Preparation of poly(p-styrenesulfonic acid) grafted multi-walled carbon nanotubes and their application as a solid-acid catalyst

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1. Introduction

Carbon nanotubes (CNTs) possess ultra-high surface area, high mechanical strength despite ultra-light weight, excellent chemical and thermal stability, and rich electronic polyaromatic structure [1–4], which make them ideal candidates for applying as carriers of biomolecular [5–7] or metallic catalyst [8–10]. Up to date, a variety of metallic nanoparticles, e.g. platinum [10,11], ruthenium [12,13], gold [14], and so on, have been loaded onto CNTs. These composites showed higher catalytic activity and selectivity than traditional metal catalysts, which was likely owing to the huge specific surface area and outstanding electronic properties of CNT [10–14].

So far, most of the applications of CNT on catalysts are limited to CNT and metallic nanoparticle composites. To our knowledge, no study concerning the use of CNT composites as solid-acid catalyst to prepare biodiesel has been reported. Biodiesel, defined as monoalkyl esters of fatty acids, has attracted great interest as a renewable and green fuel [15]. Biodiesel was mainly produced by either the transesterification of triglycerides or the esterification of fatty acids with low molecular weight alcohols [16,17]. Conventional biodiesel production process uses homogeneous base (e.g. NaOH or KOH) [18], or acid (e.g. H\textsubscript{2}SO\textsubscript{4}) [19] as catalysts. These catalysts would give rise to the corrosion of equipment, environmental problems, and expensive separation process of products from the reaction mixture. For these reasons, a variety of solid-acid catalysts, such as zeolites [20,21], heteropolyacids [22,23] and perfluorinated resin sulfonic acids [24], have been developed to avoid these defaults. However, the application of most reported solid acid catalysts was obstructed because of their poor mechanical and thermal stability, low active site available for catalytic reaction. The development of novel solid acid catalysts is still a challenging work.

Herein, poly(p-styrenesulfonic acid) grafted multi-walled carbon nanotubes (PSSA-g-MWCNTs) were prepared by in situ polymerization of sodium p-styrenesulfonate in the presence of MWCNTs, followed by refluxing with concentrated hydrochloric acid. In this reaction system, sodium p-styrenesulfonate served not only as the reaction monomer but also as an amphiphilic dispersant to disperse pristine MWCNTs in water, which is critical for the grafting PSSA onto MWCNTs. Due to the existence of copious sulfonic groups (−SO\textsubscript{3}H), PSSA-g-MWCNTs could be stably dispersed in polar solvents, such as water and methanol. This is favorable to the application of PSSA-g-MWCNTs as a solid-acid catalyst in a heterogeneous catalytic reaction. The PSSA-g-MWCNTs showed high catalytic activity in the esterification of lauric acid with methanol, and could be easily separated from the product by filtration. The catalytic activity of PSSA-g-MWCNTs showed no detectable change even after recycling after being used for three times.

Poly(p-styrenesulfonate acid)-grafted multi-walled carbon nanotubes (PSSA-g-MWCNTs) were prepared by in situ polymerization of sodium p-styrenesulfonate in the presence of MWCNTs, followed by refluxing with concentrated hydrochloric acid. In this reaction system, sodium p-styrenesulfonate served not only as the reaction monomer but also as an amphiphilic dispersant to disperse pristine MWCNTs in water, which is critical for the grafting PSSA onto MWCNTs. Due to the existence of copious sulfonic groups (−SO\textsubscript{3}H), PSSA-g-MWCNTs could be stably dispersed in polar solvents, such as water and methanol. This is favorable to the application of PSSA-g-MWCNTs as a solid-acid catalyst in a heterogeneous catalytic reaction. The PSSA-g-MWCNTs showed high catalytic activity in the esterification of lauric acid with methanol, and could be easily separated from the product by filtration. The catalytic activity of PSSA-g-MWCNTs showed no detectable change even after recycling after being used for three times.

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2. Experimental

2.1. Materials

MWCNTs, with a diameter of 10–20 nm and produced by chemical vapor deposition (CVD), were purchased from Chengdu Organic Chemicals Co. Ltd. Sodium p-styrenesulfonate was purchased from Fluka. Potassium persulfate (KPS), hydrochloric acid, lauric acid and anhydrous methanol were all purchased from Shanghai Chemical Reagent Corporation. All the reagents were used as received.

2.2. Preparation of PSSA-g-MWCNTs

Similar but different in detail to the method of Warren T. Ford [25], 2.0 g of sodium p-styrenesulfonate were dissolved into 100 mL of deionized water, and then 50 mg of MWCNTs were added. After sonication for 1 h, the black solution was kept stirring for another 3 h. 0.5 g of KPS was added as a radical initiator, the mixture was purged with dry nitrogen for 30 min to remove oxygen. The solution was kept stirring at 70 °C for 3 h, followed by at 85 °C for 1 h. After reaction, the mixture was filtered through a 0.45-μm mixing fibroid membrane, and washed with deionized water for 5 times. The black solid was refluxed with concentrated hydrochloric acid for 12 h. The mixture was filtered through a 0.45-μm mixing fibroid membrane, and then washed with deionized water for 5 times to get PSSA-g-MWCNTs as a black solid.

