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IONIC LIQUID SUPPORTED ACID-CATALYSED ESTERIFICATION OF LAURIC ACID

(Mangkin Asid Disokong pada Cecair Ionik Sebagai Mangkin dalam Tindak Balas Pengesteran Asid Laurik)

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Abstract

Ionic Liquid (IL) based on 1-n-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($BMI.NTf_2$) under acidic condition was used as catalyst for the esterification reaction of fatty acid. Various acids namely sulphuric acid, perchloric acid, *p*-toulene sulphonic acid and various chloride salts such as zinc chloride ($ZnCl_2$) and iron(III) chloride ($FeCl_3$) immobilized in ionic liquid $BMI.NTf_2$ gave acidic ILs. These acidic ILs were tested as catalysts for esterification reactions. Esterification of alcohol (methanol) with fatty acid (lauric acid) using ionic liquid $BMI.NTf_2$ combined with H_2SO_4 ($BMI.NTf_2(H_2SO_4)$) gave high activity (>85%) and selectivity (100%) observed over a period of 2 hours reaction with reaction temperature 70^{o}C. The ester became easily separated due to IL forming biphasic with product after the reaction where ester accumulated as the upper phase and IL with water produced after reaction at lower phase. Catalytic activities comparison also be studied between acidic ionic liquid $BMI.NTf_2$ with acidic ionic liquid $ChCl^{.}2ZnCl_2$ and conventional acid catalyst. These ILs were characterised by using FTIR, NMR and TGA. Results from FTIR were showed no significant difference between ILs with ILs in acidic condition. The TGA curve show $BMI.NTf_2$ thermal's decomposition is ≥400^{o}C but when $BMI.NTf_2$ combination with H_2SO_4, TGA curve show weight loss increase and becomes unstable. The advantages of ILs as catalyst are “clean process” and “green chemistry” due to its behaviour such as non-volatile, no loss of solvent through evaporation and reduced environmentally impact. This ILs-catalyst system can be recycle for futher reaction.

Keywords: 1-n-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; Choline chloride; Ionic liquids; Acidic condition; Esterification; Fatty acid

Abstrak

Cecair ionik (IL) berdasarkan 1-n-butil-3-metilimidazolium bis(triflorometilsulfonil)imida ($BMI.NTf_2$) dalam keadaan berasid digunakan sebagai mangkin dalam tindak balas pengesteran asid lemak. Pelbagai asid seperti asid sulfurik, asid perklorik, asid *p*-toulena sulfonik dan pelbagai garam klorida seperti zink klorida ($ZnCl_2$) dan ferum klorida ($FeCl_3$) dipegunkan pada cecair ionik $BMI.NTf_2$ menjadikannya ILs berasid. ILs berasid ini diuji sebagai mangkin dalam tindak balas pengesteran. Tindak balas pengesteran alkohol (metanol) dengan asid lemak (asid laurik) menggunakan cecair ILs $BMI.NTf_2$ kombinasi bersama H_2SO_4 memberikan aktiviti yang tinggi (>85%) dan selektiviti yang tinggi (100%) yang mana diperhatikan pada 2 jam tindak balas pada suhu tindak balas 70^{o}C. Produk ester yang terhasil dapat dipisahkan dengan mudah kerana ILs membentuk bifasa dengan produk selepas tindak balas di mana ester terkumpul pada fasa atas manakala cecair ionik dan air yang terhasil pula terkumpul pada fasa bawah. Perbandingan aktiviti-aktiviti mangkin juga dikaji antara IL $BMI.NTf_2$ berasid dengan IL $ChCl^{.}2ZnCl_2$ berasid dan mangkin asid konvensional. ILs ini kemudiannya dicirikan dengan menggunakan FTIR, NMR dan TGA. Keputusan yang didapati daripada FTIR menunjukkan tiada perbezaan antara ILs dengan ILs dalam keadaan berasid. Keluk TGA menunjukkan penguraian terma $BMI.NTf_2$ adalah ≥400^{o}C tetapi apabila kombinasi $BMI.NTf_2$ bersama H_2SO_4, keluk TGA menunjukkan kehilangan berat meningkat dan menjadi tidak stabil. Kelebihan menggunakan ILs sebagai mangkin adalah kerana ILs ini merupakan "proses bersih" dan "kimia hijau" kerana sifatnya yang tidak meruap, tiada kehilangan pelarut melalui penyejatan dan mengurangkan kesan kepada alam sekitar. Sistem mangkin-ILs ini boleh diguna semula untuk tindak balas berikutnya.

