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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 N₂ 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.

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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 H₂SO₄ 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

PSFA-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 PSFA-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 PSFA-CNT-*x*, where *x* represents the mass ratio of the PSFA-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 tempera-

ture. 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

PSFA-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 PSFA-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

Fig. 1. N₂ adsorption-desorption isotherms of (1) CNT, (2) PFSA-CNT-0.1, (3) PFSA-CNT-0.2, (4) PFSA-CNT-0.3, (5) PFSA-CNT-0.4, and (6) PFSA-CNT-0.5.

Fig. 2. SEM images of pristine CNT ((a) and (c)) and PFSA-CNT-0.3 ((b) and (d)).

images that polymer functionalization does not affect the tubular structure of the CNTs. The polymer was well deposited on the surface of the pore channels, which is in agreement with the results of the N₂ adsorption measurements. These CNT materials have a nanodimension ranging from 20 to 30 nm.

The thermal behavior of PFSA-CNT materials is shown in Fig. 4. A significant decrease in the mass percentage at ~350 °C is observed, which can be attributed to the desorption or de-

Fig. 3. TEM images of pristine CNT ((a) and (c)) and PFSA-CNT-0.3 ((b) and (d)).

Fig. 4. TG curves of (1) pristine CNT, (2) PFSA-CNT-0.3, and (3) PFSA-PTFE solution.

composition of the perfluorosulfonic acid functional group from the catalyst surface because the PFSA-PTFE copolymer shows a similar mass loss (the decrease at 50 °C is related to the desorption of solvent). The slow decrease in the mass percentage above 600 °C is because of the decomposition of the CNTs, which also occurs for the pristine CNT material.

Fig. 5 shows the FT-IR spectra of the CNT materials after polymer modification, together with that of PFSA-PTFE for comparison. The peaks at 620 and 1070 cm⁻¹ confirmed the existence of the sulfonic group. All were consistent with FT-IR spectra of the pure PFSA-PTFE sample, suggesting the successful introduction of PFSA onto the surface of the CNTs.

Table 1

Textural and acidic properties of PFSA-CNT catalysts.

Sample	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)	Acid site amount ^a (mmol/g)	S amount ^b (mmol/g)
CNT	153	0.87	22.6	—	—
PFSA-CNT-0.1	147	0.81	21.9	0.06	0.13
PFSA-CNT-0.2	121	0.63	20.9	0.13	0.21
PFSA-CNT-0.3	101	0.54	21.6	0.21	0.30
PFSA-CNT-0.4	97	0.54	22.1	0.26	0.37
PFSA-CNT-0.5	91	0.54	23.8	0.24	0.40

^a Obtained by neutralization titration. ^b Measured by XRF.

Fig. 5. FT-IR spectra of (1) PFSA-CNT and (2) PFSA-PTFE.

3.2. Acidity of the catalysts

The amount of acid sites on the PFSA-CNT samples was evaluated by neutralization titration, and the results are listed in Table 2. The amount of acid sites linearly increases with PFSA loading at the beginning, reaching a maximum at PFSA-CNT-0.4, and then decreases with further increase of PFSA loading, indicating that the deposited PFSA cannot be well dispersed at that time because of the limitation of the surface of the CNTs.

The acidity of the catalysts was also characterized by potentiometric titration with *n*-butylamine. The initial electrode potential indicates the maximum acid strength of the acid sites, and the amount of *n*-butylamine consumed, where the plateau is reached, indicates the total number of acid sites. The evaluated results are listed in Table 2, which are consistent with the results of neutralization titration.

The acid sites can be classified by their acid strength according to the following scale: $E > 100$ mV (strong), $0 \text{ mV} < E < 100$ mV (medium), and $-100 \text{ mV} < E < 0$ mV (weak) [22,23]. The increase in the total acid amount after modification was mainly caused by the increase of the acid sites with strong acid strength, which confirmed the strong acid strength of PFSA itself.

3.3. Stability of the catalysts

The thermal stability of the PFSA-CNT-0.3 sample was tested by calcining it at different temperatures for 4 h. The results

Table 2

Acidity of PFSA-CNT catalysts obtained by potentiometric titration.

