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Sulfonated porous carbon catalyzed esterification of free fatty acids

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ABSTRACT

The esterification of free fatty acids (FFA) with methanol is studied using Sulfonated Porous Carbon (SPC) as catalyst. In compare to the amorphous sugar catalyst and protonated Nafion, the proposed catalyst shows stability and high efficient performance in biodiesel production. The highest initial rate of oleic acid conversion is obtained at catalyst loading of 1 mmol H^+ and mole ratio of MeOH/Oleic acid of 10. The prepared Sulfonated Porous Carbon reused at least three times without loss of activity.

Keywords: Sulfonated Porous Carbon, Esterification, Fatty acids, Solid acid.

1. Introduction

Esterification reaction is one of the most important processes in organic synthesis and has been extensively used in chemical industry [1-4]. Esterifications are usually catalyzed by proton-donor mineral acids such as sulfuric, p-toluenesulfonic and hydrochloric acid in liquid phase [5]. The catalytic activity of Brønsted acids as homogeneous catalysts is high. However, such acid catalysts require special processing in the form of neutralization, which involves costly and inefficient catalyst separation from products. The present tendency is to replace these catalysts by solid acid catalysts. A variety of solid acid catalysts have been reported such as zeolites [6] La/zeolite beta [7], MCM-41 [8], Amberlyst-15 [9] and Nafion [10]. However, the heterogeneous acid catalyst commonly is hydrophilic, and its activity will be decreased by the water produced from the esterification of free fatty acid (FFA) or exhibited low surface area which may limit the accessibility to active sites. In addition, many of these catalysts are expensive.

Recently, new various carbon base solid acids (CBSAs) have been reported to esterificate of fatty acids. The CBSAs show the higher catalytic performance and higher stability versus other solid acids such as sulfonated mesoporous silica's. These catalysts can cheaply produced by incomplete carbonization of sulfopolycyclic aromatic hydrocarbons or sulfonation of incompletely carbonized sugar, starch or cellulose [11-14]. However, these materials are soft aggregate of polycyclic aromatic carbons and aromatic molecules are leached out during liquid-phase reactions above 100 ºC or, the nonporosity of CBSA exhibit low surface area which may limit the accessibility to active sites [15].

Porous carbon materials and products based on them have been attracted because of their huge scientific applications and in industry [16, 17]. They are use as supports for different catalytic processes, fuel cells and capacitors. Porous carbon materials with high surface areas and well developed porosities are used widely during the years because; they can fulfill most of the desirable properties required for a suitable catalyst support. The stability in aggressive media at elevated temperature, feasibility of control parameters of the porous structure surface area in a broad range, surface is hydrophobic and the physicochemical properties are the major advantages of porous carbon materials [18-33].

In the present study, Sulfonated Porous Carbon (SPC) were prepared and evaluated for esterification of oleic acid (palmitic acid and stearic acid) with methanol and ethanol, and its catalytic performance was compared with other acidic catalysts.

2. Experimental

General experimental information

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. The specific surface area and mean pore diameter (dp) were calculated from adsorption isotherms of nitrogen at 77 K using the standard Brunauer-Emmett-Teller (BET) equation and were obtained on a NOVA 2200, Quantachrome Corporation. GC-Mass analysis was carried out using Fisons TRO 1000 spectrometer.

Preparation of SPC

Pine wood powder was used as precursor to prepare of porous carbon material. In a typical procedure, wood powder (10 g) was impregnated with $ZnCl_2$ by immersion in aqueous solution of HCl (1.0 M, 50 ml) containing $ZnCl_2$ (20 g) under mechanical agitation at 25 ºC for 15 h. After that, the supernatant liquid was separated by filtration and the remaining solid was oven-dried at 80 ºC for 24 h. Then, the $ZnCl_2$-impregnated wood powder was placed in a boat like small size ceramic container and heated gradually from room temperature to 500 ºC. The heating gradient was not faster than 10 ºC min $^{-1}$. The heating time at maximum heat (500 ºC) treatment

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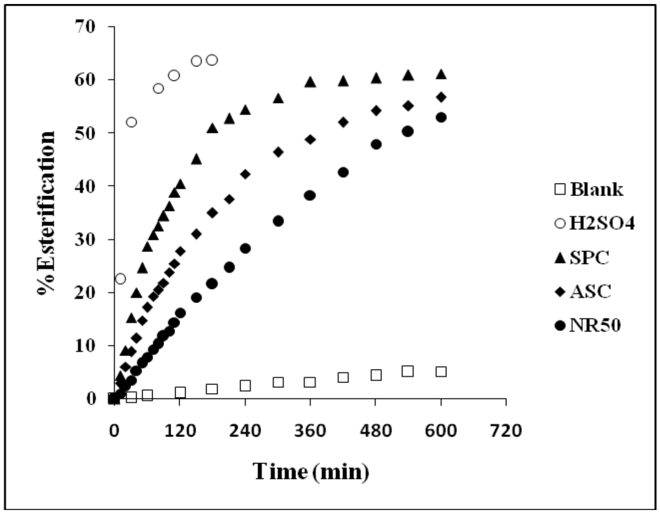

