



US007951749B2

(12) **United States Patent**
Yang et al.

(10) **Patent No.:** **US 7,951,749 B2**
(45) **Date of Patent:** **May 31, 2011**

(54) **ENHANCING HYDROGEN SPILLOVER AND STORAGE**

(75) Inventors: **Ralph T. Yang**, Ann Arbor, MI (US);
Yingwel Li, Ann Arbor, MI (US);
Anthony J. Lachawiec, Jr., Ann Arbor, MI (US)

(73) Assignee: **The Regents of The University of Michigan**, Ann Arbor, MI (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 128 days.

(21) Appl. No.: **11/820,954**

(22) Filed: **Jun. 21, 2007**

(65) **Prior Publication Data**

US 2010/0019196 A1 Jan. 28, 2010

Related U.S. Application Data

(63) Continuation-in-part of application No. 11/442,898, filed on May 30, 2006.

(60) Provisional application No. 60/751,744, filed on Dec. 19, 2005, provisional application No. 60/725,337, filed on Oct. 11, 2005.

(51) **Int. Cl.**

B01J 20/08 (2006.01)

B01J 20/20 (2006.01)

(52) **U.S. Cl.** **502/415**; 502/417

(58) **Field of Classification Search** 502/415,
502/417

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,314,857	A *	5/1994	Koontz	502/258
6,297,185	B1 *	10/2001	Thompson et al.	502/101
6,559,094	B1 *	5/2003	Korotkikh et al.	502/326
6,596,055	B2 *	7/2003	Cooper et al.	95/116
6,596,243	B1 *	7/2003	Fujii et al.	422/177
6,930,193	B2	8/2005	Yaghi et al.	

OTHER PUBLICATIONS

Dillon, et al., "Storage of Hydrogen in Single-Walled Carbon Nanotubes", *Nature*, vol. 386, Mar. 27, 1997, pp. 377-379.

Ye, et al., "Hydrogen Adsorption and Cohesive Energy of Single-Walled Carbon Nanotubes", *Applied Physics Letters*, vol. 74, No. 16, Apr. 19, 1999, pp. 2307-2309.

Wang et al., "Computer Simulations of Hydrogen Adsorption on Graphite Nanofibers", *Journal of Physical Chemistry B*, vol. 103, No. 2, Jan. 14, 1999, pp. 277-281.

Liu, et al., "Hydrogen Storage in Single-Walled Carbon Nanotubes at Room Temperature", *Science*, vol. 286, Nov. 5, 1999, pp. 1127-1129.

Chen, et al., "High H₂ Uptake by Alkali-Doped Carbon Nanotubes Under Ambient Pressure and Moderate Temperatures", *Science*, vol. 285, Jul. 2, 1999, pp. 91-93.

Yang, Ralph T., "Hydrogen Storage by Alkali-Doped Carbon Nanotubes—Revisited", *Carbon*, 38 (2000), pp. 623-626.

Dillon, et al., "Hydrogen Storage Using Carbon Adsorbents: Past, Present and Future", *Appl. Phys. A* 72 (2001), pp. 133-142.

Tibbetts, et al., "Hydrogen Storage Capacity of Carbon Nanotubes, Filaments, and Vapor-Grown Fibers", *Carbon* 39 (2001), pp. 2291-2301.

Cheng, et al., "Mechanism of Hydrogen Sorption in Single-Walled Carbon Nanotubes", *J. Am. Chem. Soc.* 2001, 123, pp. 5845-5846.

Simonyan, et al., "Hydrogen Storage in Carbon Nanotubes and Graphitic Nanofibers", *Journal of Alloys and Compounds*, 330-332 (2002), pp. 659-665.

Lueking et al., "Hydrogen Spillover From a Metal Oxide Catalyst onto Carbon Nanotubes—Implications for Hydrogen Storage", *Journal of Catalysis* 206 (2002), pp. 165-168.

