



## Effect of anodic alumina pore diameter variation on template-initiated synthesis of carbon nanotube catalyst supports

S. Sigurdson<sup>a</sup>, V. Sundaramurthy<sup>a</sup>, A.K. Dalai<sup>a,\*</sup>, J. Adjaye<sup>b</sup>

<sup>a</sup> Catalysis and Chemical Reaction Engineering Laboratories, Department of Chemical Engineering, University of Saskatchewan, 5 Campus Drive, Saskatoon, SK, S7N 5A9, Canada

<sup>b</sup> Syncrude Edmonton Research Centre, Edmonton, AB, T6N 1H4, Canada

### ARTICLE INFO

#### Article history:

Received 1 November 2008

Received in revised form 10 February 2009

Accepted 11 February 2009

Available online 21 February 2009

#### Keywords:

Carbon nanotubes  
Anodized alumina  
Pore diameter  
Catalyst support  
Hydrotreating

### ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) are a potential alternative to commonly used heterogeneous catalyst supports due to their high surface area, structural integrity, and controllable dimensional characteristics. Synthesis of MWCNTs with specific pore diameters can be achieved by chemical vapor deposition (CVD) of a carbon source onto an anodic aluminum oxide (AAO) template. AAO films consist of pore channels in a uniform hexagonal arrangement that run parallel to the surface of the film. These films are created by the passivation of an aluminum anode within an electrolysis cell consisting of certain weak acid electrolytes. A two-step anodization method has been developed to produce these templates. Changing the concentration of the oxalic acid electrolyte and the electrical potential of the electrolysis cell altered the structural characteristics of these AAO films, specifically the diameter of their pore channels. The AAO characteristics were examined by SEM analysis. Controlling the pore diameter of these templates enabled the pore diameter of MWCNTs synthesized by CVD to be controlled as well. After considering their thermal and structural stability, the produced MWCNTs were characterized by SEM, TEM, TGA–DTA, BET N<sub>2</sub> adsorption analysis, and DRIFT spectroscopy. Anodizing conditions of 0.40 M oxalic acid concentration and 40.0 V maximum anodizing potential were found to produce AAO films that resulted in MWCNTs with optimum surface characteristics for a catalyst support application. These MWCNTs with optimum pore diameters were synthesized for the purpose of being used as a support for NiMoS hydrotreating catalyst. This optimum grade of MWCNTs was found to produce the highest HDS and HDN activities when applied in the packed-bed processing of coker light gas oil.

© 2009 Published by Elsevier B.V.

### 1. Introduction

$\gamma$ -Alumina is the most commonly used support for industrially applied hydroprocessing catalysts. Its desirable properties include its strong mechanical and textural properties as well as the great dispersion it provides for active transition metals [1]. That being said, a negative aspect of  $\gamma$ -alumina is the strong chemical interaction that can exist between the alumina and the transition metal catalysts in their oxide phase. This can make the transition of the catalyst metal to its active phase a difficult procedure and can prevent the catalyst from reaching its maximum potential activity [2]. The opportunity presents itself to apply a catalyst support that can offer great dispersion of supported metals while providing limited interaction with the metals while they exist in the intermediate oxide phase.

From the time they were discovered by Iijima [3], the allotrope of carbon that has come to be known as carbon nanotubes (CNTs)

has sparked unprecedented interest from a wide variety of scientific fields. The simplest definition of CNTs is that they are graphitic crystal lattice sheets that possess manipulated sp<sup>2</sup> covalent bonds, allowing them to become encircled and form a cylindrical crystal structure. The methods for producing multi-walled carbon nanotubes (MWCNTs) are electric arc discharge, laser ablation, and chemical vapor deposition. Of these three methods, CVD is the most economically feasible and the most likely method to be scaled up to provide bulk production of MWCNTs. A basic description of this method is the cracking of a gaseous carbon source and the deposition of the carbon on a catalyst substrate at temperatures ranging from 650 to 900 °C. The properties of the MWCNTs synthesized by CVD method typically include inner diameters ranging from 10 to 100 nm, specific surface areas of 200–400 m<sup>2</sup>/g, and thermal resistance to air at temperatures up to ~650 °C under atmospheric conditions [4].

