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Short communication

Enhanced esterification of carboxylic acids with ethanol using propylsulfonic acid-functionalized natural rubber/hexagonal mesoporous silica nanocomposites

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ABSTRACT

Propylsulfonic acid-functionalized natural rubber (NR)/hexagonal mesoporous silica (HMS) nanocomposites (NR/HMS-SO_3H) with different acid contents were prepared via an in situ sol–gel process, and then applied as heterogeneous acid catalysts in the esterification of model carboxylic acids and palm fatty acid distillate (PFAD) with ethanol. The NR/HMS-SO_3H composites exhibited a wormhole-like framework with enhanced wall thickness, high mesoporosity, and enhanced hydrophobicity. The NR/HMS-SO_3H composites exhibited a superior catalytic performance compared to a commercial Nafion/silica composite solid acid catalyst (SAC-13) and conventional propylsulfonic acid-functionalized HMS (HMS-SO_3H). The NR/HMS-SO_3H catalyst can be regenerated and reused in the esterification.

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1. Introduction

Organic esters are important chemicals in various industrial products, which are commonly synthesized via esterification of carboxylic acids with alcohols in the presence of homogeneous acids. However, the process is energy-inefficient and environmentally unfriendly. Various acidic materials have been investigated as heterogeneous catalysts for the esterification of carboxylic acids [1–4]. Hybrid/composite-type catalysts combine good aspects of inorganic and organic materials in which the organic moieties, such as functionalized polymers [5,6], provide strongly acidic sites and hydrophobic properties, whereas the inorganic frameworks have porous structures and high surface areas. For example, SAC-13, an amorphous silica-supported Nafion® polymer containing sulfonic acid groups, has a high surface area (>200 $m^2 g^{-1}$) and nanometer-scale pores (>10 nm) that allow its application to the catalytic reaction of bulky reactants. Although it has great potential for the esterification, a considerable number of surface silanol groups (≡Si-OH) deteriorate its activity in water-sensitive reactions [7].

Hexagonal mesoporous silicas (HMSs) functionalized with organosulfonic acid groups are promising catalysts in the esterification due to their wormhole-like porous structure with high surface area and strong sulfonic acid groups [8]. Propylsulfonic acid-functionalized HMS materials (HMS-SO_3H) have been synthesized using 3-mercaptopropyltrimethoxysilane (MPTMS) as the precursor [9]. The thiol groups were then oxidized with H_2O_2 [10], yielding the sulfonic acid moieties. However, the residual silanol groups on the surface of the resulting materials contributed the hydrophilicity and retarded the reaction by readsorption of H_2O on the acid sites [11].

Recently, we successfully prepared novel mesoporous composites consisting of natural rubber (NR) as a hydrophobicity improver dispersed in the wormhole-like mesostructure of HMS (NR/HMS) [12]. Moreover, the NR/HMS composites were functionalized with propylsulfonic acid groups via the direct co-condensation method (NR/HMS-SO_3H) [13]. In this communication, we report the catalytic performance of NR/HMS-SO_3H in the esterification of model carboxylic acids and palm fatty acid distillate (PFAD) with ethanol in comparison with that of SAC-13 and HMS-SO_3H.

2. Experimental

2.1. Synthesis of acidic mesoporous catalysts

The synthesis of NR/HMS-SO_3H materials was carried out using the in situ sol–gel method as described elsewhere [13]. The molar composition of synthesis gel was 0.10 TEOS: 0.04 DDA: 5.89 H_2O: 0.37 THF: 0.01 NR: (n) MPTMS: ($7n$) H_2O_2, where $n = 0.01, 0.02$ or 0.04. The obtained acidic composite was designated as NR/HMS-SO_3H (x), where x represents the MPTMS/TEOS molar ratio used in the synthesis. The HMS-

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SO_3H materials were synthesized using the same procedure but without the addition of the NR sheet.

2.2. Characterization of acidic mesoporous catalysts

Structural and textural properties of HMS-SO_3H and NR/HMS-SO_3H materials were analyzed by powder X-ray diffraction (XRD), N_2 physisorption measurement, and transmission electron microscopy (TEM). The presence of surface functional groups in the acidic mesoporous catalysts was confirmed by in situ Fourier transform infrared (FTIR) spectroscopy. The CHNS elemental analyzer was used to quantify the composition of the functionalized materials. The concentration of sulfonic acid groups in the mesoporous catalysts was determined by acid–base titration. The monolayer adsorbed volume of H_2O (V_m) was determined by H_2O adsorption–desorption measurement. The information about characterization instruments and conditions were described in our previous report [13]. The water contact angle was examined at room temperature using a Ramé–Hart Model 200-F1 standard goniometer. Water was dropped on the powder sample, and the droplet dimension was analyzed using the software system. The experiment was repeated five times for each sample, and the averaged value was reported.

