



Short Communication

Carbon-based nanostructured catalyst for biodiesel production by catalytic distillation



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ABSTRACT

A promising carbon-based nanostructured catalyst was prepared via the following four steps: (1) thermal decomposition of organometallic compound ($C_{10}H_{14}CoO_4$) on 304 stainless steel substrate, (2) cracking of benzene to carbon nanotubes (CNTs) on the substrate using Co particle catalyst, (3) sulfurizing CNTs with Na_2S_x , and (4) oxidating the sulfurized CNTs with hydrogen peroxide. The as-prepared carbon-based catalyst was characterized by spectroscopy, scanning electron microscopy, transmission electron microscopy etc. The monolithic catalyst can serve as appropriate filler for a catalytic distillation column. Catalytic activity was examined by catalyzing the transesterification of soybean oil and methanol to biodiesel in the catalytic distillation column.

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1. Introduction

Biodiesel is gaining increased attention from researchers as an alternative fuel [1–3]. The transesterification reaction to produce biodiesel can be catalyzed by homogeneous (H_2SO_4 and NaOH) and heterogeneous (KOH/ Al_2O_3 , WO_x/ZrO_2 , Amberlyst-15, protonated nafion, zeolite etc.) catalysts [4–6]. Homogeneous catalysts are difficult to be separated from reactants and products after reaction. Meanwhile, a large amount of methanol exceeding the stoichiometric ratio is usually used and causes problems in dealing with waste reactants, catalysts and glycerol. For some solid catalysts, a reactive system containing few free fatty acids and pre-esterification is required [7].

Recently, a sulfonated carbon-based solid acid catalyst has been reported as a promising catalyst for transesterification to produce biodiesel because this catalyst can avoid some shortages of common catalysts. Many efforts have been devoted to using sulfonated carbon nanotubes (CNTs) as catalysts [8] because they possess outstanding stability and sufficient protonic acid sites. The general method is to introduce acid sites to the surface of CNTs by oxidation [9,10]. If CNT powders are directly used as catalysts in a catalytic reaction, generally, the catalyst separation will be difficult and consume a significant amount of energy. CNT powders easily adhere to vegetable oil into blocks after being used

to catalyze the transesterification. To overcome these shortages, it's desired to develop a method for synthesizing and functionalizing CNTs on stainless substrate to obtain monolithic carbonaceous catalysts with acid sites. To date, the two processes have been investigated separately by many researchers. Baddour et al. had studied the growth of CNTs and microfibers over stainless steel [11], whereas several groups had subjected CNTs to harsh acid treatment to produce acid-functionalized CNTs [12,13]. Given that surface defect sites can be easily induced with harsh acid treatment, a surface-substitution approach was also applied to produce CNT- SO_3H [14].

In this work, a carbon-based nanostructured catalyst was fabricated by growing CNTs on stainless steel and then being in situ functionalized. The CNTs reacted with Na_2S_x to generate CNT-SH at pH 6 [15]. Then, H_2O_2 was used to oxidize the -C-SH to -C- SO_3H . This approach avoids the corrosion of stainless steel substrate by harsh acid under common functionalization conditions. To date, few studies have been reported on producing monolithic solid acid materials with high stability, sufficient protonic acid sites, and excellent plasticity (i.e., can be easily shaped as desired for use as a filler for a catalytic distillation column). Numerous -C-S- covalent bonds on the surface can provide an electron-withdrawing force to resist desulfonation [16]. Meanwhile, - SO_3H groups as strong protonic acid are mainly attached on the outer surface of CNTs and provide favorable acid activities.

The as-prepared carbon-based catalyst also shows excellent performance for heat exchange and mass transfer. This monolithic carbon-based nanostructured catalyst can overcome some shortages of the current catalysts when used as a filler for a catalytic distillation column, and shows excellent performance in catalyzing the transesterification of soybean oil and methanol to biodiesel.

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2. Experimental

2.1. Catalyst preparation

The 304 stainless steel substrate was used to load the Co catalyst to produce CNTs. The substrate coated with Co precursor was heated in N_2 flow at 700 °C for 2 h. Then, the temperature was increased to 800 °C and maintained for 1 h in H_2/Ar (10:90) flow before benzene (as carbon source) was injected at about 0.06 mL/min with a syringe. The cracking process of benzene gas to CNTs lasted for 30–60 min at 800 °C.

The stainless steel substrate coated with CNTs was placed into Na_2S_x saturated solution at 85 °C with stirring for 36 h to produce the substrate coated with CNT-SH. Then, H_2O_2 was used to oxidize CNT-SH to CNT- SO_3H at room temperature. For more details, see the Supplementary material.

2.2. Catalyst characterizations

The catalysts were characterized by laser Raman spectroscopy (514.5 nm), SEM (S4800), TEM (JEM-100S), HRTEM (JEM-2100), XRD ($\lambda = 0.15418$ nm) and XPS (K-Alpha). The biodiesel samples were analyzed by gas chromatography–mass spectrometry. Neutralization titration was conducted to determine acid site densities. More details are presented in the Supplementary material.

2.3. Catalytic reactions

Fig. 1 shows the scheme and profile of the catalytic reaction system. For the detailed contents refer to the Supplementary material.

3. Results and discussion

3.1. Catalyst characterization

According to a previous report [17], the diameters of CNTs can be controlled by the size of the catalyst particles. Thus, suitable catalyst particle sizes and shapes are desired for catalysis, which require proper organo-metallic precursor and control during thermal decomposition. Surfactants such as oleylamine and triphenylphosphine are adsorbed onto the particle surface to control nanocrystal formation. Triphenylphosphine may promote monomer exchange between particles to allow uniform size distribution [18]. The TEM image of the obtained Co particle catalyst is shown in Fig. 2a. The diameters of the particles range from 5 nm to 10 nm and increase to 25 nm to 40 nm after heat treatment at 700 °C.

