ALUMINUMDODECATUNGSTOPHOSPHATE ($Al_{0.9}H_{0.3}PW_{12}O_{40}$) NANOTUBE AS A SOLID ACID CATALYST ONE-POT PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL

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Solid nanocatalyst aluminum dodecatungstophosphate ($Al_{0.9}H_{0.3}PW_{12}O_{40}$, abbreviated as AlPW) with nanotube structure was synthesized through a natural cellulose fiber template. The AlPW nanotubes, which are highly water-tolerant and acid-tolerant, can be described as green double acids, as they combine both Brønsted and Lewis acid sites. They have been applied as an efficient nanoheterogeneous catalyst for the preparation of biodiesel from waste cooking oil containing 26.89 wt% high free fatty acids (FFAs) and 1% moisture via esterification of FFAs and transesterification of triglycerides in one pot under mild conditions.

Keywords: Biodiesel; Heteropolyacid; Nanoheterogeneous catalyst; Transesterification; Esterification

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INTRODUCTION

Biodiesel, which is recognized as a ‘green fuel,’ is a promising alternative renewable fuel composed of mono-alkyl esters of fatty acid derived from either the transesterification of triglycerides (TGs) or the esterification of free fatty acids (FFAs) with short-chained alcohols. Cheap low-quality oils such as waste cooking oil (WCO) and animal fat are attractive starting materials that can help improve the economic feasibility of biodiesel (Kulkarni et al. 2006). There are two undesirable side reactions reducing the catalyst efficiency and increasing purification cost, i.e. TGs’ hydrolysis and saponification (Morin et al. 2007; López et al. 2005). Because of these reactions, feedstocks with high FFAs and moisture cannot be transesterified directly via a basic catalyst. The homogeneous acid catalysts H_2SO_4, HCl, or H_3PO_4 do not exhibit measurable susceptibility to FFAs, but are sensitive to moisture and difficult to recycle, need to operate at high temperatures, and give rise to serious environmental and corrosion problems (Liu 1994; Canakci et al. 1999; Canakci et al. 2001; Canakci et al. 2003; Widyan et al. 2002).

Solid acid catalysts offer significant advantages of eliminating separation, corrosion, toxicity, and environmental problems (Clark 2002; Okuhara 2002), and have recently attracted considerable attention for solid acids catalytic production of biodiesel (Lotero et al. 2005). Among the solid acid catalysts, mostly Brønsted acids have been used for biodiesel production, such as zeolites (Okuhara 2002), ion-exchange resins (Kiss et al. 2006), metal oxide such as sulfated zirconia, WO_3/ZrO_2, MoO_3/ZrO_2, and sugar-based catalyst (Zong et al. 2007; Lou et al. 2008). There are only few reports on homogeneous Lewis acid catalyst — carboxylic or cyanide salts of the metals (Cd, Mn, Pb, Zn) (Di Serio et al. 2005; Sreeprasanth et al. 2006). Santacesaria concluded that Brønsted acid catalysts are active mainly in esterification, while Lewis acid catalysts are more active in transesterification (Di Serio et al. 2005). So design and synthesis of solid acid catalysts containing Brønsted acid and Lewis acid in one material, with numerous strong acid sites, enhancement of water-tolerance, large pores, hydrophobic surface, and low cost are still a challenge and a task needed to be solved. Among this line and in continuation of our interest to explore new catalytic activity of heteropolyacids (HPAs) $H_3PW_{12}O_{40}$(HPW), and its salts (Cao et al. 2008; Chai et al. 2007), we now have designed and synthesized $Al_{0.9}H_{0.3}PW_{12}O_{40}$ nanotube, which has been successfully applied for the esterification of FFAs and transesterification of triglyceride to biodiesel in one pot. To the best of our knowledge, utilization of HPA solid acid nanocatalysts with double acid sites for biodiesel production from low quality WCO has not been explored in detail so far.

EXPERIMENTAL

Catalyst Preparation

The procedure for formation of the nanotube catalyst was essentially that of Chai et al. (2008): 1 mmol $H_3PW_{12}O_{40}\cdot 23H_2O$ was dissolved in 20 mL distilled water. This solution was added dropwise into 10 mL ethanol solution containing 1 mmol $Al(NO_3)_3\cdot 9H_2O$ with gentle stirring. The mixture was continuously stirred for about 30 min, then some pieces of filter paper were dipped into this solution for 15 min, and then the filter paper was thoroughly washed with water and ethanol in order to remove the HPW and aluminum nitrate which did not attach onto the surface of filter paper. Then the filter paper coated with Al salt of HPW was dried by airflow. This procedure was repeated 20 times. The resultant paper/AlPW complexes were calcined in air at 673K for 6h to remove the original filter paper. The greenish-yellow powder, which was self-supporting AlPW nanotube, was obtained with a yield of 1.5g.

