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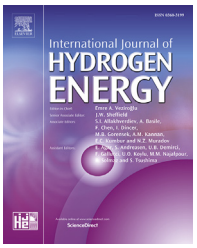

Thermodynamic assessment of carbazole-based organic polycyclic compounds for hydrogen storage applications via a computational approach

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ABSTRACT

Liquid organic hydrogen carriers (LOHCs) are promising candidates for storage and transport of renewable energy due to their reversible reaction characteristics. For the proper assessment of candidate molecules, various thermochemical properties are required, and significant experimental efforts are necessary. In this work, we suggest a systematic method for the estimation of thermochemical properties for LOHC candidate molecules combining Density Functional Theory (DFT) calculations, Conductor-like Screening Model (COSMO) and Molecular Dynamics (MD) simulations. We applied the suggested method for the assessment of previously reported LOHC materials. Based on the analysis, new candidates of carbazole-derivative compounds (*N*-acetylcarbazole, *N*-phenylcarbazole, *N*-benzoylcarbazole, and 4-methyl-4H-benzocarbazole) are suggested, and their properties are estimated and reviewed. Calculation results show that these candidates can provide high theoretical hydrogen uptake capacities above 6 wt% and optimal heats of dehydrogenation in the liquid phase. Analysis on the stereoisomerism showed that the structure-selectivity toward less stable stereoisomers of the hydrogen-rich form is preferable for the dehydrogenation process.

Introduction

Hydrogen storage is one of the essential elements of technologies for utilizing renewable energy systems. Recently, liquid organic hydrogen carriers (LOHCs) have received increasing attention because they can store a significant amount of hydrogen via a catalytic chemical reaction under ambient conditions compared with high-pressure gas compression or low-temperature cryogenic hydrogen storage [1]. Moreover, the use of LOHCs is economically beneficial because LOHCs have similar thermo-physical properties (*e.g.*,

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density, viscosity, heat capacity) to diesel oil, and thus current infrastructures for transportation can be used [2].

Thermochemical properties of LOHCs such as reaction enthalpy and equilibrium constants are essential for the initial design of hydrogen storage systems because they determine the maximum possible efficiency of the system. The thermochemical properties targets suggested by Müller et al. [3] are as follows: (1) the optimal range of enthalpy of dehydrogenation is from 39.78 to 58.60 kJ/mol H_2 and (2) negative Gibbs free energies for hydrogenation and dehydrogenation are preferable at the reaction conditions.

The enthalpies of dehydrogenation for liquid organic hydrides (*i.e.*, hydrocarbons) such as methylcyclohexane are above 67 kJ/mol H_2, typically requiring a high dehydrogenation reaction temperature around 300 °C [4]. One strategy to overcome the problem of the high reaction temperature is to incorporate heteroatoms (*i.e.*, N, S, O, B) into the molecular structure. *N*-ethylcarbazole is one of the well-known compounds for a LOHC, and a reversible reaction is possible at a low temperature ranging from 120 to 180 °C [5,6]. The presence of an *N*-heteroatom in the 5-membered ring decreases the enthalpies of dehydrogenation compared with hydrocarbon materials with similar structures like dodeca-hydrofluorene [7]. Also, ammonia borane (AB), a compound containing boron (B) and nitrogen (N), has been considered as a potential hydrogen storage candidate due to its high hydrogen storage capacity up to 19.6 wt % [8]. Campbell et al. [9] proposed BN heterocyclic compounds (N-*R*-1,2-dihydro-1,2-azaborane, R = H, Me, *t*-Bu) and demonstrated that the spent fuel of BN heterocyclics could be converted to fully hydrogenated materials under ambient conditions. Recently, Li et al. [10] proposed 2-methylindole as a potential substance for chemical hydrogen storage because of its low melting point and fast kinetic reaction rate compared with *N*-ethylcarbazole. Forberg et al. [11] developed a lignin-based energy storage system. They synthesized octahydrophenazine from a lignin hydrogenolysis product and ammonia and demonstrated that phenazine is a promising candidate suitable for reversible hydro/dehydrogenation reactions with high storage capacity.