Kata kunci: 1-n-butil-3-metlimidazolium bis(trifluorometilsulfonil)imida; Kolin klorida; Cecair ionik; Keadaan berasid; Pengesteran; Asid lemak

Introduction

Esterification of alcohol with fatty acid is the most important reaction in oleochemical industry. The products, fatty acid esters are used as raw material for emulsifiers or as oiling agents for foods, lubricants for plastics; spin finishes and textiles; paints and ink additives and for mechanical processing; surfactants; personal care emollients and base materials for perfume; Japanese candles, etc [1,2]. Esterification reaction usually uses conventionally homogeneous catalyst such as sulphuric acid, *p*-toulene sulphonic acid or phosphoric acid. There are problems when using conventional catalyst where these acid catalysts are toxic, corrosive, involve expensive separation, hard to remove from product, require large volumes of salt waste during neutralization of homogeneous acid and gave environmentally effect [1,2,3,10].

Ionic liquids (ILs) are liquids referred to a new class of solvents that consists only of ions. Ionic liquids also a green reaction media (catalyst + solvent) [3,4,5]. The using of ILs as a catalyst in esterification reaction will solve the problems of using conventionally homogeneous catalysts. This is because, the special characteristics of ionic liquids which are non-volatile, negligible vapour pressure, hence are not volatile to the environment after evaporation ensure ionic liquids to be more environmentally friendly or clean process (green chemistry) [3,5,6]. Ionic liquids are also non corrosive and an interesting aspect here is that the special solubility characteristic of ionic liquids enables a biphasic with product after reaction [4,10,11]. The catalyst can be easily to be isolated effectively from product and can be reused several times [4,10,11].

In recent years the application of ionic liquids as catalyst in esterification reaction has been widely studied especially imidazolium based ILs, also knowing the modern era of ILs [12]. Esterification reaction commonly uses imidazolium based ILs in acidic condition [7,8]. The classical ionic liquids such as 1-n-butyl-3-methylimidazolium tetrafluoroborate and hexafluorophosphate ($BMI.BF_4$ and $BMI.PF_6$) are common ionic liquids used in esterification reaction as catalysts. However, these ionic liquids are not stable under acidic condition and are easily decomposed [8]. In our study, we used ionic liquid 1-n-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($BMI.NTf_2$) under acidic condition after combination with Bronsted or Lewis acids. We also employ ChCl-based ILs or $ChCl{\cdot}2ZnCl_2$ as catalyst in the esterification reaction of fatty acid. We then make activity comparison of this catalyst with that of ILs $BMI.NTf_2$ under acidic condition by increasing reaction times. The use of ionic liquid $ChCl{\cdot}2ZnCl_2$ is being investigated to find what extent is effectiveness when choline chloride based ionic liquids as catalyst in the esterification of lauric acid. This rational is taken because imidazolium based ionic liquids is more expensive than that based on choline chloride [7].