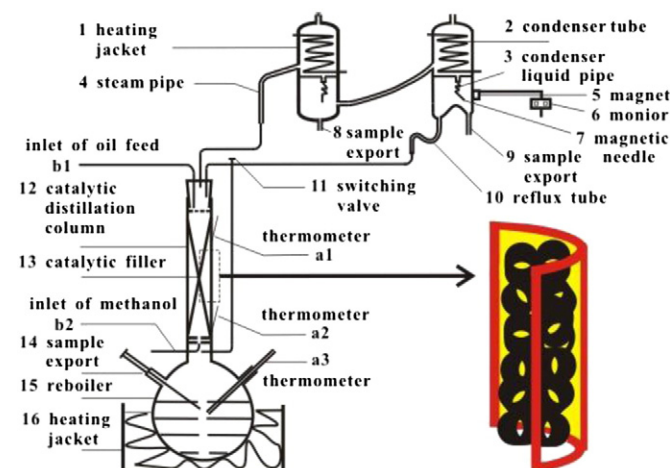


Fig. 1. Scheme and profile of the catalytic reaction system.

Fig. 2b–k shows the evolution of CNTs from pristine CNTs (c, d, e, f) and CNT-SH (g) to the oxidation product CNT- SO_3H (h, j). After oxidation, changes can be observed. Fig. 2k shows that an oxidized layer appeared outside the CNTs, 0.364 nm of the interlayer spacing is obviously bigger than 0.344 nm of normal interlayer spacing. Meanwhile, the images indicate that the tubular morphology of CNTs is maintained. The loading quantity of CNTs on stainless steel is approximately 5 mg/cm².

The samples were further characterized by energy-dispersive X-ray (EDX) line scan analysis with TEM observations. EDX microanalysis presents the proportions of C, O, and S shown in Fig. 2m. The sulfur content in CNTs is higher than the 5% reported by Planka et al. [19]. After oxidation treatment, oxygen content significantly increases and is three times more than the sulfur content, indicating that the CNT surface has abundant -COOH and -OH, besides - SO_3H .

Fig. 3a shows the Raman spectra of pristine and modified CNTs. The bands at approximately 1356 and 1585 cm^{-1} are characteristic D- and G-bands of graphite carbon. The intensities of the G-band are stronger than those of the D-band, indicating high graphitization. In the Raman spectrum of CNT-SH, new peaks at 472, 673, and 2727 cm^{-1} appear. The peak at 472 cm^{-1} is associated with the bending vibrations of S=C-S bonds [20], whereas the peak at 673 cm^{-1} is related to the stretching vibrations of C-S bonds [12,20,21]. The band at 2727 cm^{-1} is attributed to the stretching vibrations of S-H bonds [22]. The peak at 2708 cm^{-1} in the Raman spectrum of CNT- SO_3H arises from the stretching vibrations of O-H bonds in sulfonic groups [19]. Given the formation of hydrogen bonds, the stretching bands of O-H shift to lower wavenumbers.

The XRD patterns after the integration of CNTs on stainless steel substrate are shown in Fig. 3b. The strong diffraction peaks at 26.4° (002) and 43.7° (100) are associated with the hexagonal graphite structure [23], consistent with the Raman results. The peak at 44.7° is attributed to Co (111) crystal [24]. Meanwhile, it implies that Fe particles can also catalyze the cracking of benzene in terms of the Fe_2O_3 peaks in the XRD patterns. However, CNTs are easily removed from the stainless steel in subsequent treatments when catalyzed by Fe particles from the stainless steel bulk independently.

Fig. 3c–f shows the XPS spectra of the carbon-based nanostructured catalyst. Three peaks at 284.5, 286.3, and 288.7 eV are observed in the C1s spectrum. The peak at 284.5 eV is attributed to sp^2 -hybridized graphite carbon. The peak at 286.3 eV is attributed to the carbon atoms of C-OH species [25]. The peak at 288.7 eV is associated with the carbon atoms of C-S species [26]. The O1s spectrum can be deconvoluted into two peaks at 531.5 and 532.1 eV, which are assigned to the oxygen atoms of S-OH and C-OH, respectively. Two peaks appear at 168.5 and 169.7 eV in the S2p spectrum. The binding energies of S2p_{1/2} at 169.7 eV and S2p_{3/2} at 168.5 eV can be assigned to the - SO_3H group in the sulfide species [27]. The peak at 785.2 eV is assigned to the cobalt atoms of Co^{+3} species because Co particles were oxidized by H_2O_2 [28].

Neutralization titration was performed to measure the effective protonic densities of acid sites in the samples. The effective protonic acid density attached to CNTs is 3.1 mmol·g⁻¹. Compared with other acid site densities of the carbon materials (Table 1), the as prepared carbon-based catalyst materials have relatively high acid density among the carbon-based solid acids.

3.2. Catalytic results

The catalytic activity of the carbon-based nanostructured catalyst was demonstrated by catalyzing the transesterification of soybean oil and methanol to biodiesel in a catalytic distillation column. The catalysts were tailored to Raschig rings used as fillers for the catalytic distillation column. The area of the stainless steel mesh as the filler is 450 cm², which loads 2.1 g of CNTs. The feed temperature of soybean oil and methanol are 135 and 95 °C, respectively. The reboiler temperature is maintained at 95 °C to reboil unreacted methanol. Given that the boiling point of fatty acid methyl ester is significantly higher than the

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