

Effect of pore diameter variation on CNT-supported catalyst activity for hydrotreating of coker light gas oil

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Introduction

At the beginning of any hydrotreating process, the loaded catalyst undergoes an initial period of catalyst deactivation. The principle cause of this catalyst deactivation is the deposition of a carbonaceous species (i.e. coke) on the catalyst surface [1]. After initially being deposited very rapidly, the coke eventually reaches a steady-state level within the reactor. A large loss in accessible surface area is also observed along with the rapid decline in catalyst activity. This can be attributed to the pores of the catalyst support, most commonly γ -alumina, being plugged by coke deposits and prohibiting reactants to access active sites within the pore volume [2]. Based on this theory, it can be concluded that applying a catalyst support with a large average pore diameter and a maintained high surface area could help minimize the detrimental effects of the precoking phase.

Multi-walled carbon nanotubes (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 & surface chemistry, and the potential for allowing great dispersion of doped catalysts due to their high specific surface areas [3]. 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 [4]. It is at these functional group sites that catalyst metals can become chemically adsorbed to the MWCNT 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 MWCNT synthesis conditions.

The primary objective of this research project is to examine the effect that the variation of MWCNT inner diameter has on NiMo/MWCNT sulfide catalyst. This will be done by examining the hydrotreating activity of each produced catalyst as well as by using characterization techniques to analyze the change in behavior of the catalysts. The determined activity of each catalyst is to be based on the extent of hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) conversion exhibited by coker light gas oil (CLGO) after undergoing hydrotreatment.

Materials and Methods

Through obtaining the objectives of this research, parameter variation is being performed to determine the settings that provide the best hydrotreating catalyst activity. This is being performed for each of the three processes being used for this research project. The first is anodized aluminum oxide (AAO) template synthesis via electrolysis within a cooled oxalic acid cell. The second process synthesizes carbon nanotubes (CNTs) via chemical vapor deposition (CVD) of C_2H_2 on AAO templates. The third and final process is the hydrotreating of CLGO within a trickle bed reactor.

Results and Discussion

From the progress made thus far, AAO films with varying pore channel diameters were successfully grown by changing the parameters of energy potential and oxalic acid concentration in an anodization process. This was confirmed by performing SEM analysis on the surface of the AAO films. By applying these films as templates for MWCNT synthesis, CNTs were produced with inner diameters varying from approximately 60 to 80 nm as determined by TEM analysis. After performing nitric acid treatment on the surface of the CNTs in order to create functional groups, it was found via DRIFT spectroscopy that the allocated treatment time was sufficient to allow for carboxyl groups to be created on the surface of the CNTs. The variation of the inner diameters of the CNTs did not affect their thermal integrity, as was verified by TG analysis. For each grade of nanotubes produced, an initial oxidizing or decomposition temperature from their exposure to air flow was found to be approximately 590°C. The highest rate of CNT oxidation in each case was found to occur at a system temperature of 630°C. The surface characteristics of the CNTs were found to be significantly affected by changes in the structure of the AAO templates. From N_2 desorption/adsorption analysis, the analytically determined pore diameters were up to 70 nm less than those observed in the TEM images, possibly indicating a significant number of the tubes were close-ended. From the 9 different grades of AAO templates that were studied (oxalic acid concentrations of 0.30 M, 0.40 M, and 0.50 M were tested with maximum voltage profiles of 40.0 V, 50.0 V, and 60.0 V), the templates grown at a 40.0 V maximum potential and a 0.40 M oxalic acid concentration were found to result in CNTs with the most desirable structural characteristics. Specifically, CNTs with a 229 m²/g BET surface area, a 0.658 cc/g single-point pore volume, and an 11.5 nm average pore diameter were achieved from AAO templates grown under these conditions. It can be concluded from these results that these anodizing conditions would result in CNTs most applicable as a catalyst support.

From the CNTs produced with varying inner diameters due to the changing characteristics of the AAO templates, 4 grades of NiMo/MWCNT catalyst were produced with varying pore sizes. The metal loadings for each catalyst were kept constant at 2.5 wt% Ni and 13 wt% Mo. The average CNT inner diameters for each catalyst were measured from TEM images and were determined to be 67 nm, 57 nm, 71 nm, and 76 nm for the four grades of catalyst. The results of this analysis showed that the 67 nm inner diameter CNT support, which was made up of CNTs produced from the optimum anodization settings, exhibited the highest HDS and HDN activities of the four catalysts. At steady-state, the catalyst produced HDS and HDN conversions of 78% and 41%, respectively, at a reactor temperature of 370°C and at standard industrial operating conditions. Future work will include metal loading optimization, catalyst characterization, and kinetic studies for CNT supports possessing this average inner diameter.

References

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