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Short communication

Sulfamic acid: An efficient acid catalyst for esterification of FFA

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ABSTRACT

Esterification is one of the most fundamental reactions in organic chemistry. It has a great application in both laboratory work and industrial processes on account of its versatility. In this study sulfamic acid (H_2NSO_3H, SA) was used as an efficient catalyst for the synthesis of fatty acid methyl and ethyl esters (FAEEs and FAMEs) under different conditions (fatty acid type, molar ratio, temperature, and % catalyst). Esterification using methanol and ethanol resulted in a higher fatty acid alkyl ester yield. The best result was obtained with ethanol, which yielded 91.2–97.7% FAEEs. However, in the same conditions the FAMEs were obtained with lower yields. These results demonstrate that this green methodology has high potential for the synthesis of fatty acid alkyl esters.

1. Introduction

In recent years, the use of solid acids as heterogeneous catalysts has received tremendous interest in various areas of organic synthesis [1–3]. Heterogeneous solid acids are advantageous compared with conventional homogeneous acid catalysts, as they can be easily recovered from the reaction mixture by simple filtration and can be reused after activation or without activation, thereby making the process economically more viable [4]. Esterification is one of the most fundamental reactions in synthetic organic chemistry and is extensively employed for the production of alkyl esters from carboxylic acids [5–7]. Fatty acid alkyl esters (FAAEs) serve as feedstock for the production of cosmetics, detergents, surfactants, and more recently, biodiesel [8] (fatty acid methyl esters, FAMEs) [9]. In general, FAMEs are currently produced by homogeneous acid catalysis with sulfuric [10] or *p*-toluenesulfonic acid [11], which produce secondary reactions and generate pollution.

Sulfamic acid (H_2NSO_3H, SA) has emerged as a substitute for conventional Bronsted- and Lewis acid catalysts. It is a relatively stable, white crystalline solid that is odorless, non-volatile, non-hygroscopic, non-corrosive, and low-cost, and it is a highly efficient green catalyst in organic synthesis [12,13]. More specifically, sulfamic acid is a sulfur-containing amino acid with mild acidity. Interestingly, sulfamic acid exists not only in its aminosulfonic acid form, but also as $H_3N^+SO_3^-$ zwitterionic units [14] immiscible with commonly employed non-polar organic solvents [12]. It possesses distinctive catalytic features related to its zwitterionic nature and displays an excellent activity over a vast array of acid-catalyzed organic transformations. It has been extensively used for acid catalyzed reactions, such as functional group protections [15] and deprotections [16] and some important organic transformations, such as the Beckmann rearrangement [17], the Michael addition [18], imino Diels–Alder reactions [19], and Pechmann [20] and Biginelli condensations [21].

We herein report a practical method, easily separable, and highly effective catalytic system (SA/alcohol) for the synthesis of fatty acid ethyl and methyl esters (FAEEs and FAMEs).

2. Experimental

The fatty acids and sulfamic acid (98 wt.%) were supplied by Aldrich, methanol and ethanol from Merck.

2.1. General procedure

Acid-catalyzed esterification of fatty acid was carried out in 25 mL round-bottomed flasks equipped with a condenser and a magnetic stirrer. A mixture of alcohol and fatty acid, molar ratios 6:1 our 9:1, respectively, was heated to 80 °C, 100 °C our 120 °C for 3 h with and sulfamic acid 5.0% and 10% w/w (based on fatty acid) and the progress was monitored by TLC using hexane:ethyl ether (80:20 v/v) as eluent. The spots were detected in iodine chamber. After the reaction was complete, hexane was added and the mixture was filtered to recover the catalyst. The filtrate, after being washed with water to remove residual sulfamic acid was dried over anhydrous $MgSO_4$, and the solvent was evaporated to furnish the product.

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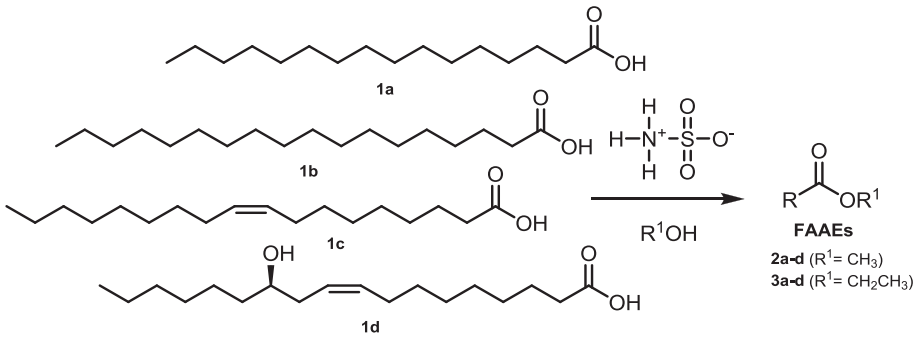

Scheme 1. Synthesis of the fatty acid alkyl esters, FAMEs **2a–d** and FAEEs **3a–d**.

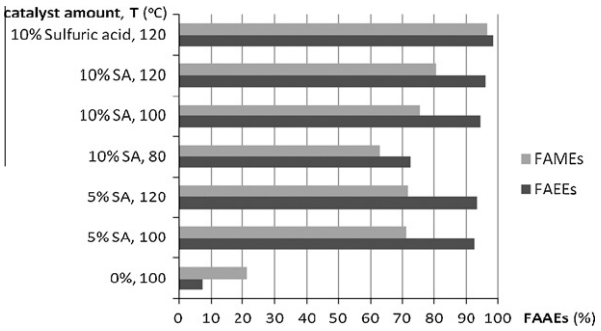

Fig. 1. The esterification of oleic acid (alcohol:FFA, 6:1) catalyzed by sulfamic acid (H_2NSO_3H).

