Fe-nanoparticles dispersed carbon micro and nanofibers: Surfactant-mediated preparation and application to the removal of gaseous VOCs

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ABSTRACT

This study describes the preparation of Fe nanoparticle-dispersed carbon microfibers (Fe-ACFs) and carbon nanofibers (Fe-CNFs) for the removal of gaseous volatile organic compounds (VOCs). Fe-ACFs were prepared by impregnating ACFs with Fe salts. Three different types of surfactants (cationic, anionic, or non-ionic) were used to achieve the segregation and monodispersion of Fe(III) ions in aqueous solutions. Fe(III) nanoparticles were produced on the ACF-surface after the calcination of Fe(III)-surfactant molecules which were transferred from the solution to the ACF during the impregnation-step. Fe-CNFs were prepared by the catalytic chemical vapor deposition (CVD) of benzene on the Fe-ACFs used as a substrate. Different analytical instruments were used to characterize the physicochemical properties of the prepared materials, including the loading and monodispersity of the Fe nanoparticles. The data showed that Fe nanoparticles of 8-nm average size were uniformly dispersed over the surface of the ACFs with a maximum loading of 0.68 mg/g when using SDS, an anionic surfactant. In this case, the relatively more uniform and dense growth of CNFs was observed. The prepared Fe-ACFs and Fe-CNFs were used to remove carbon tetrachloride (CCl_4), a persistent gaseous VOC. The results of the study show an effective method for preparing surfactant-enhanced Fe nanoparticles and carbon webs of micro- and nanofibers for the removal of persistent gaseous organic pollutants.

1. Introduction

Currently, metal nanoparticles are used in a wide range of applications, for example, in drug delivery, optoelectronics, magnetics, biomedicine, and chemical reactions [1–5]. The nanoparticles made of transition metals, such as nickel (Ni), iron (Fe), and cobalt (Co), are commonly used as catalysts for growing different carbon nanostructures, such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), and carbon nanowires (CNWs) [6–9]. In this context, there is an increasing focus on controlling the size and uniform dispersion of metal nanoparticles, especially on the surface of a porous substrate during the preparation of nanostructures. One way to achieve a controlled size and uniform dispersion of metal nanoparticles is the use of surfactants in the precursor solutions.

The literature is replete with the synthesis of metal oxide nanoparticles, such as FeO, CoO, AuO, AgO, and NiO, in either organic or aqueous solutions and using various commercially available surfactants, such as sodium dodecyl sulfate (SDS), tri-n-octylphosphine (TOPO), triton X-100, cetyl trimethylammonium bromide (CTAB), cetyl trimethylammonium chloride (CTAC), and cetylpyridinium chloride (CPC) [10–26]. In these studies, metal nanoparticles were synthesized in the solutions by reducing the different metal-salts to their respective oxides using a strong reducing agent and aging at elevated temperature. Surfactants prevented the agglomeration of metal particles in the solution.

It is important to note that it is extremely difficult to prepare nanoparticles in their metallic state because the highly reactive nanoparticles are instantly converted into their respective oxide counterparts. Therefore, in this study, activated carbon fibers (ACFs) were first impregnated with ferric nitrate salts in the aqueous solution using a suitable surfactant. The surfactant prevented Fe(III) ions from agglomerating with neighboring ions in the impregnating solution. Fe(III) oxide nanoparticles were produced on the ACF-surface after the calcination of Fe(III)-surfactant molecules which were transferred from the solution to the ACF during the impregnation-step. Next, the metal oxides were converted into the

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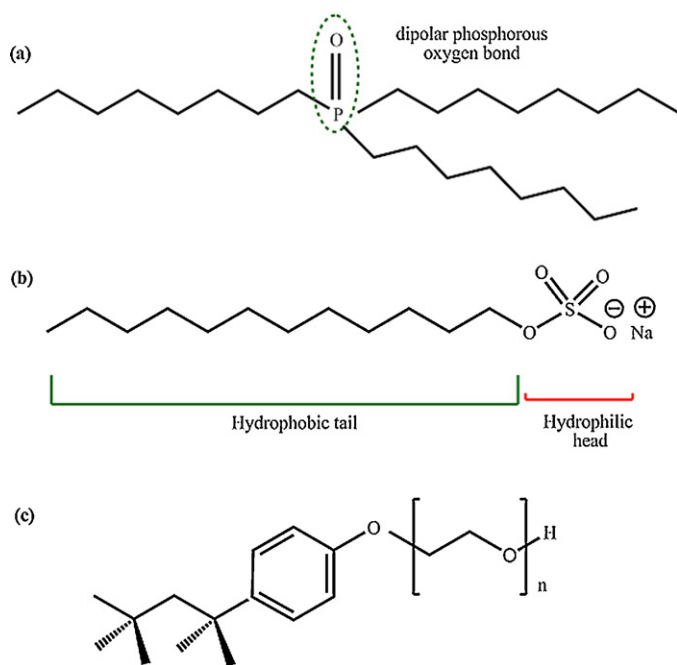
Fig. 1. Chemical structure of (a) TOPO, (b) SDS, and (c) Triton X-100.

metallic state by a reduction under a hydrogen atmosphere. The Fe-ACFs thus prepared had a significant and uniform loading of Fe nanoparticles and were subsequently used as a substrate for growing CNFs by catalytic chemical vapor deposition (CVD). The prepared Fe-ACFs and Fe-CNFs were used in removing carbon tetrachloride (CCl_4), a persistent gaseous volatile organic compound (VOC).