2.3. Synthesis of methyl laurate from lauric acid and methanol

The reaction for synthesis of methyl laurate from lauric acid and methanol was carried out at 60 °C in a three necked round bottom flask fitted with a magnetic stirrer, a thermometer and a reflux condenser. A mixture containing 4.167 g (0.0208 mol) of lauric acid, 10 g (0.3125 mol) of methanol and 0.16 g of catalyst (PSSA-g-MWCNTs) was added to the flask. Reaction sample concentrations were periodically monitored by a gas chromatograph equipped with a 30 m SE-54 capillary column and a flame ionization detector (FID).

2.4. Characterization

Fourier transform infrared spectroscopy (FT-IR) was carried out on a NEXUS-470 spectrometer using KBr pallets. Raman spectra were measured on a DIOLABram-1B Raman spectrometer using He–Ne laser at 632.8 nm as the light source. X-ray photoelectron spectroscopy (XPS) was performed on a PHI 5000C ESCA X spectrometer with Al Kα excitation (1686.6 eV). Thermogravimetric analysis (TGA) measurement was carried out on a Perkin-Elmer Pyris-1 series thermal analysis system under nitrogen atmosphere at a scan rate of 20 °C/min. Transmission electron microscopy (TEM) images were obtained on a JEOI-2100 transmission electron microscope. Samples for TEM measurements were prepared by casting a methanol solution of pristine MWCNTs and PSSA-g-MWCNTs on a carbon-coated copper grid.

3. Results and discussion

3.1. Preparation of PSSA-g-MWCNTs

To prepare polymer covalently grafted CNTs, it is critical to disperse CNTs into solvents firstly. It is well known that pristine CNTs could be temporarily dispersed in water with the aid of surfactants [26,27] or amphiphilic polymers [28,29], which are composed of hydrophilic and hydrophobic segments. We have previously prepared poly(acrylic acid) functionalized single-walled carbon nanotubes (SWCNTs) by utilizing sodium dodecylbenzene...
sulfonate (SDBS) as dispersant agent to disperse SWCNTs in water firstly [30]. Herein, sodium \( p \)-styrenesulfonate, an amphiphilic monomer, was chosen to prepare PSSA-\( g \)-MWCNTs, because that sodium \( p \)-styrenesulfonate not only acted as reaction monomer but also demonstrated a good ability to disperse pristine CNTs in water, with hydrophobic part of styrene to form \( \pi \)–\( \pi \) stacking interaction with MWCNTs and hydrophilic part of sodium sulfonate to afford hydrophilicity and electrostatic repulsion to counteract the van der Waals attractions of bare tubes.

Pristine MWCNTs could not be stably dispersed in methanol and would be totally precipitated in a few minutes (Fig. 2c). After grafted with PSSA, due to the existence of copious \( -\text{SO}_3\text{H} \) groups, PSSA-\( g \)-MWCNTs could be well dispersed in methanol to form a uniform black solution (Fig. 2d). This solution is stable, even after 6 months, no apparent deposition has been detected, which is favorable to the subsequent catalytic reaction.

The successful grafting of PSSA onto MWCNTs was also confirmed by FT-IR measurement. It could be seen from Fig. 2, compared with the FT-IR spectrum of pristine MWCNTs (Fig. 2a), that of PSSA-\( g \)-MWCNTs (Fig. 2b) displays a broad band centered at 3450 cm\(^{-1} \) (Fig. 2b), characteristic of a stretching vibrational mode of an \(-\text{OH} \) group. In addition, two obvious bands at 2920 and 2860 cm\(^{-1} \) are typical of the asymmetric and symmetric vibrational absorptions of alkane \( \text{C–H} \) bands. The strong bands at 1635 and 1386 cm\(^{-1} \) are attributed to the stretching modes of phenyl group and sulfonic group, respectively. All these typical bands suggested the presence of PSSA. X-ray photoelectron spectroscopy (XPS) was performed to evaluate the content of S element in pristine MWCNTs and PSSA-\( g \)-MWCNTs, the results are shown in Fig. S1 (Supporting Information). After grafted with PSSA, the content of S element was increased from 0.04\% in pristine MWCNTs to 0.55\% in PSSA-\( g \)-MWCNTs, which suggested the successful introducing of PSSA.

As seen from Fig. 3, both the Raman spectra of pristine MWCNTs and PSSA-\( g \)-MWCNTs show two obvious bands at 1328 cm\(^{-1} \) (D-band) and 1580 cm\(^{-1} \) (G-band). The ratios of D-band to G-band (\( D/G \)) are 1.43 for pristine MWCNTs and 1.82 for PSSA-\( g \)-MWCNTs, respectively. The increase of \( D/G \) indicated that the PSSA chain was covalently grafted onto MWCNTs.

