



Review article

Transesterification of vegetable oil into biodiesel catalyzed by CaO: A review

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ABSTRACT

Vegetable oil is one of the biomass resources generated from carbon dioxide and water with the aid of photosynthesis, and is converted into an alternative to fossil diesel fuel by transesterifying with methanol. The eco-friendly fuel, termed as “Biodiesel”, is manufactured with the help of alkali hydroxide, but its homogeneous catalysis gives rise to some technological problems: a massive amount of wastewater, soap formation and so on. Therefore, much interest has been taken in utilizing the heterogeneous catalysis of solid base for biodiesel production. Calcium oxide (CaO) is a candidate for the solid base catalyst from an economical point of view. In the present work, we reviewed CaO catalyst for the vegetable oil transesterification on the basis of a variety of the concerning research papers. After catalytic properties of the basic sites generated on CaO were described preliminarily, a mechanism on the vegetable oil transesterification catalyzed by CaO was explained. Then, procedure to prepare the active CaO catalyst, its deactivation occurring under the reacting condition and modification of CaO catalyst were discussed. Finally, the practical use of CaO catalyst for industrial biodiesel production was studied with pointing out the required future works.

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1. Introduction

The planet earth clearly tends toward warming clearly for the last several decades. It is to be feared that the global warming leads to the serious climatic change threatening human nature, so it is necessary to make great efforts at reducing greenhouse gas emissions. This is a major reason that much interest has been taken in converting biomass resources, which are generated from carbon

dioxide and water with the aid of photosynthesis, into the alternative fuel and chemicals.

Vegetable oil is one of the biomass resources and is used as a feedstock of an alternative to fossil diesel fuel. The alternative fuel, which is termed as “Biodiesel”, consists of fatty acid methyl esters produced by transesterifying vegetable oil with methanol [1]. In addition to the renewable nature peculiar to the biomass resources, biodiesel has another advantage of the good fuel properties: high flash point, good lubricity and so on [2,3]. Moreover, it was reported that emissions of both carbon monoxide and particulate was reduced by fueling the engine with biodiesel [4–6]. In 2003, European Community has decided to replace at least 5.75%

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of the yearly consumed fossil fuels with biofuels, by the year 2010. This decision accelerated the use of biodiesel and its production has been constantly growing. The total of biodiesel yearly produced in the world was 7.75 million metric tons in 2008 [7].

For the existent biodiesel production process, vegetable oil is transesterified with the help of homogeneous base catalysis of alkali hydroxide dissolved in methanol. The base-catalyzed transesterification is faster than the acid-catalyzed one for which sulfonic acid or p-toluenesulfonic acid is employed [8]. Furthermore, the reactants are accessible to the catalytic site in the homogeneous form. Thus, the existent biodiesel production process is characterized by the very fast transesterification. For instance, Freedman et al. reported that the yield of FAME produced by transesterifying sunflower oil in the presence of 1% sodium hydroxide dissolved into methanol at the temperature of 333 K was above 90% for 0.1 h [9]. Also, there is a research paper showing that 97% of palm oil was converted into its methyl esters by the base-catalyzed transesterification performed at 306 K for 1 h on a continuous-flow reaction system [10]. Here, it should be noted that methanol is the alcohol appropriate to biodiesel production from an economical and available point of view [11]. Additionally, methanol brings about the larger reaction rate than ethanol and propanol [12].

However, for the existent process, these are some technological problems resulting in costly production of biodiesel. The typical problem is a massive amount of the waste water, which is due to the purification to wash the homogeneous catalyst off the crude biodiesel with water. And besides, emulsification of biodiesel occurs during the purifying operation, which causes not only obstruction of the process operation but also loss of biodiesel.

With a view of resolving the technological problems mentioned above, Kusudiana and Saka studied a catalyst-free process in which vegetable oil was transesterified with super-critical methanol [13,14]. It took only 4 min. to convert rapeseed oil into biodiesel, even though the high temperature (523–673 K) and high pressure (35–60 MPa) were required for making methanol reach the super-critical state. The very fast transesterification was due to the large solubility of vegetable oil in super-critical methanol and intensified nucleophilic nature of super-critical methanol. Apart from the catalyst-free process, the enzymatic process can be applied to biodiesel production [15–17]. Although biocatalyst consisting of lipase allows vegetable oil to be transesterified into its methyl esters at room temperature, it takes more than 24 h to achieve the perfect conversion [18].