CCl_4 is a major hazardous chemical because of its high toxicity and carcinogenicity [27]. It is stable at room temperature, and also, may bioaccumulate in tissues, which may cause adverse health effects. CCl_4 is also categorized as a chemical warfare agent (CWA) [28]. CCl_4 has been removed by different methods (including adsorption, oxidation, and catalytic hydrolysis) and using different materials (such as the oxides of iron (Fe) and silver (Ag), activated carbon (AC), and granular activated carbon (GAC)) [27,29–34]. CCl_4 has also been removed by adsorption onto ACFs modified with different metals, such as chromium (Cr), copper (Cu), and silver (Ag) [28]. In another study, CCl_4 has been removed by bentonite-modified ammonium salts [34]. Among these materials, Fe or FeO are relatively more effective in removing CCl_4 by catalytic destruction. Considering the significantly large BET surface areas of ACFs and CNFs, the present study was undertaken to modify the ACFs and CNFs with Fe and then to utilize the Fe-impregnated ACFs and CNFs for the catalytic/adsorptive removal of CCl_4. In the latter material (Fe-CNFs), the Fe had dual roles: (1) to grow CNFs on ACFs by CVD and (2) to remove the organic species. Herein, it may be noted that the surface-functionalized ACFs and CNFs have been shown to be successful adsorbents in different environmental remediation applications, ranging from the removal of arsenic, fluorides, and phenol in water to that of SO_2, NO_x, and 2-chloroethanol in air [35–39].

2. Materials and methods

ACFs were impregnated with hydrated ferric nitrate using three different types of surfactants: (1) SDS, an anionic surfactant, (2) TOPO, a cationic surfactant, or (3) Triton X-100, a non-ionic surfactant. Fig. 1 presents the chemical structure of the surfactant molecules. SDS is an organosulfate compound consisting of a

12-carbon tail attached to the sulfate functional group. TOPO is an organophosphorus compound having uncharged alkyl chains. It also has polarity resulting from the dipolar phosphorus-oxygen (P—O) bond. TOPO is a commonly used cationic surfactant to prepare and stabilize the Fe-nanoparticles [40]. The triton molecule is neutral. In general, anionic and non-ionic surfactants facilitate the formation of small and large nanoparticles, respectively. In addition, the size and stability of the nanoparticles depend on the surface charge of the surfactant molecules and the interaction between the surfactant molecules and the metal ions [21,41,42].

In this study, the Fe-ACFs and Fe-CNFs prepared using SDS exhibited relatively superior physiochemical properties that are responsible for the enhanced adsorption capacity for CCl_4. During impregnation, the negatively charged hydrophilic head of SDS molecule binds to the positively charged Fe(III) ions produced in the solution following the dissolution of Fe salts, which prevents Fe(III) ions from agglomerating with neighboring ions. Consequently, an increasingly large amount of Fe(III) ions is transferred from the bulk solution to the ACF-surface, along with SDS. During the calcination step, SDS decomposes, which leaves behind Fe(III) oxide nanoparticles on the ACF-surface. Subsequent reduction in H_2-atmosphere converts Fe(III) particles into their pure metallic state, i.e., Fe(0) that have been further reduced in size. Fig. 2 schematically depicts the above effects.

In the case of cationic TOPO, it has the polarity resulting from the dipolar phosphorus–oxygen (P—O) bond. The electrostatic repulsion occurs between the surfactant molecule and the Fe(III) ions in the impregnating solution which inhibits the attachment of the surfactant to the Fe(III) ions. Therefore, the segregation of the Fe(III) ions or monodispersity in the impregnating solution is reduced. Triton X-100 is a neutral molecule and does not attach to Fe(III) ions. As discussed later in the manuscript, the size of Fe(0) nanoparticles on the Fe-ACFs surface was found to be smaller for SDS than for the other two surfactants (TOPO and Triton). Consequently, the CNFs grown on the ACFs in the former case were relatively denser and more uniform. The CCl_4 adsorption capacity of the Fe-ACFs and Fe-CNFs was also relatively larger when the materials were prepared using SDS.

2.1. Materials

Fe $(NO_3)_3 \cdot 9H_2O$ (purity > 99.9%), SDS (purity > 90%), Triton X-100 (purity > 99%), and benzene (purity > 99.9%) were purchased from Merck, Germany. TOPO (purity > 98%) was purchased from Alfa Aesar, Germany. The phenolic resin precursor-based ACFs were purchased from Kynol Inc., Tokyo (Japan). Hydrogen (purity > 99.999%), zero air (purity > 99.999%), nitrogen (purity > 99.999%), and CCl_4 were purchased from Sigma Gases, India.

2.2. Synthesis of Fe-dispersed ACFs (Fe-ACFs)

The as-received ACFs samples were leached for 6 h in de-ionized (DI) water at 80 °C to leach out any undesirable ions from the ACFs surface to make it conducive to metal impregnation. After leaching, the wet samples were dried for 4 h in static air at room temperature (30 ± 5 °C), which was followed by oven-drying for 12 h at 120 °C. Approximately 1.5 g of the oven-dried ACFs sample was wrapped over a perforated glass tubular reactor and then vacuum-dried for 12 h at 200 °C to remove any entrapped gases from the pores of ACFs. After drying, the ACFs sample was slowly cooled to room temperature (30 ± 5 °C).

Fe$(NO_3)_3 \cdot 9H_2O$ salts were used as an iron precursor for preparing the Fe-ACFs. The impregnating solution of Fe$(NO_3)_3 \cdot 9H_2O$ was prepared in DI water at various molar concentrations (0.1–1 M) by the incipient wetness impregnation method [36]. The Fe