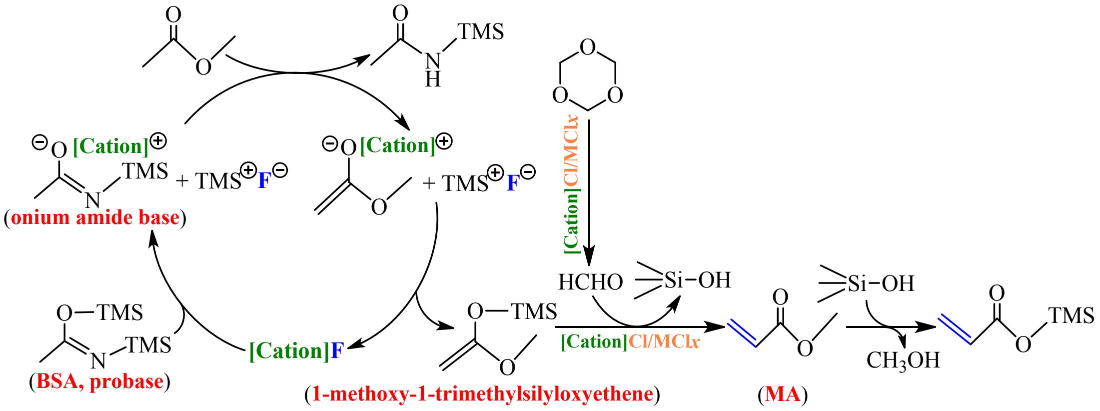
between methyl acetate and trioxane with catalysis of [Cation]F and [N3,3,3,3]Cl/MCl$_x$ gave the main product of MA. Otherwise, a small amount of byproducts of trimethylsilyl acetate and trimethylsilyl acrylate were detected (MS information were provided in **ESI**).



Scheme 1. Proposed reaction pathways for ionic liquid catalyzed direct synthesis of MA from methyl acetate and trioxane in mild liquid-phase

On the basis of these above experimental findings and confirmed substrates, the reaction pathway for MA production in this mild liquid-phase catalytic system was proposed as **Scheme 1**. The probase of BSA is firstly transformed into the strong onium amide base with catalysis of [Cation]F, followed by the α-deprotonation of methyl acetate to onium enolate and generation of *N*-trimethylsilyl acetamide. [39, 43] The highly active onium enolate will transform to 1-methoxy-1-trimethylsilyloxyethene through the interaction with trimethylsilyl group, during which the [Cation]F can be recycled. Meanwhile, the trioxane is decomposed into three units of formaldehyde with catalysis of [Cation]Cl/MCl$_x$. Then the [Cation]Cl/MCl$_x$ catalyzed condensation between the generated formaldehyde and 1-methoxy-1-trimethylsilyloxyethene, which is also called as Mukaiyama reaction, proceeds to produce MA and trimethylsilanol. While the generated trimethylsilanol will undergo transesterification with methyl acetate and

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methyl acrylate, leading to the consumption of reactant and decrease in selectivity of MA. Among all these steps, the trioxane decomposition, onium amide base generation and methyl acetate deprotonation are significantly crucial for the formation of MA in this mild liquid-phase reaction system as we considered.

