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Sulphate-Functionalized Multi-Walled Carbon Nanotubes as Catalysts for the Esterification of Glycerol with Acetic Acid[1]

Xianbing Ji[a, b], Yinxia Chen[a, b], Xiaobo Wang[a], and Weimin Liu[a]

[a] *State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, P.R. China*

[b] *Graduate School of Chinese Academy of Sciences, Beijing, P.R. China*

e-mail: wangxb@licp.cas.cn

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Abstract—Sulphate-functionalized multi-walled carbon nanotubes (S-CNTs) were synthesized by an efficient and convenient method and characterized by FT-IR and TEM methods. Catalytic activities of the S-CNTs were evaluated in the esterification of glycerol with acetic acid at low temperature under atmospheric pressure. The CNTs grafted with sulphate groups show activity and stability in this reaction. The catalyst can be recycled and reused for several times without any significant loss of its catalytic activity.

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The decline of mineral-oil-based raw materials is the driving force for the development of sustainable resources. One method to produce chemicals in a more sustainable way is to use biomass [1]. Various reactions are involved in the conversion of biomass, such as hydrogenation, oxidation, isomerization and esterification [1]. The conventional heterogeneous catalysts used for biomass transformation are alkaline earth oxides, calcined hydrotalcites and nano-MgO [2]. However, the classical heterogeneous catalysts show drawbacks, such as small surface area and partial dissolution in reaction solution. So the development of new heterogeneous catalysts is essential.

During the last few years, multi-walled carbon nanotubes (CNTs) have attracted much attention because of their potential application in various fields, including single-electron transistors [3], memory elements [4], field emission devices [5–7], chemical and biological sensors [8], catalyst and heterogeneous catalyst supports [9–15]. Many functionalized carbon nanotubes have been prepared to be useful for catalysis, including deposition of catalytic metal nanopaticles on CNTs [16–19], amino-functionalized CNTs [2], sulfonate-functionalized CNTs [20, 21], and so on. Typical synthetic routes of sulfonate-functionalized CNTs include acid-assisted thermal decomposition, electrochemical modification, and chemical reduction method [22]. Acid-assised thermal decomposition method, which involves refluxing CNTs with concentrated sulfuric acid at high temperatures, could destroy structural frameworks on the tip with limited yields. Electrochemical modification is only restricted to electrically contacted CNTs on confined electrode surface. Chemical reduction method is usually time-consuming and complex. Therefore, the development of an efficient and convenient method for the sulfonation of CNTs is important.

In this paper, chlorosulfonic acid was used as sulfonating agent instead of sulfuric acid and this technique is rarely used in catalyst preparation. The resultant sulphate-functionalized CNTs (**S-CNTs**) have been used as catalysts for the esterification of glycerol with acetic acid.

EXPERIMENTAL

Catalyst Preparation

Multi-walled carbon nanotubes (CNTs) were obtained from NTP (Shenzhen, China), which were produced by a chemical vapor deposition process. Other chemicals used were all analytical grade and used without further purification.

Sulphate-functionalized multi-walled carbon nanotubes (S-CNTs) were prepared as shown in Fig. 1. In the first step, the raw CNTs were immersed in a 37% HCl solution and sonicated for 20 min, and then the mixture was kept overnight to remove metal catalyst particles [15]. In the second step, the CNTs were immersed and dispersed in a 67% HNO_3 + 98% H_2SO_4 solution (1 : 3 by volume), sonicated and refluxed at 60°C for 2 h and then filtrated and washed with deionized water for several times, dried at 80°C for 12 h, and crushed, giving carboxyl groups modified CNTs (**CNTs-COOH**) [23]. In the third step, the CNTs-COOH reacted with $LiAlH_4$ in dry tetrahydrofuran (**THF**) at room temperature for 12 h, which results in hydroxyl group functionalized CNTs (**CNTs-CH_2OH**) [24]. Finally, 2 g of the above-obtained CNTs-CH_2OH further reacted

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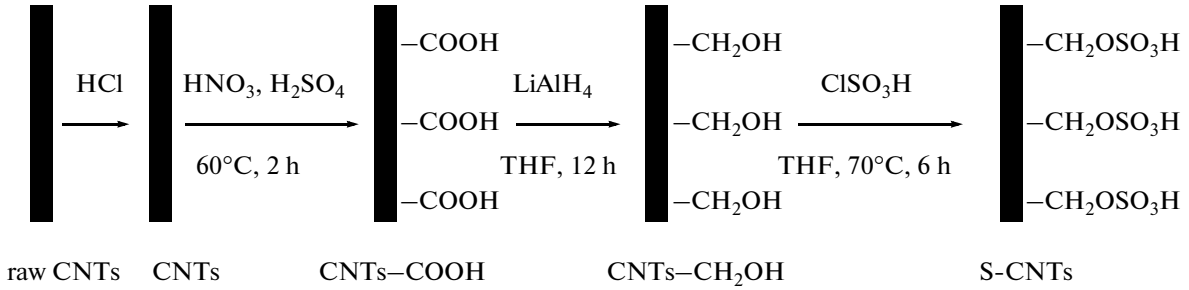