Previous work by Lapis et al. [8] and Sunitha et al. [7] deal with the application of ionic liquid $BMI.NTf_2$ with choline chloride. While the study involving the use of Lewis acid (chloride salt) combined with an ionic liquid has been carried out by Abbott et al. and Angueira et al. [9,13]. The work done by Lapis et al. reported the application of ionic liquid $BMI.NTf_2$ in acidic and basic condition on transesterification reaction of soybean oil. They found that, in this process, the acid is almost completely retained in ionic liquid phase and the biodiesel separates from the ionic liquid and the aqueous phase [8]. While Sunitha et al. study about the using of acidic ionic liquid $ChCl{\cdot}2ZnCl_2$ as catalyst for esterification of long chain carboxylic acids and long chain alcohols typically referred to as 'wax ester' [7]. However, no report has been made regarding the use of ionic liquid $BMI.NTf_2$ and $ChCl{\cdot}2ZnCl_2$ in acid or base as catalyst in the esterification reaction of fatty acid.

Experimental

Materials

1-n-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($BMI.NTf_2$) and zinc chloride (98%) were obtained from Merck. Choline chloride (ChCl) (>97%), iron(III) chloride anhydrous and lauric acid (98%) were obtained from Fluka. Sulphuric acid (95-98%) was obtained from ChemAr, perchloric acid (70%) was obtained from Riedel de Hëin, *p*-toulene sulphonic acid (98.5%) was obtained from Aldrich, stannous chloride anhydrous was obtained from Ajax Chemical and methanol (99.99%) was obtained from Fisher Scientific.

Preparation of Catalysts

BMI.NTf$_2$ (1.79 ml, 6.17 mmol) was mixed with concentrated sulphuric acid (0.34 ml, 6.17 mmol) with stirring until ionic liquid dissolved in sulphuric acid. Combination BMI.NTf$_2$ with another acid was carried out the same method. Choline chloride (20 mmol) was mixed with zinc chloride (40 mmol) and heated to 150°C with stirring until a clear colourless solution was obtained.

Characterization Procedures

Ionic liquids were characterized for ionic liquid BMI.NTf$_2$ and the combination H_2SO_4 with BMI.NTf$_2$ by FTIR, ^1H NMR and also TGA. The FTIR spectra of ionic liquids were recorded on Perkin Elmer model gx 1605. The ^1H NMR spectra of the ionic liquids were recorded after dissolution of the complex in $CDCl_3$ for BMI.NTf$_2$ and D_2O for ChCl with TMS as reference (400 MHz). TGA was performed by Mettler Toledo thermal analyzer. Weights of the samples used were between 20-30 mg and all the samples were heated at 10°C/min in nitrogen from room temperature up to 500°C.

Esterification Procedures

Esterification of lauric acid with methanol was performed in a three-neck flask at atmospheric pressure equipped with a magnetic stirrer bar, thermometer, Dean-Stark receiver, aluminium foil and reflux condenser. The mole ratios for methanol, lauric acid, ILs BMI.NTf$_2$ and H_2SO_4 are 4 : 1 : 0.1 : 0.1. While the mole ratios for methanol, lauric acid, ChCl and $ZnCl_2$ are 4 : 1 : 1 : 2 [7]. The reaction temperature was 70°C. The products were determined by gas chromatography (GC-FID, Agilent 6890) using DB-Wax column (30 m) with added internal standard. The parameter for the temperature program is the starting temperature is 100°C (3 min), ramp at 5°C min^{-1} to 250 (10 min).

Results and Discussion

Characterization using FTIR Technique

Figure 1. shows the FTIR spectra of BMI.NTf$_2$, H_2SO_4 and BMI.NTf$_2$(H_2SO_4). While, Figure 2. shows the FTIR spectra of ChCl, $ZnCl_2$ and $ChCl{\cdot}2ZnCl_2$.

