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Preparation and characterization of hydrotalcite-like compounds containing transition metal as a solid base catalyst for the transesterification

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ABSTRACT

Hydrotalcite-like compounds (HTLCs) containing Mg^{2+}, Fe^{3+} and Al^{3+} layered double hydroxide (LDH) were synthesized by co-precipitation method and calcined at 873 K for 16 h. These heterogeneous base catalysts were used for the transesterification of soybean oil with methanol to produce biodiesel. The Mg/Fe molar ratio was varied from 6 to 15, but the MgAlFe catalysts have a constant Al composition in the hydrotalcite-like structures. The catalysts were characterized by nitrogen physisorption, X-ray powder diffraction (XRD), thermogravimetric analysis (TGA), CO_2 temperature programmed desorption (CO_2-TPD), field-emission scanning electron microscope (FE-SEM), and Fourier transfer infrared spectroscopy (FTIR). The conversion of fatty acid methyl ester (FAME) has been affected by the basicity and Mg content in the MgAlFe catalysts. When MgAlFe 15 was used, the highest basicity and high conversion of FAME (81%) was obtained due to the formation of Mg^{2+}–O^{2-}, Al^{3+}–O^{2-} pairs, and the higher CO_2-desorption temperature.

1. Introduction

Transesterification is a general term used to describe an important class of organic reactions where an ester transforms into another ester by the interchange of the alkoxy moiety. The transesterification process is also called alcoholysis because the ester reacts with a short-chain alcohol. It has been known that the α-halo esters and the β-ketoesters undergo a transesterification via an acylketene intermediate [1]. The transformation between fatty acids contained in vegetable oils (e.g., rapeseed, sunflower, or soybean oil) and low-molecular weight alcohol (methanol) could form the alkyl esters of fatty acids such as FAME. This reaction is useful for the biodiesel production. However, the presence of a catalyst (a strong acid or a base) considerably accelerates the adjustment of the equilibrium process. The overall process is a sequence of three consecutive and reversible reactions, in which di- and monoglycerides are intermediates formed during the generation of alkyl esters. According to the above statements, the triglyceride reacting with alcohol (methanol) in the presence of a strong acid or base could produce a mixture of FAME and glycerol, but glycerol is a byproduct in the reaction. In general, the stoichiometric reaction requires 1 mol of triglyceride and 3 mol of alcohol. However, an excess of alcohol is used to increase the yield of the alkyl esters and allow its phase separation from the glycerol. Several parameters including the type of catalyst (alkaline or acid), alcohol/oil molar ratio, temperature, purity of the reactants (water content mainly), and the free fatty acid content have an influence on the transesterification. In reality, the application of transesterification is not restricted to laboratory scale. Several relevant industrial processes use this reaction to produce different types of compounds. For instance, the production of polyethylene terephthalate (PET), dimethylterephthalate is transformed to ethylene glycol using the zinc acetate as a catalyst [2]. If the alcohol and the ester groups have the same molecular chain, the ester groups would undergo an intramolecular transesterification to form cyclic compounds such as lactones or macrocycles [3–6].

Biodiesel is produced by a homogeneous basic catalyst such as a sodium hydroxide or a potassium hydroxide. This method has several disadvantages to overcome. Firstly, the catalyst dissolved in the methanol causes it recycle hard and the weight loss after the reaction. Secondly, large quantities of water are produced, making it be necessary to purify the ester phase. To prevent these drawbacks, the heterogeneous catalyst is used because the separation process of the heterogeneous method is relatively easy. This reaction without the formation of the soap could omit the requirements for the washing water and improve the reusability of the catalyst [7]. Generally, there are three types of heterogeneous catalysts used in the transesterification including the acidic, basic, and enzymatic catalysts. The acid catalysts include sulfonated polystyrene (SPS) [8], palmitic acid over the aluminosilicate Al-MCM-41 [9], and H_2SO_4/TiO_2–SiO_2 [10]. The basic catalysts include MgO/CaO [11] and KNO_3/γ-Al_2O_3 [12]. The alkali earth metal catalysts include $ZnO/Sr(NO_3)_2$ [13] and

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