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SO₄²⁻/ZrO₂ as catalyst for upgrading of pyrolysis oil by esterificationLu Li^a, Bin Yan^b, Huaxiao Li^b, Shitao Yu^{b,*}, Shiwei Liu^b, Hailong Yu^b, Xiaoping Ge^a^a College of Marine Science and Biological Engineering, Qingdao University of Science and Technology, Qingdao 266042, China^b College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

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ABSTRACT

Pyrolysis oil of rubber seed oil (RSO) was upgraded by methyl esterification using SO₄²⁻/ZrO₂ solid acid as catalyst. The activity and reusability of SO₄²⁻/ZrO₂ solid acid were investigated and the experiment indicated that the esterification rate could reach 99.62% and was still above 95% in the third reaction. The component of SO₄²⁻/ZrO₂ solid acid changed little after the third used. The properties of the obtained biofuel were studied and the results showed they were superior to pyrolysis oil and biodiesel, and similar to 0[#] diesel. The methyl esterification reaction kinetics was researched. The kinetics calculation indicated that the reaction order of the methyl esterification is 1.058, and Arrhenius equation can be expressed as $k_1 = 7.711 \times 10^6 e^{-\frac{47.913}{RT}}$.

1. Introduction

As the shortage of the world petrochemical energy, the rise in the price of oil and the deterioration of environment caused by automobile exhaust, there is an ever-increasing demand for alternative energy. Biofuels are carbon-neutral fuels that do not contribute to global warming, and are renewable resources with low emissions. Therefore, biofuels were paid more emphasis recently [1].

The well-known conventional biofuel that is currently used worldwide and produced from biomass is biodiesel, which is associated with fatty acid methyl esters (FAMES) produced by the transesterification of triglyceride-containing feedstocks [2]. Manayil et al. [3] has reported the catalytic upgrading of macroporous silica sulfonated fast cracking bioils. Alhassan et al. [4] improved the use of eutectic solvents (green solvents and catalysts) for the supercritical esterification of waste tyres pyrolysis oils. Kim et al. [5] reported the use of tungstate-zirconia supported ruthenium catalysts to upgrade small amounts of coke formed sawdust pyrolysis oil to hydrocarbon fuels. Jahromi et al. [6] enhanced the rosin-oil catalyzed pyrolysis by hydrodeoxygenation and achieved good results. However, transesterified biodiesel has many disadvantages. The resulting oil has low calorific value and produces large amounts of glycerol by-products, which greatly limits the popularization and application of this method. In the recent decade, pyrolysis oil has become a new trend in the preparation of biodiesel. Compared with the traditional transesterification, biodiesel prepared by pyrolysis oil has high calorific value and few by-products. Zhao and Jiang et al. [7] obtained the main alkanes and alkenes with C10–C18 carbon chains (64% of the main content) by thermal cracking of waste

oil and at the same time the heat value of the oil reached 44 MJ/kg. Li et al. [8] used USY as catalyst for cracking waste oil to obtain C8–C9 alkanes or alkenes and the heat value of the oil reached 41 MJ/kg. Xu et al. [9] got a good ignition quality (cetane number) pyrolysis oil by pyrolysing of high acid waste oil. However, the drawback of cracking oil product is that the acidity of the obtained oil product is too high. H-ZSM5, metal-impregnated MCM-41 and Y zeolite catalysts have been used for hydrocarbon cracking [10–12]. However, the cracking oils in these studies exhibited a high carboxylic acid content (acid value = 116–142) [13]. In order to reduce the acid value, it is usually necessary to increase the reaction time or the reaction temperature, which in turn causes the reaction yield to drop. The traditional base catalysts could decrease the acid value of biofuel, the catalysts would exhaust in the process and the content of salt in the biofuel would increase [14]. A possible solution to overcome this problem is esterification. Xu et al. [15] esterified pyrolysis oil products using acid catalysts to significantly reduce their acid value from 67.0 mg/g to 6.0 mg KOH/g. Those undesired products (carboxylic acids) were changed into their corresponding fatty acid esters efficiently by a continuous esterification operation [15]. Kocsisava et al. reported the esterification of degreasing acid with methanol at elevated temperatures above the boiling point of methanol [16]. In addition, the kinetics of esterification of free fatty acids with methanol have also been studied [17]. Kirumakki et al. have studied the esterification of benzyl alcohol with different types of zeolite catalysts [18]. Although the acid number of the pyrolytic products decreased dramatically after the acid-catalyzed pyrolysis reaction, it still did not meet the requirements of biodiesel for international standard (ASTM D6751). Currently, the

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esterification process is relatively mature, but is rarely used in the upgradation of pyrolysis oil. Biodiesel is mainly produced in the industry using homogeneous catalysts such as NaOH and H₂SO₄. After the reaction, the separation of the catalyst from the reaction system requires washing, centrifugation and vacuum drying to increase the reaction cost and pollutant emission [19]. Heterogeneous catalysis does not require a lot of water washing, catalyst separation is easy and high purity by-product glycerol. That is a green biodiesel production line. Heterogeneous catalysis includes solid acid and solid base catalyst. However, the use of solid base as a catalyst, the reaction conditions are mild, but met with water and easy to deactivate, and has demanded to the content of free fatty acids in raw oil. SO₄²⁻/M_xO_y can avoid the disadvantages of liquid catalyst without raw material requirements, and not easy to deactivate, therefore the use of SO₄²⁻/M_xO_y catalyst for the preparation of biodiesel has become a hot research field.