Sample	Amount of acid sites (mmol/g)			Total
	Strong ^a	Medium ^b	Weak ^c	
PFSA-CNT-0.1	0.030	0.010	0.048	0.088
PFSA-CNT-0.2	0.058	0.015	0.061	0.134
PFSA-CNT-0.3	0.171	0.018	0.035	0.224
PFSA-CNT-0.4	0.165	0.020	0.067	0.252
PFSA-CNT-0.5	0.157	0.018	0.062	0.237

^a $E > 100$ mV. ^b $0 \text{ mV} < E < 100$ mV. ^c $-100 \text{ mV} < E < 0$ mV.

Fig. 6. Amount of acid sites on PFSA-CNT-0.3 after calcination at different temperatures.

are shown in Fig. 6. The amount of acid sites on the catalyst is almost unchanged after calcination at temperatures below 300 °C compared with the fresh sample. However, when the calcination temperature is 350 °C or above, a sharp decrease is observed. Almost no acidity is detected when the calcination temperature is 400 °C. These results indicate that the temperature tolerance of the PFSA-CNT catalyst is less than 300 °C, which is in agreement with the TG results shown in Fig. 4.

The stability of the catalyst in various solvents was also tested by treating the catalyst in the solvents at different temperatures. The results are summarized in Table 3. Little change in the acidity was observed at the reflux temperature of the solvents, showing that the catalyst is stable in both polar and non-polar solvents.

3.4. Activity of the catalysts

2-*Tert*-butylhydroquinone (2-TBHQ) is an excellent antioxidant that is widely used in food industry. It is conventionally prepared by the alkylation of hydroquinone with *tert*-butanol or isobutylene. The activity of PFSA-CNT for alkylation of hydroquinone was tested and compared with that of PSA-CNT, and the results are shown in Table 4. The activity of PFSA-CNT increases with PFSA loading and exceeds that of PSA-CNT when the content of copolymer reaches $x = 0.4$. Because more acid sites were detected on PSA-CNT (0.343 mmol/g) than on PFSA-CNT-0.4 (0.252 mmol/g), the turnover frequency on PFSA-CNT is much higher.

However, the yield of TBHQ over PFSA-CNT is much lower than over PSA-CNT because of its low selectivity. More 2,5-DTBHQ and 2,5-DTBBQ were formed over PFSA-CNT than

Table 3

Acid site amount of PFSA-CNT-0.3 treated in various solvents obtained by neutralization titration.

Temperature (°C)	Acid site amount (mmol/g)		
	Ethanol	Xylene	Water
75	0.20	0.20	0.20
100	0.20	0.20	0.18
125	0.19	0.19	0.18
150	—	0.20	—

Table 4

Catalytic activity of PFSA-CNTs for hydroquinone alkylation.

Sample	Conversion (%)	Selectivity (%)				Yield (%)
		2-TBHQ ^a	2,5-DTBHQ ^b	2,5-DTBBQ ^c	TBPE ^d	
PFSA-CNT-0.1	47.9	41.3	12.6	18.3	23.7	19.8
PFSA-CNT-0.2	56.6	43.5	25.4	16.4	14.2	24.6
PFSA-CNT-0.3	66.5	39.8	34.6	14.3	10.9	26.4
PFSA-CNT-0.4	78.1	32.6	46.4	10.2	10.8	25.4
PFSA-CNT-0.5	87.5	27.4	58.4	9.01	5.26	24.0
PSA-CNT [23]	73.3	73.2	17.2	4.2	5.6	53.7

^a 2-*tert*-butyl hydroquinone. ^b 2,5-di-*tert*-butyl hydroquinone. ^c 2,5-di-*tert*-butyl benzoquinone. ^d *tert*-butyl phenol ether.

PSA-CNT, which indicates that the acid strength of PFSA-CNT is stronger because the selectivity in this reaction is related to the acid strength of the catalyst. The higher acid strength causes the higher percentage of di-alkylation and oxidation products.

To confirm the heterogeneity of this catalytic reaction, a comparative experiment was carried out as follows: alkylation was performed for the first 2 h with PFSA-CNT and then for the second 2 h both with and without PFSA-CNT. The results shown in Fig. 7 indicate that the conversion did not obviously increase without the catalyst, suggesting that no leaching occurred during the reaction or the leaching species had negligible catalytic activity. Therefore, the alkylation catalyzed by PFSA-CNT catalyst under the present conditions is a heterogeneous catalytic reaction.

