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Transesterification of soybean oil over WO_3 supported on $AlPO_4$ as a solid acid catalyst

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HIGHLIGHTS

- The catalyst was effective in the transesterification reaction of soybean oil.
- The catalyst also showed activities in the esterification of free fatty acid.
- The catalytic activity and stability of the catalyst were investigated.

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ABSTRACT

$WO_3/AlPO_4$ catalysts were prepared by impregnation of $AlPO_4$ with ammonium metatungstate. Powder X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, and thermo gravimetric and differential thermal analysis (TG–DTA) demonstrated that the tungsten compound was incorporated into $AlPO_4$ forming the catalyst with an enhanced acidity. When transesterification of soybean oil over the catalysts was performed, the catalyst with 30 wt.% WO_3 loading and calcined at 1073 K, exhibited the best catalytic activity with a conversion of 72.5%. The transesterification was optimal at 453 K for 5 h with a methanol/oil ratio of 30:1 and catalyst dosage of 5 wt.%. Free fatty acid (FFA) and water did not affect the catalytic activity. The catalyst proved to be stable over four transesterification cycles as it lost only 4% of its activity after being reused four times. The catalyst could be used for the transesterification of low-cost oils for biodiesel production.

1. Introduction

Currently, biodiesel is generally produced by transesterification of vegetable oil using a soluble basic catalyst, such as NaOH, KOH or $NaOCH_3$. These homogeneous catalysts are inexpensive, but suffer from sensitivity to moisture and free fatty acid (FFA). Therefore, the alkali-catalyzed transesterifications commonly requires the use of valuable, refined vegetable oils with less than 0.5 wt.% FFAs and anhydrous conditions (Li and Xie, 2008), and low-cost oils usually containing large amounts of FFAs and water cannot be used (Ramachandran et al., 2011). Homogeneous acid catalysts have the potential to replace alkali catalysts since they do not show measurable susceptibility to FFAs and can catalyze esterification and transesterification simultaneously; however, high reaction temperatures, slow reaction rates, high methanol-to-oil molar ratios, separation of the catalysts, serious environmental and corrosion related problems need to be considered for the utilization of liquid acid catalysts for biodiesel production (Lotero et al., 2005). Some of these problems can be avoided with the use of heterogeneous acid catalyst since they are reusable, can be separated easily from the reaction mixture and yield products with higher purity since washing process can be eliminated (Semwal et al., 2011). Moreover, the heterogeneous acid catalysts have the ability to simultaneously catalyze the transesterification of triglycerides and the esterification of FFAs (Kulkarni et al., 2006). Several solid acid catalysts have been prepared and used for the preparation of biodiesel, including sulfated zirconia (López et al., 2008), WO_3/ZrO_2 (López et al., 2008; Furuta et al., 2006), SO_4^{2-}/SnO_2 (Furuta et al., 2004), $SO_4^{2-}/SnO_2–SiO_2$ (Lam and Lee, 2011), SnO_2/SiO_2 (Xie et al., 2012), tungstated zirconia (López et al., 2007; Ramu et al., 2004) and WO_3/MCM-14 (Jiménez-López et al., 2011; Jiménez-Morales et al., 2010).

Aluminum phosphate is an attractive support for a variety of catalysts. For example, $AlPO_4$ was employed as a support for nickel catalysts used in hydrogenation reactions (Marcelin et al., 1983). $Co/AlPO_4$ catalysts were prepared and used for Fischer–Tropsch synthesis (Bae et al., 2009). High surface area and large average pore size are the main advantages for using amorphous $AlPO_4$ as a support. Amorphous aluminum phosphate is built of tetrahedral units of AlO_4 and PO_4 and is structurally similar to the silica (Bautista et al., 1998). This type of structure provides a feature of large surface area and high thermal stability and allows for easy

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