Commercial sodium poly(\( p \)-styrenesulfonate) (PSSNa) homopolymer, purchased from Fluka (reported \( \text{Mw} = 6530 \), polydispersity < 1.2), was chosen as control to evaluate the grafting ratio of PSSA on MWCNTs by TGA. As shown in Fig. 4, PSSNa homopolymer (Fig. 4c) and PSSNa-\( g \)-MWCNTs (Fig. 4b) show weight losses of 39.4 wt\% and 10.4 wt\%, respectively. In view of that pristine MWCNTs do not show obvious weight loss during the whole heating process (Fig. 4a). The grafting ratio of PSSNa could be calculated as 26.4 wt\%. Assume that all the sodium sulfonate groups (\(-\text{SO}_3\text{Na} \)) were turned into sulfonic groups (\(-\text{SO}_3\text{H} \)) in the

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**Fig. 5.** TEM images of (a) and (b) pristine MWCNTs, (c) and (d) PSSA-\( g \)-MWCNTs.

**Fig. 6.** (a) Gas chromatograph spectrum and (b) lauric acid conversion of esterification reaction of lauric acid with methanol at 60 °C using PSSA-\( g \)-MWCNTs as catalyst.
HCl reflux process, according the grafting ratio of PSSNa (26.4 wt%), with a simple mathematical and chemical conversion from PSSNa to PSSA, the calculated grafting ratio result of PSSA on MWCNTs should be 23.6 wt%.

The TEM images of PSSA-g-MWCNTs (Fig. 5c and d) show that the morphology of MWCNTs is well retained, indicating that the graft of PSSA does not affect the tubular structure of MWCNTs. As seen from Fig. 5a, pristine MWCNTs are tangled together, due to the van der Waals attractions between tubes. After grafted with PSSA, PSSA-g-MWCNTs (Fig. 5c) display much better dispersibility than pristine MWCNTs. Because PSSA-g-MWCNTs contain many sulfonic groups, which can afford adequate electrostatic repulsions to vanquish the van der Waals attractions between tubes. Furthermore, due to the covalent graft of PSSA, the surface of PSSA-g-MWCNTs (Fig. 5d) looks much coarser than that of pristine MWCNTs.

3.2. Esterification reaction using PSSA-g-MWCNTs as solid-acid catalyst

The prepared PSSA-g-MWCNTs were utilized as solid-acid catalyst to catalyze the esterification of lauric acid with methanol, a conventional reaction to synthesize biodiesel [30]. Gas chromatography (GC) was used to monitor the reaction. It could be seen from Fig. 6a, besides the peaks of methanol and lauric acid at 2.21 min and 4.61 min respectively, a new peak appeared at 4.07 min (Fig. 6a), characteristic of methyl laurate, which indicated the successful esterification of lauric acid and methanol catalyzed by PSSA-g-MWCNTs. As shown in Fig. 6b, the conversion of lauric acid increased with the extension of reaction time. After reaction for 6 h, the conversion of lauric acid was as high as 52.8%.

Sulfated zirconia is reported to be the most promising candidate among a various list of solid acid catalysts [31–33]. Using sulfated zirconia as catalyst, the conversion of dodecanedioic acid with methanol increases at higher amounts of catalyst and higher temperatures. Typically, the conversion with 1 wt% catalyst at 120 °C is 64% [32]. In our experiment, the esterification reaction took place at a much lower temperature (60 °C), while the conversion of lauric acid was similar to the most promising solid acid catalysts reported.

After reaction, the PSSA-g-MWCNTs could be easily separated by filtration, which is favorable to the product post-processing and the cyclic utilization of PSSA-g-MWCNTs. To evaluate the recycling ability of PSSA-g-MWCNTs, an experiment was designed as following: the resultant mixture was filtered through a 0.45-μm mixing fibroid membrane and washed with diluted H2SO4 (0.2 M). The obtained PSSA-g-MWCNTs were reused as solid-acid catalyst in the esterification of lauric acid and methanol with the similar reaction condition. The GC results showed that the conversion of lauric acid was no detectable change even after 3 times recycles. All the results above suggest that PSSA-g-MWCNTs possess high catalytic activity and good recycling ability.

4. Conclusions

In present work, PSSA-g-MWCNTs were successfully prepared by the in situ polymerization of sodium p-styrenesulfonate in the presence of MWCNTs, followed by flushing with concentrated HCl. The graft ratio of PSSA evaluated by TGA was 23.6 wt%. Due to the existence of copious sulfonic groups, PSSA-g-MWCNTs could be well dispersed in methanol to form a stable black solution. The PSSA-g-MWCNTs were applied as solid-acid catalyst in the esterification of lauric acid with methanol and showed high catalytic activity. The promising advantages of PSSA-g-MWCNTs used as solid-acid catalyst are that they could be easily separated from the product by filtration and their excellent recycling ability.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.matchemphys.2010.11.021.

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