Rubber seed oil (RSO), which is extracted from rubber seeds, is reasonably priced and more readily available compared to other vegetable oils [20,21]. What's more, the production of RSO is rich in China per year, therefore biodiesel produced by pyrolysis oil of rubber seed oil (RSO) has extremely objective application prospects. In the present study, the methyl esterification of pyrolysis oil of RSO using SO₄²⁻/ZrO₂ solid acid as catalyst was investigated. The activity and reusability of SO₄²⁻/ZrO₂ solid acid and the properties of biofuel were studied. The reaction kinetics of methyl esterification was researched.

2. Experimental section

2.1. Materials

Zirconium (VI) oxychloride octahydrate (ZrOCl₂·8H₂O), ammonia (25%–28%), sulfuric acid (98%), methanol (99.5%), potassium hydroxide (99.8%), ethanol absolute (99.7%). The above reagents are analytically pure. Homemade pyrolysis oil of RSO.

2.2. Synthesis of solid acid SO₄²⁻/ZrO₂

The SO₄²⁻/ZrO₂ catalyst was synthesized by mixing zirconium hydroxide powder and 1 mol/L H₂SO₄ solution. Zirconium hydroxide powder was sulfated by impregnation with 10 mL of H₂SO₄ solution per gram of Zirconium hydroxide powder for 24 h, then dry for 24 h at 100 °C and calcinations at 550 °C for 4 h to obtain SO₄²⁻/ZrO₂ solid acid. Finally, in order to reduce the effect of mass transfer on the experiment, we sieved the catalyst with a 30-mesh sieve.

2.3. Characterization of catalysts

The structure of catalysts was characterized by FT-IR. The KBr disc method was performed using a FT-IR spectrometer (BRUKER TENSOR 27). A certain amount of sample was pressed into a sheet with a diameter of 10 mm. The sheet was placed in a vacuum sample cell and pretreated at 400 °C and less than 10⁻³ Pa for 2 h. After the temperature was lowered to room temperature, pyridine was adsorbed at 2 Pa. After 15 min at 150 °C, the pyridine adsorbed on the surface of the sample was removed, and the infrared spectrum of the sample was measured at room temperature. The FT-IR spectra were recorded in the wave number range from 400 to 4000 cm⁻¹.

2.4. Methyl esterification of pyrolysis oil

According to a certain mass ratio, pyrolysis oil of RSO, methanol and SO₄²⁻/ZrO₂ solid acid was put into the high-pressure reaction kettle, which was in Numerical Show Constant Temperature Oil-bathing. The stirring rate was adjusted to 300 rpm. The reaction was carried out at certain temperatures for certain time. The acid value of product was investigated through KOH – ethanol solution titration method. The esterification rate was calculated as followed.

$$\text{Esterification rate/\%} = \left(1 - \frac{A}{B}\right) \times 100\%$$

A – the acid value of biofuel; B – the acid value of pyrolysis oil.

2.5. The kinetics on methyl esterification of pyrolysis oil

The SO₄²⁻/ZrO₂ solid acid, RSO cracking oil and methanol were added to the autoclave at a ratio of 0.05:1:1.25 and reacted at 90 °C, 100 °C, 110 °C, 120 °C for a certain period of time. And we calculated the rate of esterification per reaction.

The dynamic model in this work relies on the following assumptions:

- Theoretically, the esterification reactions are all reversible reactions, but in this reaction, the methanol is in a large excess, so it can be considered that the reaction is irreversible.
- The rate of non-catalytic reaction is negligible compared to the catalytic reaction.
- The chemical reaction takes place in the oil phase.
- Methanol has a large excess and the methanol concentration remains constant throughout the process.

Under these conditions, the reaction is assumed to be a quasi-homogeneous reaction. After the experiment was completed, the acid value of the reaction substrate was measured using KOH-ethanol standard solution. Then according to different temperatures measured at different time experimental data, using origin 8.0 can obtain the instantaneous reaction speed. Linear fitting of the relationship between $\ln\left(-\frac{dC_A}{dt}\right)$ and $\ln C_A$ using least squares method to obtain the reaction order and correlation coefficient at different temperatures. Logarithm to Arrhenius gives formula. The Arrhenius parameter of the esterification reaction can be obtained by the relationship between the reaction rate constant and the inverse of the thermodynamic temperature. Finally, linearly fitting $\ln K$ to $1000/T$ to get Arrhenius parameters.

3. Results and discussion

3.1. Selection of catalysts

Different catalysts were chosen to catalyze the esterification of pyrolysis oil of RSO (Table 1). As shown in Table 1, Compared with similar literature, the catalytic activity of SO₄²⁻/ZrO₂ was the same as H₂SO₄ and Na₂CO₃ and significantly higher than mesoporous and microporous catalysts, such as MCM-41, SBA-15 and USY [22]. The esterification rate of pyrolysis oil was high and the acid value of pyrolysis oil reduced from 70.65 mg·g⁻¹ to 0.27 mg·g⁻¹ using SO₄²⁻/ZrO₂ as catalysts. Therefore, this research adopted SO₄²⁻/ZrO₂ as catalyst and the effect of esterification reaction conditions on the esterification reaction was investigated detailed.

Table 1
Catalytic activity of different catalysts.

Catalytic	Na ₂ CO ₃	2 mol/ LH ₂ SO ₄	SO ₄ ²⁻ /ZrO ₂	MCM-41	SBA-15	USY
Acid value of pyrolysis oil/mg·g ⁻¹	80.34	80.34	70.65	78.88	72.53	78.88
Acid value of product/mg·g ⁻¹	5.76	4.37	0.27	62.88	55.32	58.65
Esterification rate/%	92.83	94.56	99.62	20.28	23.73	25.65

Reaction condition: reaction time 6 h, reaction temperature 100 °C, *m*(methanol):*m*(pyrolysis oil) = 1.25:1, *m*(catalyst):*m*(pyrolysis oil) = 5%.

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