

CARBON NANOTUBES AS A PREMIUM CATALYST SUPPORT MATERIAL

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Introduction

Carbon nanotubes are a special carbon material having a highly graphitic nature and nanoscale dimensions. These tubular filaments were first observed 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-tube 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. 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 [8,9], 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. In this paper, a comprehensive investigation of applying carbon nanotubes as support for noble metals and metal carbides will be discussed.

Experimental

Carbon nanotubes used in this study were FIBRIL™ Nanotubes, made commercially by Hyperion Catalysis International Inc. The raw material (Purity > 99%) was first activated

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with nitric acid to generate abundant surface functional groups. Palladium nitrate purchased from Alfa Chemical was then impregnated or ion-exchanged onto nanotube surface with various metal loadings. Carbon nanotube-supported transition metal carbide catalysts, primarily Mo and W carbides, were prepared via a proprietary technique [10]. Mo or W precursor was first deposited on carbon nanotubes, and the mixture was then subject to a controlled calcination and reduction process to form Mo or W carbide phases. Catalytic activities of these samples were evaluated in several model reactions such as hydrogenation of cyclohexene and nitrobenzene, and hydrodesulfurization of thiophene.

Results and Discussion

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). 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.

Carbon nanotube supported noble metal catalyst

Pd particles were found to support on carbon nanotubes in a highly dispersed state with average particle size of 1.7 nm at 1 wt%, and 2.5 nm at 5 wt% loading respectively. Catalytic activities of supported Pd catalysts were evaluated with comparison to a commercial Pd catalyst supported on activated carbon made by Precious Metal Corporation. As shown in the Fig.1, with the same loading and particle sizes, Pd catalyst exhibited nearly doubled activity in cyclohexene hydrogenation on carbon

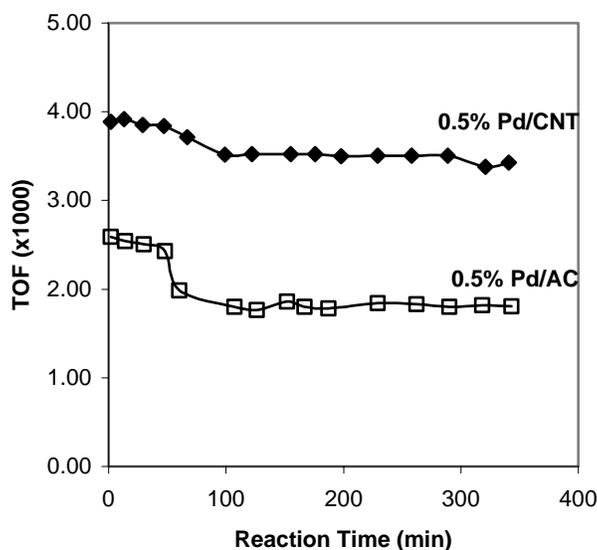


Figure 1. Comparison of catalytic activities of Pd/CNT versus Pd/AC (PMC catalyst) during hydrogenation of cyclohexene.

nanotubes than on activated carbon. The structural and electronic impact from the carbon nanotube substrate was linked to this enhanced catalytic performance.

Carbon nanotube supported metal carbide catalyst

When used as support medium for Mo and W carbides, carbon nanotubes were found being served not only as a reducing agent but also as a structural template. Two distinct morphologies of Mo carbide were obtained through manipulation of process parameters, namely highly dispersed carbide particles (3~8 nm), and highly porous freestanding assemblages of stoichiometric Mo carbide nanorods. It was also discovered that carbon nanotubes offered superior advantages to form nanoscale Mo carbides as compared to other carbonaceous materials such as graphite and activated carbon. When these materials were used to make supported Mo carbides, the reaction produced much larger particles with mixed molybdenum phases. This sequence of these events was consistent with the notion that a strong interaction between MoO_3 and carbon nanotube support induced a spontaneous dispersion of Mo oxides so as to form nanoscale oxide and carbide particles.

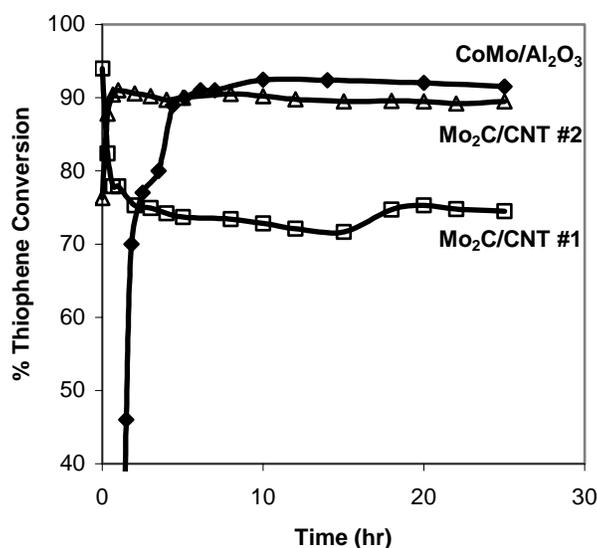


Figure 2. Vapor phase HDS of thiophene at 400°C over $\text{Mo}_2\text{C}/\text{CNT}$ catalysts as compared to $\text{CoMo}/\text{Al}_2\text{O}_3$ catalyst.

As shown in Fig.2, the nanoscale Mo carbide catalysts exhibited promising catalytic activities during hydrodesulfurization of thiophene. A steady turnover rate of 2.4 h^{-1} was observed with a CNT-supported catalyst at 400°C after 24 hours, which was the highest among those reported in the literature under similar conditions [11]. Although the bulk carbide phase was retained during reaction as indicated from X-ray diffraction, the surface information revealed by X-ray photoelectron spectroscopy indicated decreased carbide signal intensity with simultaneous emergence of S^{2-} species after the reaction. Thus it is clear that a thin layer of sulfided Mo was generated on the surface of carbide nanoparticles and attributed as the active phase for the reaction. Further modification of our catalyst formulation substantially enhanced the catalytic activity and stability, which

became essentially comparable to those of an alumina supported Co-Mo catalyst. The selectivity towards alkene was, however, improved significantly, which can have great implication of lowering hydrogen consumption and energy saving.

Conclusions

Carbon nanotubes have proved to be a premium support material for a variety of catalysts including noble metals, transition metals and transition metal carbides, nitrides or derivatives thereof. Carbon nanotube-supported catalysts possess better thermal and mechanical properties as compared to those supported on activated carbon and are free of micropores. The nanoscale dimensions of carbon nanotubes can enable the formation of either highly dispersed catalyst particles or rigid porous assemblages of catalyst nanorods. A possible electronic effect-induced catalyst-support interaction could further enhance catalytic performance in term of selectivity.

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