Journal of Cleaner Production 183 (2018) 67–76

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Microwave-assisted preparation of coal-based heterogeneous acid catalyst and its catalytic performance in esterification

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ARTICLE INFO

Article history:
Available online 14 February 2018

Keywords:
Biodiesel
Esterification
Coal-based heterogeneous acid catalyst
Microwave irradiation

ABSTRACT

Powder coal is carbonized under nitrogen atmosphere and then treated with concentrate sulfuric acid with the assistance of microwave radiation for heterogeneous acid catalyst synthesis and the capability in catalyzing esterification of oleic acid with methanol for biodiesel production is subsequently studied. The catalysts are characterized by N_2 adsorption-desorption, ultimate analysis, X-ray diffraction, Raman spectra, attenuated total reflectance-Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and acid amount tests to obtain the physicochemical property. Microwave irradiation is a faster and simpler process than the conventional heating, and the sulfonation duration can be shortened to be 5 min. Under the carbonization temperature of 250 °C for 30 min and sulfonation temperature of 75 °C for 5 min, the synthesized catalyst gains the acid amount of 1.73 mmol g^{-1} and esterification efficiency of 98.1% is achieved with the catalyst dosage mass percentage of 10 wt%, molar ratio of methanol to oleic acid of 12, esterification temperature of 65 °C and esterification duration of 180 min, where the commercial Amberlyst-15 catalyst only presents the efficiency of 71.5% under the same condition. Though the catalytic capability is crippled during the recycling reusage, it can be easily regenerated with its mostly original catalytic activity.

1. Introduction

The continuous consumption of fossil fuels is inevitable due to the promotion of economic development and improvement of life quality, and it causes the energy shortage and environmental pollution in turn (Lai et al., 2016). Biodiesel is regarded as a promising alternative to the fossil diesel because it is environmental benign, renewable and biodegradable. Besides, biodiesel possesses similar properties with the conventional petroleum-based diesel to guarantee its application directly or blended with the fossil fuel at an arbitrary ratio. Biodiesel is a mixture of monoalkyl esters of long-chain fatty acids, and produced from vegetable and animal oils/fats by transesterification and esterification with short-chain alcohols in the presence of acid or base catalysts or supercritical pressure condition (Hájek et al., 2017; Huang et al., 2015). The alkali-catalyzed transesterification is the common commercial process with high catalytic activity and short reaction duration (Alaba et al., 2016; Cheng et al., 2014), but it is restricted by the high cost of raw materials and production process. Acidic oils such as crude vegetable oils or waste cooking oils have been proposed as the potential resources due to the low cost and abundant availability (Konwar et al., 2014), where the base catalysts are not applicative as saponification generated by free fatty acids (FFAs). Compared with base catalysts, the acid ones are not sensitive to the raw materials quality and can convert FFAs into esters before the base catalyzed transesterification (Bala et al., 2017). Employment of the conventional mineral acid of concentrated H_2SO_4 or HCL for the acidated oils pretreatment is restricted by the strong corrosion, difficult recyclability and environmental unfriendly drawbacks (Xia et al., 2012). To qualify the esterification as a “green” process, heterogeneous acid catalysts, such as mesoporous silica based materials (Kocík et al., 2016), zeolite (Alaba et al., 2016), sulfonated mesoporous ZnO (Soltani et al., 2016) and carbon-based acid (Konwar et al., 2014), etc, gradually appear and they are easily separated from the liquid reactants through physical filtration.

Among various heterogeneous acid catalysts, sulfonated carbon-based ones are reported to be promising in biodiesel production due to the advantages of chemical inertness, thermal stability and structural diversity, where incomplete carbonization to form aromatic hydrocarbon structure followed by sulfonation with

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https://doi.org/10.1016/j.jclepro.2018.02.145
0959-6526/

Nomenclature

YLC	Yulin Coal
N_2	Nitrogen
FFAs	Free fatty acids
HCL	Hydrochloric acid
H_2SO_4	Sulfuric acid
NaCl	Sodium chloride
NaOH	Sodium hydroxide
KOH	Potassium hydroxide
ZnO	Zinc oxide
$CT_1(x)$-$ST_2(y)$	C and S are for carbonization and sulfonation, T_1, x and T_2, y represent the temperature and duration of carbonization and sulfonation process, respectively
ζ	Catalyst dosage mass percentage, wt%
γ	Molar ratio of methanol to oleic acid
T_e	Esterification temperature, °C
τ_e	Esterification duration, h
η	Esterification efficiency, %
XRD	X-ray diffraction
FTIR	Fourier transform infrared
XPS	X-ray photoelectron spectroscopy
S_{BET}	Specific surface area, $m^2\,g^{-1}$

concentrated H_2SO_4 or fuming SO_3 is frequently used. Besides, the carbon-bearing materials are relatively cheap and widely available, where biochar (Kastner et al., 2012), glycerol (Devi et al., 2009), rice husk (Li et al., 2014) and de-oiled canola meal (Rao et al., 2011), etc, have been reported. Coal is a polycyclic aromatic hydrocarbon polymer and mainly consists of carbonaceous organic compounds, where the aromatic rings are connected to oxygen-containing functional groups and alkyl side chains. Use of coal as the support material gains increasing attentions in recent years, besides the conventional applications of power generation, gasification and liquefaction, etc. To date, Babajide et al. (2010) utilized fly ash to prepare heterogeneous basic catalyst via wet impregnation under the potassium nitrate effect to catalyze transesterification. Zhong et al. (2014) synthesized a trichloroacetic acid modified coal tar pitch heterogeneous catalyst and studied the activity in catalyzing esterification for ethyl acetate production. However, synthesis of the heterogeneous acid catalyst from coal for biodiesel production is barely reported.

