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Density Functional Theory and Reaction Thermodynamics: Assessment of new Molecules for the Liquid Organic Hydrogen Storage Technology

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PURPOSE OF THE ABSTRACT

As global warming is forcing our societies out of fossil fuels, new carbon-free energy vectors such as dihydrogen (H2) are developed, and new forms of storage must follow accordingly. Indeed, despite exhibiting the highest energy density per unit of mass of all chemical fuels, H2 is the lightest molecule in the Universe, challenging our current storage technologies.1,2

Liquid organic hydrides also known as Liquid Organic Hydrogen Carrier (LOHC) are promising as they promote the use of an easily transportable (liquid) recyclable intermediate to store vast amounts of H2 (TWh of energy) in a condensed and controllable fashion (chemical binding) over a long period of time (year).3 H2 can be released at will through a dehydrogenation of the H2-rich intermediate, yielding the H2-poor intermediate, which can be used to close the cycle. Whilst several couples such as Methylcyclohexane/Toluene, 18H-Dibenzyltoluene/Dibenzyltoluene or 12H-N-Ethylcarbazole/N-Ethylcarbazole are already well studied in the literature, the determination of other suitable couples is still under investigation.4?6 Indeed, the dehydrogenation energy cost of the state-of-the-art LOHC couples as well as their synthesis from non-renewable feedstock are issues left to be tackled.7

Herein we use Density Functional Theory (DFT) to describe the energy levels of new potential LOHC molecules and the reaction thermodynamics of the hydrogenation/dehydrogenation. In this framework, we assess various possible intermediates through their thermodynamic properties, characterizing the enthalpy as the energy needed for their dehydrogenation reaction. The appropriate methodology is benchmarked for a class of compounds containing C, H, O and N atoms by computing the reaction energy for known LOHC couples and new couples are modelled thereafter.

A new potential carrier is proposed, with properties on par with the state-of-the-art LOHC couples with advantages on the eco/toxicological safety and potential production by renewable feedstock.8 Preliminary results show great promises for the heterogeneously catalysed hydrogenation and features different side reactions during the dehydrogenation depending on the nature of the catalyst. The mechanism and limitations of the side reactions are then rationalized. The comparison between DFT-modelling and experiment of the reaction enthalpy is also addressed to appraise its value for the development of the LOHC technology.

FIGURES

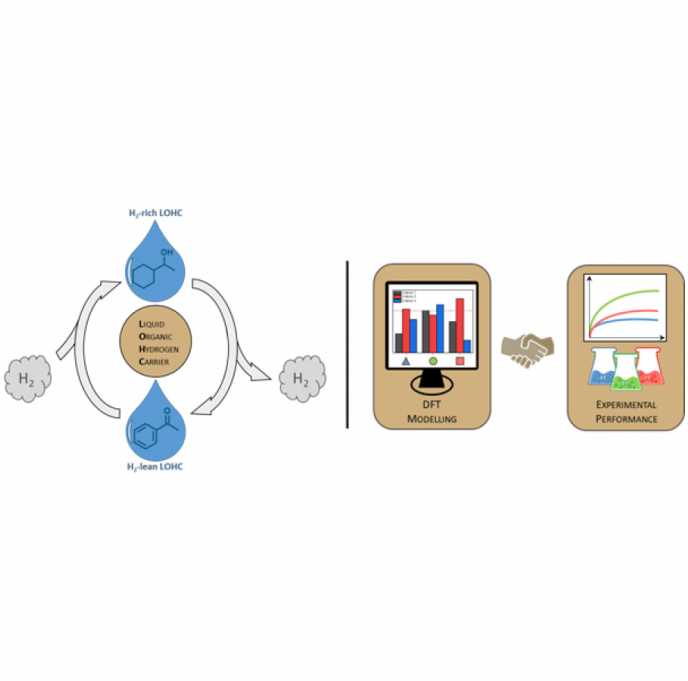

FIGURE 1

Combining the computational and experimental approaches to assess new potential Liquid Organic Hydrogen Carriers (LOHC)

Left: LOHC cycle with the new couple 1-Cyclohexylethanol/Acetophenone

Right: Combining computational and experimental approachs

FIGURE 2

KEYWORDS

LOHC | Hydrogen | Hydrogen storage | DFT

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