



An investigation on the catalytic capacity of dolomite in transesterification and the calculation of kinetic parameters



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HIGHLIGHTS

- The activated dolomite was used as the transesterification catalyst.
- The dolomite presented the stronger catalytic capability than the calcium oxide.
- The kinetic parameters of the transesterification were calculated.

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ABSTRACT

The catalytic capacity of dolomite in transesterification was investigated and the kinetic parameters were calculated. The activated dolomites as transesterification catalyst were characterized by X-ray diffraction, nitrogen adsorption and desorption and Hammett indicator method, where the original dolomite was analyzed by thermogravimetric and X-ray fluorescence in advance. Its potential catalytic capacity was validated from aspects of the activated temperature and the reused property, where the reliability of the experimental system was also examined. Then, influences of the catalyst added amount, the mole ratio of methanol to oil, the transesterification temperature and the transesterification time on the catalytic capacity were investigated. Finally, kinetic parameters of the transesterification catalyzed by the activated dolomite were calculated.

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1. Introduction

Biodiesel is normally produced through transesterification using the vegetable oil or the animal fat, where the main composition is triglycerides, as the feedstock under the catalytic effect. Compared with the fossil diesel, advantages of the biodiesel are renewable and environmental benign (Atabani et al., 2012; Borges and Diaz, 2012). Broad researches about the catalyst, which is critical to transesterification, have been conducted over the past decades. In the primary stage, the homogeneous catalysts were mentioned, where the high conversion of triglycerides into fat acid methyl esters was achieved, but the post-treatment process to purify biodiesel was energy guzzling for the solubility of the homogeneous catalysts in the products. Then, the heterogeneous catalyst was developed, which simplified the transesterification by facilitating the separation and the purification, and it has been demonstrated to be more environmental (Lam et al., 2010; Leung et al., 2010).

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The heterogeneous catalyst works including adsorption of reactants onto the catalyst surface, transesterification reaction on the catalyst surface and desorption of the product from the catalyst (Filippis et al., 2005). CaO is representative of the basic heterogeneous catalysts, but its application in transesterification is restricted for requirement of the large amount of catalyst, the high molar ratio of methanol to oil and the long reaction time (Nurfitri et al., 2013). The rigorous transesterification conditions should be ascribed either to the slow reaction for the weak basic strength or to the mass transfer limitation in the three-phase transesterification system of oil-methanol-catalyst. So, these two aspects were normally taken as the breakthrough.

To strengthen basic strength, the common used method was to impregnate active sites of the sodium or the potassium into the heterogeneous catalysts (Fan et al., 2012; Jairam et al., 2012; Olutoye et al., 2011). But, improved capacity of the impregnated catalyst was exhibition of the homogeneous composition and the most obvious defect was leaching of the homogeneous active sites into the liquid product (Alonso et al., 2007; Capek et al., 2014). Meanwhile, cost for the catalyst preparation was boosted. So, creating a more developed texture to accelerate physical adsorption of

the reactants onto the catalyst surface was also considered as a promising method. The hydration–dehydration method to modify the natural calcite for large surface area has been demonstrated to be available in improving the catalytic capacity (Yoosuk et al., 2011). But, this method also increased the cost because of the twice-calcination process. Therefore, it is urgent to explore the efficient and inexpensive transesterification catalysts for biodiesel production.

Dolomite is the natural mineral substance and abundantly distributed in China. It is dominantly composed of the carbonates of calcium and magnesium with small quantity of ferrum, aluminum, silicon, etc. Considering its low cost, weak toxicity and environmental benign, dolomite could be used as building materials and ceramics resources (Sedmale et al., 2006; Sugranetz et al., 2013). The previous studies demonstrated that decomposition product of dolomite was the mixture of CaO and MgO, and it therefore gained potential as transesterification catalyst (Ilgen, 2011; Ngamcharussrivichai et al., 2010; Wang et al., 2013; Wilson et al., 2008; Yoosuk et al., 2011). MgO was not the effective composition in catalyzing transesterification, but its appearance acted as role of the supporter. As a result, texture of the dolomite after activated was different from the carbonate or the hydrate of the pure calcium.

