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Optimization of the activity of KOH/calcium aluminate nanocatalyst for biodiesel production using response surface methodology



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ABSTRACT

In this study, alumina and calcium aluminate were prepared through microwave combustion method (MCM) and then were modified by potassium hydroxide as solid base catalysts. The catalytic activities were evaluated in the transesterification reaction of canola oil. The characteristic properties of the samples determined by XRD, FTIR, TG, BET surface area, basicity by Hammett indicator, SEM and EDX showed that the alpha phase of alumina and monocalcium aluminate $(CaAl_2O_4)$ were successfully synthesized by MCM. However, the samples showed less basicity and activity whereas these properties were meaningfully increased by KOH loading. Moreover, the surface area of monocalcium aluminate was increased from 38.9 to 48.1 m²/g by loading of potassium components. To obtain a catalyst with highest activity and basicity, the calcium oxide and potassium group precursor dosages on aluminum oxide were optimized using the response surface methodology (RSM). The optimal parameters obtained were calcium oxide/alumina molar ratio of 1.48:1 and 23 wt.% potassium hydroxide to CaO-Al₂O₃. The yield in the optimal condition was 96.7% (the predicted yield was 98.3%) where the transesterification reaction was performed in conditions of 65 °C, 3.5 wt.% catalyst, 12:1 molar ratio of methanol-to-oil and 4 h reaction time. The catalyst maintained its activity for at least three times.

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1. Introduction

Biodiesel is a very popular alternative fuel that is renewable, biodegradable and non-toxic which is commonly produced through transesterification of triglyceride with methanol in the presence of a catalyst. Recently, heterogeneously biodiesel production is widely in consideration to avoid the drawbacks of the homogeneous biodiesel production process and reducing the production costs [1]. In this process, solid base catalysts are extremely utilized due to their higher activity during the transesterification reaction and performing the reaction at a shorter time in comparison to the solid acid catalyst. In this case, many metal oxide catalysts were promoted using the base components such as alkali hydroxide [2-4] and alkaline earth metal oxide [5,6]. The effects of potassium hydroxide and calcium oxide have been extensively evaluated as active phases on the support catalysts due to their high basicity and cheaper resources [7,8]. Many support catalysts have been examined which among them alumina provides more specific surface area, larger distribution of pore sizes and higher stability for active

phases [9]. Alumina promoted by calcium oxide [10–12] and potassium hydroxide [13–16] is meaningfully applied in the biodiesel production. However, according to our knowledge, extensive studies have not yet been performed on the effects of both potassium hydroxide and calcium oxide loading on alumina. Moreover, the researchers reported that the mixture of calcium oxide and alumina could result into many phases of calcium aluminate that are able to affect the basicity and activity due to the presence of different ratios of Ca-to-Al [17–19].

Scientists have applied various catalyst preparation methods that among them, the wet chemical processes such as sol-gel, coprecipitation, impregnation and hydrothermal methods are often utilized. However, these methods require long time, usually more than 2 days for the catalyst preparation which makes these techniques uncommercial, due to consuming expensive raw materials and requiring many processing steps. Nowadays, researchers have proposed other novel methods for producing the catalyst in a short time such as the combustion method. Combustion synthesis is a two-step process: first formation of the precursor and then autoignition. This auto-ignition is often termed as the self-propagating high temperature synthesis [20]. Combustion synthesis is particularly an easy, safe and rapid production process wherein the main advantages are savings made in the energy and time. The

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