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Chemical hydrides: A solution to high capacity hydrogen storage and supply

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Abstract

Cycloalkanes are good candidate media for hydrogen storage (6.5 wt% and 60–62 kg H_2/m^3). A novel approach for the supply of hydrogen, through liquid organic hydrides (LOH) using catalytic reaction pair of dehydrogenation of cycloalkanes and hydrogenation of corresponding aromatics is a useful process for supply of hydrogen. Hydrogenation of aromatics is relatively well-established process. However, the efforts are needed to develop efficient catalyst for dehydrogenation of cycloalkanes. In this paper we review the dehydrogenation of cycloalkanes as useful reaction for storage of hydrogen in chemical hydrides.

Keywords: Hydrogen storage; Liquid organic hydrides; Delivery to fuelling station; Cycloalkanes

1. Introduction

Onboard storage and supply of hydrogen for fuel cell is an important issue in the successful application of PEMFC. Also the transportation of H_2 from production facilities to the fuelling station needs to be considered for successful application of hydrogen economy [1,2]. Hydrogen being very flammable gas its transport involves several safety issues. The safety issues are related to the lower and higher explosion limits for H_2 concentration in air, low ignition energy in air and requirement of high pressure (typically 300–500 psi) storage or some times cryogenic temperatures, if it is transported in liquid form. These problems can be overcome if the hydrogen is either adsorbed on some materials such as carbon nano-tubes or chemically stabilized such as in the case of metal hydrides or alanates. Several studies report the development of hydrogen storage materials such as metal hydrides [3–6], Mg-based alloys [7,8], carbon materials [9–16], boron compounds [17], chemical hydrides [18], etc. While developing such hydrogen storage materials, capacity of the material in terms of weight and volume basis is an important factor to be considered. With a limited capacity it would result in weight penalty and CO_2 emissions associated with transportation. Also the adsorption and desorption kinetics is to be sufficiently fast to provide continuous H_2 supply. Another important requisite is to transport the hydrogen containing media at close to atmospheric temperature and pressure conditions and possibly using the existing infrastructure such as lorries.

Hydrogen containing chemicals which are useful for storage of hydrogen include methanol, ammonia and cycloalkanes. At STP all these are in liquid phase and therefore provide advantage of possibility of using existing infrastructure being used for gasoline. The hydrogen storage capacities of these chemical hydrides may range in the scale of 6–8 wt%. Earlier it was thought that since the chemical storage method is non-reversible, the compounds cannot be used in cycles. In view of this supply of hydrogen through liquid organic hydrides (LOH) using catalytic reaction pair of dehydrogenation of cycloalkanes such as methylcyclohexane, cyclohexane and decalin; and hydrogenation of corresponding aromatics is a useful process for supply of hydrogen to PEMFC. This is one of the most promising methods to store, transport and supply with in situ generation of hydrogen due to several advantages associated with this system which include; CO_x free hydrogen at fuelling stations, reversible catalytic reactions, recyclable reactants and products and relatively high hydrogen contents (6–8% on weight basis and about 60–62 kg H_2/m^3 on volume basis). Particularly,

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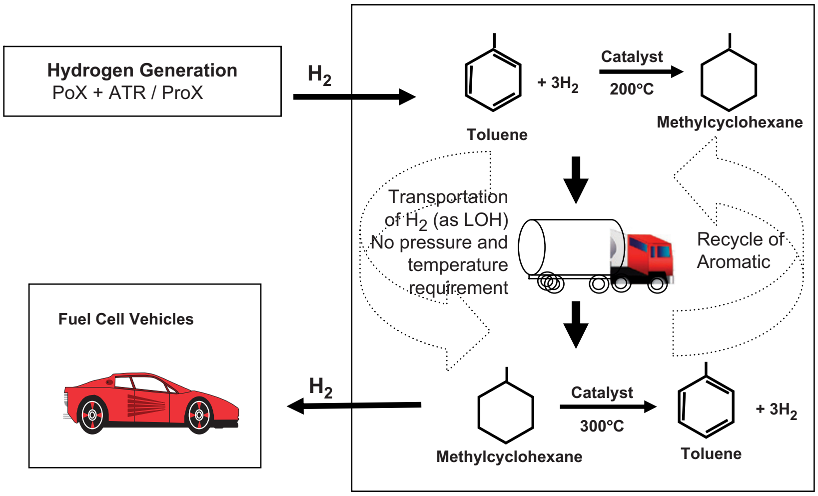

