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1-Methylimidazolium Chlorosulfate ($[HMIm]SO_3Cl$): A Novel Ionic Liquid with Dual Brønsted–Lewis Acidity

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A novel acidic ionic liquid, 1-methylimidazolium chlorosulfate ($[HMIm]SO_3Cl$), with dual Brønsted–Lewis acidity was synthesized. This compound provided better catalytic performance in esterification and dehydration of fructose to 5-hydroxymethylfurfural (HMF) than acidic ionic liquids with only Brønsted or Lewis acidity.

Rececently, interest has increased in the use of ionic liquids as novel solvents or catalysts in synthetic chemistry.[1] Acidic ionic liquids are an important subset of functional ionic liquids. They can be used as efficient reaction media or catalysts for a variety of reactions that are usually catalyzed by conventional acidic catalysts such as $AlCl_3$, H_2SO_4, HNO_3, or HCl.[2] In comparison with these conventional catalysts, acidic ionic liquids usually improve catalytic performance, enhance reaction rates, and provide higher yields and easier product separation/catalyst recycling.

The many different acidic ionic liquids that have been synthesized can be classified as either Brønsted or Lewis acids, according to the acidic groups they possess. Few studies have reported preparation of acidic ionic liquids with both Brønsted and Lewis acid sites. In contrast, some solid acids such as dealuminated HY zeolite or mesoporous Al-Zr-TUD-1 can have both Brønsted and Lewis acid sites, and a synergistic effect between these sites has been proposed.[3]

Combination of Brønsted and Lewis acidity within ionic liquids can impart new properties. For example, it is well established that Lewis acidic chloroaluminate ionic liquids can become superacidic in the presence of protons. This is one of the few examples of an acidic ionic liquids with Brønsted–Lewis dual acidity. Recently it was revealed that incorporation of an acidic ionic liquid with a Lewis acid co-catalyst can efficiently increase the catalytic performance for certain reactions.[4] Thus, synthesis of acidic ionic liquids with both Brønsted and Lewis acid sites is important for expanding both the scope and application of acidic ionic liquids.

We previously reported synthesis of SO_2Cl-based Lewis acid ionic liquids.[4b] As a continuation of this, we herein report a novel ionic liquid with dual Brønsted–Lewis acidity, 1-methylimidazolium chlorosulfate ($[HMIm]SO_3Cl$). This ionic liquied can be easily synthesized by reaction of 1-methylimidazolium hydrogen sulfate ($[HMIm]HSO_4$),[5] a common Brønsted acid ionic liquid, with $SOCl_2$. Our primary results showed that $[HMIm]SO_3Cl$ provides better catalytic performance in esterification and dehydration of fructose to HMF than both its Brønsted acid precursor and the SO_2Cl-based Lewis acid ionic liquid reported previously.[4b]

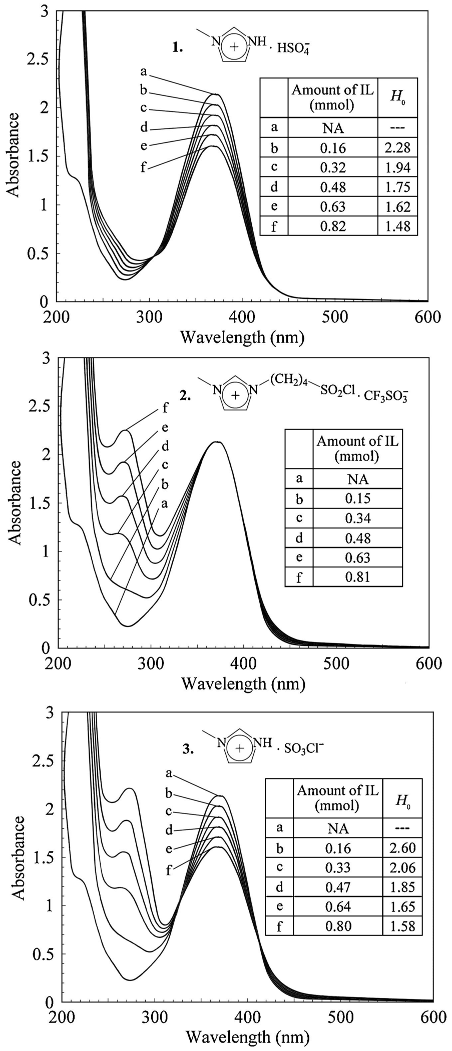
To prepare $[HMIm]SO_3Cl$, 5 g of $SOCl_2$ was added dropwise to 10 g of $[HMIm]HSO_4$ in a 50 mL flask in an ice water bath. Then the reaction mixture was stirred for 12 h at room temperature. After another 2 h of reaction at 80 °C, excess $SOCl_2$ was removed from the reaction mixture via vacuum distillation. The remaining yellow liquid was washed with diethyl ether three times, and dried under vacuum at room temperature. The structure of $[HMIm]SO_3Cl$ was confirmed by NMR and HRMS analyses (see Supporting Information).[11]

Usually, the acidity of Brønsted acid ionic liquids can be quantitatively characterized by Hammett acidity function based UV–visible spectroscopy.[6] Our previous study has shown that this method can also be qualitatively applied to Lewis acid ionic liquids.[7] In the current study, the acidity of $[HMIm]SO_3Cl$ was investigated by UV–visible spectroscopy using *p*-nitroaniline as an indicator and methanol as the solvent. For comparsion, the Brønsted acid ionic liquid $[HMIm]HSO_4$, which was used as the precursor of $[HMIm]SO_3Cl$, and Lewis acidic ionic liquid 3-methyl-1-(4-chlorosulfonylbutyl)imidazolium trifluoromethanesulfonate ($[MSCBI]CF_3SO_3$) were also analyzed. The results are summarized in Figure 1.