2.3. Esterification of various carboxylic acids with ethanol

Esterification of carboxylic acids with ethanol was carried out in a 50-mL three-neck round-bottom flask equipped with a magnetic stirrer and a reflux system. The cooling water temperature (5 °C) was controlled by bath circulating equipment. Before being used, the catalyst was dried at 100 °C for 2 h. The reaction temperatures were set at 80 °C, 100 °C and 120 °C using an oil bath when the acid reactants were acetic acid (AR grade, TCI), octanoic acid (AR grade, TCI) and lauric acid (AR grade, TCI), respectively. Other typical operating parameters were the molar ratio of ethanol:carboxylic acid of 2:1, catalyst loading of 1 wt% (based on the carboxylic acid weight), and reaction time of 8 h. The batch system was checked for any possible leaks prior to the experiment. The product composition was analyzed with a Shimadzu GC-2014 gas chromatograph equipped with a 30-m DB-5 capillary column and a flame ionization detector (FID). The quantitative analysis was performed according to an internal standardization method. *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA) (>98.5%, Aldrich) was used as derivatizing agent. In all cases, the weight loss of reaction mixture was <10 wt%.

2.4. Esterification of PFAD with ethanol

The esterification of commercial PFAD (Morakot Industries Public Co., Ltd. (Thailand)) with ethanol was carried out in a 100-mL PTFE-lined autoclave reactor equipped with a magnetic stirrer. Typically, 6.75 g of PFAD was melted by heating at 70 °C, and then poured into the reactor together with adding ethanol (4.18 g) and a catalyst (5 wt% of PFAD). Subsequently, the reactor was tightly sealed and heated to 120 °C under vigorous stirring. The reaction temperature was controlled by a silicone oil bath. After 5 h, the reaction mixture was filtered to recover the solid catalyst. The excess ethanol and H_2O as by-product were removed using a rotary evaporator. The reaction mixture was analyzed for its composition in an on-column mode with an Agilent 7890A gas chromatograph (GC) equipped with a 30-m HP-5 column, and a FID. The free fatty acid (FFA) conversion was determined according to an external standardization method using methyl heptadecanoate (AR grade, Fluka) as the reference standard.

3. Results and discussion

3.1. Physicochemical properties of acidic mesoporous catalysts

The physicochemical properties of acidic mesoporous catalysts are summarized in the Supplementary Information (SI) Table S1. The XRD analysis indicated that the materials retained the mesostructure ordering after forming the NR/HMS composite and the functionalization with propylsulfonic acid group (Fig. S1: SI). The N_2 physisorption isotherms and the BJH pore size distribution of all functionalized materials confirmed their mesoporosity (Fig. S2: SI). Both HMS-SO_3H and NR/HMS-SO_3H exhibited framework-confined mesoporous channels with a wormhole-like structure similarly to HMS, as revealed by TEM images (Fig. S3: SI). The wall thickness of HMS-SO_3Hs and NR/HMS-SO_3Hs was increased by 44–61% and 56–66%, respectively, when compared to that of the pristine HMS (Table S1: SI), indicating that the propylsulfonic acid groups were attached on the silica wall. This observation was consistent with the FTIR results (Fig. S4: SI). The larger wall thickness expansion for NR/HMS-SO_3H suggests that the NR molecules were dispersed in the silica matrix [14]. HMS-SO_3H and NR/HMS-SO_3H exhibited an increase in the acidity with the MPTMS/TEOS ratio (Table S1: SI). At a similar MPTMS loading, NR/HMS-SO_3H possessed slightly lower acidity than HMS-SO_3H.

The presence of organic moieties increased the water contact angle by 5.6 and 6.8 times for HMS-SO_3H and NR/HMS-SO_3H, respectively (Fig. 1). Moreover, the volume of H_2O adsorbed on the functionalized materials was lower than that of the pure silica HMS (Table S1: SI). The reduction of H_2O affinity was explained by the extent of the exposed surface silanol groups that were diminished upon the functionalization, as evidenced by the FTIR analysis (Fig. S4: SI). In addition, the incorporated NR created a hydrophobic environment around the mesoporous framework.

3.2. Esterification of various carboxylic acids with ethanol

Fig. 2 shows the conversion profiles of model carboxylic acids with ethanol in the presence of various acidic mesoporous catalysts. Within the first hour, the HMS-SO_3H (0.2) catalyst gave the highest conversion

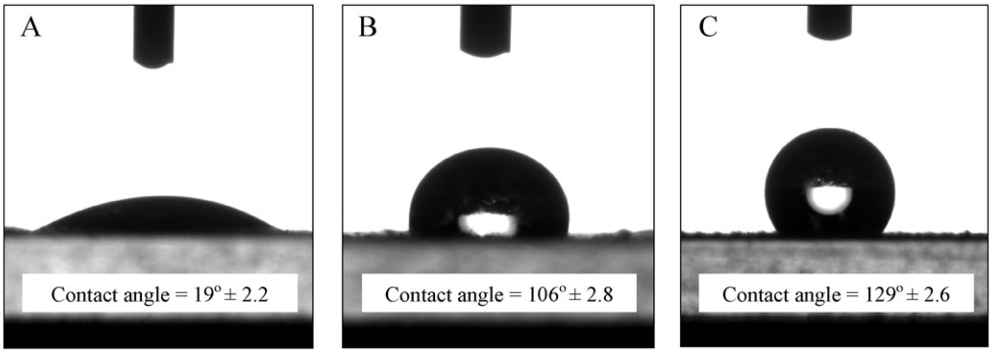

Fig. 1. Water contact angles of (A) pure silica HMS, (B) HMS-SO_3H (0.1) and (C) NR/HMS-SO_3H (0.1).

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