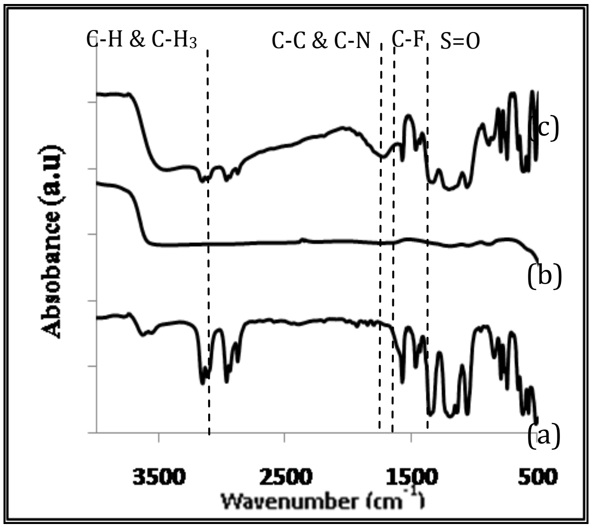

Figure 1: FTIR spectra (a) BMI.NTf$_2$, (b) H_2SO_4, (c) BMI.NTf$_2$(H_2SO_4)

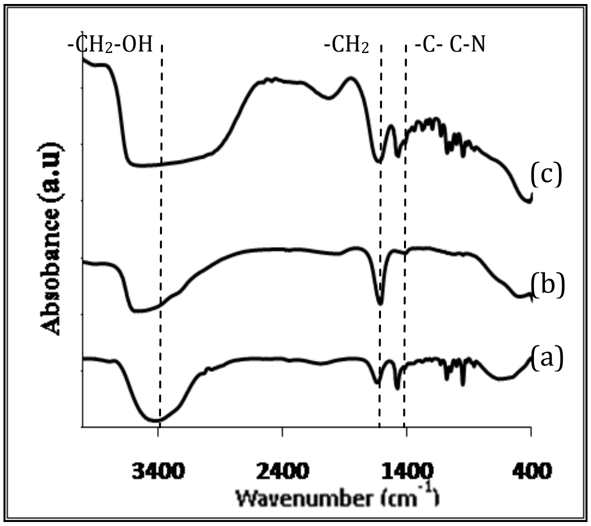

Figure 2: FTIR spectra (a) ChCl, (b) $ZnCl_2$, (c) $ChCl{\cdot}2ZnCl_2$

From Figures 1. and 2. no significant difference was shown, can see that when acids were added to BMI.NTf$_2$ or choline chloride it is just physical mixture between combined acids and ionic liquids. FTIR spectra from Figure 1. shows a band near 2970 cm^{-1}, indicating C-H and CH_3 stretching (C-H, C-H_3 = 2850 - 2980 cm^{-1}), a band near 1590 cm^{-1} showing the C-C and C-N stretching (C-C, C-N = 1650 – 1590 cm^{-1}), a band near 1400 cm^{-1} shows C-F stretching (C-F = 1000 – 1400 cm^{-1}) and a band near 1140 cm^{-1} shows that the S=O stretching in sulphonamides group (1140 – 1350 cm^{-1}). In Figure 1. when sulphuric acid was added to BMI.NTf$_2$ a band near 1140 cm^{-1} is getting broad. This might indicate the presence of sulphuric acid. In Figure 2., FTIR spectra show a band near 3420 cm^{-1} showing the -CH_2-OH stretching (-CH_2OH = 3250 – 3420 cm^{-1}), a band near 1475 cm^{-1} showing -C-H_2 stretching (-C-H_2 = 1450 – 1475 cm^{-1}) and a band near 1230 cm^{-1} shows the presence -C-C-N in amine group (-C-C-N = 1100 – 1230 cm^{-1}).

