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Article

Preparation and catalytic performance of perfluorosulfonic acid-functionalized carbon nanotubes

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ABSTRACT

Perfluorosulfonic acid-functionalized carbon nanotubes were prepared by liquid deposition of the perfluorosulfonic acid-polytetrafluoroethylene copolymer and characterized by N_2 adsorption, scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectroscopy, and acid-base titration. The effects of reaction temperature and the type of solvent were investigated. The results showed that these solid acids are very stable in both polar and non-polar solvents and can maintain their acidity up to 300 °C. Higher activity and better stability were observed over these materials in the alkylation of hydroquinone compared with poly(styrene sulfonic acid)-grafted carbon nanotubes.

1. Introduction

Acid-catalyzed reactions are the most important processes in fine chemical, pharmaceutical, and petrochemical industries. A significant number of acid-catalyzed reactions, such as the Friedel-Crafts reaction, esterification, hydration, and hydrolysis, are still carried out using liquid acids such as H_2SO_4 and HF as catalysts, leading to a series of problems such as the harmful effects on the environment, corrosion of apparatus, and difficulties in separating the reactants and products. Thus, there is a strong drive and major trend to replace these hazardous liquid acid catalysts with environmentally benign reusable solid acid materials, which provide much greener syntheses and processes [1]. In addition, many conventional solid acid catalysts lose their activity in water participating reactions because of the easy chemisorption of water on their active sites. Therefore, water-tolerant solid acid catalysts with high efficiency desperately need to be developed [2].

Carbonaceous materials functionalized with sulfonic acid groups have emerged as a promising solid acid material because of their inherent advantages of resistance to acidic and basic media and easily tunable properties [3–5]. Sulfonate-functionalized porous carbon-based solid acid materials can usually be prepared by direct sulfonation of ordered mesoporous carbon with sulfuric acid at elevated temperature [6,7], incomplete carbonization of sulfopolycyclic aromatic hydrocarbons [3], or sulfonation of incompletely carbonized organic compounds [4,5]. These materials have already exhibited high catalytic activity for various liquid-phase acid-catalyzed reactions, such as hydration of 2,3-dimethyl-2-butene, esterification of acetic acid, transesterification of triacetin, the Biginelli reaction, and oxidation of aldehydes to carboxylic ac-

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ids [5,8–10]. However, the stability of the resultant materials in the above cases is not satisfactory, especially in polar media, because of the leaching of polycyclic aromatic hydrocarbon-containing $–SO_3H$ groups [8,11]. In addition, a large amount of concentrated sulfuric acid is used in their preparation process, which is harmful to the environment. Furthermore, catalyst swelling is another important parameter that can remarkably affect the catalytic activity, indicating that sulfopolycyclic aromatic compounds are not suitable catalysts in non-media reactions (e.g., gas-phase reactions) [8].

Carbon nanotubes (CNTs) have attracted a lot of interest since their discovery in 1991 [12] because of their unique structural, mechanical, and electronic properties [13]. Because CNTs themselves have little catalytic activity, acidic functional groups need to be introduced, specifically onto the surface of CNTs, for their application to acid-catalyzed reactions. CNT-based acid catalysts have been synthesized by directly sulfonating CNTs [14–17], but the activity or the stability of the obtained catalysts was not ideal [14,17]. Sulfonated multi-walled carbon nanotubes have also been obtained by direct synthesis, resulting in higher stability [18]. CNT-based acid catalysts can also be synthesized by directly functionalizing CNTs with polymers. Poly(styrene sulfonic acid)-functionalized CNTs (PSA-CNTs) have been synthesized by in situ radical polymerization [19]. High activity and good stability can be achieved over this catalyst although the stability needs to be further improved [20].

In this work, perfluorosulfonic acid-functionalized CNT (PSFA-CNT) samples were prepared. Their textural, structural, and acidic properties were characterized by N_2 adsorption, scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and titration methods. The catalytic activity and stability of the samples for alkylation of hydroquinone with *tert*-butanol were tested and compared with PSA-CNTs.

2. Experimental

2.1. Catalyst preparation

PFSA-CNT samples were synthesized by liquid deposition. Typically, 500 mg of multi-walled carbon nanotubes (purity >99.5%, Chengdu Organic Chemical Co. Ltd.) was dispersed in a certain amount of PFSA-polytetrafluoroethylene (PTFE) copolymer solution (5 wt% solution, Alfa Aesar), and the mixture was then diluted with ethanol solution (75%) until the total mass of the mixture was 25 g. After sonication for 40 min, the solution was stirring overnight at room temperature. The obtained black solid was then dried at 100 °C. The final product is designated as PFSA-CNT-*x*, where *x* represents the mass ratio of the PFSA-PTFE copolymer to CNT.

2.2. Catalyst characterization

The N_2 adsorption-desorption isotherms were measured on a Micromeritics ASAP 2000 instrument at liquid N_2 temperature. The specific surface areas of the samples were calculated from the adsorption isotherms by the Brunauer-Emmett-Teller (BET) method. FT-IR spectra of the samples were recorded on a Nicolet Avatar-360 spectrometer. TGA was performed using a PerkinElmer TGA7 instrument under a flowing N_2 atmosphere at a heating rate of 10 °C/min. SEM studies were carried out with a Philips XL30 using an accelerating voltage of 15 kV. TEM images were taken using a JEOL JEM 2100 instrument. The sulfur content was measured by elemental analysis on a Bruker-AXS (S4 EXPLORER) elemental analyzer.

2.3. Acidity measurement

The density of surface acid sites was measured by a neutralization titration method [21]. In brief, the sample was added into an aqueous solution of NaCl (in excess), and HCl formed because of the exchange of Na^+ for protons on sulfonic groups, which were titrated with a standard solution of NaOH. The acidity was also measured by potentiometric titration [22,23]. The solid was suspended in acetonitrile, agitated for 3 h, and then titrated with 0.1 butylamine (mol/L) in acetonitrile. The electrode potential variation was recorded with a METTLER TOLEDO FE20 potentiometer.

2.4. Catalytic testing

Alkylation of hydroquinone was carried out in a stainless steel autoclave with a PTFE liner using magnetic stirring. Typically, 0.5 g hydroquinone, 1.0 g *tert*-butanol, and 0.2 g catalyst were added in the autoclave accompanied with 2 g xylene as solvent. The reaction lasted 4 h. The products were analyzed with a GC122 gas chromatograph equipped with a SE-54 capillary column (30 m × 0.25 mm × 0.3 μm) and a flame ionization detector.

3. Results and discussion

3.1. Structure of the catalysts

PFSA-CNT samples with different perfluorosulfonic acid loadings were prepared. Their N_2 adsorption-desorption isotherms were recorded and are shown in Fig. 1. Similar isotherms were observed for all the samples, showing that modification by perfluorosulfonic acid has little effect on the pore structure of the CNTs.

Table 1 summarizes the textural properties of the prepared samples. The samples maintained a large surface area and pore volume after modification although slightly lower than that of the pristine CNTs.

The SEM images of the CNT materials before and after modification are shown in Fig. 2. Significant differences can be observed in the morphology of the CNTs before and after modification. The PFSA-CNTs are arranged in ordered sheets, while the pristine CNTs are disorganized and entwined without any order. A similar change was observed for PSA-CNTs [20].

The size and structure of the functionalized CNT materials can be determined by TEM (Fig. 3). It is clear from the TEM