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Article

Brönsted acid surfactant-combined dicationic ionic liquids as green catalysts for biodiesel synthesis from free fatty acids and alcohols

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ABSTRACT

Quaternary ammonium Brönsted acid surfactant-combined dicationic ionic liquids (BASDILs) based on zwitterionic 1,2-bis[*N*-methyl-*N*-(3-sulfopropyl)-alkylammonium]ethane betaines and various anions were prepared and characterized. BASDILs possess properties similar to those of phase-separated catalysts and were applied to the catalytic synthesis of biodiesel from free fatty acids and alcohols. Several factors were investigated and the results indicated that [C_{12}Sb][*p*-$CH_3C_6H_4SO_3$] was the optimal catalyst, with good catalytic performance and reusability under mild conditions.

1. Introduction

Because of environmental concerns and the ongoing depletion of fossil fuels, biodiesel has attracted considerable attention during the past decade as an alternative, green and renewable fuel [1]. Biodiesel is generally produced from vegetable oils or animal fats by transesterification of triglycerides [2–4] or by esterification of free fatty acids (FFAs) with short-chain aliphatic alcohols [5–9]. However, the mineral acids that are employed for this purpose in industrial processes cannot be recycled and have other disadvantages [10]. In addition, the rate of the esterification reaction with heterogeneous catalysts is adversely affected by mass transfer limitations resulting from the heterogeneous reaction conditions [11]. Hence, it would be beneficial to replace existing esterification methods with more environmentally benign processes.

Various ionic liquids (ILs) have been used as catalysts for preparing biodiesel from long-chain FFAs and can be easily recycled [12–14]. In particular, SO_3H-functionalized ILs have been successfully used as catalysts and reaction media for biodiesel production, resulting in excellent performance and high yields [15–20]. Among these, the dicationic ILs have received significant attention [21] because of their higher stability as compared with their monocationic analogues. Fang et al. [22] used halogen-free dicationic acidic ILs in the synthesis of biodiesel from FFAs and alcohols, while Zhang et al. [23] prepared three dicationic basic ILs for biodiesel production from soybean oil. Aghabarari et al. [24,25] reported the use of acidic ILs based on bentonite as catalysts for the esterification of oleic acid with short-chain alcohols. However, the relatively high

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cost of ILs containing the imidazolium cation hinders their industrial applications. Thus, a more efficient, simple and biodegradable catalyst need to be developed.

In the present work, we prepared quaternary ammonium Brönsted acid surfactant-combined dicationic ILs (BASDILs, Scheme 1) and explored their application as green catalysts for biodiesel production from FFAs and alcohols. To gain an understanding of the acidity-activity relationship, the Hammett method was also employed to evaluate the acidity of the BASDILs.

2. Experimental

2.1. Synthesis of BASDILs

BASDILs were synthesized according to our previously described protocol [26]. The zwitterionic 1,2-bis[*N*-methyl-*N*-(3-sulfopropyl)-alkylammonium]ethane betaines (C*n*Sbs) were prepared by the reaction of *N,N'*-dimethylethylenediamine with *n*-alkyl bromide, followed by reaction with 1,3-propanesulfonate. Zwitterion acidification was subsequently accomplished by mixing the zwitterions with *p*-toluenesulfonic acid monohydrate.

2.2. Measuring the acidity of BASDILs

The Brönsted acidity of the ILs was determined by employing Hammett functions (H_0) together with UV-visible spectroscopy data acquired on a Perkin Elmer Lambda 35 UV-Vis spectrophotometer, following a previously reported procedure [18,27,28]. In this process, the BASDIL and the indicator 4-nitroaniline (pK_a = 0.99) were both dissolved at respective concentrations of 35 and 110 μmol/L in anhydrous ethanol.

