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Mechanochemical preparation and characterization of CaO·ZnO used as catalyst for biodiesel synthesis

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ABSTRACT

In this study, the synthesis of biodiesel or fatty acid methyl esters (FAME) from sunflower oil and methanol using CaO·ZnO catalyst was investigated. Catalyst was synthesized by ball milling of $Ca(OH)_2$ and ZnO powder mixture with the addition of water (BMH), as well as solely by ball milling of mentioned powders (BM) and subsequent calcination at 700 °C in air atmosphere. For comparison, the CaO·ZnO mixed oxide was also prepared using usual coprecipitation procedure (CP) followed by calcination at 700 °C of the formed calcium zinc hydroxide hydrate. The BMH, BM and CP catalysts were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), infrared spectroscopy (FTIR), particle size distribution measurement and scanning electron microscopy (SEM and SEM-EDS). In addition, specific surface area (BET), solubility in methanol at 60 °C and alkalinity (Hammett indicator method) were also determined. The activity of BMH, BM and CP catalysts for biodiesel synthesis were tested at 60 °C and 1 bar, using molar ratio of sunflower oil to methanol of 1:10 and with 2 wt% of catalyst based on oil weight.

1. Introduction

Due to the limitation of fossil fuel and its toxicity today's research is directed towards alternative renewable sources. Biodiesel is non-toxic and biodegradable renewable fuel derived from vegetable oils, animal fats or used cooking oils. Biodiesel (FAME, Fatty Acid Methyl Esters) is usually produced by transesterification of triglycerides, the main constituent of vegetable oil, with methanol or ethanol. The most important parameters that affect the rate of transesterification are reaction temperature, type and concentration of catalyst as well as alcohol to oil molar ratio [1].

In order to improve the rate of transesterification and yield of FAME the reaction of transesterification could be catalyzed by homogeneous (alkalies and acids) or heterogeneous catalysts. Nowadays, homogeneous base catalysts are the most frequently used in industry, since the process is faster under mild reaction conditions compared to acid catalyzed reaction. However, their utilization in vegetable oils transesterification very often forms soaps as undesirable byproducts, which in turn generates large amounts of wastewater during the separation of the catalyst and formed products. Heterogeneous catalyst could overcome mentioned drawbacks of homogeneous catalysts; they can reduce production costs, be reused, regenerated [2] and, finally, heterogeneous catalysts could be operated in continuous processes.

A variety of solid catalysts for biodiesel production has been investigated. Those include alkaline earth base oxides [3–12], zeolites and modified zeolites [13], hydrotalcites [14], and alkali or alkaline earth oxides on porous support [15–17]. Some of them are produced using complex and expensive procedures, which is a big disadvantage for their industrial application.

Among the heterogeneous base catalysts, CaO is the most studied due to its low price and desired activity (Table 1). The catalytic activity of CaO strongly depends on calcination temperature [3,5] and used precursor [3,6]. Since CaO, known to be active in methanolysis reaction (yield over 90% after 90 min [3]), tends in smaller extent to be leached by methanol [7] it is important to improve its properties by fixing it to some support, e.g. silica [15], alumina [16], or ZnO [17]. The support is usually a porous material providing higher surface area, with catalytic activity ranging from very small to none.

One of the catalysts showing excellent activity under moderate reaction conditions (reaction time 3 h, FAME yield 94% and catalyst can be reused up to 3 times with FAME yield above 90% [18]) is the mixture of CaO and ZnO oxides [17–20]. It might be obtained by calcination of calcium zinc hydroxide hydrate (calcium zincate dihydrate – $CaZn_2(OH)_6{\cdot}2H_2O$) synthesized by coprecipitation of ZnO and $Ca(OH)_2$ added to 20% KOH solution [19]. Proposed method of $CaZn_2(OH)_6{\cdot}2H_2O$ synthesis consists of several steps. One of them is long-lasting, as is the washing of formed calcium

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