

RESEARCH NOTE

Hydrogen Spillover from a Metal Oxide Catalyst onto Carbon Nanotubes—Implications for Hydrogen Storage

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Hydrogen storage on multiwalled nanotubes (MWNTs) was dependent on the degree of catalyst removal. At atmospheric pressure, removal of the catalyst decreased the uptake from 0.6% to below detection limits. Hydrogen uptake of the metal oxide catalyst ranged from 0.25 to 0.98%, depending on surface area. Normalization by metal content and temperature-programmed desorption studies suggest hydrogen dissociation and subsequent spillover to the MWNT. Metal-support interactions were key to the spillover; dry mixing of the MWNT and catalyst did not enhance storage, whereas *in situ* production increased storage by 40%. The moderate temperature range of this material suggests a novel material for hydrogen storage applications. © 2002 Elsevier Science (USA)

Key Words: hydrogen storage; carbon nanotubes, multi-wall; metal oxides.

INTRODUCTION

Although much excitement was generated when Dillon *et al.* first reported that single-walled carbon nanotubes (SWNTs) had the potential to store up to 5–10% hydrogen at moderate temperatures and pressures (1), the excitement has somewhat waned as recent claims of hydrogen storage capacities for carbon materials have fallen short of the U.S. Department of Energy (DOE) target of 6.5% by weight. Claims that have exceeded the DOE target for carbonaceous materials have not been reproducible by other laboratories (2–4). In other hydrogen uptake studies, three common features exist: slow uptake, partial irreversibility of adsorbed species, and the use of transition metals in synthesis (Fe, Co, or Ni) which may not be completely removed during purification. Hydrogen spillover from metals to carbon surfaces is well documented (5, 6). *Ab initio* molecular orbital studies show that adsorption of hydrogen atoms is exothermic and stable on the graphite basal plane (7). The preliminary work presented here shows strong

experimental evidence that the residual catalyst present in the system participates in hydrogen adsorption.

METHODS

Multiwalled carbon nanotubes (MWNTs) were synthesized using a procedure similar to that developed by Chen *et al.* (8). In brief, a Ni_{0.4}Mg_{0.6}O catalyst was first reduced in 100 ml of hydrogen/min for 15 min, then reacted with 200 ml of methane/min at 650°C in a vertical flow reactor or *in situ* on the thermogravimetric analyzer (TGA). For the MWNT produced externally, the catalyst was removed by dissolution in 6 M HNO₃ either at room temperature (MW-H) or by acid reflux (MW-HR) prior to the hydrogen uptake experiments. The MWNTs were examined with a JEOL 4000 EX high-resolution transmission electron microscope (HRTEM) operated at 400-kV accelerating voltage and a Phillips XL30 FEG scanning electron microscope (SEM). An estimate of the local metal composition was made using the energy-dispersive X-ray spectroscopy detector on the SEM. The metal composition for the acid-treated MWNTs was measured by neutron activation analysis using P-tube irradiation for magnesium analysis and in-core irradiation for nickel. The metal composition for the MWNTs produced *in situ* (MW-TGA) was determined from the normalized weight gain. A Micromeritics ASAP 2010 was used to conduct surface area measurements using standard BET methods with nitrogen at 77 K.

Hydrogen adsorption experiments were performed on a Shimadzu thermogravimetric analyzer. For *in situ* MWNT production, 10 mg of the catalyst was loaded onto the quartz sample holder and treated until a predetermined MWNT yield was obtained, as evidenced by the mass gain of the sample. For the acid-treated carbon fibers, 20 mg of MWNT was pretreated by hydrogen reduction for 1 h at 700°C. In both cases, the samples were then cooled in hydrogen to room temperature at 5°C/min, maintained at room temperature for 1 h, then reheated at a rate of 5°C/min. The TGA experiment was a dynamic, rather than equilibrium,

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measurement. Temperature-programmed desorption experiments were conducted by varying the heating rate from 1 to 10°C/min. Residual water was removed from the analysis gas via an activated carbon bed maintained at 77 K. The total flow rate of analysis gas was 100 ml/min; a separate set of experiments confirmed that this flow rate was sufficient to eliminate external mass transfer limitations. All weight gains/losses reported are after correction by a quartz blank calibration; temperature calibrations were made using a standard copper sulfate method.

