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Recent Researches in Communications, Electronics, Signal Processing & Automatic Control

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Synthesis and Characterization of Modified Carbon Nanotubes with Silica-supported Preyssler Nano Particles and Study of Their Catalytic Activities in Synthesis of β-acetamido Ketones/Esters

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Abstract: In this work, a novel structured silica-supported Preyssler nano particles /carbon nanotube composite is synthesized. Multiwalled carbon nanotubes (MWCNTs) were synthesized by catalytic chemical vapor deposition method (CVD). The characterization of the materials by the Fourier transform infrared spectroscopy (FTIR), and Transmition electron microscopy (TEM), showed that the functionalization of MWCNTs by silica-supported Preyssler nano particles was successfully achieved via impregnation method. It has been found that the synthesized composite with 30 wt% loading is highly active catalyst in synthesis of β-acetamido ketones/esters and shows high yields in this reaction. This catalyst can be easily recovered and reused for many times without a significant loss in its activity.

Key-Words: Silica-supported Preyssler nanoparticles, Multiwalled carbon nanotubes, Catalyst, β-acetamido ketones/ester, Functionalization, Heteropolyacid.

1 Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991, researchers have taken interest in their unique structure and physical properties. This interest is still continuing at present, and research into the practical application of CNTs has recently become popular [1]. They have been attracted much attention in material science, sensor technology, catalysis, and biomedical fields [2]. However, the low chemical reactivity of raw CNTs leads to some limitations in their applications [3]. For most of these applications, nanotubes require functionalization, such as changing some of the graphite properties, supporting or attaching different groups, especially inorganic particles for future utilization of modified nanotubes.

Heteropolyacids (HPAs) are a large and diverse class of inorganic oxides which have attracted a great deal of interest in both academia and chemical industry due to their unique properties, such as strong Bronsted acidity, structure alterability, high proton mobility, redox behavior and environmental friendliness [4, 5]. Therefore, modifying CNTs with HPAs will make CNTs more attractive in various fields. Also, the electrochemical properties of HPAs may be fully maintained when they are introduced to CNTs [6].

Recently, HPAs have been investigated as modifying of CNTs. Pan et al. modified CNT with phosphomolybdic acid (HPMo) through chemisorption and found that catalysts supported on modified CNTs presented higher performance for methanol oxidation as compared with catalysts supported on CNTs [6]. Seo et al. deposited HPMo on Pt/CNTs catalysts and the HPMo-Pt/CNTs catalysts showed at least 50% higher catalytic mass activity with improved stability for the electrooxidation of methanol than Pt/CNTs [7]. Kim et al reported that HPMo can facilitate the electrooxidation of intermediate species such as CO and diminish the poison of catalysts [8].

Anyway, in spite of extensive investigations on modifying CNTs by different HPAs, modification of CNTs with sodium 30-tungstopentaphosphate, the so-called Preyssler anion, has been largely overlooked. Preyssler anion has exclusive properties and excellent stability. It is ideal model for the construction of hybrid systems, so it is regarded as

the potential candidate to be transformed into nanometer-sized materials. Thus, in recent years, we have devoted to the design and controlled fabrication of nanostructured Preyssler [9].
Encouraged by our recent results with Preyssler [10-16], in the present work, we used MWCNTs materials as nanostructured porous supports for immobilization of spherical Preyssler nanoparticles. In our previous work, we investigated performance and capability of Preyssler, in pure form, for chemical modification of MWCNTs [17]. Also, in continuation of our works with Preyssler catalyst, we synthesized silica-supported Preyssler nano particles [9]. In order to perform a new contribution to the field of nanotechnology, it is of great interest to know what occurs if the silica-supported Preyssler nanoparticles (spherical morphology) is used in chemical modification of MWCNTs. Interestingly, we have found that the silica-supported Preyssler nanoparticles fills MWCNTs more effective than Preyssler's anion in pure form.
CNTs provide large surface areas and can also facilitate electron transfers to reactive sites, and such properties make them attractive materials for applications in both sensors and electrocatalysis. Also we checked catalytic activity of them in synthesis of β-acetamido ketones and esters.