Transesterification Reaction

The waste cooking oils (FFAs content: 26.89 wt%; acid value: 53.8 mg KOH/g; water content: 1wt% being measured gravimetrically using the method AOCS Ai2-75 at 376K) was kindly provided by a local company and used without any treatment. The transesterification of WCO was carried out in a 50mL round reactor, provided with thermometer, mechanical stirring, and condenser. The system was preheated to 338K, then 8g of waste frying oil was added. When the system reached 338K, 29mL of methanol and 3.0 wt% of catalyst AlPW were added with stirring at 300 rpm in order to keep system uniform in temperature and in suspension.

The transesterification was performed over a specified time, and 2mL samples were withdrawn at 4h, 6h, 8h, 10h, 12h, and 14h to determine the concentrations of biodiesel by ^{1}H NMR, and the acid value was determined by titration (Xie et al. 2006). The experiment was prolonged for about 14h, by which time the conversion to esters was complete. After cooling, the mixture formed two layers: the upper layer consisted of methyl esters, FFSAs, triglycerides, and intermediates; the lower layer contained glycerin, AlPW, and the excess of methanol. The methyl esters were treated by activated carbon to dehydrate and discolor. The glycerin layer was distilled — the residual methanol being gathered at 323K using a rotary evaporator, and kept for reuse. The catalyst AlPW was decanted at the bottom of the reactor, so it was easily separated and reused after soaking in methanol to remove the polar compounds such as glycerol, and drying under vacuum at 353K.

RESULTS AND DISCUSSION

Catalyst Characterization

From elementary analysis, the contents of the material were W, 75.42; P, 0.92; Al, 0.76 %. It can be seen that the ratio of W: P: Al was 12:1:0.9, corresponding to the formula of $Al_{0.9}H_{0.3}PW_{12}O_{40}$ (AlPW). The IR spectrum (Fig. 1a) of the AlPW nanotubes confirmed that AlPW nanotube kept a Keggin structure. The X-ray powder diffraction (XRD) pattern (Fig. 1b) of the sample showed some differences due to the partial substitution of Al ion. However, the primary structure of HPAs still remained intact. The morphology and microstructure of the prepared AlPW were investigated by transmission electron microscopy (TEM) (Fig. 2). Typical TEM images showed that the sample displayed tube-like shapes obtained by burning out the fibers from the middle of the material. The average length of the tubes was about 35 nm, the width of the tubes was about 2 nm, and the inner width was about 1 nm. The acidic properties of the nanocat-alyst AlPW were studied by NH_3-TPD (Fig. 3a) and Hammett indicator methods. The acid strength of AlPW lay between $Ho = -13.75$ and -14.52, which is lower than that of pure HPW or CsPW ($H_0 \leq -13.16$) (Okuhara et al. 1992). FTIR spectra of adsorbed pyri-dine were recorded to distinguish the type of acid sites on the catalyst AlPW at 300K. The FTIR spectra of adsorbed pyridine on pure HPW showed typically intense bands at 1533, 1638, and 1545cm^{-1} that are characteric of Brønsted type acidity (Parry et al. 1963). In the FTIR spectra of adsorbed pyridine on AlPW (Fig. 3b), the intense band at 1480 cm^{-1} is attributed to Lewis acid sites, and the bands at 1603, 1540 cm^{-1} are related to Brønsted acid sites. It can be concluded that compared with pure HPW, the Lewis acid sites were introduced by partial exchanging of H with Al ions. Thus AlPW maintained its Brønsted acidity and increased in Lewis acidity, which might be considered as being advantageous for catalyzing simultaneous esterification and transesterification of waste cooking oil.