Kinetic studies

With the understanding of cation and anion effects on catalytic performance of [Cation]F and [Cation]Cl/MCl$_x$-type ionic liquids, the kinetic studies on this whole transformative process was conducted. As described in **Scheme 1**, the main reaction networks include generation of onium base, enolization of methyl acetate to 1-methoxy-1-trimethylsilyloxyethene, decomposition of trioxane into formaldehyde monomer, and condensation between 1-methoxy-1-trimethylsilyloxyethene and formaldehyde to MA. To simplify the kinetic investigation, the trioxane decomposition into formaldehyde without methyl acetate was carried out separately. It has reached a general agreement that the trioxane observes a two-step decomposition mechanism on either Brønsted or Lewis acid sites, namely the C-O activation caused ring opening and formation of a linear trioxymethylene intermediate, followed by further decomposition into three formaldehyde units. [33, 48] **Fig. 6a** shows the concentration evolution of trioxane during decomposition reaction without methyl acetate at 20-35^{o}C, which fits the first-order model well in the region of acceptable deviation less than 5%, and the corresponding rate constants are summarized in **Table 2**. The pre-exponential factor and activation barrier of trioxane decomposition can be calculated as 1.80×10^{5} min^{-1} and 41.2 ± 0.3 kJ mol^{-1} from the Arrhenius plot, as shown in **Fig. 6b**. Compared with the activation

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barrier of 120.1 kJ mol^{-1} obtained in concentrated hydrochloric solution, [49] it can be considered [N3,3,3,3]Cl/AlCl$_3$ with 67 mol.% AlCl$_3$ is an efficient ionic liquid catalyst for the trioxane decomposition into formaldehyde, which will provide supplementary reference in the research field of trioxane decomposition.

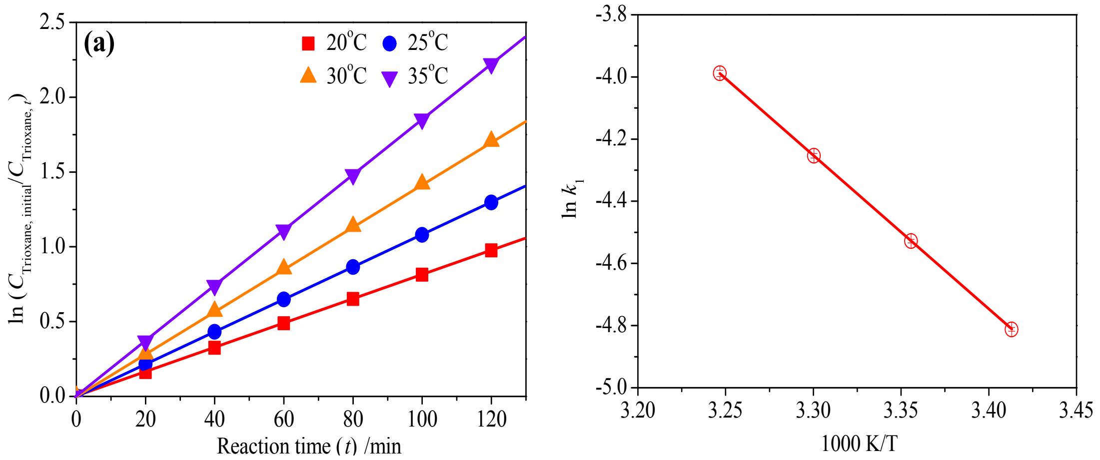

Fig. 6. Concentration evolution of trioxane (a) and Arrhenius plot (b) for kinetic investigation of trioxane decomposition at the reaction condition of 0.1 mol/L trioxane in 20 mL CH_2Cl_2 and 5 mol.% of [N3,3,3,3]Cl/AlCl$_3$ with 67 mol.% AlCl$_3$

Table 2 Rate constants of trioxane decomposition at 20-35°C

T /°C	Kinetic equation	Rate constant (k_1) ×10^3 /(min^{-1})
20	$\ln (C_{\text{Trioxane, initial}}/C_{\text{Trioxane, }t}) = (8.13 \pm 0.05) \times 10^{-3}t$	8.13 ± 0.05
25	$\ln (C_{\text{Trioxane, initial}}/C_{\text{Trioxane, }t}) = (10.80 \pm 0.05) \times 10^{-3}t$	10.80 ± 0.06
30	$\ln (C_{\text{Trioxane, initial}}/C_{\text{Trioxane, }t}) = (14.21 \pm 0.10) \times 10^{-3}t$	14.21 ± 0.10
35	$\ln (C_{\text{Trioxane, initial}}/C_{\text{Trioxane, }t}) = (18.53 \pm 0.19) \times 10^{-3}t$	18.53 ± 0.19

