Novel Organometallic Fullerene Complexes for Vehicular Hydrogen Storage

A.C. Dillon, E. Whitney, C. Engtrakul, C. J. Curtis, K.J. O'Neill, P.A. Parilla, L.J. Simpson, M.J. Heben, Y. Zhao, Y-H. Kim and S. B. Zhang

National Renewable Energy Laboratory, 1617 Cole Blvd, Golden, CO 80401, USA

Theoretical studies have predicted that scandium may bind to the twelve five-membered rings in C_{60}. It would then be possible to stabilize four dihydrogen ligands (H_2) on each Sc atom with a binding energy of ~ 30 kJ/mol, with a ~7.0 wt% reversible hydrogen capacity(*1*), ideal for vehicular hydrogen storage. However, wet chemical synthesis of the calculated η^5-coordinated fullerene complex is unprecedented. The chemistry of C_{60} is generally olefinic (i.e., η^2-coordination, in which the metal is coordinated to two carbon atoms contributing two electrons to the bonding). Another theoretical investigation has suggested that the lithium fulleride, $Li_{12}C_{60}$, may be promising for onboard vehicular hydrogen storage applications(*2*). In this study, the Li atoms are centered over each of the twelve five-membered rings in C_{60}, and hydrogen is stored with a capacity of ~ 9 wt% and a reversible binding energy of ~ 7 kJ/mol. However, again experimental challenges in synthesizing this molecule are anticipated as Li generally clusters in the octahedral voids of the fcc lattice of C_{60} crystals.

Recently we have probed new synthetic techniques in order to coordinate C_{60} with either Fe, Sc, Cr, Co or Li. The new compounds were characterized with ^{13}C solid-state nuclear magnetic resonance, Raman spectroscopy, electron paramagnetic spin resonance, transmission electron microscopy and nanoprobe energy dispersive x-ray spectroscopy. All of the structures were found to have unique binding sites for hydrogen employing the technique of temperature programmed desorption. Furthermore, the $Fe(C_{60})$ complex has a reversible hydrogen storage capacity of 0.5 wt% at 77 K with an H_2 overpressure of 2 bar (with unaltered C_{60} having an undetectable hydrogen capacity). The extensive characterization techniques indicate that C_{60}-Fe-C_{60}-Fe-C_{60}-chain structures of an undetermined length are formed and that η^5-coordination is demonstrated. Interestingly, the specific surface area of the $Fe(C_{60})$ compound is only ~ 50 m^2/g indicating that a mechanism other than surface physisorption may be occurring. A $Li_{12}C_{60}$ compound has also been synthesized. In good agreement with the theoretical studies, the experimentally determined hydrogen binding energy for the compound is approximately 7 kJ/mol. However, the reversible capacity at 77 K and 2 bar is only ~ 0.3 wt%. The difference between the experimental and theoretical capacity is attributed to significant differences in structure. Collectively however, these results suggest that synthesis of organometallic fullerene complexes should be further explored for vehicular hydrogen storage applications.

1. Y. Zhao, Y.-H. Kim, A. C. Dillon, M. J. Heben, S. B. Zhang, *Physical Review Letters* **94**, 155504 (2005).
2. Q. Sun, P. Jena, Q. Wang, M. Marquez, *JACS* **128**, 9741 (2006).