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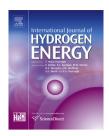
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2016) 1-17



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Review Article

An overview of organic liquid phase hydrogen carriers

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ARTICLE INFO

Article history:
Received 22 February 2016
Received in revised form
20 July 2016
Accepted 20 July 2016
Available online xxx

Keywords:
Hydrogen carriers
Hydrocarbons
Hydrogen content
Enthalpy of dehydrogenation
Methylcyclohexane

ABSTRACT

An overview study for assessing the feasibility of using organic compounds as hydrogen carriers is conducted. A literature survey and preliminary molecular modeling work have been carried out. Different classes of compounds have been investigated in the literature. Those are cycloalkanes, polycyclic alkanes, heteroatoms-containing hydrocarbons and even ionic liquids. In addition to experimental work where catalyst development and reactor design were sought for efficient and selective dehydrogenation of organic carriers, computational modeling work had also been conducted by different research groups, principally to search for compounds with low enthalpy of dehydrogenation. Among the different compounds considered, the ones that meet more or less the required physical (liquid in all state), toxicity/environmental, stability (to be recycled) and cost criteria for hydrogen storage and delivery purposes are within the cycloalkanes class. Methylcyclohexane only seems to be the appropriate candidate. The economic viability of using such compounds is however pending to the releasable hydrogen content as the maximum value is only about 7.2wt%. Among catalysts usually cited for the dehydrogenation of the organic compounds, noble metal supported ones and mono or bi-metallic catalysts especially are having better performances in terms of activity and selectivity. Although the combination of catalysts and organic compounds will give different reactivity and selectivity, the polycyclic alkanes and heteroatom-containing hydrocarbons will usually be more susceptible to side reactions during dehydrogenation forming coke, additional partially dehydrogenated and decomposed products as well. No data are available as to the life time of the catalyst in such reaction, but it is expected that deactivation might be a concern. Different reactor configurations were considered in pursuit of high conversions while limiting side reactions. Finally the computational modeling data obtained are in agreement with the ones found in the literature. Although heteroatom-containing polycyclic hydrocarbons are found to present lower enthalpy of dehydrogenation that would be suitable for on-board dehydrogenation, as mainly sought by the different research groups, their application as organic carrier seems quite difficult in regards of their hydrogen content, their physical properties and the cost of synthesis.

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http://dx.doi.org/10.1016/j.ijhydene.2016.07.167

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Please cite this article in press as: Bourane A, et al., An overview of organic liquid phase hydrogen carriers, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016/j.ijhydene.2016.07.167

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Introduction

The fossil fuels that are today the primary energy sources are challenged, as societies in developed countries at least, are requesting use of alternative energy sources that are cleaner and sustainable. Hydrogen was found to be a promising alternative energy carrier for decades already but the realization of a hydrogen economy is still facing multiple obstacles. For the hydrogen production, steam methane reforming, partial oxidation of fossil fuels or even water electrolysis are the current established methods while new methods like thermochemical water splitting using nuclear or solar heat or other biological techniques are in early development phases. In addition to its production, hydrogen storage and delivery technologies are currently in commercial use but by the chemical and refining industries only [1].

Hydrogen is indeed presently produced in limited number of plants and to be used at the required location it is currently transported by road via cylinders, tube trailers, and cryogenic tankers. It is then stored as a discrete gas or liquid.

However for a widespread hydrogen use in energy application and especially in transportation, hydrogen delivery, storage and even conversion technologies barriers have to be overcome [2].

Among options for meeting at least the delivery and storage challenges and keeping oil as a hydrogen source, one of

the promising methods would be through the catalytic reaction pair of dehydrogenation of saturated organic materials and the subsequent hydrogenation of their corresponding aromatic products. The organic compound would indeed act as a hydrogen carrier.

A vision of a global hydrogen energy chain using the organic hydrogen carrier approach would involve hydrogenation of the organic compound near gas or oil fields with a large reduction in the CO2 emission, as the generated CO2 through the hydrogen production process is planned to be captured and injected into the ground for instance. The hydrogen carrier would be transported to the consumer countries by the usual sea-going chemical tankers, and it would be stored in tanks on land, before being delivered to the hydrogen stations by chemical trucks or even pipes used for conventional fuels. The organic compound would then be either dehydrogenated at the hydrogen station or directly onboard the vehicle. This latter option seems quite difficult to implement on a technical level and it would also be easier to deal with CO2 generated through energy provided for the reaction at the station as well. This overall scheme has a low potential risk regarding safety and a small loss of hydrogen through the transportation and also low cost, as the storage and transportation would be carried out in the liquid state under ambient pressure and temperature.

Organic molecules that can undergo reversible hydrogenation and dehydrogenation reactions have been investigated

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