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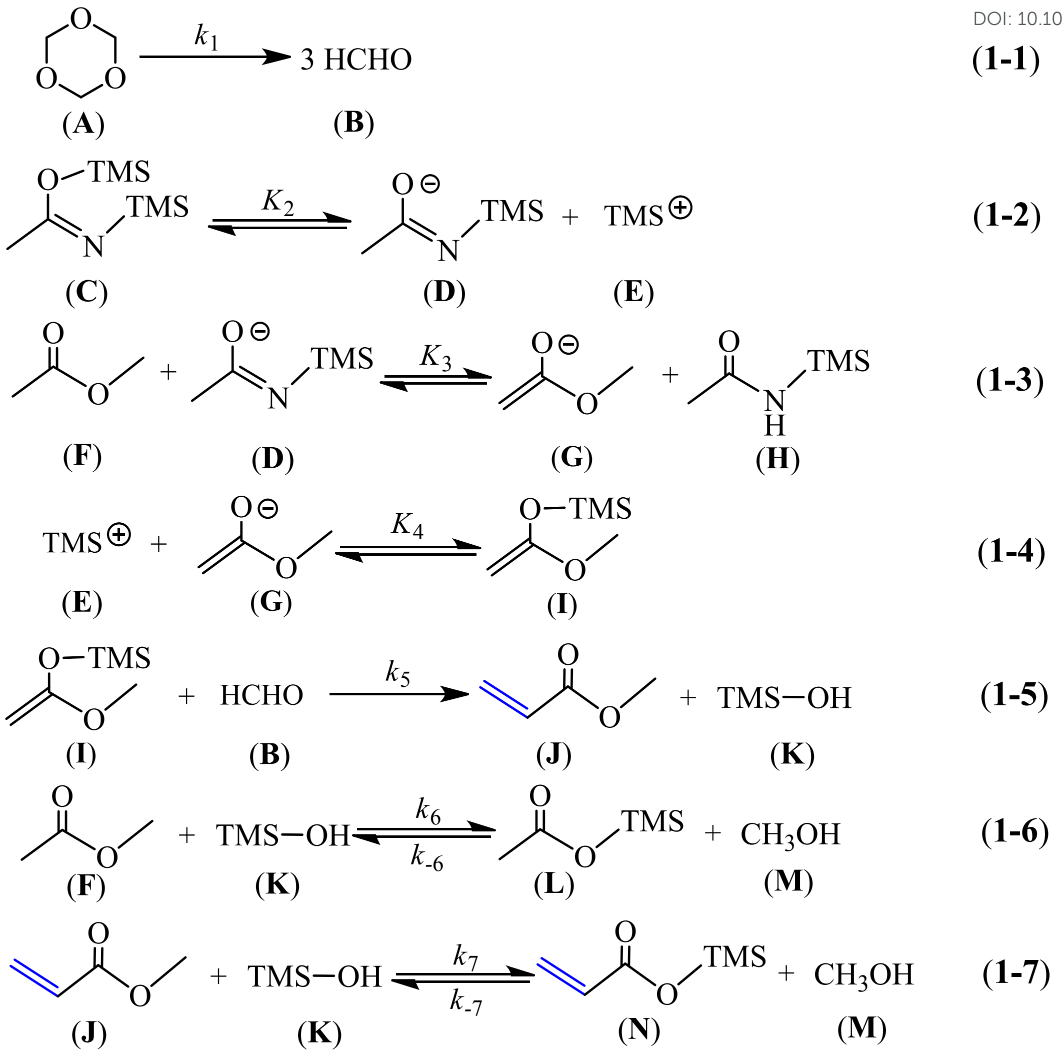

