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Communication

Preparation and properties of zirconia nanotube-supported 12-tungstophosphoric acid catalyst

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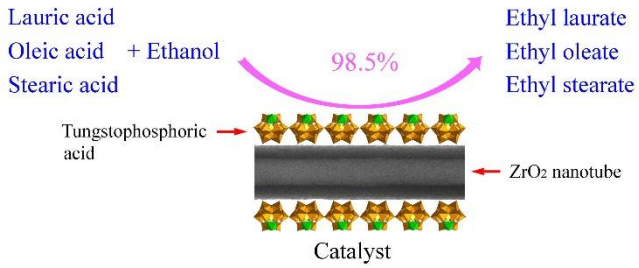
Graphical abstract



Zirconia nanotube-supported $H_3PW_{12}O_{40}$ (HPW) catalysts exhibit high catalytic activities in the synthesis of fatty acid ethyl ester.

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ABSTRACT

Zirconia nanotube-supported $H_3PW_{12}O_{40}$ (HPW) catalysts were obtained by loading HPW onto zirconia nanotube arrays which were prepared through anodization of zirconium foil in the mixture of formamide and glycerol (volume ratio=1:1) containing 1 wt% NH_4F and 1 wt% H_2O. The samples were characterized through scanning electron microscope, X-ray diffraction, infrared spectra and thermogravimetric analysis. Various factors affecting the catalytic activities have been investigated. The catalysts, prepared through pretreating the nanotube carrier at 400 °C, followed by loading with 35 wt% HPW and calcining at 200 °C, possess high catalytic activities in the synthesis of fatty acid ethyl ester. Under the optimal reaction conditions, the conversion percentages of lauric acid, oleic acid and stearic acid are all higher than 98.5%.

Keywords: Zirconia Nanotube arrays Catalyst Tungstophosphoric acid Esterification

The exhausting petroleum resources and serious air pollution caused by burning of fossil fuel promote people to look for new kinds of clean energy [1], among which biodiesel has arisen increasing attention due to its advantages such as renewable, degradable and pollution-free [2-4]. Preparation methods of biodiesel can be divided into physical, chemical and biological method. The main defect of physical method is that its product quality cannot achieve the user's requirement and the biological method has disadvantages such as poor stability and long production cycle. The main chemical methods include splitting method and transesterification method [5]. Most attention has been focused on the transesterification method because coke and carbon deposition problem is difficult to be dissolved in splitting method [6].

Transesterification reaction is reversible, thus, to achieve complete transesterification reaction, low boiling point alcohol is generally replaced with high boiling point alcohol and the low boiling point alcohol must be separated timely. However, when biodiesol is prepared through transesterification reaction, methanol or ethanol is used to replace glycerol in vegetable oils, which is unfavorable to complete the transesterification reaction. The main chemical composition of vegetable oils is triglyceride of fatty acids. Incompolete transesterification reaction would result in the generation of mono- and di-glyceride of fatty acids, both of which have surface activity and lead to higher glycerol content in the products [7].

As it is well known, the technology of obtaining glycerol and fatty acids from oil hydrolysis has been well developed and industrialized. Consequently, based on the oil hydrolysis technology, an ideal preparation method of biodiesol is direct esterification of fatty acid with low-carbon alcohol. The existing problems in transesterification method can be overcome in direct esterification method