RESULTS AND DISCUSSION

HRTEM and SEM micrographs have been used to confirm the presence of MWNTs; the outer diameter of the MWNTs is fairly consistent at 15 nm, while the inner diameter ranges from 2 to 8 nm (Fig. 1). The metal content of the different MWNT samples is summarized in Table 1; room-temperature acid treatment left residual catalyst (MW-H), whereas no residual metal was detected for the sample treated by acid reflux (MW-HR). The SEM micrographs show that the residual metal oxide for the MW-H sample was evenly distributed along the length of the nanotube. The SEM micrographs also indicate that the tubular carbon nanotubes remained intact after both acid treatments.

A comparison of the TGA hydrogen adsorption experiments for the nanotube samples versus the original catalyst shows that the catalyst is a necessary component for hydrogen uptake under the nonequilibrium experimental conditions (Fig. 2). Removal of the catalyst by acid reflux (MW-HR) eliminates hydrogen uptake when compared to

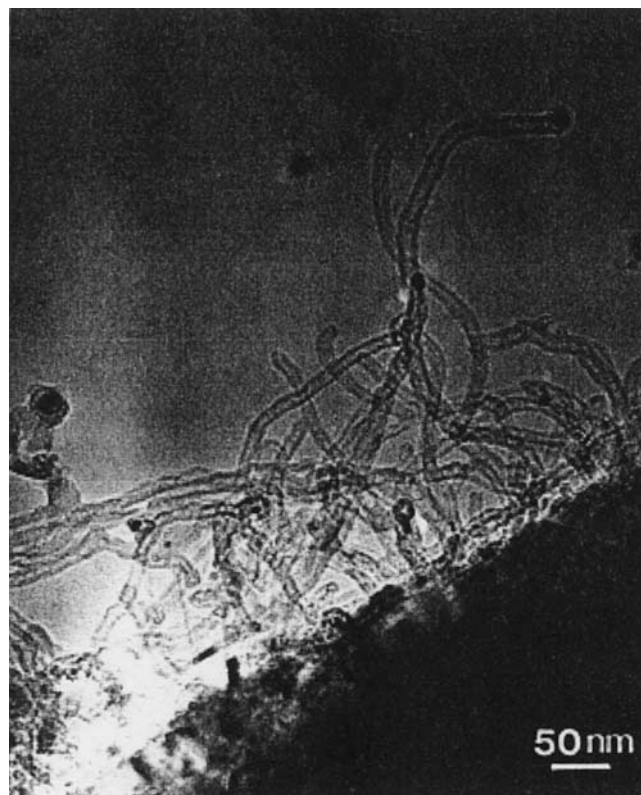


FIG. 1. Transmission electron micrograph of MWNTs as prepared.

the 0.6–0.7% uptake by the nanotubes with residual catalyst (MW-H). Although the hydrogen uptake of the catalyst is not as extensive as the nanotube–catalyst sample, the two sorbents have qualitatively similar behavior. This can

TABLE 1

Comparison of Hydrogen Uptake for Catalyst Vs MWNT Samples

Sample	Description	Ni content (wt%)	Mg content (wt%)	BET surface area (m ² /g)	H ₂ uptake (g/g)	H : O atomic ratio (est)
MW-H-726	MWNT treated in 6 M HNO ₃	17.4 (NAA)	1.9 (NAA)	184	0.65%	1.38
MW-H-727	MWNT treated in 6 M HNO ₃	17.7 (NAA)	2.2 (NAA)	184	0.58%	1.23
MW-HR	MWNT treated in 6 M HNO ₃ at 200°C	ND (EDX)	ND (EDX)	93.3	ND	ND
Catalyst						
MWGO-0100	Catalyst used to make MW-H and MW-HR	43.4	27.0	ND	0.25%	0.13
MWGO-1000	Increase catalyst surface area by varying heat treatment	43.4	27.0	3.9	0.47%	0.25
MWGO-0201	Increase catalyst surface area by varying heat treatment	43.4	27.0	19.9	0.98%	0.51

Note. NAA, measured by neutron activation analysis; EDX, measured by electron dispersive X-ray on SEM.

