

PHYSICAL ACTIVATION OF MULTI-WALLED CARBON NANOTUBES FOR HYDROGEN STORAGE

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Introduction

As energy demand increases throughout the world, the need for clean energy sources, that do not impact the urban air quality as well as the global climate, increases accordingly (1). Hydrogen has been touted as the fuel to satisfy this future energy need due to its very benign combustion product, namely water. However, several questions remain as to how this will be accomplished. Storage of this energy gas is a vital element of the proposed “hydrogen economy.” There are several options for hydrogen storage under research, including alloys and intermetallics, sodium and lithium alanates, nanocubes, and carbon nanotubes (2). In particular, carbon nanotubes may provide the highly anticipated answers to the challenging hydrogen storage quest due to its potential to form a light-weight storage material that can satisfy the 6-7 wt% benchmark storage target set by Department of Energy (3). Although unaltered carbon nanotubes are capable of adsorbing some H₂, activating nanotubes can substantially increase the potential for adsorption (4). Accordingly, this paper focuses on the activation of multi-walled carbon nanotubes with physical agents such as carbon dioxide gas and oxygen.

Experimental

The multi-walled nanotube sample was obtained from Nanostructured & Amorphous Materials, Inc. The activation was conducted at 550°C under a flow of carbon dioxide or air. The surface area was measured using a Micromeritics ASAP 2000 under N₂ at 77K. A thermogravimetric analyzer, Cahn TGA-151, was used to conduct pressure-composition isotherm measurement studies of the hydrogen absorbed where the pressure and time related uptake of hydrogen and the associated kinetics was followed as a function of the modified composition of the activated carbon nanotubes. During a typical hydrogen adsorption test about 200 to 400 mg of sample is placed into the analyzer and degassed using helium or nitrogen gas. Following degasification the system is pressurized to the desired pressure using dry H₂ gas. While reaching the desired pressure the sample is held isothermal at room temperature and the weight change of the sample is monitored. Any increase in weight is attributed to an uptake of H₂ into the sample.

Results and Discussion

Figure 1 shows the changes in surface area after activation in air at 550°C for a multi-walled carbon nanotube sample. As the MWNT sample is activated with air up to

10 minutes there is a 50% increase in the surface area of the resultant activated sample compared with the original MWNT. Beyond 10 minutes activation there is a significant decrease in overall surface area from about 140 m²/g at 10 minutes down to about 10 m²/g at 20 minutes. The results indicate that air attacks the MWNT selectively leaving behind metallic catalyst and amorphous carbon that yield very little surface area compared to the carbon nanotubes. From TEM analysis on the pristine MWNT it was estimated that the sample was about 20 to 30% pure MWNT with the remainder being mainly amorphous carbon. The weight loss for the 10 minutes activated sample was about 10% indicating that about 1/3 to 1/2 of the carbon nanotube structure has been oxidized at this point. After 20 minutes close to 20 wt% was lost corresponding to the low surface area of the resulting sample. The results suggest that MWNT can easily be activated using air or oxygen.