MWCNTs have garnered interest as potential heterogeneous catalyst support structures due to the resistance they possess to acidic/basic conditions, the possibility of controlling their porosity and surface chemistry, and the potential for allowing great dispersion of doped catalysts due to their high specific surface areas [5].

\* Corresponding author. Tel.: +1 306 966 4771; fax: +1 306 966 4777.  
E-mail address: [ajay.dalai@usask.ca](mailto:ajay.dalai@usask.ca) (A.K. Dalai).

Nitric acid treatments can create oxygen functionalities, such as hydroxyl and carboxyl groups, on the outer and inner walls of the MWCNTs necessary for depositing catalyst metals [6]. It is at these functional group sites that catalyst metals can become chemically adsorbed to the CNT surface while in the oxide active phase. The pore diameter (i.e. the inner diameter) of the nanotubes can be controlled by variation of the synthesis conditions used to produce the CNTs. Increasing the size of the pore diameters often lead to a decrease in the specific surface area of the substance. This creates the need to find an adequate balance between these two properties in order to find the optimum catalyst activity for a given reaction application.

When aluminum is anodized as part of an electrolysis cell in the presence of certain weak acid electrolytes – such as chromic acid, phosphoric acid, or oxalic acid – a porous anodic aluminum oxide (AAO) film develops on the surface of the anode. These porous films develop due to electrolytes which dissolve the resulting oxide film at an appreciable rate. The pores develop in a remarkably uniform hexagonal array of pore channels, with each channel separated by an aluminum oxide barrier [7]. These channel formations are made possible by the transport of aluminum and oxygen ions through an amorphous aluminum oxide barrier layer due to electric field conditions [8]. The electrolyte anions adhere to the anode and increase  $O^{2-}$  ion production at the barrier layer surface. Trivalent or divalent ions, such as the four aforementioned electrolytes, adsorb more readily than monovalent ions to the positively charged alumina surface. As water molecules also adsorb to the anode surface, hydrogen bonding occurs between the hydrogen atoms of the water molecules and the oxygen atoms of the oxyanions. The weakening of the bonds that make up the  $H_2O$  molecule result in the donation of  $O^{2-}$  ions from the water to the alumina barrier layer [9]. Of the four previously mentioned weak acid electrolytes, oxalic acid results in the production of thicker, more manageable anodic films that do not readily dissolve into the electrolyte solution [10].

In the last decade, AAO films have been implemented as templates for synthesizing many different types of functional nanostructured materials [11]. The first such use of these films for this application was in 1995, when Masuda and Fukada published a two-step anodization method for producing AAO film that is widely used today [12]. For any given AAO template application, it would be highly useful if the diameter of the pore channels could be controlled in order to achieve a desired pore structure. Zhao et al. [13] examined the change in the pore diameter and wall thickness of AAO film from varying the constant electrical potential of the cell, as well as from changes in the oxalic acid electrolyte concentration. The results of this study showed that the pore diameter of the films increased linearly with increases in the oxalic acid concentration and the anodizing voltage. It was found that low voltages (i.e. less than 30 V) resulted in disordered pore arrangements, while high voltages (i.e. beyond 60 V) resulted in wall cracking and pore merging. The above study suggests that the conditions for AAO growth can be tuned in order to produce a template for the synthesis of CNTs that can provide an optimum catalyst support structure.

There have been numerous studies performed based on the application of AAO films as templates for MWCNT synthesis [14–24]. The common link between each of these studies is the use of AAO template in place of a more typical catalyst substrate in a chemical vapor deposition process. The carbon that is deposited along the inner walls of the channels forms MWCNTs with outer diameters equivalent to that of the AAO pores. These reactions typically occur in a continuous gas flow quartz tube reactor at temperatures ranging from 550 to 800 °C. The pore diameters within the AAO templates applied in these studies varied from 30 to 230 nm. An observed trend was that templates in the absence of any catalyst substrate with pore diameters less than roughly 60 nm produced close-ended MWCNTs, while pore diameters more than roughly

60 nm produced open-ended nanotubes. For usage as a catalyst support, it would be beneficial for the MWCNTs to be open-ended to allow catalyst metals and reactant fluids to access the inner wall surface area of the tubes.