Characterization using ^{1}H NMR Measurement

Figures 3. Figure 4. show the ^{1}H NMR (400 MHz, $CDCl_3$ and D_2O, TMS) spectrum of BMI.NTf$_2$ and choline chloride respectively. Figure 3. shows the chemical shift at 0.99 ppm ($-CH_2-C\underline{H_3}$), 1.40 ppm ($-C\underline{H_2}-CH_3$), 1.66 ppm (HOD), 1.90 ppm ($-CH_2-C\underline{H_2}-$), 3.97 ppm ($C\underline{H_3}-N-$), 4.20 ppm ($-C\underline{H_2}-CN-$), 7.29 ppm ($CDCl_3$ solvent) 7.32 ppm ($-N-C\underline{H}-CH-$) and 8.79 ppm ($-N=C\underline{H}-N$), respectively. Figure 4., the chemical shifts occured at 3.20 ppm ($3CH_3$'s in $-N-C\underline{H_3}$), 3.53 ppm ($-N-C\underline{H_2}-CH_2-$), 4.06 ppm ($-CH_2-C\underline{H_2}-OH$) and 4.80 ppm ($D_2O$ solvent).

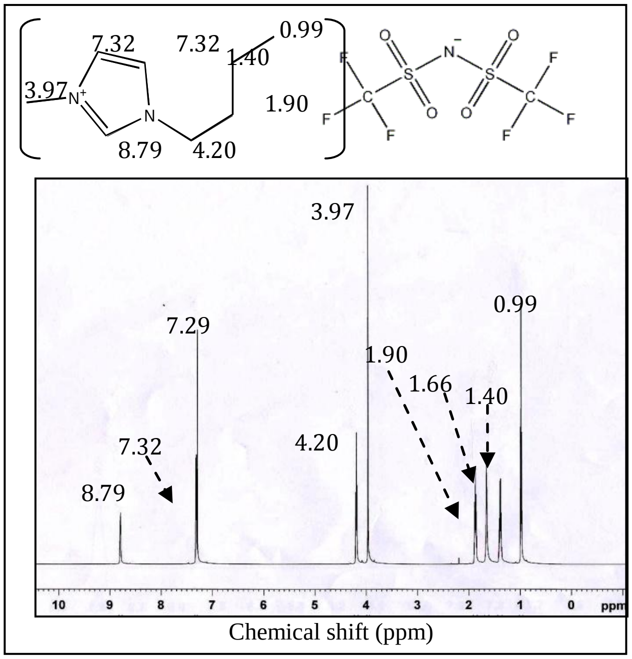

Figure 3. ^{1}H NMR spectrum of BMI.NTf$_2$

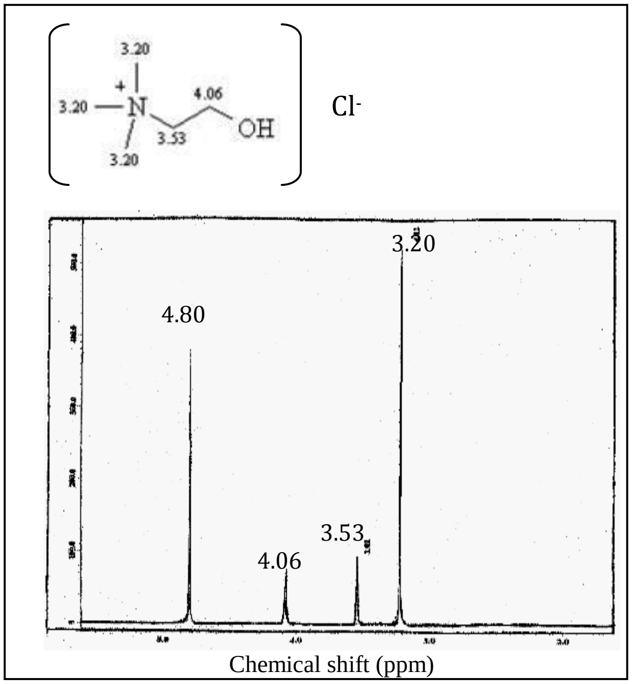

Figure 4: ^{1}H NMR spectrum of ChCl

Characterization using TGA Technique

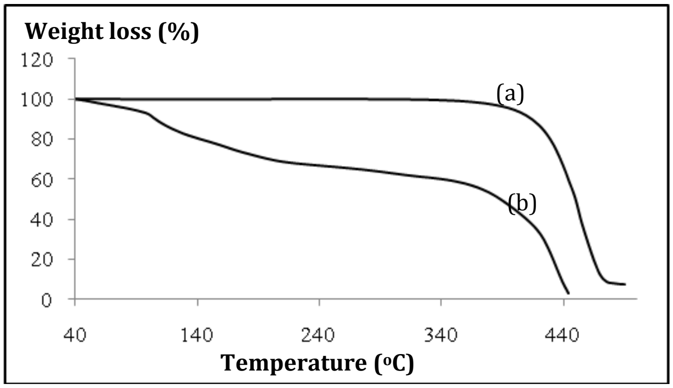

Figure 5: TGA curves of (a) $BMI.NTf_2$ and (b) $BMI.NTf_2(H_2SO_4)$