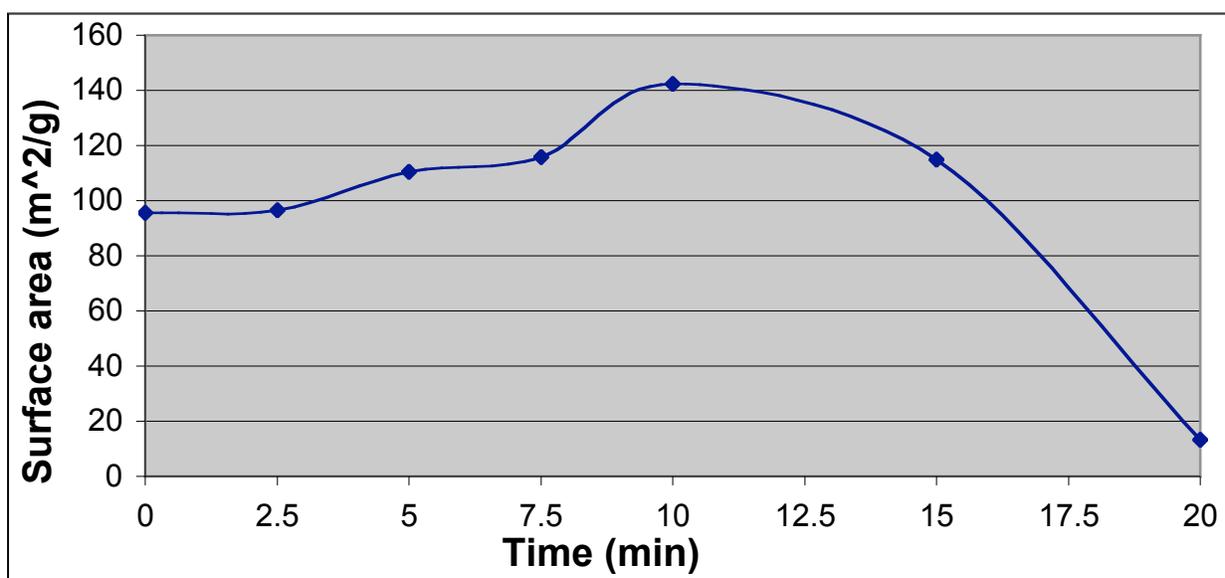


Figure 1. Activation of multi-walled nano-tubes in air at 550°C.

Figure 2 shows the MWNT activated in carbon dioxide at 550°C up to 960 minutes. After the first 100 minutes very little change in the surface area has occurred although about 10 wt% of the sample has been lost. This indicates that oxidation using carbon dioxide may preferentially attack the amorphous carbon at shorter activation times. Extending the activation time to 250 minutes resulted in an 18 wt% loss and a 35% increase in the surface area suggesting that the MWNT are being activated. The difference in activation for air (Figure 1) and CO₂ (Figure 2) indicates that there is a great potential for physical activation of MWNT to generate activated samples for hydrogen storage with various adsorption sites.

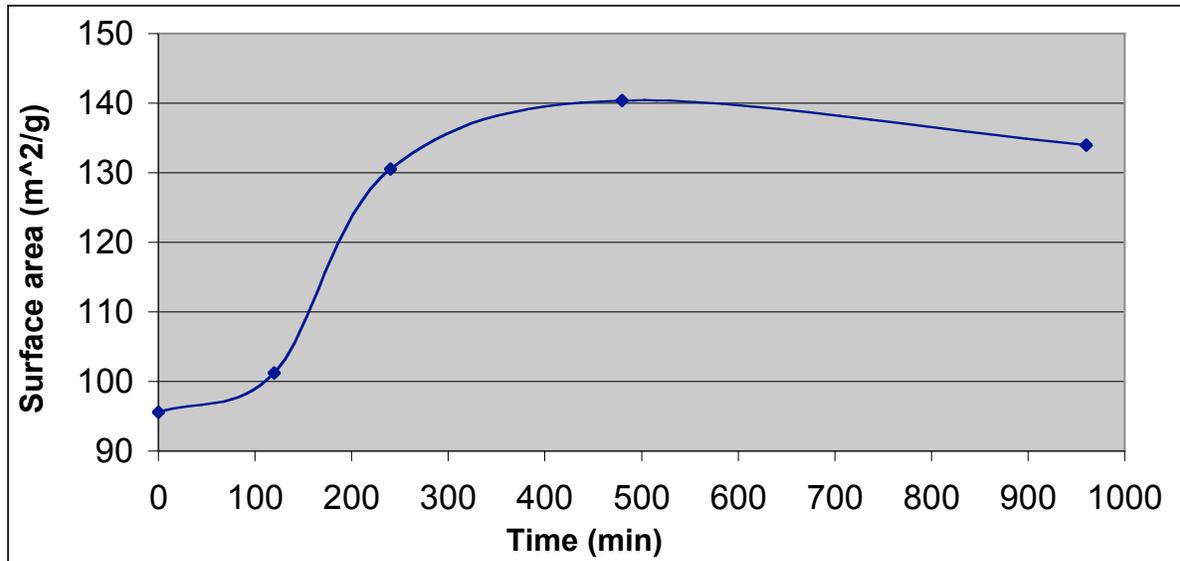


Figure 2: Activated multi-walled nano-tubes in CO₂ at 550°C up to 960 min.

Conclusions

Figure 1 indicates that the MWNT structure is made accessible for hydrogen storage using air activation at relatively low temperatures. Typical MWNT structures are several nanometer thick with about 20-30 layers of carbon. Hence, most of the carbon is therefore not accessible for hydrogen adsorption due to encapsulation by the outer layer. Further, the extreme length of the multi-walled carbon nanotubes compared to their diameter is limiting the storage of hydrogen within the MWNT themselves. Hence, liberating the structure through partial oxidation as shown above can significantly introduce hydrogen adsorption sites in MWNT.

References

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