Scheme 2. Proposed elemental steps for direct synthesis of MA from methyl acetate and trioxane with catalysis of [N3,3,3,3]F and [N3,3,3,3]Cl/AlCl$_3$ in the presence of BSA

Based on the kinetic studies on trioxane decomposition and the reaction pathways illustrated in **Scheme 1**, the elemental steps including trioxane decomposition (1-1), onium amide base generation (1-2), methyl acetate enolization (1-3 and 1-4), aldol condensation (1-5) and transesterification (1-6 and 1-7) were proposed in **Scheme 2**. In addition, the steps of onium amide base generation, methyl acetate enolization and transesterification were considered as reversible. Compared with the much slower condensation between 1-methoxy-1-trimethylsilyloxyethene and formaldehyde, both of onium amide base generation and methyl acetate enolization steps, which are also involved in highly active intermediates of **D**, **E** and **G**, are regarded as fast equilibrium. So the equilibrium equations can be expressed as (3)-(5) according to the steady state theory.

$$C_D C_E = K_2 C_C \quad (3)$$

$$C_G C_H = K_3 C_D C_F \quad (4)$$

$$C_I = K_4 C_E C_G \quad (5)$$

So the concentration of intermediate **I** can be expressed by equation (6).

$$C_I = \frac{K_2 K_3 K_4 C_C C_F}{C_H} \quad (6)$$

Then the governing series of design equations can be obtained from (7) to (16).

$$\frac{dC_A}{dt} = -k_1 C_A \quad (7)$$

$$\frac{dC_B}{dt} = 3k_1 C_A - \frac{k_5 K_2 K_3 K_4 C_B C_C C_F}{C_H} \quad (8)$$

$$\frac{dC_C}{dt} = -\frac{k_5 K_2 K_3 K_4 C_B C_C C_F}{C_H} \quad (9)$$

$$\frac{dC_F}{dt} = -\frac{k_5 K_2 K_3 K_4 C_B C_C C_F}{C_H} - k_6 C_F C_K + k_{-6} C_L C_M \quad (10)$$

$$\frac{dC_H}{dt} = \frac{k_5 K_2 K_3 K_4 C_B C_C C_F}{C_H} \quad (11)$$

$$\frac{dC_J}{dt} = \frac{k_5 K_2 K_3 K_4 C_B C_C C_F}{C_H} - k_7 C_J C_K + k_{-7} C_M C_N \quad (12)$$

$$\frac{dC_K}{dt} = \frac{k_5 K_2 K_3 K_4 C_B C_C C_F}{C_H} - k_6 C_F C_K + k_{-6} C_L C_M - k_7 C_J C_K + k_{-7} C_M C_N \quad (13)$$

$$\frac{dC_L}{dt} = k_6 C_F C_K - k_{-6} C_L C_M \quad (14)$$

$$\frac{dC_M}{dt} = k_6 C_F C_K - k_{-6} C_L C_M + k_7 C_J C_K - k_{-7} C_M C_N \quad (15)$$

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$$\frac{\mathrm{d}C_{\mathrm{N}}}{\mathrm{d}t} = k_7 C_{\mathrm{J}} C_{\mathrm{K}} - k_{-7} C_{\mathrm{M}} C_{\mathrm{N}} \qquad (16)$$

After that, the computational regression for the mechanism-based kinetic model was performed by using Runge-Kutta method on MATLAB software, during which the temperature and concentration distribution under all the reaction conditions were considered as uniform. **Fig. 7** shows the concentration evolution of methyl acetate and MA over reaction time at 20-35^{o}C, which are also compared with the results calculated from kinetic model. The obtained parameters from model regression with experimental concentrations are summarized in **Table 3**.