2 Results and Discussions

MWCNTs were synthesized via chemical vapor deposition (CVD) method. In this work, bimetallic combination of Fe and Co was used. The catalytic activity of these metals strongly depends on their electronic structure. We have checked the catalyst/support ratio. When both Fe and Co were present in 5%, most of the products were MWNTs. We suggest that Fe plays a major role in the catalytic CVD process and Co might play co-catalyst role in this process. Calcium carbonate was used as support catalyst. Application of $CaCO_3$ support showed high density and purity of CNT products. The synthesis process was carried out in two steps: In the first step, bimetallic catalyst was deposited on the $CaCO_3$ substrate. Then, acetylene gas as a carbon source was introduced in the reaction chamber. In this stage, metal carbides are formed and then these materials are converted to carbon atoms by using energy source. These carbons will get diffused towards substrate, which is coated with catalyst and nanotubes grow over the metal catalyst. Fig. 1 shows TEM images of the carbon nanotubes. This Figure shows a bamboo-like structure. The inner and outer diameters are about 20 nm and 35 nm, respectively.

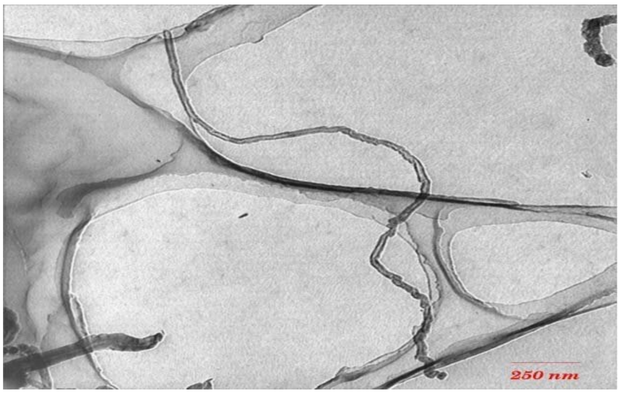

Fig.1. TEM images of the CNTs.

At the other stage, the functionalization of MWCNTs by silica-supported Preyssler nanoparticles was successfully achieved via impregnation method. All functionalization methods of carbon nanotubes can be divided into two major groups including: endohedral functionalization and exohedral functionalization [18, 19]. In endohedral functionalization, nanotubes are functionalized by filling them with different nanoparticles.
Fig. 2 presents typical TEM images of the modified CNTs with silica-supported Preyssler nanoparticles.

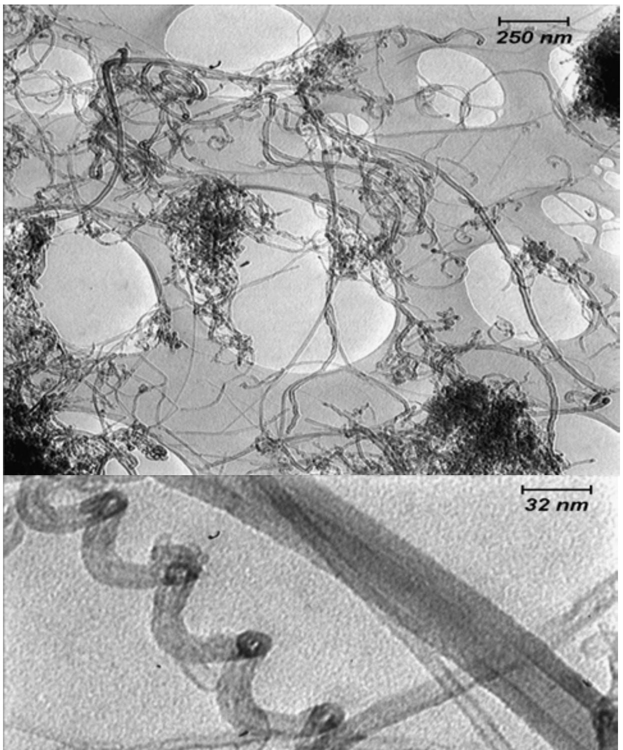

Fig.2: TEM images of the modified CNTs with silica-supported Preyssler nano particles

Our results show that, the chemical modification of MWCNTs by silica-supported Preyssler nano particles was successfully achieved *via* endohedral method. Based on the novel properties of both Preyssler anion and CNTs, such structures may find wide applications, especially in electrocatalysis.

The existence of heteropolyacid $[NaP_5W_{30}O_{110}]^{14-}$ in the MWCNTs was also confirmed by infrared spectroscopy. The asymmetric stretching frequency of the terminal oxygen was observed at 960 cm^{-1} and the P-O asymmetric stretching frequency was noted at 1080 cm^{-1} and 1165 cm^{-1}. The prominent P-O bands at 960, 1080, and 1165 cm^{-1} were consistent with a C_{5V} symmetry anion. Also, IR spectra showed a peak at about 1578 cm^{-1}, corresponding to the IR active phonon mode of CNTs [20].