Fig. 1. The esterification yield of oleic acid, conditions: 1 mmol H^+, [MeOH]/[OA] =10 and 80 ºC.

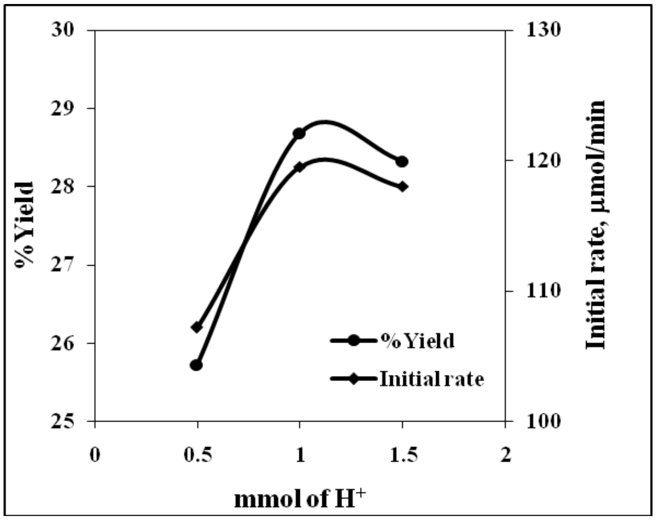

Fig. 2: The effect of catalyst dosage on the yield in time duration of 60 min and initial rate of esterification catalyzed by SPC.

temperature was 1 h. Thereafter, the sample was washed by heating in the aqueous HCl solution (5 %, 100 ml) at 100 ºC for 1 h. Then, the resulting solid was filtered and rinsed with warm distilled water (50 ºC) to confirm that the wash solution is free of zinc ions. The resultant activated porous carbon material was finally dried at 80 ºC in an oven for approximately 24 h. Then, the activated porous carbon material (5 g) was heated for 15 h in oleum (18-24 wt% SO_3, 100 ml) at 150 - 180 ºC under N_2 in order to introduce SO_3H. After heating and then cooling to room temperature, distilled water (400 ml) was added to the mixture. The black precipitate was filtered and repeatedly washed with boiling distilled water until impurities such as sulfate ions were no longer detected in the wash water. The sample was finally dried overnight in an oven at 80 ºC to afford the sulfonated acid catalyst.

The acid density of SPC was 4.03 mmol g^{-1} which measured using NaOH (0.01 mol L^{-1}) as titrant through acid-base potentiometric titration [31-34].

General reaction procedure

Reactions were carried out in a 50 mL three-neck round bottom glass flask with a reflux condenser to minimize methanol losses. The flask was submerged in an oil bath placed on a temperature-controlled magnetic stirring hotplate. The reaction temperature was monitored by thermocouple as well as mercury thermometer, and held within ±1 ºC.

Catalytic esterification of oleic acid ($C_{17}H_{33}COOH$) with methanol (methanol; 0.25 mol, oleic acid; 0.025 mol) was performed under N_2 atmosphere at 80 ºC. All tested catalysts except sulfuric acid were evacuated at 100 ºC for 1 h prior to reaction to remove adsorbed water, and the catalyst acid amount used in the reaction was always 1 mmol H^+ [(0.05 g, H_2SO_4), (0.25g, SPC), (0.28 g, ASC) and (1.25 g, NR50)] . The liquid phase during reaction was analyzed by a gas chromatograph-mass spectrometer.

3. Results and Discussion

Esterification catalyzed by sulfonated porous carbon

The catalytic performance of prepared SPC was investigated for the esterification of oleic acid with methanol. The conversion of oleic acid measured as a function of time at 80 ºC over the SPC, amorphous sugar catalyst (ASC) [14], protonated Nafion (NR50) and concentrated sulfuric acid (Fig. 1). The compositions, surface areas, acid densities, added amount (H^+ = 1 mmol), and initial rate of methyl oleate formation (catalytic activity) for all samples are

Table 1.

Characterization and catalytic activity of homogeneous and heterogeneous catalysts in esterification reaction of oleic acid with methanol.