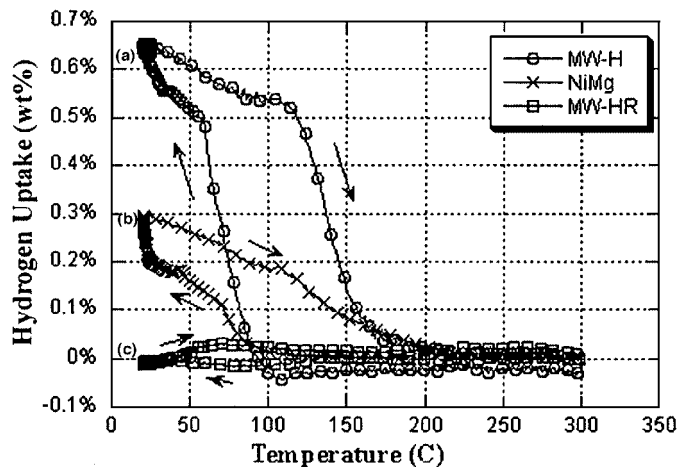


FIG. 2. TGA adsorption profile for (a) an acid-treated MWNT (MW-H), (b) the $\text{Ni}_{0.4}\text{Mg}_{0.6}\text{O}$ catalyst, and (c) the MWNT with extended acid treatment to remove the residual catalyst (MW-HR). The data has been normalized by subtracting the mass of a quartz blank.

be explained by the increase in catalyst surface area on acid-deposition on the nanotube surface, as observed in SEM micrographs. The TGA experiment was not designed to be an equilibrium measure; thus, the available surface area of the active component will affect the rate of hydrogen uptake. Varying the catalyst surface area using different calcination conditions has provided additional evidence for this: increasing the catalyst surface area fivefold doubled the hydrogen uptake (Table 1). However, the increase in hydrogen uptake cannot be solely attributed to an increase in surface area, as discussed below.

It is not surprising that the metal oxide catalyst would participate in hydrogen uptake, as both magnesium oxides and dilute transition metal–magnesium oxides are active in hydrogen exchange reactions (9, 10). It should also be noted that the conditions under which the samples were treated were not sufficient to reduce the bulk of the metal oxide, as evidenced by X-ray diffraction data (data not shown). On the ionic crystal lattice structure of metal oxides, hydrogen molecules are thought to dissociate into a proton and a hydride, associated with the anion and cation, respectively (9). However, pretreatment of MgO as well as NiO–MgO solutions at elevated temperatures and/or in the presence of hydrogen atoms may form active catalytic centers corresponding to a lattice vacancy populated by an electron (10). These results may also provide a basis with which to reinterpret and optimize other hydrogen storage measures in light of any residual catalyst present in the system; the use of transition metals in nanotube synthesis is common, in arc-discharge as well as catalytic vapor decomposition methods.

The hydrogen storage capacity of a metal oxide at equilibrium is not expected to be competitive with current hydrogen adsorbents based on stoichiometric calculations.

However, the possibility of using active catalytic sites to dissociate hydrogen, which can then freely migrate to the catalytic support, is a somewhat novel idea for reaching DOE hydrogen storage targets. If the hydrogen uptake reported here is normalized per catalyst lattice site (estimated from the metal content), the hydrogen storage in the nanotube–catalyst sample (MW-H) surpasses that of the pure catalyst (Table 1). Treating the catalyst *in situ* to produce MWNTs provides an additional hydrogen reservoir and increases the uptake by 40%; dry mixing of the MWNTs and the catalyst did not increase hydrogen uptake (Table 2). Thus the MWNTs appear to provide an additional hydrogen storage reservoir when there are appropriate catalyst–support interactions. By optimizing not only the properties of the catalyst but also the catalyst–support interactions and the conditions of hydrogen spillover, the hydrogen storage capacity of the metal oxide catalyst will be increased.

Temperature-programmed desorption TPD experiments for the MW-H system result in a desorption activation energy of 97 kJ/mol (Fig. 3). Although the Redhead analysis used to obtain this number is merely an estimate, the magnitude suggests a chemisorption process. The value of 97 kJ/mol was less than that calculated from a Redhead analysis of TPD experiments with the pure NiMgO catalyst, which resulted in a desorption activation energy of 115 kJ/mol. This suggests that hydrogen is more loosely bound to the carbon of the MW-H sorbent than to the catalyst. The desorption activation energy for the MW-H is less than the 113 kJ/mol theoretical value for H atoms on the basal plane of planar graphite (7). The catalyst-free system (MW-HR) did not have substantial hydrogen uptake when compared to the nanotube–catalyst system. This suggests that the metal oxide acts to dissociate hydrogen, which is then free to migrate to the surface of the MWNT. This is consistent with the results of Yang and Yang (7) which show that hydrogen atoms are stabilized on the graphite lattice.