Chambers et al., "Hydrogen Storage in Graphite Nanofibers", *The Journal of Physical Chemistry B*, vol. 102, No. 22, May 28, 1998, pp. 4253-4256.

Ahn et al., "Hydrogen Desorption and Adsorption Measurements on Graphite Nanofibers", *Applied Physics Letters*, vol. 73, No. 23, Dec. 7, 1998, pp. 3378-3380.

Park et al., "Further Studies of the Interaction of Hydrogen With Graphite Nanofibers", *J. Phys. Chem. B*, 1999, 103, pp. 10572-10581.

Gupta et al., "Further Studies on Microstructural Characterization and Hydrogenation on Behaviour of Graphite Nanofibers", *Intl. J. of Hydrogen Energy* 26 (2001), pp. 857-862.

Browning et al., "Studies into the Storage of Hydrogen in Carbon Nanofibers: Proposal of a Possible Reaction Mechanism", *Nano Letters* 2002, vol. 2, No. 3, pp. 201-205.

Lueking et al., "Hydrogen Storage in Graphite Nanofibers: Effect of Synthesis Catalyst and Pretreatment Conditions", *Langmuir* 2004, 20, pp. 714-721.

Chahine et al., "Low-Pressure Adsorption Storage of Hydrogen", *Intl. J. Hydrogen Energy*, vol. 19, No. 2 (1994), pp. 161-164.

Lamari et al., "Thermal Effects in Dynamic Storage of Hydrogen by Adsorption", *Environmental and Energy Engineering*, vol. 46, No. 3, Mar. 2000, pp. 632-646.

Orimo et al., "Hydrogen in the Mechanically Prepared Nanostructured Graphite", *Applied Physics Letters*, vol. 75, No. 20, Nov. 15, 1999, pp. 3093-3095.

Yang et al., "Ab Initio Molecular Orbital Study of Adsorption of Atomic Hydrogen on Graphite: Insight into Hydrogen Storage in Carbon Nanotubes", *Carbon* 40 (2002), pp. 437-444.

Khoobiar, S., "Particle to Particle Migration of Hydrogen Atoms on Platinum-Alumina Catalysts From Particle to Neighboring Particles", *Notes*, vol. 68, No. 2, Feb. 1964, pp. 411-412.

Sinfelt et al., "Kinetic Evidence for the Migration of Reactive Intermediates in Surface Catalysis", *Migration of Intermediates in Surface Catalysis*, Nov. 5, 1963, pp. 3365-3367.

Connor, Jr. et al., "Spillover in Heterogeneous Catalysis", *Chem. Rev.* 1995, 95, pp. 759-788.

Srinivas et al., "Direct Observation of Hydrogen Spillover on Carbon-Supported Platinum and Its Influence on the Hydrogenation of Benzene", *J. of Catalysis* 148, (1994), pp. 470-477.

Lueking et al., "Hydrogen Spillover to Enhance Hydrogen Storage—Study of the Effect of Carbon Physicochemical Properties", *Appl. Catalysis A: General* 265 (2004), pp. 259-268.

Boudart, et al., "On the Slow Uptake of Hydrogen by Platinized Carbon", *Journal of Catalysis* 18 (1970), pp. 46-51.

Levy et al., "The Kinetics and Mechanism of Spillover", *Journal of Catalysis* 32 (1974), pp. 304-314.

(Continued)

Primary Examiner — Stuart Hendrickson
(74) *Attorney, Agent, or Firm* — Dierker & Associates, P.C.

(57) **ABSTRACT**

Methods for enhancing hydrogen spillover and storage are disclosed. One embodiment of the method includes doping a hydrogen receptor with metal particles, and exposing the hydrogen receptor to ultrasonification as doping occurs. Another embodiment of the method includes doping a hydrogen receptor with metal particles, and exposing the doped hydrogen receptor to a plasma treatment.

7 Claims, 4 Drawing Sheets