2.1 Catalytic synthesis of β-acetamido ketones and esters

The synthesis of β-acetamido ketones and esters in the presence of a catalytic amount of the modified CNTs studied under reflux conditions in acetonitrile as solvent. The results are shown in Table 1.

Obviously, this catalyst renders synthesis of β-acetamido ketones and esters. The advantages of this method are reusability of catalysts, easy work-up procedure and high yields. Simple experimental procedure as well as high yield and selectivity, makes this method useful addition to the methodologies that require green super acid solid catalyst.

Table 4. Synthesis of β-acetamido ketones and esters using catalytic amount of modified CNTs.

Aldehyde	Carbonyl compound	Time (min)	Yield (%)	M.p (Found)	M. p (Reported)
4-ClC_6H_4CHO	$C_6H_5COCH_3$	45	82	149	146-148 [a]
C_6H_4CHO	$C_6H_5COCH_3$	45	70	103	102-104 [a]
4-$NO_2C_6H_4CHO$	$C_6H_5COCH_3$	50	72	151	148-149 [a]
4-$CH_3C_6H_4CHO$	$C_6H_5COCH_3$	55	86	109	112-114 [a]
C_6H_4CHO	$CH_3O_2CCH_2COCH_3$	50	62	132	129-131 [a]
4-ClC_6H_4CHO	$CH_3O_2CCH_2COCH_3$	45	64	134	130-132[a]

[a] [21,24]

3 Experimental

3.1 Synthesis of MWCNTs by catalytic chemical vapor deposition method

MWCNTs were synthesized by catalytic decomposition of acetylene in the temperature range of 650-800°C over bimetallic catalyst supported on $CaCO_3$. As catalyst, the bimetallic combination of Fe(III) and Co(II) was used. For being precise, a calculated amount of metal salts $Co(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ was mixed with a few drops of distilled water and subsequently $CaCO_3$ powder was added to the mixture. After mixing well, the result in powder was dried in an oven at 120°C overnight and then collected as dry powder. The total concentration of catalysts was about 5 wt.%. The decomposition of acetylene was carried out in a horizontal reactor at different temperatures. Approximately 500 mg of the prepared supported catalysts (Fe(III),Co/$CaCO_3$) was placed in a quartz boat, which was inserted in a ceramic tube under nitrogen flow. A continuous nitrogen flow was kept until the final temperature was reached and then acetylene was let through with a gas flow of 100 mL/min for 20 min to 40 min. After rinsing the system with nitrogen, the reaction product was collected from the boat.

For purification, raw MWCNT samples were sonicated (30 W) in diluted nitric acid (30% HNO_3) for 30 min at room temperature, filtered, washed several times with distilled water, and finally dried at 120°C overnight.

3.2 Impregnation method

Purified MWCNTs were used as support materials. Prior to impregnation, the CNTs were treated with 30 wt.% HNO_3 at 100°C overnight, washed with distilled water, and dried at 120°C for 6 h. All modified samples were prepared with incipient wetness impregnation of nano Preyssler anion solution on treated MWCNTs. Using sequential impregnation method, modified samples were prepared with Preyssler anion loadings of 30 wt.%. After impregnation step, the sample was dried at 120°C and calcined at 350°C for 3 h with a heating rate of 10°C/min under argon flow.

3.3 Catalytic test

A mixture of ketone or methylacetoacetate (1 mmol), aromatic aldehyde (1.1 mmol) and acetyl chloride (4 mmol) in acetonitrile was mixed with a catalytic amount of nano catalyst. The progress of reaction was monitored by TLC and GC. After completion of the reaction, the mixture was poured into cold water, which resulted in precipitation of the desired β-acetamido ketones/esters. The precipitated solid was filtered and washed with diethylether. The pure product was obtained by recrystallization.

3.4 Reusability of the catalyst

The catalyst could be recycled after evaporation of solvent from the residue. The residue then washed with diethylether, dried at 130°C for 1 h and re-used in another reaction. The recycled catalyst was used for three reactions without observation of appreciable loss in its catalytic activities.

4 Conclusion

In this contribution, an organic–inorganic nanostructure contains nanosized inorganic building blocks in organic material has been achieved by impregnation method. Organic–inorganic nanostructure showed an excellent potential in synthesis of β-acetamido ketones/esters.

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