Compared with the other heterogeneous transesterification catalysts (Borges and Diaz, 2012; Helwani et al., 2009; Lam et al., 2010), such as alkaline earth oxides, hydrotalcites, zeolite, supported catalysts and anion-exchange resin, the published papers about dolomite as transesterification catalyst have not been comprehensively reported. Ngamcharussrivichai et al. (2010) revealed that dolomite activated at 800 °C could supply highly active mixed oxide and under the transesterification condition of the catalyst amount 6%, the molar ratio of methanol to oil 30, the reaction time 3 h, the efficiency of 98.0% was achieved. Also, dolomite was modified through a conventional precipitation method using nitrate salt solutions of alkali earth metals and trivalent metals, and it was found that the activated temperature was a crucial factor (Ngamcharussrivichai et al., 2007). Wang et al. (2013) showed that activated dolomite presented large pore sizes and high active site densities and no loss of capacity was observed after regeneration. Yoosuk et al. (2011) took a controlled hydration–dehydration process to modify dolomite and an excellent efficiency of 93.3% was achieved within 90 min. Ilgen (2011) found that the maximum capacity of dolomite as transesterification catalyst was obtained at the activation temperature 850 °C, the molar ratio of methanol to oil 6, the catalyst amount 3% and the reaction time 3 h. Further, Ilgen (2012) calculated kinetic parameters of the rate constant and the reaction order. Wilson et al. (2008) activated dolomite at 900 °C to increase the surface area and the effective transesterification was realized. Discrepancies in these studies drove more fundamental investigations to be conducted. Especially for the kinetics on dolomite as the transesterification catalyst, which was critical to the reactor design and the process simulation, available information was rare (Ilgen, 2012).

In this study, the catalytic capacity of dolomite in transesterification was investigated. The chemical composition of dolomite was analyzed by X-ray fluorescence (XRF) spectrum analyzer. Then dolomite was calcined for activation and the temperature was determined by thermogravimetric analysis (TGA). The outcomes of calcinations at different temperatures were further checked for the crystalline phase analysis through X-ray diffraction (XRD). Meanwhile, the achieved catalysts were characterized by nitrogen adsorption and desorption instrument for the textural parameters measurement and Hammett indicator method for the basic strength determination. Based on characterizations for the activated dolomite, the catalytic capacity in transesterification was tested from aspects of the activated temperature, the catalyst

added amount, the mole ratio of methanol to oil, the transesterification temperature and the transesterification time. Also, the re-used property of dolomite as the transesterification catalyst was investigated for the stability estimation. Finally, kinetic parameters of the reaction order, the reaction rate constant, the activation energy and the pre-exponential factor were calculated. For comparison, the calcium oxide (analytical reagent) was also mentioned occasionally.

2. Methods

2.1. Catalyst preparation and characterization

Dolomite was purchased from Zibo, in Shandong Province, China, and its chemical composition (Ca 21.8%, Mg 13.31%, Si 1.33%, Fe 0.34%, Al 0.19%, Na 0.12%, K 0.08%, S 0.31%, O 19.77%, others 0.50%, loss 42.25%) was analyzed by XRF on the WDX-200X fluorescence spectrum analyzer, Bandwise Technology Development Co., Ltd, China. After the loss of volatile (42.25%), the main composition of dolomite included calcium, magnesium and oxygen, which could be hypothetically formulated as $\text{CaMgO}_{2.27}\text{M}$ (M indicated the mixture of silicon, ferrum, aluminum, sodium, potassium, sulfur, etc.). Further, crystalline phases of the calcium and the magnesium existing in the original dolomite and the activated dolomite were ascertained through XRD.

To activate dolomite used as the transesterification catalyst, TGA was conducted on the TGA/SDTA 851e thermogravimetric analyzer, Mettler-Toledo Instruments Co., Ltd, Switzerland, and the initial sample was weighted to 10 ± 0.1 mg in an aluminum oxide ceramic crucible of 5 mm depth and 5 mm diameter. During the experiment, gas flux of nitrogen (99.99% purity) was kept at 30 mL/min and dolomite was heated from 25 °C to 1000 °C at the temperature heated rate of 5 °C/min. TG curve, which detected mass loss signal with a resolution of 0.1 µg, was continuously recorded.

According to the TGA result, dolomite activation temperatures were selected and the activation process was conducted through calcination in the muffle furnace under the air atmosphere. To check the outcomes of calcination at the different temperatures, crystalline phase of the activated dolomites were analyzed by XRD. The Advanced D8 X-ray diffraction analyzer, Bruker Instruments Co., Ltd, Germany, was used for XRD analysis, which used Cu K α radiation with voltage at 40 kV electricity at 100 mA, scanning range from 10° to 90°, scanning speed of 4°/min and step size of 0.02°.

Textural parameters of the transesterification catalyst were measured through nitrogen adsorption and desorption instrument, Micromeritics ASAP 2020, USA. After the catalyst was desorbed under vacuum at 573 K, the parameters were isothermally measured at 77 K using nitrogen as the adsorbed substance. Then, surface area was calculated by Brunauer-Emmett-Teller (BET) equation and average particle size with pore area distribution was calculated through Barrett-Joyner-Halenda (BJH) model.

Hammett indicator method was used to test basic strength. About 0.1 g of the activated dolomite was shaken with 5 mL cyclohexane and three drops of diluted Hammett indicator (0.5 wt% by methanol). After that, basic strength was obtained according to color variation. Hammett indicators included bromthymol ($H_- = 7.2$), phenolphthalein ($H_- = 9.8$), 2,4-dinitroaniline ($H_- = 15.0$) and 4-nitroaniline ($H_- = 18.4$).

2.2. Transesterification experiments

The feedstock of transesterification was the commercial peanut oil, which was the major edible oil in China and made great

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