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R&D NOTE

Spent FCC Catalysts: An Untapped Resource of Carbon Nanotubes?

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Introduction

In this work, we explore the possibility of using the existing petroleum refinery infrastructure for the large-scale synthesis of carbon nanotubes (CNTs). In this context, we define large-scale as being of the order of 10,000 tons of CNTs per plant per year. Coke deposition on heterogeneous catalyst surfaces, generally in the form of amorphous, graphitic or filamentous carbon,[1] leads to catalyst deactivation in many hydrocarbon processes. For several decades research focused on eliminating coke formation on catalyst surfaces; more recently, however, the interesting physical and chemical properties of filamentous carbon were realized, and the industrial applications of these are now being explored in detail. Carbon filaments with graphene planes parallel to the axis of the fiber are termed nanotubes (CNTs), while those with herringbone or stacked structures are known as nanofibers (CNFs).[2] On the basis of publication frequency, CNTs with predefined structure and functionality already play a central role in the field of nanotechnology,[3] and will become increasingly important as large-scale synthesis techniques are further developed. While CNFs and CNTs are currently produced commercially via catalytic chemical vapor deposition (CVD), for example, Hyperion Catalysis International (USA), Showa Denko (JPN), Thomas Swan and Co. (UK), and Nanocyl (Belgium), the CNTs produced are less graphitized than those produced via arc discharge.[4] The degree of graphitization in a nanotube is a common measure of CNT quality. Therefore, there remains a trade-off between quality and quantity, because arc discharge production methods are inherently difficult to scaleup, for example, due to vacuum conditions and batch processing.

Currently, the limited supply of CNTs impedes both research and the development of mass consumer applications, and, thus, there is an urgent requirement to develop large-scale synthesis processes. A promising technique for CNT synthesis, which is easily scalable, is fluidized-bed catalytic chemical vapor deposition (FBCVD).[5] This is analogous to fluidized-bed catalytic cracking (FCC) technology used in the petroleum industry for manufacturing petroleum products. Hence, we feel there is value in examining whether the existing refinery infrastructure can be utilized for large-scale CNT production. In this work, we report for the first time, CNTs observed on the surface of spent FCC catalysts, that is, those discarded at the end of their useful life. We contend that this supports the idea of using FBCVD as a viable large-scale technique for CNT production; if a suitable catalyst, optimized for nanotube synthesis, was used in place of the traditional FCC catalyst, the existing infrastructure could be utilized with few modifications for the large-scale supply of CNTs.

Samples of spent FCC catalyst were sourced from a commercial petroleum refinery operating in Sydney, Australia. Typically, spent FCC catalyst is an off-white, free-flowing powder, between 50 μm and 70 μm in dia., which has undergone several reaction-regeneration cycles before being discarded. The samples analyzed here were "unregenerated". The chemical composition of the spent catalyst (measured using electron dispersive X-ray analysis) was 95% alumina, silica, magnesium oxide and kaolin, approximately 2 wt % transition metal oxides, for example, iron, nickel and vanadium; carbon and rare earth oxides made up the balance. The as-received sample was characterized using; (1) transmission electron microscopy (TEM), and (2) thermogravimetric analysis coupled with mass spectrometry (TGA/MS).

For the TEM studies, 100 mg of the as-received powder was mixed with 10 mL of dimethylformaldyhide solution (Sigma-Aldrich), and subjected to ultrasonication (Branson S450) for five minutes. One drop of the supernatant mixture

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was loaded onto a 200 mesh copper TEM grid, dried overnight and examined at 120kV (Philips CM120). TEM images of the surface of individual particles show that much of the carbon present is in the form of spherical particles (Figure 1a) and fibers (Figure 1b). However, CNTs between 10 nm and 20 nm in dia., and lengths largely in the submi-

