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Determination the Hydrogen Stored in Carbon Nanotubes by NO Titration Method

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Abstract: A novel method was established to determine the H_2-storage capacity in carbon nanotubes. According to $2NO+2H_2$ (or 4H) = N_2+2H_2O reaction, the H_2-storage capacity in carbon nanotubes could be calculated. The H_2-storage capacity in carbon nanotubes is at least 2.89 wt%.

Keywords: NO, titration, hydrogen storage, carbon nanotubes.

With the diminution of fossil fuel resources and the increase in pollution, energy and environment have become a public concern. Mankind is in need of a new but clean energy resource. The use of hydrogen appears to be the answer. One of the technical challenges in hydrogen utilization is H_2-storage. At present, materials for storing hydrogen are alloys such as $LaNi_5$ and FeTi; the storage capacity is around 1.4 wt%, too low for practical application. Another problem with these alloys is that they turn into powder due to volume changes that occur in absorption and desorption. Since the discovery of carbon nanotubes (CNTs) in 1991, scientists have devoted a lot of attention on this material and many reports have been published. Recent studies are mainly focused on applications. Dillon *et al.*[1] speculated that the H_2-storage capacity of pure Single-Walled CNTs is 5-10 wt% (133 K, 0.04 MPa); there was only 0.1% Single-Walled CNTs in their samples and they reported that H_2 can be absorbed at room temperature. Chambers *et al.*[2] reported a 67 wt% H_2-storage capacity (25°C, 120 atm) of carbon nanofibers. Ye *et al.*[3] reported that the H_2 absorption capacity of Single-Walled CNTs was 8.25 wt% (80 K, 100atm). Liu *et al.*[4] reported a H_2-storage capacity of 4.2 wt% (25°C, 10 MPa). Chen *et al.*[5] reported that at ambient pressure, a lithium-based Multi-Walled CNTs could store 20 wt% of H_2 in the 473-653 K range whereas a potassium-based one can adsorb 14 wt% at room temperature. However, Yang[6] pointed out that the results of Chen *et al.* are unreliable due to the presence of H_2O and Li_2O (or LiOH hydrates) but agreed that lithium addition could enhance the H_2-storage capacity.

Up to now, the results among the reports on H_2-storage over single- and multi-walled CNTs are inconsistent; inevitably causing controversies[7-9]. Why there are so much discrepancies in the measurements of H_2-storage? There are a number of reasons. First, the CNTs materials studied were different in texture and diameter. Second, the error is large and the uncertainty lies on the determination methods that are based on weight or pressure changes. Since the CNTs samples examined were in small quantities (a few mg) and the hydrogen densities were small, trace amount of impurities in the H_2 source would cause large errors in gravimetric methods; this is especially so if the impurity is water. For methods based on pressure measurement, the error could be large as well. Based on our previous work[10], according to the $NO+H_2$ (or 2H)$\rightarrow H_2O+\frac{1}{2}N_2$ reaction, the H_2-storage capacity can be determined by the NO-titration method. The reaction is conducted at 573 K. At this temperature, CNTs would not be oxidized. None has reported this method before.

The CNTs material was synthesized *in situ* by means of CH_4 decomposition on reduced-$LaCoO_3$ at 973 K. The CNTs was first purified in a HCl solution at 353 K for 2 h, and then dried at 373 K and calcined in air at 773 K for 4 h.

The typical feed gas containing 60000 ppm NO in He was passing through 30 mg of catalyst at a total flow rate of 20 $mL\cdot min^{-1}$ (regulated by a Tylan mass flow controller) in a downward manner. The sample was first heated in a H_2 or He flow at 573 K for 120 min and subsequently purged with He for 30 min before the feed gas was introduced.

The effluent was analyzed on-line by chromatography (GC) using a thermal conductivity detector.

Figure 1 shows NO conversion *versus* reaction time and **Figure 2** shows N_2 activity *versus* reaction time.

Figure 1 NO conversion *versus* reaction time at 573 K

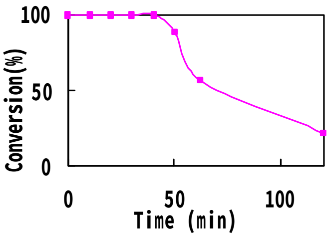
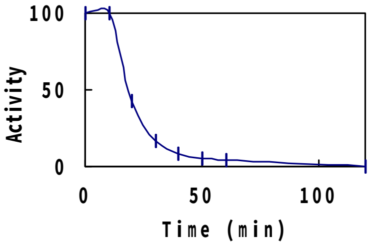


Figure 2 N_2 activity *versus* reaction time at 573 K



NO conversion and N_2 activity are defined as follows:

$$\text{NO conversion (\%)} = 100 - \frac{\text{NO detected in outlet}}{\text{NO in the feed gas}} \times 100$$

$$N_2 \text{ activity (\%)} = \frac{N_2 \text{ detected in experiment}}{\text{The theoretical amount of } N_2 \text{ by NO decomposition in feed gas}} \times 100$$

On He-pretreated sample, no N_2 was observed, so we ascribe the generation of N_2 to the reaction between stored hydrogen and NO.

From **Figure 1** and **Figure 2**, we can obtain that at the first 10 minutes, NO in the feed gas was completely reduced to N_2 by hydrogen stored in the CNTs. We calculate the H_2–storage capacity based on the following formula expression:

$$2NO+2H_2=N_2+2H_2O$$

$$n_{\text{H2-storage}} = \frac{\text{NO concentration}\times\text{feed gas flow rate}\times\text{reaction time}}{\text{NO molecular weight}}$$

$$= \frac{\dfrac{60000\ \text{ppm}\times 20\ \text{mL}\cdot\text{min}^{-1}\times 10\ \text{min}\times 101325\times 720}{10^{6}\times 8.314\times 285\times 760}}{30}$$

$$=4.86\times 10^{-4}\ (\text{mol})$$

$$H_2\text{-storage in CNTs (wt\%)} = \frac{n_{\text{H2-storage}}\times 2}{\text{CNTs weight}}\times 100$$

$$= \frac{4.86\times 10^{-4}\times 2}{33.6\times 10^{-3}}\times 100$$

$$= 2.89$$

This method was more accurate than the methods of weight or pressure change, it is not influenced by the impurities such as a little water or oxygen. The result was convincible, and this field is still in need of further investigation.

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