Base of Figure 5. the TGA curves show that the thermal stability of $BMI.NTf_2$ (Figure 5.(a)) is ≥400°C. This is prove from literature review before that the using ionic liquids immidazolium with anion NTf_2 which gives ionic liquids salts with thermal stability of up to 400°C. This occured because of delocalization of the negative charge, the anion and cation is probably less associated and more mobile than triflate anion. However when combining $BMI.NTf_2$ with H_2SO_4 the weight loss slowly increase and making it less stable than pure $BMI.NTf_2$. This is so maybe due to the presence of H_2SO_4 which causes the ionic liquid $BMI.NTf_2$ to be less stable.

Esterification Reaction

Table 1 : Esterification of lauric acid with methanol using $BMI.NTf_2$ combined with H_2SO_4 and $ChCl^{.}2ZnCl_2$

Entry	Reaction Time [h]	Catalyst (ILs)	Conversion [%]
1	5	$BMI.NTf_2$	24.9
2	2	$BMI.NTf_2\ (H_2SO_4)$	86.8
3	4	$BMI.NTf_2(H_2SO_4)$	88.9
4	5	$BMI.NTf_2(H_2SO_4)$	89.2
5	6	$BMI.NTf_2(H_2SO_4)$	92.2
6	8	$BMI.NTf_2(H_2SO_4)$	90.0
7	5	ChCl	9.0
8	2	$ChCl^{.}2ZnCl_2$	9.9
9	4	$ChCl^{.}2ZnCl_2$	23.4
10	5	$ChCl^{.}2ZnCl_2$	19.5
11	6	$ChCl^{.}2ZnCl_2$	36.8
12	8	$ChCl^{.}2ZnCl_2$	46.3

Reaction condition: Methanol:lauric acid, 4:1, temperature = 70^oC

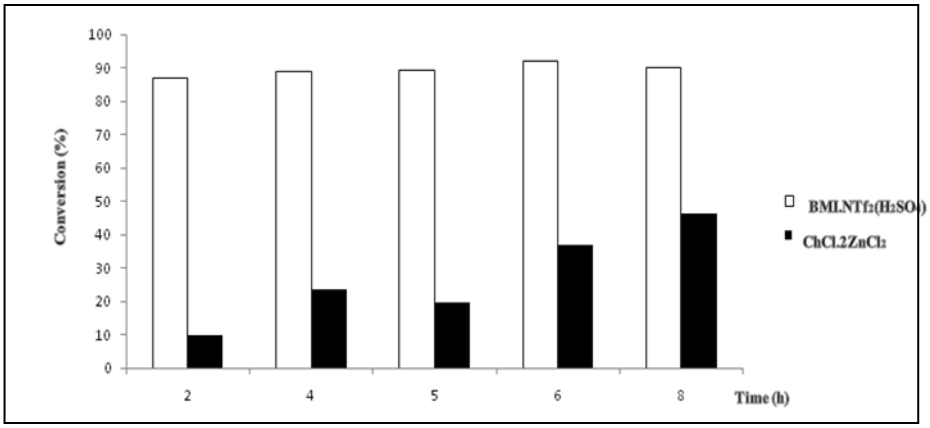

Figure 6. Catalytic activity of $BMI.NTf_2(H_2SO_4)$ and $ChCl^{.}2ZnCl_2$ for esterification of lauric acid

