

Carbon Nanotubes As A Premium Catalyst Support Material

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Carbon nanotubes are a special carbon material having a highly graphitic nature and nanoscale dimensions. These tubular filaments were first observed from steam cracker when electron microscopes came into wide use around 1950s [1], however, intentional synthesis of carbon nanotubes in bulk quantity wasn't successful till 1983 [2]. Without formal presentation, this invention was mostly unknown to the open public. These synthetic graphite fibrils have the morphology similar to those later made by Iijima using arc-discharge method in 1991 [3], but unlike the buckytubes, they are produced as aggregates uncontaminated with amorphous carbon or other graphitic non-tubular structures. Since 1991, intense interest on carbon nanotubes has risen exponentially due to their perceived novel physical and chemical properties as well as huge potential in many technological applications. The studies on applying carbon nanotubes as commercial catalyst support materials are, however, very limited partially due to their availability and concern of manufacture cost. A few studies have been reported in the literatures on hydrogenation of nitrobenzene [4], hydroformylation [5] and selective hydrogenation [6,7].

It is well acknowledged that both electronic and structural features of small metal clusters can significantly differ from those of bulk metal when the particle size decreases down to several nanometers. The choice of support materials becomes more important because of their capability of conveying to a catalyst thermal stability, high surface area and optimizing it for a particular process. Compared to conventional support materials, carbon provides some unique advantages such as mechanic and thermal stability, chemical inertness, etc [8]. Currently, carbon is used as catalyst support in a variety of chemical and refinery processes. Activated carbon supported precious metal has been applied extensively in the reactions such as liquid phase hydrogenation, carbonylation, and hydrochlorination, etc. In some cases of severe reaction conditions, carbon becomes the only choice for the support medium because oxides like silica dissolve in strong acidic or basic environment. When carbon nanotubes are used as catalyst support, the dimensions of nanotubes should stabilize fine dispersions of catalytic nanoparticles since the radius of curvature of an 8-nm diameter nanotube will limit the size of a stable particle that can be supported on it at nanoscale dimensions. Furthermore, carbon nanotubes can be oxidized to yield high concentration of various surface oxygenated groups [9,10], which provide control of surface hydrophilicity or hydrophobicity and access to a wide range of anchoring sites for deposition or nucleation of catalyst precursors using standard impregnation or ion exchange techniques.

Carbon nanotubes used in this study were FIBRIL™ Nanotubes, made commercially by Hyperion Catalysis International Inc. The surface area of fibril nanotubes is ~250-300 m²/g measured using BET method. This area is consistent with calculated geometric surface area and the density of nanotubes (ca. 1.9-2.0 g/cm³), taking into account the hollow core (~3 nm), confirming that the measured surface area is wholly exterior geometric surface. In addition, the micropore (pore size < 2 nm) volume and area of these nanotubes are less than 0.01 cc/g and 1 m²/g respectively. As compared to the total pore volume (1~1.5 cc/g) and surface area,

the contribution by micropore is negligible. In a separate investigation, carbon nanotubes were found exhibiting easier filterability as compared to commercial activated carbons.

Various reactions including hydrogenation, isomerization, and hydrodesulfurization over carbon nanotubes supported noble metals, metal carbides and nitrides were investigated in the current study. It was discovered that carbon nanotube supported catalysts exhibited excellent performance in many categories. The high electrical conductivity associated with carbon nanotubes opens up the possibility of altering the electronic balance of metal-support system, which in turn could influence the chemisorption, bond rupture of adsorbed reactant molecules, and consequently changing the selectivity. The ability to create virtually micropore-free supports make carbon nanotubes even more attractive for some particular reactions when steric factor becomes rate limiting.

Finally, carbon nanotubes have been further converted into other support materials with controlled porosity. For example, Si carbide nanotubes/nanorods can be prepared using carbon nanotubes as precursor [11,12]. The geometric shape and porosity of carbon nanotubes were retained in the newly formed materials. This creates a potential for making a broad range of catalyst support materials with controlled morphology and improved physical properties.

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