Conversion of palm fatty acid distillates to renewable biofuel additives over Ti-grafted mesoporous silica nanospheres

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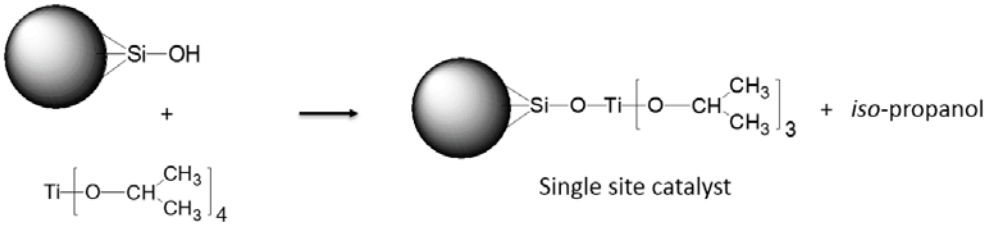
Abstract: The titanium-grafted mesoporous silica nanospheres (denoted the Ti/m-SiO_2 catalyst) as efficient Lewis solid acid catalysts were synthesized for the conversion of palm fatty acid distillates (PFAD) to fatty acid methyl esters (FAME) with saturated fatty acid tails. This study has shown that the PFAD waste could be transformed into PFAD-derived FAME molecules with high oxidation stability through the solid acid-catalyzed esterification. Consequently, the PFAD-derived FAME molecules could be used as renewable biofuel additives added to petro-diesel or petro-diesel/biodiesel blends, preventing to form insoluble gums and sediments in storage in the tropical monsoon climates.
Keywords: palm biomass waste, solid acid catalyst, biodiesel and bio-additive.

1. Introduction

Due to strong demand for food and biodiesel feedstock, the Thai palm oil market is promptly increased to 12.6 million tons/year in 2015, being the world's third largest producer of palm oil behind Indonesia and Malaysia, and the industry is highly optimistic about its future growth. In the oleochemical industry, the crude palm oil is pretreated by refining, bleaching and deodorizing (RBD) processes to form high-quality RBD palm oil for food and biodiesel feedstock, accompanying with a lot of PFAD waste with high acid value (at least 10% of crude palm oil). However, PFAD is carelessly treated by burning or disposing as manures, causing serious environmental problems, such as air and land pollutions. In this study, we have designed a novel solid acid catalyst of the Ti/m-SiO_2 catalyst with enhanced activity and reduced cost for the conversion of PFAD with methanol to PFAD-derived FAME with saturated fatty acid tails. The PFAD-derived FAME with high oxidation stability and low production cost can be used as biofuel additives for stabilizing petro-diesel and biodiesel/petro-diesel blends in storage in the tropical monsoon climates.

2. Experimental

The mesoporous silica nanospheres with average particle size of 150-500 μm and average pore diameter of around 15 nm (denoted m-SiO_2) were purchased from Fuji Silysia Chemical Company Ltd., and used as cost-effective support without further pretreatment. For the preparation of the Ti/m-SiO_2 catalyst (see Scheme 1), the mesoporous silica nanospheres were dried at 100 °C under vacuum, followed by grafting with a mixture of titanium tetraisopropoxide and acetylacetonate (50 mol% to Ti) in 200 mL of deoxygenated toluene at 50 °C under nitrogen atmosphere. The Ti/Si molar ratio was kept at 0.03. The Ti/m-SiO_2 catalyst was then obtained by washing the grafting sample with deoxygenated toluene (100 mL) and dehydrated methanol (300 mL), followed by calcining at 500 °C for 3 h. For the catalytic study, the esterification of PFAD with methanol to PFAD-derived FAME over the m-SiO_2 and Ti/m-SiO_2 samples was carried out by a stainless-steel batch-type reactor at 100-200 °C for 1 h using a PFAD/methanol molar



Scheme 1. Preparation of Ti-grafted SiO_2 nanospheres as the single site catalyst for synthesis of biofuel additives.

Table 1. Physicochemical properties of the mesoporous silica nanospheres with and without Ti grafting.