Table 1
Esterification of fatty acids using 10% sulfamic acid (H_2NSO_3H).

Entry	FFA	Alcohol	Alcohol:FFA (mol)	T (°C)	FAAEs (%)
1	Palmitic acid	CH_3OH	6:1	100	**2a** (78.4)
2	Palmitic acid	CH_3CH_2OH	6:1		**3a** (91.2)
3	Estearic acid	CH_3OH	6:1	100	**2b** (69.7)
4	Estearic acid	CH_3CH_2OH	6:1		**3b** (92.1)
5	Ricinoleic acid	CH_3OH	6:1	100	**2d** (87.9)
6	Ricinoleic acid	CH_3CH_2OH	6:1		**3d** (96.7)
7	Oleic acid	CH_3OH	6:1	100	**2c** (75.4)
8	Oleic acid	CH_3CH_2OH	6:1		**3c** (94.5)
9	Oleic acid	CH_3OH	9:1	100	**2c** (83.6)
10	Oleic acid	CH_3CH_2OH	9:1		**3c** (95.4)
11	Oleic acid	CH_3OH	9:1	120	**2c** (84.1)
12	Oleic acid	CH_3CH_2OH	9:1		**3c** (95.7)

3. Results and discussion

The ability of this H_2NSO_3H/alcohol system for esterification of fatty acids **1a–d** was compared between methanol and ethanol (Scheme 1). In a typical experimental procedure, the free fatty acid (FFA) was heated in the desired alcohol in the presence of sulfamic acid (SA). The product was separated from the system with hexane extraction and the H_2NSO_3H was recovered by filtration.

The conversion of fatty acids **1a–d** into fatty alkyl esters **2a–d** and **3a–d** was determined by measuring the acid value (*AV*, mg KOH/g) at the end of the reactions, which was easily obtained from the expression C (%) = $AV_o - AV_f/AV_o \times 100$. The free fatty acids in the obtained fatty acid alkyl esters were determined as the oleic acid percentage according to the AOCS official method Ca 5a-40 [22].

The initial experiments were performed with oleic acid (**1c**) and 0%, 5% and 10% catalyst (H_2NSO_3H) at various temperatures and a molar ratio of alcohol to FFA of 6:1 to understand the effect of sulfamic acid on the FFA level (Fig. 1). To compare the esterification process, the reaction using a molar ratio of alcohol to FFA of 6:1 in ethanol and methanol catalyzed by sulfuric acid was performed.

In general, increasing the concentration of sulfamic acid and temperature led to positive effects on the esterifications process. Excellent yields of ethyl esters, 94.5% and 96.2%, were obtained using 10% sulfamic acid and ethanol at 100 °C and 120 °C, respectively. However, in the same conditions the methyl esters were obtained with lower yields (62–80%). According to the literature, when sulfamic acid in methanol and ethanol is used for the synthesis of quinoxalines, the remarkable efficiency of the sulfamic acid/MeOH system is explained by a better synergistic effect between the sulfamic acid in its zwitterionic form and the MeOH [23]. In the esterification of fatty acids with a sulfamic acid/MeOH system, this cooperativity was not observed. Fig. 1 reveals that ethanol promoted 20% higher conversions than methanol.

To evaluate the acid-catalyzed esterification process, reactions using a molar ratio of alcohol to FFA of 6:1 with other fatty acids (i.e. C16:0, C18:0 and C18:1(OH)) in ethanol and methanol catalyzed by sulfamic acid were investigated at 100 °C for 3 h with constant stirring (Table 1).

According to Table 1, esterification of other fatty acids **1a**, **1b** and **1d** using ethanol resulted in higher FAEEs yields than methanol (Table 1, entries 1–6). We next examined the catalytic activities of the H_2NSO_3H/alcohol system in the esterification of oleic acid using a molar ratio of alcohol to FFA of 9:1 at 100 °C and 120 °C for 3 h with constant stirring (Table 1, entries 9–12). However, within the experimental conditions, an increase in the alcohol amount to 9:1 (alcohol:FFA) in the esterification of oleic acid did not significantly increase the yield of FAMEs and FAEEs more than 6:1 (alcohol:FFA). In addition, after the esterification reaction in the presence of methanol and ethanol the catalyst was recuperated by filtration in 80% and 70% yield, respectively. The catalyst was washed with hexane and alcohol and was dried to constant weight in an oven at 60 °C. After treatment the catalyst was reused without recrystallization. The results indicate that the activity of H_2NSO_3H rapidly decreased during the repeated experiments. In the first cycle the yields of ethyl esters decreased to 72%, and in the second cycle to 25%. These results demonstrated that the sulfamic acid was partially hydrolyzed under the reaction temperature from the water originated in the esterification [24,25].

4. Conclusions

SA/EtOH and MeOH were introduced as excellent catalytic systems for the synthesis of fatty acid alkyl esters. In comparison with previously reported methods, this novel and practical method had the advantages of mild conditions and near quantitative yields of FAEEs and FAMEs. The best results for acid esterification were

obtained with ethanol, yielding 91.2–97.7% of the possible FAEEs. These data demonstrate that the present protocol has high potential as a practical method for the synthesis of fatty esters from FFAs. Another attractive feature of this green methodology is its ready application in industrial processes due to easily manipulation of the SA. Encouraged by these results, we are examining the catalytic activities of the H_2NSO_3H/alcohol system in the pretreatment of vegetal oil containing significant amounts of FFA for biodiesel production.

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