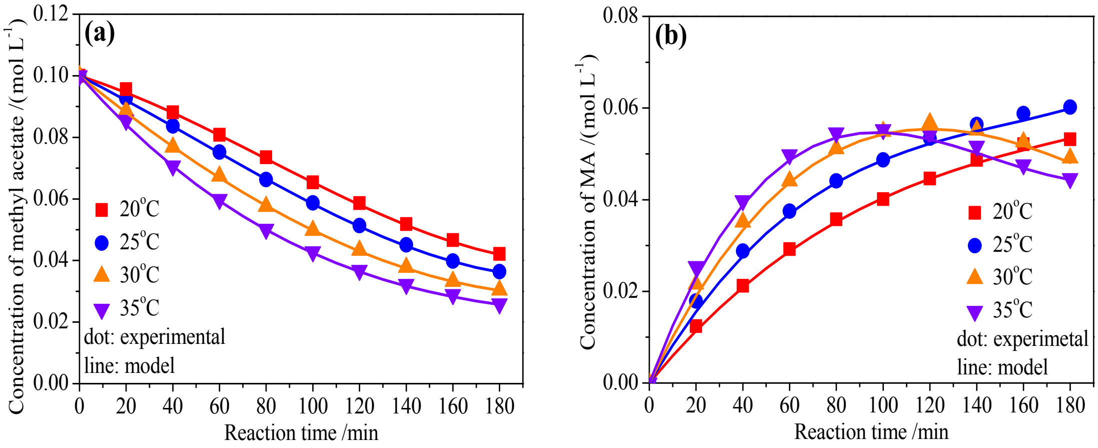

Fig. 7. Concentration evolution of methyl acetate (a) and MA (b) over reaction time at the reaction condition of 0.1 mol/L trioxane, methyl acetate and BSA in 20 mL CH_2Cl_2, 5 mol.% of [N3,3,3,3]F and [N3,3,3,3]Cl/$AlCl_3$, 20-35^{o}C.

It can be seen from **Fig. 7** that the concentrations of methyl acetate at 20-35^{o}C decrease rapidly in 140 min and then the tendency becomes slower. For the concentration of MA, it increase fast before 140 min at 20^{o}C and 25^{o}C, and then the trend becomes stable. However, it appears a peak value and then decrease over reaction time at 30^{o}C and 35^{o}C, due to the transesterification with trimethylsilanol. According to the equilibrium and rate constants presented in **Table 3**, it can be concluded that the generation of onium amide base and deprotonation of methyl acetate are both

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endothermic, while the formation of 1-methoxy-1-trimethylsilyloxyethene is exothermic. In addition, the transesterification of methyl acetate with trimethylsilanol is easier than that of MA due to the electron donor effect of C=C bonds in MA. By comparing the experimentally detected concentrations with the calculated data from kinetic model, the deviation is less than acceptable 5%, suggesting the established model and obtained parameters should be believable at the temperatures from 20°C to 35°C and reaction time before 180 min.

Table 3 The obtained kinetic parameters at 20-35°C

Temperature /°C Parameter	20	25	30	35
$k_1 \times 10^3$ /(min^{-1})	8.13 ± 0.05	10.80 ± 0.06	14.21 ± 0.10	18.53 ± 0.19
$K_2 \times 10^2$	8.39 ± 0.08	8.82 ± 0.11	9.26 ± 0.10	9.71 ± 0.09
K_3	0.54 ± 0.01	0.55 ± 0.01	0.57 ± 0.02	0.59 ± 0.01
K_4	1.80 ± 0.02	1.65 ± 0.01	1.52 ± 0.01	1.40 ± 0.01
$k_5 \times 10^2$ /(L mol^{-1} min^{-1})	5.16 ± 0.06	6.60 ± 0.09	8.36 ± 0.13	10.52 ± 0.11
$k_6 \times 10^3$ /(L mol^{-1} min^{-1})	4.40 ± 0.05	6.80 ± 0.10	10.35 ± 0.18	15.57 ± 0.31
$k_{-6} \times 10^3$ /(L mol^{-1} min^{-1})	5.87 ± 0.08	8.65 ± 0.10	12.59 ± 0.19	18.10 ± 0.31
$k_7 \times 10^3$ /(L mol^{-1} min^{-1})	3.29 ± 0.04	5.21 ± 0.07	8.13 ± 0.15	12.49 ± 0.19
$k_{-7} \times 10^3$ /(L mol^{-1} min^{-1})	5.06 ± 0.09	7.66 ± 0.11	11.43 ± 0.21	16.84 ± 0.32