The hydrogen uptake reported here is moderate when compared to other reported results, but it should be emphasized that these results are at atmospheric pressure. Hydrogen spillover is proportional to the square root of pressure (5); thus we expect the MW-H sample to be competitive

TABLE 2
Comparison of Hydrogen Uptake for Dry Mixing
Vs *In Situ* Production

Description	Mixing method	MWNT content (wt%)	H ₂ uptake (g/g)	H:O atomic ratio (est)
NMGO-1000		0.0	0.47%	0.25
MW10Cat	Dry	4	0.43%	0.24
MC50Cat	Dry	15	0.41%	0.25
MW201a	Dry	100	0.03%	ND
MW-TGA	<i>In Situ</i>		0.65%	0.36

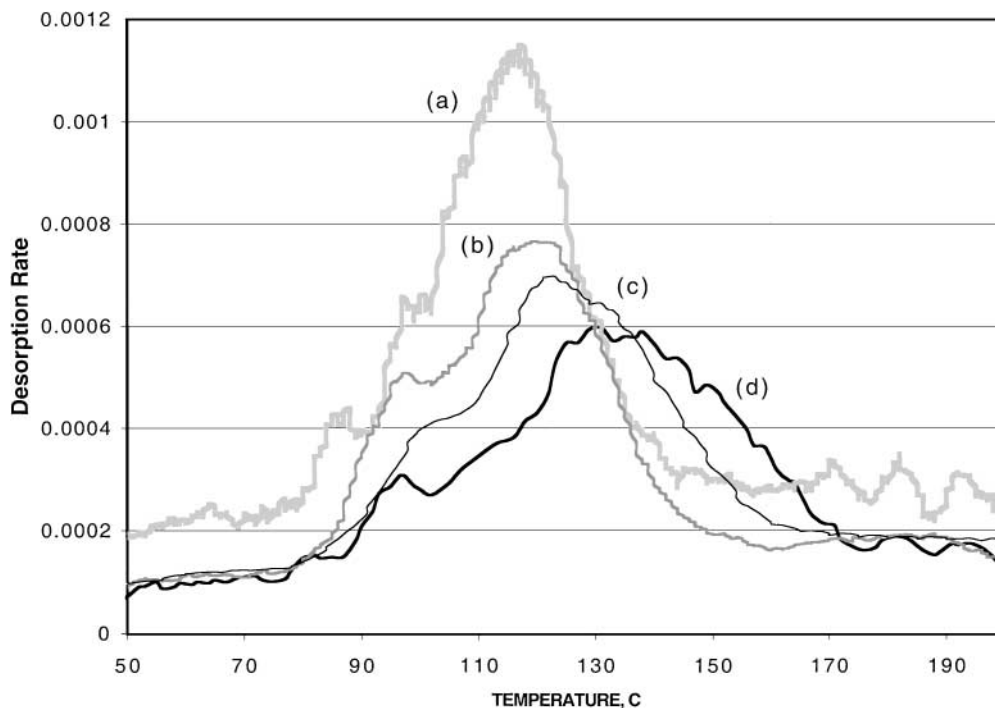


FIG. 3. Temperature-programmed desorption experiments of the acid-treated nanotubes containing residual catalyst (MW-H) showing the shift of the maximum desorption temperature with heating rate: (a) 1°C/min; (b) 2.5°C/min; (c) 5°C/min; and (d) 10°C/min. Redhead analysis of this data resulted in a desorption activation energy of 97 kJ/mol.

under high-pressure conditions. When attempting high-pressure experiments, it will be necessary to reproduce the pretreatment conditions that result in the final metal dispersion and metal-support interactions. In addition, exposure to oxygen may inactivate the active centers on the metal oxide (9). The chemical and thermal treatments are key in producing chemical bridges between the nanotube and the metal oxide catalyst; chemical bridges enhance the rate for spillover (5, 6, 11).

Perhaps the most important feature of the observed hydrogen uptake for both the MW-H and NiMgO catalyst samples is that the process is reversible at moderate temperatures (Fig. 2). This suggests that the system has operating advantages over both metal hydrides and cryogenic physisorption onto carbaceous materials. Optimization of hydrogen spillover to the MWNT surface will increase the total hydrogen storage capacity on a total weight basis. In the current case, the active temperature range for adsorption is between 25 and 100°C. Desorption begins at approximately 100°C and initial results indicate that the onset of desorption is a function of pretreatment conditions. Thus, the results show strong promise for potential hydrogen storage materials, namely the elimination of cryogenic conditions and the reduction of the necessary desorption temperature.

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