Assessment of LOHCs requires comprehensive reviews of thermodynamic properties. Arlt and coworkers [3,12] reported surveys on thermodynamic properties LOHCs including *N*-ethylcarbazole and amine borane-based compounds. They also published studies on carbazole and *N*-alkylcarbazoles, which are helpful for understanding the influence of alkyl-chain length on the thermodynamic characteristics [13,14]. Such review of thermodynamic properties requires a significant amount of experimental efforts.

Development of estimation technology using thermodynamic correlations and molecular-modeling enables us to reduce efforts in the screening of candidate LOHCs among millions of components. In this paper, we propose a systematic computation-based estimation for thermodynamic properties of LOHCs and assessment scheme by comparing the hydrogen storage capacity, melting point, enthalpies of dehydrogenation, and Gibbs free energy of dehydrogenation in the gas phase. In the proposed method, molecular configurations were constructed by Density Functional Theory (DFT) methods, and enthalpies of dehydrogenation in the gas phase were computed. Heat effects associated with phase change were estimated by the COSMO-RS method or thermodynamic correlations. Finally, molecular dynamics (MD) simulations predicted densities of components, which are closely related to the volumetric storage capacities. Based on the analysis of thermochemical properties of seven components previously reported (Table 1), we further suggested additional carbazole-based candidate molecules (acetylcarbazole, phenylcarbazole, benzoylcarbazole, and 4-methyl-4H-benzocarbazole) and properties were evaluated using the same manner. The proposed method can be used for assessment of any candidate molecule at the early stage of development.

Computational details

Density functional theory calculation

Atomic arrangement and electronic structures of candidate LOHC molecules were calculated using DFT method implemented in the DMol^3 program [15]. Three types of exchange-correlation functionals (GGA-PBE [16], mGGA-TPSS [17], Hybrid GGA-B3LYP [18]) were used to compare the feasibility of calculating the enthalpies of dehydrogenation in the gas phase. The atomic orbitals were composed of double and triple numerical basis sets plus polarization functions (DNP, TNP). All core electrons were explicitly included for relativistic effects. The Grimme dispersion correction model [19] was used in all cases to describe long-range electron correlations. The SCF convergence criterion was within 1.0×10^{-6} Hartree per atom.

In many cases, a component can be locally stable for several conformers. We used the following procedure to obtain the structure of conformers. Initial structures of conformers were generated by the Boltzmann jump method where molecular torsion angles were randomly changed, and then the generated structures were optimized with the COMPASS force field [20]. Five conformers which have lower energies were selected, and they were further optimized by density functional theory (DFT) calculations. For carbazole-derivatives, the hydrogen-rich form of the hydrogen carriers may have different configurations of hydrogen in the 5-membered ring depending on the surface condition of the catalyst. Morawa Eblagon et al. [21] reported three stereoisomers when *N*-ethylcarbazole was fully hydrogenated, as shown in Fig. 1 (Stereoisomers type A, type B, and type C). For simple comparison of properties, as shown in Table 1, stereoisomer A was only used for calculations. For reaction equilibrium calculations of newly suggested carbazole derivatives (perhydro-*N*-ethylcarbazole, -acetylcarbazole, -phenylcarbazole, -benzoylcarbazole, and 4-methyl-4H-benzocarbazole), all three possible configurations were used in the calculations.

Vibrational frequencies were calculated to determine the thermochemical properties using the harmonic oscillation approximation. Most quantum chemical calculation methods (including DFT and Hartree-Fock) overestimate the zero-point vibrational energy (ZPVE) because the anharmonicity effect is neglected [22]. One of the strategies to adjust vibrational frequencies is to introduce a scaling factor (0.89–1.06) into the vibration energy [23]. Many ZPVE scale factors have been reported and evaluated for various functionals such as BLPY,

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