Fig. 1. Scheme of the S-CNTs preparation.

with 3 ml chlorosulfonic acid in dry THF at 70°C for 6 h, and 0.2 g of anhydrous potassium carbonate was added for neutralizing the HCl, giving the final sulphate-functionalized multi-walled carbon nanotubes (S-CNTs).

Catalyst Characterization

The S-CNTs were investigated with FT-IR method (IFS66V/S FT-IR, Bruker). The morphology of the catalysts was determined by a high-resolution transmission electron microscopy (**HR-TEM**) on the apparatus JEOL JEM 2010 type (accelerating voltage 200 kV). The quantity of the surface sulphate groups was characterized by acid-base titration with NaOH as titrant and the total number of acid groups was calculated to be 3.32 mmol/g.

Catalytic Activity Test

The catalytic performance of the S-CNTs was investigated in the esterification of glycerol with acetic acid. The experiment was performed in a three-neck flask equipped with thermometer and refluxing condenser. Glycerol (0.05 mol), acetic acid (0.25 mol) and catalyst (0.015 mol) were mixed at room temperature, and then the mixture was heated with stirring at 85°C for 2 h. As work-up, the catalyst was separated by filtration under vacuum, washed with ethanol for several times and dried at 80°C for the next use. The samples of the reaction mixture were analyzed by GC-MS.

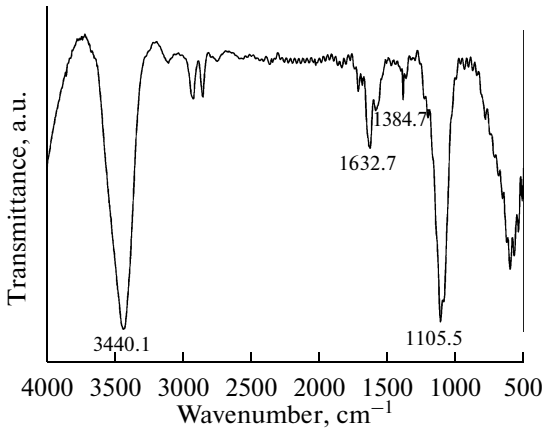

Fig. 2. FT-IR spectra of S-CNTs.

RESULTS AND DISCUSSION

Characterization

Figure 2 shows the FT-IR spectra of the S-CNTs in the range 4000–500 cm^{-1}. The bands at 3440.1 and 1632.7 cm^{-1} are attributed to the stretching vibration and deformation vibration of water OH groups, respectively. The bands at 1105.5 and 1384.7 cm^{-1} are assigned to the symmetric and asymmetric vibrations in a sulphate group, respectively [25]. The results confirm that the sulphate group is successfully modified on the surface of CNTs.

TEM was used to study the morphology of the S-CNTs and representative TEM images are presented in Fig. 3. The low magnification image (Fig. 3a) displays that uniform S-CNTs are observed with an average tube diameter of 25 nm. Figure 3a also shows that a significant contrast between the centre and edge of the material suggesting tube morphology and an on-top view (examples indicated with arrows) further proves that the material comprised hollow tubes. Higher magnification image (Fig. 3b) shows that the prepared materials consist of multiwall tubes with an average graphene sheet spacing of 3.4 Å. Thus, the morphology of the CNTs keeps the perfect structure during the acidic treatment and the oxidation reaction.

Catalytic Performances of S-CNTs

Figure 4 shows the effect of different catalysts on the esterification of glycerol with acetic acid. S-CNTs result in the most active catalyst with a conversion of 75.9% after 2 h. The yield of monoglyceride is 47.75%, while the diglyceride and triglyceride is 27.65 and 0.5%, respectively. The unmodified CNTs reach a conversion of 2.2% after the same time, which have no effect on the conversion of acetic acid. The results above show that the S-CNTs have excellent activity as

