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Ph-SO_3H-modified mesoporous carbon as an efficient catalyst for the esterification of oleic acid

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ABSTRACT

Mesoporous carbon materials with thin pore walls (~1.7 nm) were synthesized using low-cost γ-Al_2O_3 as a hard template and *in situ* polymerized resorcinol–furfural resin as the carbon precursor. Compared with sugar, resin, a widely used carbon precursor, has higher carbon yield and simplifies the synthetic process. Ph-SO_3H modified mesoporous carbon was synthesized by covalent grafting of Ph-SO_3H groups on mesoporous carbon via the diazonium salt. The resulting materials were characterized by means of nitrogen adsorption analysis, TEM, ^{13}C NMR, XRD, FTIR and sulfur elemental analysis. The modified carbons were shown to possess high surface area (~1000 m^2/g), a bimodal pore size distribution and high strong acid density (1.86 mmol H^+/g). These sulfonated carbons were used as solid acid catalysts in the esterification of oleic acid and methanol, a key reaction in biodiesel production. Compared with the traditional solid acid Amberlyst-15, the optimized carbon catalyst exhibited much higher activity with a rate constant (1.34 h^{-1}) three times to that of Amberlyt-15 and a turnover frequency (TOF) of 128 h^{-1} eight times that of Amberlyst-15. The efficient catalytic ability was attributed to the high surface area and a proper mesopore texture. This carbon catalyst could then be easily separated from the product by filtration. The catalyst was reused six times, and no distinct activity drop was observed after the initial deactivation.

1. Introduction

Due to its renewable feedstock and low CO_2 emission, biodiesel produced from vegetable oil is considered a sustainable fuel to replace conventional diesel [1]. The production of biodiesel usually involves the transesterification of triglycerides catalyzed by a homogeneous base, such as NaOH, KOH or $NaOCH_3$ [1–3]. However, the free fatty acid (FFA) contained in the crude vegetable oil will be saponified by the basic catalysts. Therefore, a pre-esterification process is necessary to convert FFA into the corresponding esters before transesterification. Conventionally, the catalysts for pre-esterification are liquid H_2SO_4, which is toxic, corrosive and costly to neutralize, separate and recycle. Therefore, the development of a green and easily separated acid catalyst has received much attention [4].

Among heterogeneous catalysts, carbon-based solid acid is ideal for many reactions owing to such advantages as chemical inertness, mechanical stability, structural diversity and surface hydrophobicity. For the pre-esterification of FFA, much work has focused on sulfonated carbon as the solid acid [5–16]. Using inexpensive biomass (sucrose [6], glucose [7,9], starch [10,11] or biochar [12]) as the carbon precursor, the pioneering work in this area synthesized carbon catalysts through direct carbonization of precursors followed by sulfonation in concentrated H_2SO_4 [5–16]. Such catalysts performed well in the esterification of fatty acid, but direct carbonization led to carbon catalysts with low porosity and low surface area, which is unfavorable for reactant accessibility to active sites. Moreover, the carbon yield of sugar is low. For instance, the theoretical carbon yield of sucrose is 40%, while the actual yield is only approximately 20% [17].

A new type of sulfonated ordered mesoporous carbon (OMC) has been developed for FFA pre-esterification [18–21]. In this work, the organic precursors were first impregnated into the pores of an ordered mesoporous silica template (typically SBA-15) and carbonized, and then the template was removed by treatment with HF solution. The remaining carbon materials were sulfonated by concentrated H_2SO_4 [18,19] or 4-benzene-diazoniumsulfonate (4-BDS) [20,21] to yield OMC-based solid acids with high surface area and large pores. This improved texture facilitates the diffusion of fatty acid molecules with long carbon chains to the active site, thereby increasing the catalytic efficiency. In most cases, silica templates must be prepared beforehand through multiple steps, which inevitably increase the cost of this type of catalysts.

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