It was concluded after reviewing various MWCNT synthesis studies from AAO templates that there are three distinct advantages of using this method for producing CNT catalyst supports. These advantages are: (1) the capacity to synthesize open-ended nanotubes; (2) the lack of nanotube entanglement when synthesized due to parallel AAO pore channels; (3) the ability to directly control the diameter of the synthesized MWCNTs by varying the process parameters for AAO film production.

There have been a limited number of studies applying MWCNTs as a support for hydrotreating catalyst. The effectiveness of an MWCNT-supported CoMo sulfide catalyst was tested in one study based on the HDS of thiophene and the HDN of pyrrole [25]. The MWCNTs for this study were synthesized by CVD of  $CH_4$  or CO in the presence of a NiMgO catalyst precursor [26]. The inner diameters of these tubes ranged from 3 to 5 nm and were determined to have a specific surface area of approximately 140  $m^2/g$ . CoMo catalyst supported on these MWCNTs was found to have superior HDS and HDN activities when compared to an activated carbon support by using model feeds as a basis of comparison. A separate publication compared the HDS and HDA activity of MWCNT and  $\gamma-Al_2O_3$ -supported CoMo sulfide catalyst using a dibenzothiophene solution as a basis of comparison [27]. The MWCNT-supported CoMo catalyst was found to be slightly less active than the  $\gamma-Al_2O_3$  support. The MWCNTs used for this study had a reported specific surface area of 189  $m^2/g$  and pore diameter of 8.9 nm. Only one study was found that applied a “real world” feedstock (in this case, light gas oil derived from Athabasca bitumen) [2]. The MWCNTs used for this study were synthesized by a CVD method that used ferrocene as a metallic catalyst and toluene as a carbon source [28]. The CNTs produced from this method possessed inner diameters ranging from 10 to 15 nm and a specific surface area of 112  $m^2/g$ . The optimum metal loadings of Ni and Mo were found for this CNT support and its HDS and HDN activity was compared to a  $\gamma-Al_2O_3$  support with similar loadings. The MWCNT-supported catalyst displayed slightly higher HDS and HDN activity than the  $\gamma-Al_2O_3$ -supported catalyst when compared on a weight basis. When compared on a volume basis, the  $\gamma-Al_2O_3$  catalyst had slightly higher activity.

For each of the three applications of MWCNT supports for hydrotreating discussed, it should be noted that the inner diameters of the tubes were rather small, ranging from 3 to 14 nm. This would have made the pores possibly susceptible pore clogging due to coke deposition. It is also worth noting that the SEM and TEM images of the MWCNTs from the hydrotreating studies showed considerably twisted morphologies, leading to considerable entanglement and decrease to the accessible surface area. These three noted problems would be expected to be rectified through the application of the previously mentioned AAO template synthesis method.

After reviewing all available publications pertaining to the synthesis of MWCNTs using an anodic alumina template, no studies were found on the effect of varying the anodization conditions of AAO electrolysis has the physical properties of the resulting MWCNTs. Specifically, how varying the electrolyte concentration and anodization voltage during AAO synthesis changes the inner diameter, wall thickness, and BET properties (surface area, pore volume, and pore diameter) of the final CNT product. Furthermore, no studies were found where MWCNTs synthesized by this method were applied as a catalyst support in a packed-bed hydrotreating application. In this study, different grades of AAO templates were synthesized by varying both the oxalic acid concentration of the electrolyte solution and the maximum anodizing voltage of the electrolysis cell. The different AAO grades were characterized and then separately applied as templates for synthesis of MWCNTs by

Download English Version:

<https://daneshyari.com/en/article/67001>

Download Persian Version:

<https://daneshyari.com/article/67001>

[Daneshyari.com](https://daneshyari.com)