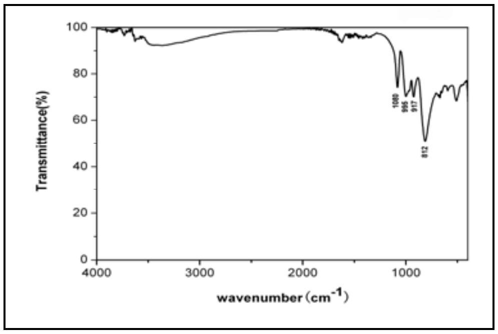

Fig. 1a. IR spectrum of AlPW nanocatalyst

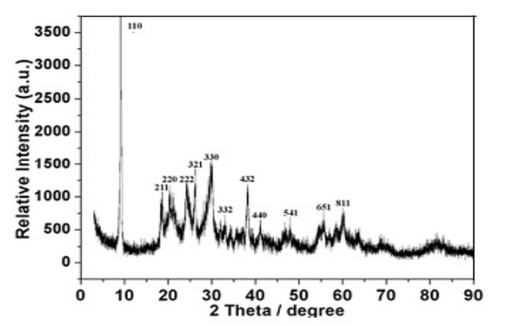

Fig. 1b. XRD patterns of AlPW catalyst

Fig. 2. Typical TEM image of AlPW nanotube

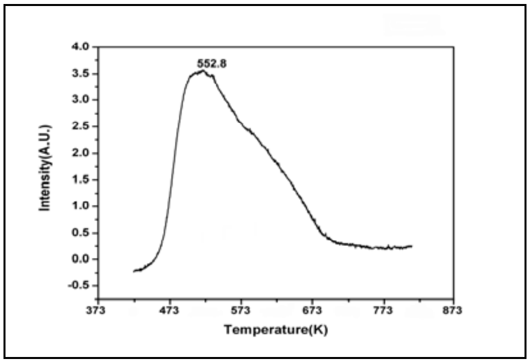

Fig. 3a. NH_3-TPD profile of AlPW nanotube

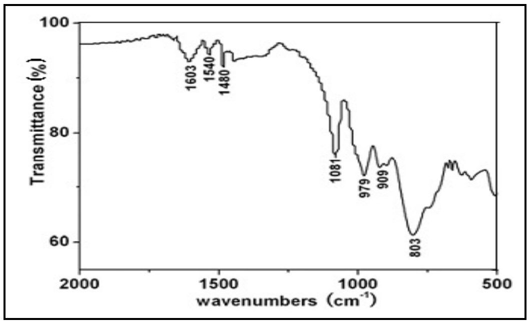

Fig. 3b. IR spectrum of adsorbed pyridine at 300 K of AlPW

From the above results it can be concluded that partial exchanging of protons with Al ions can introduce Lewis acid sites into pure HPW molecules and thereby modify the acid strength of pure HPW via Lewis acid sites assisting Brønsted acid sites.

Catalytic Activity

In order to estimate the efficiency of the AlPW nanocatalyst, we compared the catalytic effects of four solid catalysts AlPW nanotube, AlPW salt with non-nanotube structure, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW), and HPW (Fig. 4). The catalytic activities of the four different catalysts were 96, 87.3, 82.4, and 42.6%, corresponding to AlPW nanotube, AlPW non-nanotube, CsPW, and HPW. The results showed a remarkable enhancement in the reactivity, and the conversion was observed with AlPW nanotube, while the AlPW nanocatalyst afforded a high conversion of WCO above 96% at 338K, 1: 34 oil/methanol ratio, 14h, catalyst 3wt%. It can be seen that the catalytic activity of AlPW nanocatalyst was suitable for the biodiesel production from the WCO. The catalysts CsPW and HPW are pure Brønsted acid catalysts, while AlPW catalyst contains Brønsted acid and Lewis acid double acid sites, and acid strength could be enhanced through the Lewis acid sites assisting the Brønsted acidity. Thus, the higher catalytic activity is attributed to the cooperative effect of Lewis acid sites and Brønsted acid sites. The nanotube structure is also a good help for increasing catalytic activity, owing to its higher surface area ($278m^2/g$).