Catalyst	Acid density[a] (mmol H^+/g)	Added amount [b](g)	Surface area (m^2/g^{-})	Initial rate, μmol/min	Ref.
No -Catalyst		-		2.1	-
H_2SO_4	20.4	0.05	-	165.3	-
SPC	4.0	0.25	905	119.5	This work
SPC[c]	4.0	0.25	905	108.6	This work
ASC	3.5	0.28	3.5	71.8	[14]
NR50	0.8	1.25	0.1	32.7	[10]

[a] Determined by titration with NaOH.

[b] Acid-catalyzed (H^+ = 1mmol)

[c] Esterification of oleic acid with ethanol under similar condition

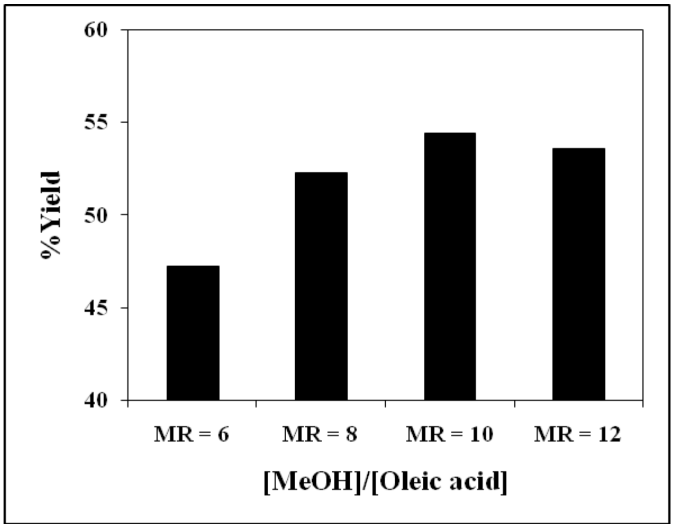

Fig. 3: The effect of mole ratio of Methanol to oleic acid on the yield of esterification catalyzed by SPC.

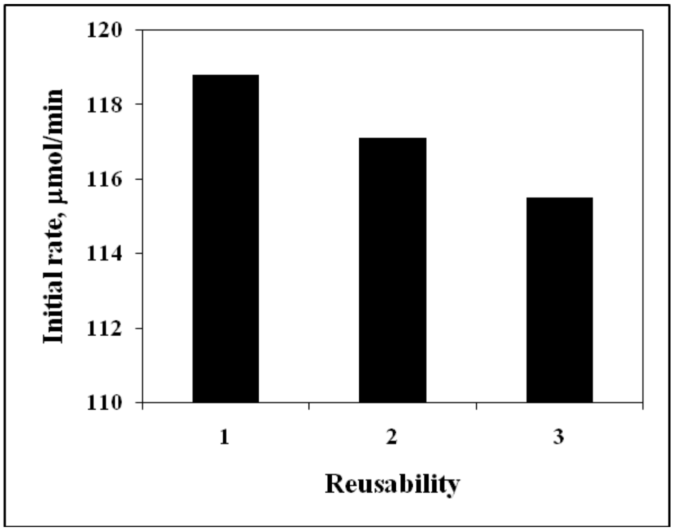

Fig. 4: The reusability of the catalyst (SPC) in the esterification of oleic acid.

summarized in Table 1. In the absence of acid catalyst, the conversion of oleic acid was only 5.15% in duration 10 h after beginning of reaction. As seen, the H_2SO_4 homogeneous catalyst shows the highest activity with a conversion of more than 60% in less than 120 min and initial rate 165.3 µmol/min. Among heterogeneous catalysts, SPC, ASC and NR50, the prepared sulfonated porous carbon with initial rate of 119.5 µmol/min indicate a higher catalytic activity in methyl oleate formation reaction. The yield of esterification was obtained 40.5, 27.9 and 16.3% for SPC, ASC and NR50 catalyst, respectively, using the same equivalent H^+ at time 120 min.

The higher catalytic activity of sulfonated porous carbon is due to high specific surface area, high acid site density, high density of mesoporous (which provide good access to the SO_3H groups on the surface of the carbon material) and hydrophobicity.

Removing water throughout the reaction process (e.g., using a Dean–Stark device or anhydrous sodium sulfate) is not show significantly effect to improvement in the rate and yield of reaction. This result is due to two reasons: i) at high mole ratio of MeOH to oleic acid, a large amount of methanol could decrease the inhibition of water on esterification by accelerating the reaction [35], and ii) hydrophobic substrate of SPC catalyst is due to superior performance on catalyzed formation of methyl oleate. Because, the catalyst can lead to effective absorption of the long chain fatty acid molecules and leaching of byproduct water, especially at the beginning stage [36-38].