3.5. Reusability of the catalysts

The reusability of the PFSA-CNT catalyst was also tested. After the reactions, the PFSA-CNT catalyst was filtered off, washed with ethanol, dried at 100 °C, and then reused in the next reaction. The reaction data for the first three runs are

Fig. 7. Conversion of hydroquinone with (1) and without (2) the PFSA-CNT catalyst.

Table 5

Reusability of the PFSA-CNT-0.3 catalyst.

Run	Conversion (%)	Selectivity (%)				Yield (%)
		2-TBHQ	2,5-DTBHQ	2,5-DTBBQ	TBPE	
1	66.5	39.8	34.6	14.3	10.9	26.4
2	68.4	40.8	34.4	12.8	11.0	27.9
3	66.1	38.4	34.1	15.6	11.1	25.4

listed in Table 5. No noticeable deactivation was observed in these cycle processes. Compared with PSA-CNT and sulfonated carbon-based solid acid, whose hydroquinone conversions drop from 73.3% to 56.6% [20] and from 91% to 48% [11], respectively. After three runs under the same reaction conditions, the PFSA-CNT catalyst is much more stable and reusable. The enhanced stability may be caused by the higher stability of perfluorosulfonic group than the styrene sulfonic group.

4. Conclusions

Perfluorosulfonic acid-functionalized carbon nanotubes can be obtained by simply depositing the perfluorosulfonic acid-PTFE copolymer on the surface of CNTs. These materials are very stable in both polar and non-polar solvent and can maintain their acidity up to 300 °C. Higher activity and better stability were observed in the alkylation of hydroquinone with *tert*-butanol compared with poly(styrene sulfonic acid)-grafted carbon nanotubes. The catalyst can be reused after simply washing it with ethanol, and no obvious decrease of activity was observed using the recycled catalyst. The excellent catalytic behavior comes from the strong acid strength and high stability of the perfluorosulfonic group.

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Graphical Abstract

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Preparation and catalytic performance of perfluorosulfonic acid-functionalized carbon nanotubes

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Perfluorosulfonic acid-functionalized carbon nanotubes were prepared and exhibit higher activity and better stability in the alkylation of hydroquinone than poly(styrene sulfonic acid)-functionalized carbon nanotubes.

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全氟磺酸功能化碳纳米管的制备及其催化性能

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摘要: 采用全氟磺酸-全氟乙烯共聚物的液相沉积方法制备了全氟磺酸功能化碳纳米管催化剂, 利用N₂吸附、扫描电子显微镜、透射电子显微镜、傅里叶变换红外光谱以及酸碱滴定等方法对材料的结构和酸性进行了表征, 考察了温度和溶剂对催化剂稳定性的影响。结果表明, 催化剂在极性和非极性溶液中均十分稳定, 并且具有良好的热稳定性, 使用温度可达300 °C。该催化剂在对苯二酚与叔丁醇的烷基化反应中表现出优异的催化性能, 其催化活性与稳定性均高于聚苯乙烯磺酸功能化的碳纳米管催化剂。

关键词: 碳纳米管; 全氟磺酸; 酸性; 稳定性; 对苯二酚; 叔丁醇; 烷基化反应

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1. 前言

酸催化反应是化工领域中最重要反应。然而, 在许多传统的工业生产中, 诸如水解、水合、酯化和Friedel-Crafts反应等, 还经常使用包括硫酸和氢氟酸在内的液体酸作为催化剂。这类酸催化剂在实际使用时存在许多问题: 其强腐蚀性容易对生产设备造成破坏; 其废液会造成环境污染; 催化剂与原料和产物不易分离等。用固体酸作为催化剂可以很好地解决这些问题, 因此开发新型绿色固体酸催化材料是目前化学工业的当务之急^[1]。

如今已有不少固体酸催化剂被应用于工业生产, 如以各种沸石分子筛为催化剂的催化裂解、二甲苯异构化和甲苯歧化等反应, 以固体超强酸为催化剂的C₅/C₆异构化反应等。然而, 对于有水参与的液相反应, 固体酸成功的例子较少, 主要原因是传统的固体酸催化剂容易在有水存在的环境中失活, 因此亟需开发新型高效不怕水的固体酸催化剂^[2]。