Lengthy duration is required for sulfonation, which is 10 h for the carbonized seed powder (Dawodu et al., 2014), 10 h for the vegetable oil asphalt and 5 h for the sugar cane bagasse (Chin et al., 2012) in oil bath. In comparison with surface thermal conduction of the conventional method, microwave irradiation can convey the heat power straight to the reactants (Soltani et al., 2016). Moreover, polar molecules can selectively absorb microwave energy and non-polar molecules are inert to the microwave dielectric loss, which dramatically accelerates reaction rate and greatly reduces reaction duration from hours to minutes (Zhang et al., 2012). In fact, microwave irradiation is especially appropriate for the sulfonation with concentrate H_2SO_4 and Maza et al. (2011) have successfully introduced microwave for the efficient and fast O-sulfonation of heparin oligosaccharide intermediates. However, the microwave assisted sulfonation for heterogeneous acid synthesis for biodiesel production has barely received attention in the literature.

Given the above issues, a series of coal-based heterogeneous acid catalysts are synthesized with microwave assistance under the variant carbonization and sulfonation conditions to optimize the catalytic capability in esterification of oleic acid with methanol. Meanwhile, the catalysts are characterized by N_2 adsorption and desorption, ultimate analysis, X-ray diffraction (XRD), Raman spectra, attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), X-ray photon spectroscopy (XPS) and acid amount tests to explain the catalytic performance. Then, influences of the catalyst dosage mass percentage, molar ratio of methanol to oleic acid, esterification temperature and duration on the catalytic capability are investigated. For comparison, commercial Amberlyst-15 catalyst is mentioned. Finally, reused property of the coal-based heterogeneous acid is studied. The subject in this manuscript has been rarely reported in the previous studies and it hopes to supplement the fundamental insight in biodiesel production catalyzed by the carbon-based heterogeneous acid.

2. Materials and methods

2.1. Materials and equipment

The coal powder is collected from Yulin, in Shaanxi province, China. The phosphoric acid (Sinopharm Chemical Reagent Co.,Ltd, Shanghai, China) with purity of 85% and sulfuric acid (Laiyang Fine Chemical Plant, Shandong, China) with purity of 98% are of analytical grade. Sulfonation and esterfication process are performed in a microwave synthesis reactor (MCR-3, lenk industrial development Co., Ltd, Shanghai, China), which is operated at atmospheric pressure with the frequency of 2450 MHz.

2.2. Catalyst synthesis

Coal powder is sieved between 74 and 125 μm and dried at 105 °C to remove moisture in advance. 15 g of dried coal powder is impregnated with 30 g of phosphoric acid (85%) and stirred at room temperature for 2 h. The slurry is dried at 105 °C in oven overnight and carbonized under nitrogen atmosphere at the designed temperature (distributed from 250 °C to 450 °C and the first investigated parameter for the carbon-based heterogeneous acid synthesis) in a tubular reactor for the given duration (prolonged from 30 min to 240 min and the second investigated parameter for the carbon-based heterogeneous acid synthesis). Afterwards, the carbonized sample is washed repeatedly with the hot distilled water (exceeding 80 °C) until the filtrate is neutral and then dried at 105 °C till to mass constant.

Then, about 5 g of the carbonized support and 75 mL of the concentrated sulfuric acid are consecutively poured into a 500 mL round-bottomed three-necked flask, which is placed in the microwave irradiation synthesis reactor, and heated at the designed temperature (distributed from 60 °C to 135 °C and the third investigated parameter for the carbon-based heterogeneous acid synthesis) for a given duration (prolonged from 1 min to 120 min and the fourth investigated parameter for the carbon-based heterogeneous acid synthesis) for sulfonation. Throughout the sulfonation, uniform mixture effect and constant temperature control are guaranteed by a magnetic stirrer and thermocouple. At termination, the suspension is cooled and washed with the hot distilled water thoroughly to be pH neutral. Then, it is dried at 105 °C in oven. The obtained carbon-based heterogeneous acid catalyst is defined as $CT_1(x)$-$ST_2(y)$, where C and S are for carbonization and sulfonation, T_1, x and T_2, y represent the temperature and duration of carbonization and sulfonation process, respectively.

2.3. Catalyst characterizations

Microstructure parameters of the catalysts are measured via a TriStar II 3020 surface area and porosity analyzer (Micromeritics