Fig. 1. Schematic of hydrogen storage and supply system.

the approach is most useful to transport the hydrogen from centralized generation facilities to fuelling stations. A schematic of catalytic reaction pair of hydrogenation of toluene and dehydrogenation of methylcyclohexane for hydrogen storage and supply is depicted in Fig. 1. Several studies have been reported on cycloalkanes as carrier for hydrogen and particularly development of dehydrogenation catalysts. The important issues being addressed by these reports are dehydrogenation temperature, dehydrogenation rates for various cycloalkanes, hydrogen evolution rates and reactor type for efficient heat transfer. Considering the development in this important field addressing hydrogen storage which is of current interest, this paper was envisaged to review state-of-art and to identify the future scope of research.

2. Cycloalkanes for hydrogen storage

Several cycloalkanes may be used as hydrogen carrier as LOH include cyclohexane, methylcyclohexane, teralin, decalin, cyclohexylbenzene, bicyclohexyl, 1-methyldecalin, etc. A few reactions of dehydrogenation of cycloalkanes are depicted in Fig. 2. One mole of cycloalkane has potential to transport 3–6 mol of hydrogen. The endothermic energy requirement for these reactions is in the range of 64–69 kJ per mole of H_2 this is much lower than energy that could be obtained by oxidation of H_2, 248 kJ/mol. Hydrogen storage capacities of cycloalkanes and other storage media are compared in the Table 1 along with boiling and melting points. Due to high boiling points of cycloalkanes, the present infrastructure such as oil tankers and tank lorries can be used for the long-term storage and long-distance transportation of hydrogen in the form of LOH.

3. Catalysts for dehydrogenation of cycloalkanes

Noble metal catalysts particularly Pt and bimetallic catalysts Pt–M (M = second metal) are well reported for highly selective dehydrogenation of cycloalkanes. Dehydrogenation of

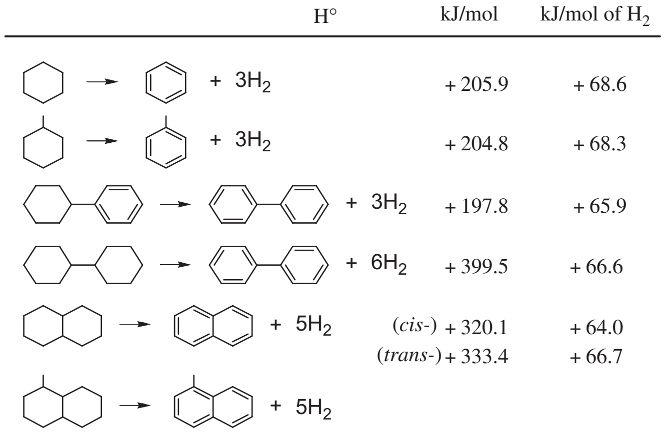

Fig. 2. Various potential cycloalkanes with hydrogen storage capacity and endothermic energy requirement.

Table 1
Hydrogen storage capacity of various media and their physical properties

Storage media	Hydrogen content		Boling point (°C)	Melting point (°C)
	wt%	mol/L		
Cyclohexane	7.2	27.77	80.7	6.5
Methylcyclohexane	6.2	23.29	101	−126.6
Tetralin	3.0	14.72	207	−35.8
cis-decalin	7.3	32.44	193	−43.0
trans-Decalin	7.3	31.46	185	−30.4
cyclohexylbenzene	3.8	17.63	237	4
bicyclohexyl	7.3	32.0	227	3
cis-syn-1-methyldecalin	6.6	29.31	213.2	−68
trans-anti-1-methyldecalin	6.6	28.52	204.9	−68
$LiH + H_2O$	7.8	4.1	–	680
$LiBH_4 + 4H_2O$	8.6	2.4	–	268
$LaNi_5H_6$	1.4	6.2	–	–
$MmNi_{4.5}Al_{0.25}Co_{0.25}H_{3.4}$	1.2	4.8	–	–
Liquid H_2 (with tank)	100 (5.11)	–	−252.9	–