Solid base can lead to the heterogeneous catalytic process, which promises the cost reasonable biodiesel production. Since the solid base catalyst is easy to separate from the transesterified product, there is some expectation that the fixed-bed reactor system advantageous to process operation is applied to biodiesel production. Also, the solid base catalyst is active in the transesterification at the temperature around boiling point of methanol. For the purpose of studying the heterogeneous catalytic process, many researchers tested a variety of solid base for the catalytic activity. Xie et al. prepared potassium loaded on alumina as the solid base catalyst and the prepared catalyst was employed for transesterification of soybean oil at reflux of methanol [19]. Under the same transesterifying condition, they examined the solid base catalysis of the magnesium–aluminum (Mg–Al) mixed oxide that was prepared by calcining the corresponding hydrotalcite [20]. Shibasaki-Kitagawa et al. elucidated that anion-exchange resin catalyzed a transesterification of triolein which is a model of vegetable oil [21].

From the economical point of view, we have focused our attentions on calcium oxide (CaO) as a candidate for the solid base catalyst. A major source of calcium oxide is limestone having the advantages of good availability and cheap cost. Moreover, calcium oxide can be prepared from the waste matters consisting of

calcium carbonate, such as mollusk shells. The use of the waste matters is not only effective in enhancing the cost advantage of CaO catalyst but also related to recycle of the naturally mineral resources. In addition to the economical advantage, the superior catalytic performance of CaO is described in a number of papers reviewing utilization of solid base for the heterogeneous catalytic reaction to produce biodiesel [22–25]. Also, there is a research paper in which CaO was compared with other solid bases in order to verify the superior catalytic performance [26]. CaO catalyst was more active in transesterification of soybean oil with methanol than anion-exchange resin and the Mg–Al mixed oxide. Potassium loaded on alumina resulted in the faster transesterification, but was very inferior in the reusability to CaO catalyst.

In the present work, we reviewed CaO catalyst for the transesterification of vegetable oil into biodiesel in detail, on the basis of a variety of the concerning research papers. After catalytic properties of the basic sites generated on surface of CaO were described preliminarily, a mechanism on the vegetable oil transesterification catalyzed by CaO was explained with related to its peculiarities: variation in the catalytically active phase and the homogeneous contribution. Then, procedure to prepare the active CaO catalyst, its deactivation occurring under the reacting condition and modification of CaO catalyst were discussed. Finally, the practical use of CaO catalyst for the industrial biodiesel production was studied with pointing out the required future works.

2. Properties of basic sites on surface of CaO

According to a research paper reported by Iizuka et al., solid base catalysis of CaO originates in its surface oxygen anion [27]. CaO is one of alkaline earth metal oxides which are formed out of ionic crystal and Lewis acidity of the metal cation is very weak due to its small electronegativity. Therefore, the conjugated oxygen anion displays the strong basic property. In their research paper, the basic sites generated on surface of CaO were identified on IR spectra that were measured in the presence of acidic molecular probe such as benzaldehyde. The presence of the acidic molecular probe resulted in appearance of a new band of OH groups at 3650 cm^{-1} , in addition to a band assigned to the isolated OH groups, which appeared at 3750 cm^{-1} in the absence of the acidic molecular probe. They came into conclusion that the new band of OH groups was due to abstraction of proton from the acidic molecular probe on the surface oxygen anion. Also, it seemed that the isolated OH groups functioned as the basic sites, since the corresponding IR band shifted toward the low wavenumber in the presence of the acidic molecular probe. The experimental fact that the isolated OH groups were formed on surface of CaO calcined even *in vacuo* was verified by XPS and LEED studies, carried out by Liu et al. [28].

The basic properties of the surface can be determined by CO_2 -TPD measurement, which is based on CO_2 adsorption–desorption process operated *in vacuo*. Prior to the measurement, CaO is heated at the temperature required for the perfect evolution of CO_2 and H_2O , generally around 1000 K [29]. It is the scientifically common sense that CaO is exposed to air as a result and the ambient CO_2 and H_2O are combined strongly with the basic sites. Therefore, the pre-treatment mentioned above is essential to collection of the exact CO_2 -TPD data. After the pre-treatment, CO_2 is adsorbed on the fresh surface of CaO, and then the adsorbed CO_2 is evolved by heating up again. The total of the evolved CO_2 and a temperature at which the amount of the evolved CO_2 is maximized correspond to the amount of the basic sites and the representative strength of basic sites, respectively. Zhang et al. reported the basic properties of alkaline-earth metal oxides from data collected by CO_2 -TPD measurement [30]. The strength of the basic sites was

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