The Brønsted acid $[HMIm]HSO_4$ showed a typical increase of acidity, in terms of H_0, with an increase of its concentration in methanol. The peaks at 270–280 nm gradually intensified for the Lewis acidic $[MSCBI]CF_3SO_3$. These peaks indicate the presence of the Lewis acidic SO_2Cl in the molecular structure of $[MSCBI]CF_3SO_3$. $[HMIm]SO_3Cl$ exhibited features of both Brønsted and Lewis acid ionic liquids, which clearly demonstrated that it had dual Brønsted–Lewis acidity.

1-Methylimidazolium bromide ([HMIm]Br) is an analogous ionic liquid to $[HMIm]HSO_4$. Some previous studies suggested that the nitrogenic proton in [HMIm]Br is not labile, and that [HMIm]Br cannot be viewed as a Brønsted acid.[8] However, the UV–visible spectra of $[HMIm]HSO_4$ and $[HMIm]SO_3Cl$ indicate that both the nitrogenic proton and the hydrogen sulfate proton contribute to the Brønsted acidity of $[HMIm]HSO_4$. The respective contributions of these protons to the acidity H_0 can be determined by considering the change in H_0 after HSO_4^- is converted to SO_3Cl^-. Due to the absence of the hydrogen sulfate proton, the Brønsted acidity of $[HMIm]SO_3Cl$ was slightly less than $[HMIm]HSO_4$ when dissolved in methanol at the same concentration.

Esterification is one of the most frequently employed probe reactions for examing the performance of acidic ionic liquids.[9] We investigated the catalytic activity of $[HMIm]SO_3Cl$ for esterification, and compared it to control experiments using $[HMIm]HSO_4$ and $[MSCBI]CF_3SO_3$. $[HMIm]SO_3Cl$ gave higher product yields than $[HMIm]HSO_4$ and $[MSCBI]CF_3SO_3$ (Table 1). This can be attributed to the presence of both Brønsted and Lewis acid sites in $[HMIm]SO_3Cl$, which provides many active sites for the reaction. It should be noted that the activity of $[HMIm]HSO_4$ was very low for the



	Amount of IL (mmol)	H_0
a	NA	---
b	0.16	2.28
c	0.32	1.94
d	0.48	1.75
e	0.63	1.62
f	0.82	1.48

	Amount of IL (mmol)
a	NA
b	0.15
c	0.34
d	0.48
e	0.63
f	0.81

	Amount of IL (mmol)	H_0
a	NA	---
b	0.16	2.60
c	0.33	2.06
d	0.47	1.85
e	0.64	1.65
f	0.80	1.58

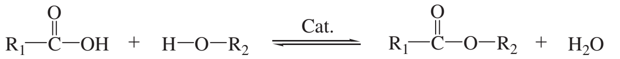
Figure 1. UV–visible spectra of *p*-nitroaniline in methanol in the presence of different acidic ionic liquids: (1) [HMIm]HSO_4, (2) [MSCBI]CF_3SO_3, and (3) [HMIm]SO_3Cl. Conditions: *p*-nitroaniline, 0.025 g L^{-1}; and methanol, 10 g.

esterification reaction. Similar results were observed in previous studies.[5]

The catalytic activity of [HMIm]SO_3Cl was also examined for dehydration of fructose to HMF, which is a major route for conversion of biomass to useful chemicals. We have previously used [MSCBI]CF_3SO_3 as catalyst for this reaction.[7] [HMIm]SO_3Cl gave an 83% yield of HMF, which was higher than that with [HMIm]HSO_4 (71%) or [MSCBI]CF_3SO_3 (77%).[10]

In conclusion, we synthesized a novel ionic liquid, [HMIm]SO_3Cl, that had dual Brønsted–Lewis acidity. This ionic liquid had higher activity in esterification and dehydration of fructose to HMF than ionic liquids with only Brønsted or Lewis acidity. We believe this will lead to further applications in acid-catalyzed reactions, and additional studies are underway.

Table 1. Esterification catalyzed by different acidic ionic liquids[a]



$$R_1-\overset{O}{\overset{\|}{C}}-OH + H-O-R_2 \xrightleftharpoons{\text{Cat.}} R_1-\overset{O}{\overset{\|}{C}}-O-R_2 + H_2O$$

Run	R_1 Acid	R_2 Alcohol	Temp /°C	Time /min	Yields IL 1	IL 2	IL 3
1	CH_3	C_2H_5	60	90	4.0	79.5	85.2
2	CH_3	$C_6H_5CH_2$	80	120	3.2	74.2	82.6
3	CH_3	*n*-C_6H_{13}	60	60	3.0	60.0	78.5
4	CH_3	*n*-C_8H_{17}	80	150	5.1	79.0	85.5
5	CH_3	*i*-C_3H_7	60	90	3.8	75.2	80.8
6	CH_3	*t*-C_4H_9	60	90	4.0	76.5	79.6
7	*n*-C_7H_{15}	C_2H_5	80	90	4.2	78.5	84.2
8	C_6H_5	C_2H_5	80	120	3.5	71.0	80.2

[a]Acid: 0.02 mol, alcohol: 0.03 mol, and IL: 0.2 mmol. IL 1: [HMIm]HSO_4, IL 2: [MSCBI]CF_3SO_3, and IL 3: [HMIm]-SO_3Cl.

References and Notes

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11 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.