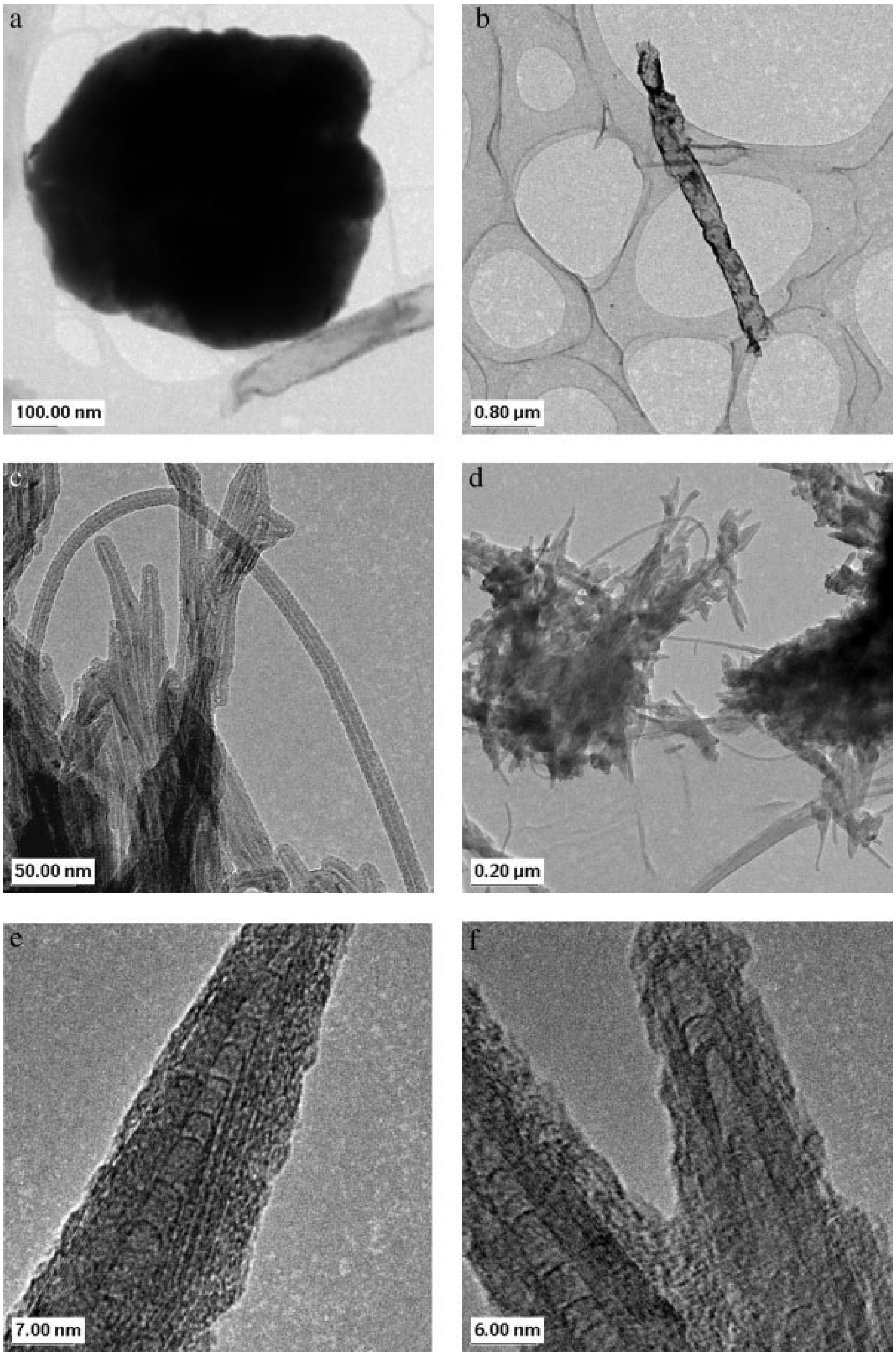

Figure 1. TEM images of carbon nanomaterials present in samples of spent fluidized-catalytic cracking (FCC) catalyst.

These included; (a) amorphous carbon particles, (b) nanofibers, and (c) nanotubes. Most of the CNTs have short lengths in the submicron region, and are coated with amorphous carbon. Figure 1d shows filamentous and amorphous carbon engulfing a catalyst particle rendering it inactive. Magnification of the tip of the nanotubes. Figure 1e and f shows single-sheet shell conical-shaped terminations, which are similar to CNTs prepared via arc discharge.[6]

cron region were also observed (Figure 1c,d). We note that the CNTs present were generally of low-quality, but interestingly, had "cone-shaped" terminations with single-sheet shells, similar to CNTs prepared via arc discharge.[6]

TGA/MS (TA Instruments SDT Q600, Thermostar GSD301) was used to investigate the quantity of carbon in the as-received samples. 20mg of spent catalyst was loaded into an alumina crucible, and then oxidized in a 5% O_2/Ar mixture, at heating rates of 5°C/min, 10°C/min and 20°C/min. Effluent-gas analysis by mass spectrometry showed an increase in the mass numbers 44, 43, 28 and 27, during each run typically between 250 and 400°C; this is indicative of carbon oxides. The overall weight loss suggested a total carbon content of 1%. There was insufficient sensitivity in the mass loss signals to accurately determine the quantity of carbon nanotubes in the sample.

These observations support the notion that the large-scale synthesis of CNTs using a similar fluidised-bed process is possible by "optimizing" the conditions required for their growth, that is, using a catalyst that is designed to promote carbon growth rather than retard it. Even without this, however, at the annual turnover rate of spent FCC catalyst (reported to be approximately 750,000 metric tons[7]) there is the equivalent of 7.5 metric tons of CNTs produced yearly by petroleum refineries, which is currently "lost", assuming that 0.1% of the carbon material synthesized is CNTs. While the degree of graphitisation of these CNTs is inferior to those synthesized by arc discharge techniques, they might well be suitable for lower end applications, for example, in sporting equipment.

We note also that recovering CNTs present at 0.01% per unit weight of catalyst is challenging using existing purification techniques. However, an "optimized" FBCVD process would potentially be capable of producing six to 10 times the active (metal) catalyst weight in CNTs.[8] Nonetheless, comparatively few researchers have investigated the growth of CNTs specifically using a fluidized bed. We argue that more research is necessary to optimize both the synthesis and purification processes.

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