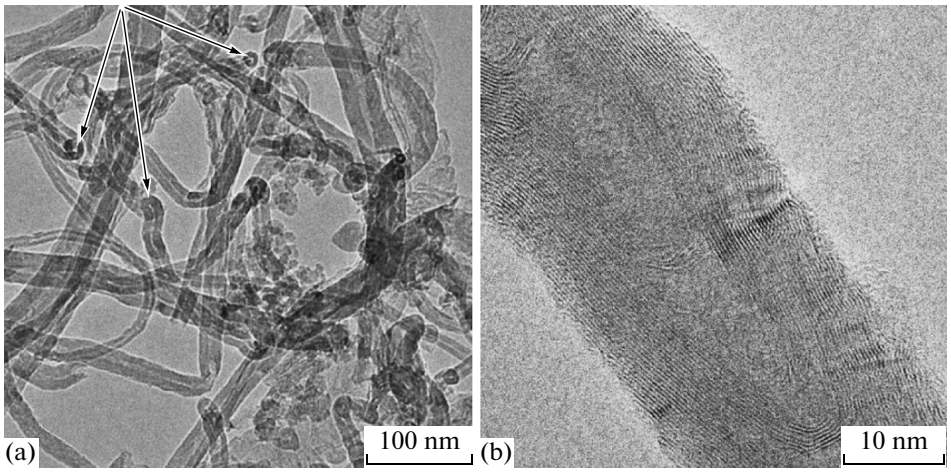

Fig. 3. TEM images of S-CNTs: (a) low magnification, (b) high magnification.

catalyst for the esterification of glycerol with acetic acid. The functional group can effectively improve the catalyst activity of CNTs.

Recycling tests were carried out in order to study the stability of the S-CNTs. In this study, the conditions were the same as the catalytic activity test. After each run, the catalyst was separated from the reaction mixture, washed with methanol for several times and dried at 80°C for the next use. Acid-base titration was performed on the used catalyst and the reaction products after each reaction were analyzed by GC-MS. Figure 5 shows that only a slight deactivation was detected by regenerating the catalyst after each run. After 4 recycles, 72.7% conversion is still maintained. The analysis of the solution by GC-MS did not present the characteristic peaks of $-OSO_3H$, probably because the concentration of the $-OSO_3H$ leached into the solution was so lower that it was impossible to detect. Titration data shows that after 4 recycles the total number of acid groups is 3.20 mmol/g. The slight deactivation may be due to the leaching of a small amount of the anchored $-OSO_3H$ and the inevitable loss of catalyst during the recycling test in the batch reactor. The results of the activity and stability of the S-CNTs demonstrate that the grafting of sulphate groups onto CNTs is a suitable method to obtain active and stable catalysts for application in liquid phase reactions.

In summary, an efficient and practical method for preparing S-CNTs is proposed. The raw CNTs are used as the substrate to form S-CNTs for the purpose of further improving the utilization of active materials. TEM reveals that the morphology of the S-CNTs keeps the perfect structure. This work implies that CNTs grafted with sulphate groups show activity and stability when used as catalysts for the estification of glycerol with acetic acid.

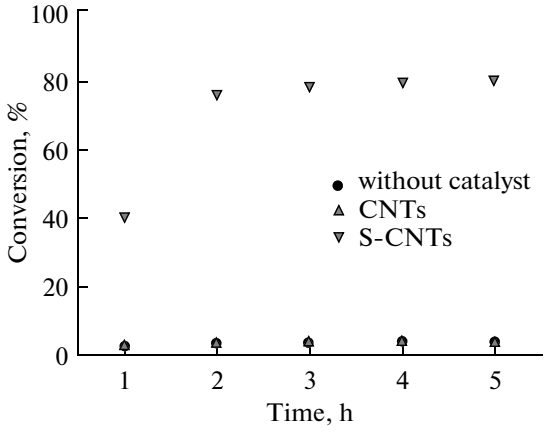

Fig. 4. Effect of different catalysts on the esterification of glycerol with acetic acid.

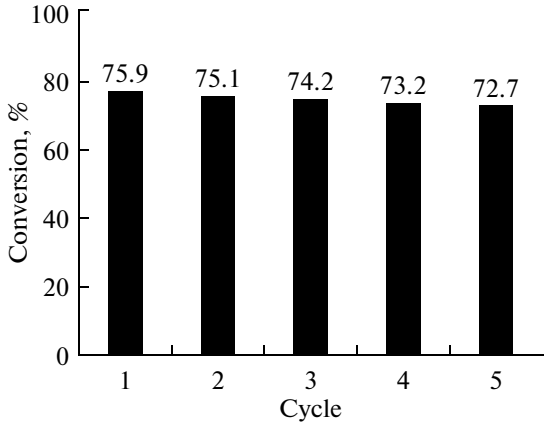

Fig. 5. Influence of reuse of S-CNTs catalysts on the esterification of glycerol with acetic acid.

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