With these rate and equilibrium constants at different temperatures in hand, the activation barriers and enthalpies of related reaction steps can be calculated from Arrhenius and Van't Hoff plots, which are shown in **Fig. 8** and **Table 4**. It reveals that the thermal effects of these equilibrium reactions are relatively small due to the low enthalpy, which is also consistent with the fact of room-temperature reaction. Compared with the trioxane decomposition and condensation steps, the transesterification of methyl acetate and MA with trimethylsilanol show higher activation barrier. With these kinetic and thermodynamic informatics, this novel ionic

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liquid catalyzed mild liquid-phase system for direct synthesis of MA from methyl acetate and trioxane can be understood in more details. Besides, it will be regarded as a reference for the new catalyst design and catalytic system development in this research area.

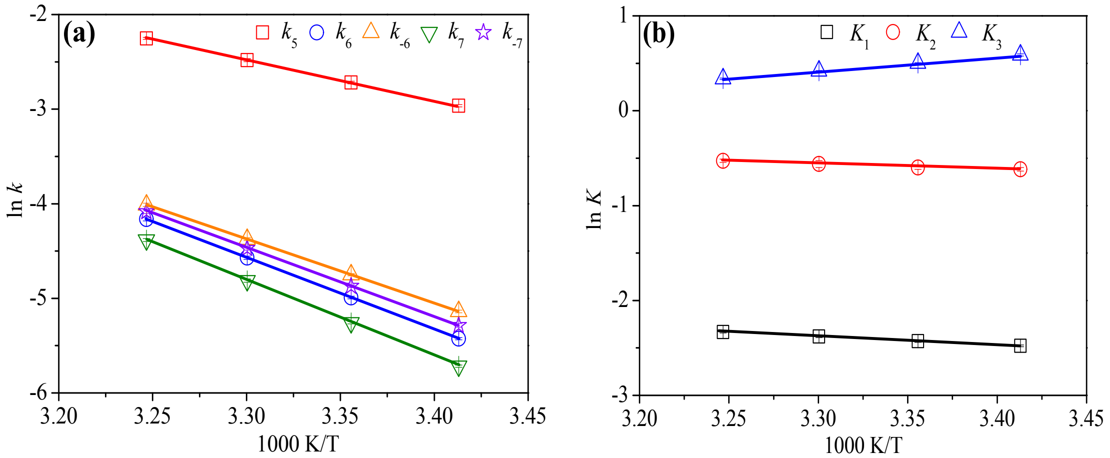

Fig. 8. Arrhenius (a) and Van't Hoff (b) plot for calculation of activation barrier and enthalpy

Table 4 Activation barrier, pre-exponential factor and enthalpy of related reaction steps

Reaction step	Pre-exponential factor	Activation barrier /(kJ mol^{-1})	Enthalpy /(kJ mol^{-1})
A→B	1.80×10^{5} min^{-1}	41.2 ± 0.3	-
C↔D + E	1.68	-	7.3 ± 0.2
D + F↔G + H	3.01	-	4.2 ± 0.4
E + G↔I	1.02×10^{-2}	-	-12.6 ± 0.3
B + I→J + K	1.15×10^{5} L mol min^{-1}	35.6 ± 0.6	-
F + K→L + M	8.22×10^{8} L mol min^{-1}	63.2 ± 1.1	-
L + M→F + K	6.42×10^{7} L mol min^{-1}	56.3 ± 0.8	-
J + K→M + N	2.56×10^{9} L mol min^{-1}	66.7 ± 0.7	-
M + N→J + K	2.62×10^{8} L mol min^{-1}	60.1 ± 0.9	-