Table 2 Esterification of lauric acid with methanol in combination with various acids to $BMI.NTf_2$

Entry	Catalyst	Ratio[a]	Conversion [%]
1	H_2SO_4	-	97.8
2	$BMI.NTf_2(H_2SO_4)$	1 : 1	89.2
3	$HClO_4$	-	97.8
4	$BMI.NTf_2(HClO_4)$	1 : 1	71.9
5	PTSA	-	95.9
6	$BMI.NTf_2$(PTSA)	1 : 1	98.3
7	$ZnCl_2$	-	66.7
8	$BMI.NTf_2(ZnCl_2)$	1 : 2	84.2
9	$FeCl_3$	-	94.1
10	$BMI.NTf_2(FeCl_3)$	1 : 2	76.8

Reaction condition: Methanol:lauric acid, 4:1, temperature= 70^oC, 5 hours reaction

[a] The mole ratios of $BMI.NTf_2$ to Lewis acid/Bronsted acid

Esterification of lauric acid with methanol was carried out using $BMI.NTf_2$ combined with H_2SO_4 ($BMI.NTf_2(H_2SO_4)$) and $ChCl^{\cdot}2ZnCl_2$ (Table 1) with increasing time of reaction and when using conventional homogenous catalyst (Table 2). All selectivity using these catalysts show high selectivity (100%). In Table 1, all $BMI.NTf_2(H_2SO_4)$ show good catalytic activity, (>85%) conversion except $BMI.NTf_2$ without any combination with acid showing result 24.9% conversion. This means H_2SO_4 influenced catalytic activity. From catalytic activity combination of $BMI.NTf_2$ and H_2SO_4, conversion increased with number of hours of reaction. Catalytic activity of $ChCl^{\cdot}2ZnCl_2$ also increases with time of reaction. Without any combination with $ZnCl_2$, it gives only 9.0% conversion. However, catalytic activity of $ChCl^{\cdot}2ZnCl_2$ for esterification of lauric acid is very low (conversion, 9.0-46.3%) than $BMI.NTf_2(H_2SO_4)$ (conversion, >85%) (see Figure 6). As observed here, catalytic activity using $BMI.NTf_2(H_2SO_4)$ is better than using $ChCl^{\cdot}2ZnCl_2$ in the esterification of lauric acid.

Catalytic activity of combination ionic liquid $BMI.NTf_2$ with other acid was also carried out (Table 2). When combination $BMI.NTf_2$ with Bronsted acid and Lewis acid, the catalytic activity shows small decrease compared to using homogeneous acid catalyst without combination with $BMI.NTf_2$ except combination $BMI.NTf_2$ with PTSA and $FeCl_3$, where the conversion increased. As explained here, all acids increase catalytic activity in the esterification reaction compared to catalytic activity using $BMI.NTf_2$ without any combination.

Conclusion

As conclusion the esterification using ionic liquid $BMI.NTf_2$ in combination with Bronsted acid and Lewis acid gave high conversion and selectivity. Although these combination ionic liquids showed nearly similar activity as homogeneous acid catalysts, these ionic liquids have their own advantage such as the acid was retained in the ionic liquid phase and easily to separated out because ionic liquid has different phase with product but different with conventional homogeneous acid catalysts. This is because conventional homogeneous acid catalysts are difficult to separate and needs high cost for separation and neutralization. Using these combination ionic liquids has some advantages such as high activity and selectivity like homogeneous catalyst, non-corrosive, ease to separate, easy to prepare, low cost and eco-friendly as these ionic liquids are non-volatile.

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