碳基磺酸化固体酸作为一类有前景的固体酸催化剂具有诸多优异的性质, 该类催化剂不怕水, 在酸、碱介质中十分稳定, 表面性质可调^[3-5]。通常情况下碳基磺酸

化固体酸可以通过高温下直接磺酸化有序介孔碳材料^[6,7]或对含磺酸基团的稠环化合物进行不完全碳化来制备^[3],也可以将有机化合物材料进行不完全碳化后再磺酸化得到^[4,5]。这些催化剂已被应用于一些液相催化反应中,如2,3-二甲基-2-丁烯水合反应、乙酸酯化反应、三乙酸甘油酯酯交换反应、biginelli反应以及醛氧化制羧酸的反应,并且表现出优良的催化性能^[5,8–10]。然而这些催化剂的稳定性还不尽如人意,尤其是在高温极性介质中,催化剂表面的 $-\text{SO}_3\text{H}$ 基团容易脱落^[8,11]。催化剂制备过程中大量硫酸的使用也会造成一定的环境污染。同时,此类催化剂的活性与溶胀效应密切相关,因此这类碳基磺酸化固体酸不适用于无溶剂存在的气相反应体系^[8]。

碳纳米管自1991年被Iijima^[12]发现以来,由于其独特的结构、优异的物理化学特性、较大的表面积和易于修饰的表面性质,受到了广泛关注^[13]。碳纳米管本身不具备酸催化性能,要使其在催化领域得到应用必须在其表面修饰上酸性基团。将碳纳米管直接磺酸化制得的碳基固体酸^[14–17],其酸性和稳定性并不理想^[14,17],而采用直接合成法制备的磺酸化多壁碳纳米管具有更好的稳定性^[18]。我们课题组^[19]提出了利用高分子聚合物对碳纳米管进行功能化,并且成功地利用原位聚合法制备得到了聚苯乙烯磺酸功能化的碳纳米管催化剂(PSA-CNT)。该催化剂具有较高的酸量和较好的催化性能,但是其稳定性仍需进一步改进^[20]。

本文制备了一系列修饰量不同的全氟磺酸功能化碳纳米管催化剂,利用 N_2 吸附、扫描电子显微镜、透射电子显微镜、红外光谱、热重分析、电位滴定和酸碱中和滴定等方法对催化剂的结构和酸性进行了表征,考察了催化剂在对苯二酚与叔丁醇的烷基化反应中的催化活性和稳定性,并与聚苯乙烯磺酸功能化的碳纳米管催化剂(PSA-CNT)进行了比较。

2. 实验部分

2.1. 催化剂的制备

全氟磺酸功能化碳纳米管通过液相沉积法制备。将500 mg多壁碳纳米管(成都有机化学有限公司产品,纯度>95%)加入到一定量的5 wt%全氟磺酸-全氟乙烯共聚物的杂醇溶液(Alfa Aesar产品)中,用75%乙醇稀释至25 g,以低能超声处理40 min使碳纳米管分散均匀后,再电磁搅拌过夜。将得到的黑色块状物放入100 °C的烘箱中过夜。所得材料记为PFSA-CNT- x ,其中 x 是指全氟

磺酸-全氟乙烯共聚物与多壁碳纳米管的质量比。

2.2. 催化剂的结构表征

用美国麦克公司的ASAP-2000型自动吸附分析仪测定样品的 N_2 吸附等温线,比表面积由BET方法得到,孔径和孔体积利用BJH方法算得。用美国尼高力(Nicolet)公司Avatar-360型傅里叶红外光谱仪采集样品的红外光谱。用美国珀金埃尔默(PerkinElmer)公司TGA7型热重分析仪分析样品的热稳定性, N_2 气氛,升温速率10 °C/min。用荷兰Philips公司XL30型扫描电镜观察样品形貌。用日本电子公司JEM 2100型透射电子显微镜观察样品的特征结构和形貌。用德国Bruker-AXS公司S4 EXPLORER型X射线荧光光谱测定S含量。

2.3. 催化剂的酸性表征

催化剂表面酸量通过酸碱中和滴定方法测定^[21],将0.1 g催化剂加入到30 mL NaCl溶液(2 mol/L)中,室温下搅拌3 d,使催化剂表面 H^+ 离子和 Na^+ 离子交换达到平衡。催化剂过滤之后,清液用NaOH溶液(10 mmol/L)滴定。表面酸量还通过电位滴定法测定^[22,23],即将催化剂加入到一定量乙腈中,搅拌3 h,然后用正丁胺的乙腈溶液(0.1 mol/L)滴定,电位变化用Mettler Toledo FE20型pH计(梅特勒-托利多国际贸易(上海)有限公司)测定。