Recycling test of ionic liquids

After the reaction, the mixture of [N3,3,3,3]F and [N3,3,3,3]Cl/AlCl$_3$ catalysts can be separated and recovered through high reduced pressure distillation method, owing to the special property of ultralow vapour pressure of ionic liquids. Then the catalyst

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mixture was recycled for synthesis reaction and the catalytic activity can still remain 80% of the fresh one after ten times' reuse, which is shown in **Fig. 9**. And the generated silicon compounds of *N*-trimethylsilyl acetamide and trimethylsilanol can be reused for synthesis of BSA, [50] despite it has not been conducted in this work. Compared with the *in-situ* generated ionic liquid catalyzed liquid-phase system, [33-36] the catalyst and activation reagent of methyl acetate, namely the probase BSA, can be recycled, although the yield of MA achieved in this work is lower.

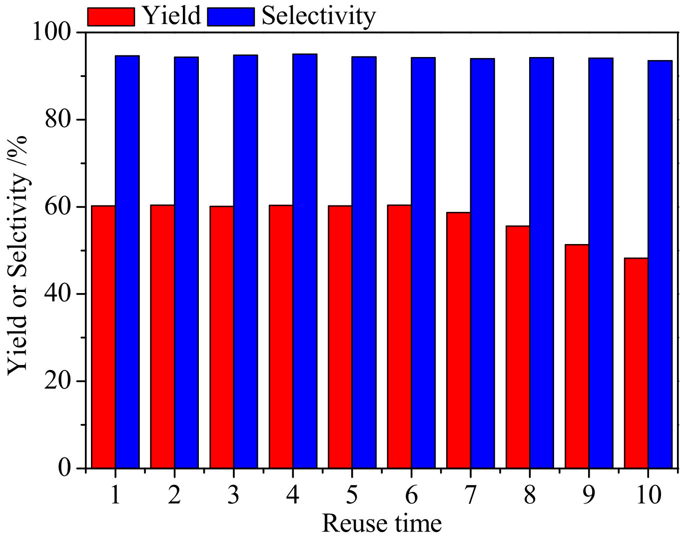

Fig. 9. Recycling test of [N3,3,3,3]F and [N3,3,3,3]Cl/$AlCl_3$ ionic liquids at the reaction condition of 0.1 mol/L trioxane, methyl acetate and BSA in 20 mL CH_2Cl_2, 5 mol.% of [N3,3,3,3]F and [N3,3,3,3]Cl/$AlCl_3$, 25°C.

Conclusion

In this work, an ionic liquid catalyzed mild liquid-phase system was developed for direct synthesis of MA from methyl acetate and trioxane, during which the decomposition of trioxane into formaldehyde and deprotonation of methyl acetate proceeded with catalysis of [Cation]F and [Cation]Cl/MCl (M = Cu^+, Fe^{3+}, Zn^{2+} and Al^{3+}) ionic liquid, respectively. Both of cation and anion of ionic liquid have significant effects on yield and selectivity of MA, resulting from the steric hindrance, Lewis acid

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site density and strength. The side reactions of transesterification between methyl acetate (or MA) with generated trimethylsilanol will decrease the yield and selectivity of MA. As a result, up to 60.2% yield with 94.6% selectivity toward MA was achieved by using [N3,3,3,3]F and [N3,3,3,3]Cl/$AlCl_3$ with 67 mol.% $AlCl_3$ in the presence of BSA at 25°C. The kinetic studies revealed the activation barrier of trioxane decomposition (41.2 ± 0.3 kJ mol^{-1}) was higher than that of condensation between 1-methoxy-1-trimethylsilyloxyethene and formaldehyde (35.6 kJ mol^{-1}), indicating the production of MA was determined by formaldehyde generation.

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