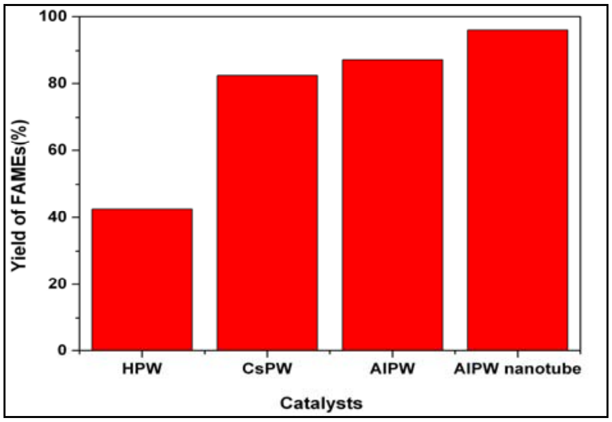

Fig. 4 . Profiles of the production of biodiesel by different catalysts. Reaction condition: molar ratio of methanol/oil =34:1, 3 wt% of catalyst, temperature = 338K, time =14h

Effect of methanol/oil ratio

The transesterification reaction stoichiometry requires three moles of alcohol per mole of triglyceride to yield three moles of fatty acid methyl esters (FAMEs) and one mole of glycerin. Since the transesterification is reversible, an excess of methanol needs to be used. Dube (Zheng et al. 2006) advocated the use of large excess quantities of methanol (245:1) while using sulfuric acid as catalyst. According to our previous reports, using pure HPW as homogeneous catalyst, the conversion of such high FFAs oil reaching 87%, required a high methanol/oil ratio (70:1) and 4Å zeolites as the water sorbent (Cao et al. 2008; Chai et al. 2007). We selected molar ratios of methanol to oil from 26:1 to 34:1 (Fig. 5) at 338K. The yield of FAME increased from 56.4 to 96.1% on increasing the methanol to oil ratio from 26:1 to 34:1 after 14h reaction time.

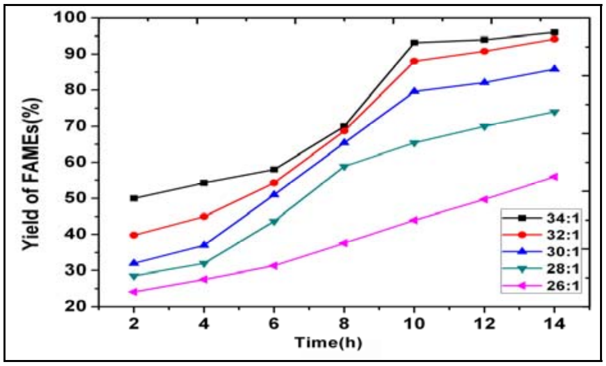

Fig. 5. Effect of molar ratio of methanol to oil on the yield of FAMEs using AlPW nanocatalyst, 3 wt% catalyst, temperature = 338K , time =14h

The final acid value of the product decreased to 1.6, which is consistent with an FFA content of about 0.8%. The conversion of FFAs in the WCO to biodiesel was calculated from the means of the acid value (*AV*) of the oil layer with the following equation (Wang et al. 2007): The conversion (%) = $(1—AV_{OL}/AV_{WCO})\times 100\%$, in which

OL and WCO refer to biodiesel oil layer and waste cooking oil. The conversion of FFAs under catalyzing by AlPW is 97.1%. From this, it can be seen that the esterification of FFAs was almost complete, indicating that AlPW is effective for the esterification of FFAs in the presence of triglycerides.

Effect of catalyst weight

The effect of the catalyst amount on the yield of FAMEs is shown in Fig. 6. An increase in the yield of FAMEs from 36.5% to 96.1% was apparent when the amount of the AlPW nanocatalyst increased from 2 to 3.25 wt%, and the acid catalyst process attained maximum yield at 3 wt% of the catalyst. The increase in the yield of FAMEs with an increase in the catalyst usage can be attributed to an increase in the availability of the number of catalytically active sites.

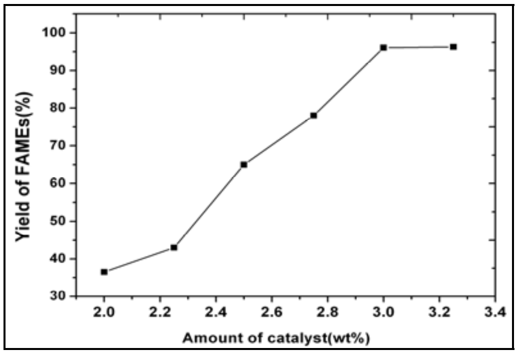

Fig. 6. The influence of catalyst amount on the yield of FAMEs, molar ratio of methanol/oil =34:1, temperature =338K and time =14h

Water tolerance test

To investigate the effect of water content on catalytic activity, the experiment was carried out by adding some excess water to the mixture under the same conditions (methanol/oil = 34:1, temperature 338K, catalyst 3 wt%, 14 h). The result (Fig. 7) indicated that AlPW nanocatalyst exhibited above 80.5% catalytic activity for the transesterification of WCO with 5 wt% water content, while the catalytic activity was little affected by the water as the water content < 5 wt%. When increasing the water content from 5 wt% to 10 wt%, the yield of biodiesel decreased from 80.5% to 11.8%, showing that the AlPW is relatively water-tolerant as water content in the range of 1 wt% to 5wt%.