2.4. 催化性能的测试

对苯二酚与叔丁醇烷基化反应在内衬有聚四氟乙烯的不锈钢高压釜中进行,使用磁力搅拌并通过油浴控制反应温度。反应条件如下:对苯二酚0.5 g,叔丁醇1.0 g,二甲苯2.0 g作为溶剂,催化剂0.20 g,在150 °C反应4 h。产物使用配有SE-30毛细管色谱柱(30 m $\times$ 0.25 mm $\times$ 0.3 μm)的GC122型气相色谱仪分析。

3. 结果与讨论

3.1. 催化剂的结构

制备了一系列修饰量不同的全氟磺酸功能化碳纳米管催化剂。图1为功能化前后样品的 N_2 吸附-脱附等温线。可以发现,样品等温线的形状非常相似,说明全氟磺酸-全氟乙烯的修饰对碳纳米管本身结构的影响很小。

表1列出了上述样品的比表面积、孔体积和平均孔径。碳纳米管的比表面为153 m^2/g ,孔体积为0.87 cm^3/g 。与碳纳米管相比,全氟磺酸-全氟乙烯修饰后样品的比表面积和孔体积有所下降,考虑到样品中碳纳米管的实际含量,比表面积下降的程度并不大。

图2给出了碳纳米管和功能化碳纳米管的SEM照片。可以看出,功能化后碳纳米管的聚集形式发生了明显变

化. 高分子修饰前碳纳米管无规则地缠绕在一起, 呈现出杂乱无章的状态, 但在修饰之后, PFSA-CNT总体呈片状, 单根碳纳米管之间的排列也表现出一定的方向性, 这与聚苯乙烯磺酸功能化的碳纳米管(PSA-CNT)的情况十分相似^[20].

图3为碳纳米管和功能化碳纳米管的TEM照片. 可以看到, 功能化后碳纳米管的管状结构没有改变. 聚合物在碳纳米管表面分散良好. 这也与上述N₂吸附表征结果一致. 同时也可以看到, 功能化碳纳米管样品的管径为20–30 nm, 比修饰之前有所增加.

图4给出了碳纳米管、功能化碳纳米管和全氟磺酸-全氟乙烯聚合物(5 wt%杂醇溶液)的热重曲线. 可以看到, 聚合物本身(曲线(3))在350 °C有一个明显的失重, 这是磺酸基团的脱除或分解所致(50 °C处失重是溶剂挥发造成的). 样品PFSA-CNT的热重曲线(2)在350 °C也有同样的趋势, 表明修饰后全氟磺酸基团的稳定性与修饰前相同, 而温度高于600 °C时的缓慢失重为碳纳米管的失重, 这在碳纳米管的失重曲线(1)上也可以观察到.

将功能化碳纳米管以及全氟磺酸-全氟乙烯的红外光谱作了对比, 结果见图5. 从PFSA-CNT的光谱图上可以看到, 在620和1070 cm⁻¹处出现了磺酸基的特征峰, 说明全氟磺酸基团被成功引入到碳纳米管表面.

3.2. 催化剂的酸性

利用酸碱滴定测试了样品的酸量, 结果见表1. 随着全氟磺酸-全氟乙烯修饰量的增加, 样品的酸量几乎线性增加, 样品PFSA-CNT-0.4的酸量最高. 继续增加修饰剂量, 催化剂的酸量并未增大. 这可能是由于碳纳米管比表面积较小, 使得过量的全氟磺酸-全氟乙烯不能很好地分散到碳纳米管表面.

为了同时考察催化剂的酸强度和酸量, 我们采用电位滴定法对样品进行了表征, 样品总酸性位数目由正丁胺的消耗量得到. 按照文献建议^[22,23], 我们指定电位超过100 mV的酸性位为强酸位, 0–100 mV为中强酸位, –100–0 mV为弱酸位, 得到的结果列于表2. 电位滴定得到的数据与酸碱滴定的结果基本一致. 另外, 修饰剂量增加造成的样品总酸性位数目的增加主要来自强酸性位($E > 100$ mV)的增加, 这也验证了全氟磺酸-全氟乙烯自身的强酸性.