2.3. Esterification reaction

The esterification reactions were carried out in a 10-ml tube with a reflux condenser. Portions of the catalyst (0.020–0.316 mmol) and of oleic acid (7.9 mmol, 2.23 g) were transferred into the reactor and preheated prior to the addition of the alcohol. Upon reaching the desired reaction temperature (25–70 °C), methanol (0.32–1.28 ml) was added into the reactor and the reaction was initiated. The reaction mixture was vigorously stirred at a constant rate for all runs. The oleic acid-methanol molar ratio, reaction time and temperature were all varied according to an experimental design. Upon reaction completion, the reactor was cooled to room temperature and phase separation was observed. Excess methanol was evaporated under vacuum and the IL settled to the bottom of the flask because it was immiscible with the ester, which formed the upper layer. Thus, the biodiesel could be separated by simple decantation and the catalyst was easily recycled by removal of water. The conversion of oleic acid was determined by acid–base titration [18].

3. Results and discussion

3.1. Acidity of BASDILs

The Hammett acidity function (H_0) can effectively express the strength of an acid in an organic solvent, and the H_0 values of the different BASDILs are summarized in Table 1. These data allow an assessment of the effect of the BASDIL structure on H_0. The results demonstrate that the acidity increased with elongation of the hydrocarbon chain (entries 2 and 3) and plateaued when the number of carbon atoms exceeded eight (entries 4, 5 and 9). Moreover, the acidity of BASDILs with different anions decreased in the order $[C_{12}Sb][Tos]$ > $[C_{12}Sb][HSO_4]$ > $[C_{12}Sb][CH_3SO_3]$ > $[C_{12}Sb][Br]$ (entries 5–8), in accordance with the acidity of the anionic counterparts.

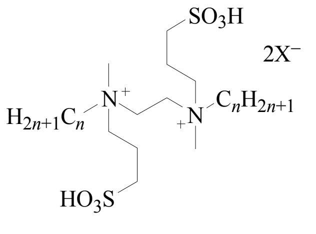
3.2. The catalytic performance for the esterification of oleic acid with methanol

To simplify the screening process, oleic acid was used as a model substrate, since it is a major and key component of low quality feedstock. The catalytic performance of different

Table 1
H_0 values of different BASDILs in ethanol.

Entry	BASDILs	[I] (%)	[IH] (%)	H_0
1	blank	100	0	—
2	$[C_4Sb][Tos]$	96.53	3.47	2.43
3	$[C_8Sb][Tos]$	77.15	22.85	1.52
4	$[C_{10}Sb][Tos]$	78.03	21.97	1.54
5	$[C_{12}Sb][Tos]$	77.63	22.37	1.53
6	$[C_{12}Sb][HSO_4]$	82.97	17.03	1.67
7	$[C_{12}Sb][CH_3SO_3]$	87.64	12.37	1.84
8	$[C_{12}Sb][Br]$	95.06	4.93	2.28
9	$[C_{14}Sb][Tos]$	78.61	21.39	1.55

Condition for UV-Vis spectra measurements: solvent anhydrous ethanol, indicator 4-nitroaniline at 110 μmol/L, BASDIL 35 mmol/L, 25 °C.



1: $n = 4$, $X^- = p\text{-}CH_3(C_6H_4)SO_3^-$, $[C_4Sb][Tos]$;
2: $n = 8$, $X^- = p\text{-}CH_3(C_6H_4)SO_3^-$, $[C_8Sb][Tos]$;
3: $n = 10$, $X^- = p\text{-}CH_3(C_6H_4)SO_3^-$, $[C_{10}Sb][Tos]$;
4a: $n = 12$, $X^- = p\text{-}CH_3(C_6H_4)SO_3^-$, $[C_{12}Sb][Tos]$;
4b: $n = 12$, $X^- = HSO_4^-$, $[C_{12}Sb][HSO_4]$;
4c: $n = 12$, $X^- = CH_3SO_3^-$, $[C_{12}Sb][CH_3SO_3]$;
4d: $n = 12$, $X^- = Br^-$, $[C_{12}Sb][Br]$;
5: $n = 14$, $X^- = p\text{-}CH_3(C_6H_4)SO_3^-$, $[C_{14}Sb][Tos]$;

Scheme 1. Structures of the BASDILs.