Catalyst recycling

The recycling of catalyst is a crucial step, owing to the reduction the cost of biodiesel production. The recyclability of the catalyst was studied under the reaction conditions of 338K, 3 wt% catalyst, 14 h, and 34:1 methanol/oil molar ratio. The catalyst can be reused with treatment by soaking in methanol to remove the polar compounds such as glycerol and drying under vacuum at 353K. The experiments were repeated six times, and the yield of conversion to fatty acid methyl esters is shown in Fig. 8. It shows that there was no considerable change in the activity of the catalysts even after six reaction cycles.

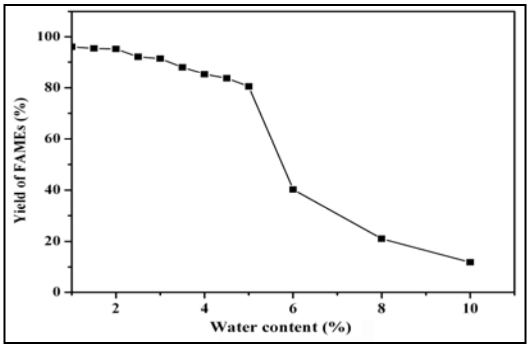

Fig. 7. The influence of water content on the catalytic activity of AlPW nanocatalyst. Conditions: molar ratio of methanol / oil = 34: 1, temperature = 338K, time = 14h, 3 wt% catalyst

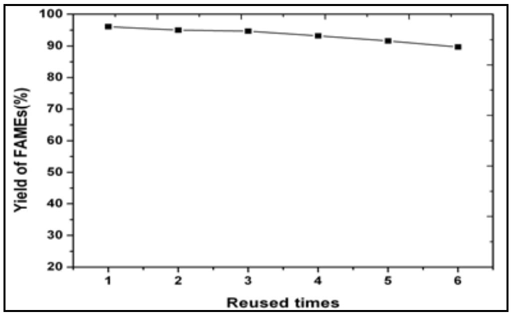

Fig. 8. The catalyst activity in six reaction cycles. Conditions: molar ratios of methanol / oil = 34: 1, temperature 338K, time = 14h, 3 wt% catalyst

To test for leaching of the AlPW nanocatalyst, the catalyst was filtered hot after reaction for 8h (ca. 70 % ester conversion), and the filtrate allowed reaction to continue for a further 2h at the same temperature of 338K. From the result, it can be seen that the conversion of fatty acid methanol ester was only 70.6%, which indicates a little leaching of AlPW into the mixture. The elementary analytical result showed that the content of W was 1446ppm. The total amount of AlPW leaching through six runs of the reaction reached 0.79% of the starting amount of AlPW. So our solid acid catalyst was found to be relatively stable and could be reused up to a minimum of six reaction cycles.

CONCLUSIONS

1. AlPW nanotube with double acid sites, i.e., Brønsted acid sites and Lewis acid sites, has been synthesized and used as a nanoheterogeneous acid catalyst for the production of biodiesel from low-cost waste cooking oil containing 26.89 % FFA and 1% moisture.
2. The solid acid AlPW nanotube exhibits high catalytic activity and stability towards biodiesel production under mild reaction conditions. Most importantly, the activity of the AlPW nanotubes is not considerably affected by the FFAs content in WCO and is

relatively water-tolerant for 5% water content. In other words, nanotube AlPW is acid-tolerant and water-tolerant.

3. The better catalytic activity came from introduction of Lewis acid sites to pure HPW by partial exchange of H^+ ions by Al^{3+} ions, high acid strength by Lewis site-assistance of Brønsted sites, high surface area, and nanotube structure.
4. The above facts probably contribute to high catalytic activity for the simultaneous esterification and transesterification of waste cooking oil, and this AlPW catalyst can be comparable to other acid catalysts, such as Fe-Zn double-metal cyanides and starch-derived catalyst, when producing biodiesel using feedstocks having relatively high FFAs and water contents.

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