3.3. 催化剂的稳定性

以PFSA-CNT-0.3为代表测试了全氟磺酸功能化碳纳米管的热稳定性. 将样品在不同温度下焙烧4 h后测试其酸量, 并与焙烧前的样品进行对比, 结果如图6所示.

在300 °C以下焙烧的样品酸量未出现变化, 当焙烧温度超过300 °C时, 样品酸量大幅下降; 而当焙烧温度达到400 °C时, 样品已基本没有酸性. 结果表明, 催化剂的适用温度不宜超过300 °C, 这也与图4热重分析结果相一致.

为了进一步探讨催化剂的适用范围, 我们还考察了上述样品在不同温度下不同溶剂中的溶脱性能. 将0.1 g催化剂加入到10 mL溶剂中, 在不同温度下加热搅拌4 h, 随后离心过滤, 干燥后的催化剂用中和滴定方法测其表面酸量, 结果列于表3. 该样品在三种溶剂中不同回流温度下处理后酸量均未出现明显下降, 说明该催化剂在极性和非极性溶液中均十分稳定.

3.4. 催化剂的催化性能

2-叔丁基对苯二酚(TBHQ)具有良好的抗氧化性能, 其作为防腐剂广泛应用在食品行业中. 传统的制备方法是通过苯二酚与叔丁醇烷基化反应. 表4列出了PFSA-CNT催化剂对上述烷基化反应的催化性能, 并与PSA-CNT催化剂进行对比. 结果表明, PFSA-CNT催化剂的活性随着全氟磺酸-全氟乙烯修饰量的增加而增大. 当聚合物与碳纳米管的质量比达到0.4时, 其活性超过了PSA-CNT催化剂. 由于PFSA-CNT-0.4催化剂的酸量为0.252 mmol/g, 低于PSA-CNT的酸量(0.343 mmol/g), 说明PFSA-CNT催化剂的TOF值更高.

同时, 以PFSA-CNT为催化剂时, 目的产物TBHQ选择性较低, 反应生成了更多的2,5-DTBHQ和2,5-DTBBQ副产物. 这是由于上述反应的选择性与催化剂的酸强度密切相关, PFSA-CNT催化剂的酸强度过高, 从而导致二烷基化产物(2,5-DTBHQ)和氧化产物(2,5-DTBBQ)等副产物的大量生成.

在液相反应中, 固体催化剂活性中心容易脱落到溶液中, 使反应过程存在均相催化的可能. 为了验证反应的多相性, 设计了一个对比实验. 烷基化反应在催化剂存在下进行2 h, 再离心过滤去掉催化剂后继续反应2 h, 结果见图7. 可以发现, 除去催化剂后, 对苯二酚的转化率几乎保持不变, 这证明PFSA-CNT催化剂催化的烷基化反应确实为多相催化反应. 即使反应过程中有少量磺酸基团脱落, 在反应溶液中也起不到催化作用.

3.5. 催化剂重复使用性能

以PFSA-CNT-0.3为代表, 考察了催化剂的重复使用性能. 催化剂在反应后, 经过滤, 用乙醇洗涤, 于100 °C干燥过夜后, 直接用于下一次反应, 反应结果列于表5. 在3次循环反应中, 样品PFSA-CNT-0.3没有出现明显失活;

而在相同反应条件下, PSA-CNT经3次循环后对苯二酚转化率从73.3%下降到56.6%^[20], 磺酸化的碳基固体酸上的转化率则从91%下降到48%^[11]. 这说明样品PFSA-CNT更加稳定, 具有极好的重复使用性. 这是由于全氟磺酸的稳定性高于对苯乙烯磺酸钠, 从而使样品PFSA-CNT的稳定性优于PSA-CNT.

4. 结论

通过液相沉积方法制备的全氟磺酸功能化的碳纳

米管催化剂在极性和非极性溶剂中均可以保持稳定, 热稳定性可以达到300 °C. 与聚苯乙烯磺酸功能化的碳纳米管催化剂相比, 该催化剂具有更高的酸催化能力, 含有0.25 mmol/g酸量的催化剂在烷基化反应中活性就超过了0.34 mmol/g酸量的聚苯乙烯磺酸功能化的碳纳米管催化剂. 催化剂具有很好的重复使用性能, 通过洗涤即可直接用于下一次反应, 反应3次后活性几乎不变. 该催化剂优异的催化性能来源于高酸强度和稳定的全氟磺酸基团.