Effect of parameters in esterification reaction

The esterification reaction of oleic acid catalyzed by SPC at dosage of 0.5, 1.0 and 1.5 mmol of H^+ were done at mole ratio of 10 for MeOH/OA and 80 °C. The yield of reaction in duration time of 60 min and initial rates are indicated in Fig. 2. The yield of 25.72% was at 0.5 mmol H^+ and increase to 28.68% with increasing of H^+ amount to 1.0 mmol at time 60 min. While, the more increasing of SPC catalyst did not show any improvement of esterification reaction (yield 28.32% at 1.5 mmol of H^+). In high amounts of catalyst, the rate of esterification will be increased and water will be formed in a shorter time. The acidic hydroxyl groups were deactivated by the hydration of these groups when water is present. So, the catalyst loading of 1 mmol H^+ is optimum.

The effect of mole ratio of MeOH/Oleic acid on the efficiency of esterification reaction catalyzed by SPC (1 mmol H^+) at time 240 min was shown in Fig. 3. The reaction temperature was 80 ºC. As seen, the esterification yield increase with increasing of mole ratio up to MR = 10 and then decrease in upper mole ratio. The conversion of FFA is obtained 54.5% at time 240 min using ratio 10:1 of MeOH:FFA. The esterification is a reversible reaction. Therefore, the excess of methanol as a reactant can aid to progress of reaction in methylester formation. However, a drop in esterification yield can observed at MR > 10. The hydrophilic functional groups ($-SO_3H$) bonded to carbon sheets is due to increasing the hydrophilic property of SPC. The rate of conversion and thus water production increases at higher mole ratio of alcohol to FFA (>10). At present of much amounts of water, the acidic hydroxyl groups (–OH, Brönsted acid sites) is reduced because of hydration of these groups. Also, the active sites of sulfonated porous carbon are flooded at present of excess amounts of methanol and the conversion of FFA decreases at higher mole ratios of methanol to oleic acid. Therefore, the mole ratio of 10 recommend as an optimum amount.

Since the reaction temperature was also expected to affect the conversion of FFA, the reaction at 40, 60 and 80 ºC, keeping the remaining reactions parameters constant, was studied at presence of sulfonated porous carbon. The initial rate of conversion FFA was 97.3, 109.6 and 119.5 µmol/min at temperature of 40, 60 and 80 ºC, respectively. The endothermic of the reaction is due to increasing of reaction rate with increasing of temperature. This result corroborates those obtained by Trubiano et al [15].

The esterification of other free fatty acids

Catalytic esterification of palmitic and stearic acid (0.025 mol) with methanol (0.25 mol) at 80 ºC were also successfully conducted with the SPC catalyst (1 mmol H^+). The initial rate of methylstearate and methylpalmitate formation is 111.1 and 127.5 µmol/min, respectively. Among FFA esterification reactions, palmitic acid show slightly faster initial rate than oleic acid (Table 1) and stearic acid. The initial rate of the esterification decreases slightly with increasing the carbon chain length of the fatty acid, possibly resulting from the steric hindrance effect of the carbon chains.

The esterification of olecic acid with ethanol

The esterification of oleic acid with ethanol (EtOH) at present of SPC as catalyst was studied at optimized conditions of [EtOH]/[Oleic acid] = 10, 1 mmol of H^+ and 80 ^oC. The initial rate is obtained 108.6 µmol/min. Thus, the proposed catalyst shows a suitable reactivity in esterification reaction of free fatty acids with ethanol.

The reusability of catalyst

To check the reusability and recyclability of the catalyst (SPC), we have carried out the esterification of oleic acid under similar reaction conditions. The catalyst was separated by filtration after completion of the reaction. It has also been dried and used for subsequent experiments after adding fresh substrate under similar reaction conditions. For three catalytic cycles, the initial rate of methyl oleate formation is obtained 118.8, 117.1 and 115.5 µmol/min (Fig. 4). However, the reaction time was found to increase gradually with the comparable yields of the methyl oleate in subsequent recycle experiments.

4. Conclusion

The sulfonated porous carbon prepared from pine wood powder can used as a catalyst in esterification of free fatty acids such as oleic, palmitc and stearic acid. The high specific surface area and acid density are the advantages of proposed catalyst in compare to amorphous sugar catalyst and protonated Nafion. The highest initial rate of free fatty acid conversion can obtained at 1 mmol H^+, mole ratio of alcohol to acid of 10 and 80 ºC.

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