Catalysts	S_{BET} (m^2 g^{-1})	V_{total} (cm^3 g^{-1})	Φ_p (nm)	NH_3 uptake (mmol g^{-1})			FAME Yield (%)
				Total	Strong[a]	Weak	
3Ti/m-SiO_2	157	0.98	16	0.79	0.38	0.41	82
m-SiO_2	188	1.22	18	0.75	0.24	0.51	36

a. the differential heat of NH_3 adsorption > 70 kJ mol^{-1}.
b. the differential heat of NH_3 adsorption < 70 kJ mol^{-1}.

ratio of 28-56. The resulted products were thoroughly analyzed according to the specifications of international fuel standards, such as EN14214.

3. Results and discussion

The XRD pattern and SEM image showed that the m-SiO_2 and Ti/m-SiO_2 samples are amorphous silica nanosphares with the average particle sizes of 150-500 μm. The corresponding N_2 physisorption result showed that both of them contained a classic type IV isotherm with a parallel H1 hysteresis loop at the relative P/P_0 region of 0.75-0.9, indicating the presence of ultra-large mesopores (Fig. 1(a)). Table 1 showed that the surface area (S_{BET}), total pore volume (V_{Total}) and pore size (Φ_p) of the Ti/m-SiO_2 sample is slightly lower than that of the m-SiO_2 sample, presumably due to the structural shrinkage by the grafting method. The acidic strength and capacity of the m-SiO_2 and Ti/m-SiO_2 samples were examined by the differential heat of NH_3 adsorption technique [1]. It is apparent that the Ti/m-SiO_2 sample contained new acidic sites with strongly acidic strength, which are associated with the grafting of Ti species with Lewis acidic nature based on the study of the DRIFT spectra. In contrast, the m-SiO_2 sample only had weakly acidic sites, corresponding to surface silanol groups.

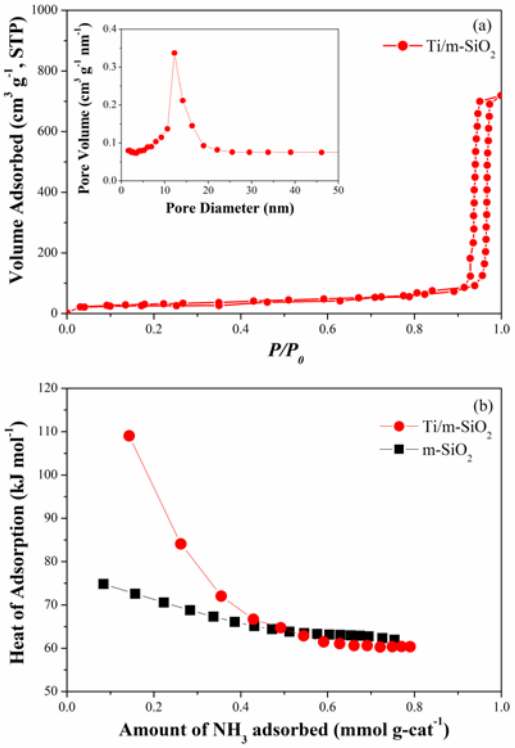


Figure 1. (a) N_2 adsorption-desorption isotherm and pore size distribution, and (b) differential heat of NH_3 adsorption over the m-SiO_2 and Ti-m-SiO_2 samples.

The esterification of PFAD with methanol over the m-SiO_2 and Ti/m-SiO_2 samples was examined using a methanol/PFAD molar ratio of 28 at 150 °C for 1 h. Obviously, the Ti/m-SiO_2 sample was superior to the m-SiO_2 sample in synthesis of PFAD-derived FAME molecules, due to the grafting of Ti species with Lewis acid character as the catalytically active sites. Note that the PFAD-derived FAME molecules with saturated fatty acid tails are naturally stable in air. It is suggested that the PFAD-derived FAME molecules can be used as biofuel additives for protection of the petro-diesel or high blends consisted of biodiesel and petro-diesel from the degradation under ambient condition. In other words, the PFAD-derived FAME molecules synthesized by the PFAD waste are renewable biofuel additives and it can avoid the formation of insoluble gums and sediments when the petro-diesel and high-blends are stored in the tropical monsoon climates.

4. Conclusions

We have prepared a cost-effective and efficient solid acid catalyst of the Ti-grafted mesoporous silica nanospheres for the esterification of the PFAD waste with methanol to form the PFAD-derived FAME molecules, which showed high oxidation stability and suitable for adding to petrol-diesel or high-blends as biofuel additives in the tropical monsoon climates.

References

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