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# Hydrogen delivery through liquid organic hydrides: Considerations for a potential technology

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## ABSTRACT

Carrying hydrogen in chemically bounded form as cycloalkanes and recovery of hydrogen via a subsequent dehydrogenation reaction is a potential option for hydrogen transport and delivery. We have earlier reported a novel method for transportation and delivery of hydrogen through liquid organic hydrides (LOH) such as cycloalkanes. The candidate cycloalkanes including cyclohexane, methylcyclohexane, decalin etc. contains 6 to 8 wt% hydrogen with volume basis capacity of hydrogen storage of 60–62 kg/m<sup>3</sup>. In view of several advantages of the system such as transportation by present infrastructure of lorries, no specific temperature pressure requirement and recyclable reactants/products, the LOH definitely pose for a potential technology for hydrogen delivery. A considerable development is reported in this field regarding various aspects of the catalytic dehydrogenation of the cycloalkanes for activity, selectivity and stability. We have earlier reported an account of development in chemical hydrides. This article reports a state-of-art in LOH as hydrogen carrier related to dehydrogenation catalysts, supports, reactors, kinetics, thermodynamic aspects, potential demand of technology in field, patent literature etc.

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## 1. Introduction

In order to meet the ever increasing energy demand without causing further damage to the environment, zero carbon emission fuel such as hydrogen is required [1,2]. There is consensus on the hydrogen as a clean energy option. An efficient method for hydrogen storage, transportation and delivery to point of usage is a prerequisite for any hydrogen-fueled energy system [2]. Among wide variety of hydrogen storage technologies liquid organic hydrides provide several advantages such as relatively higher hydrogen capacity on both the weight and volume basis [1,2]. The candidate liquid organic hydrides reported comprise cyclic alkanes such as methylcyclohexane, cyclohexane, decalin, etc. The physico-chemical properties and hydrogen storage capacities for

cyclohexane, methylcyclohexane and decalin are listed in Table 1.

Considering the boiling point and melting point, cycloalkanes are in liquid phase at ambient conditions with prevailing temperature of 20–40 °C. This facilitates the transportation of cycloalkanes using simple transport means such as lorries. Further, properties of methylcyclohexane, as one of the candidate media for hydrogen storage, (Table 2) are comparable to that of gasoline and diesel which makes it possible to transport using present fuel transportation methods.

Due to simple reaction mechanism, the dehydrogenation reaction is considered as favorable process for hydrogen abstraction from cycloalkanes. The mechanism involves adsorption of cycloalkane over metal catalyst (particularly Pt) with either simultaneous or rapid subsequent dissociation of

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**Table 1 – Hydrogen storage capacities for cycloalkanes such as cyclohexane, methylcyclohexane and decalin and their physical properties.**

Sr. No.	Properties	Cyclohexane	Methylcyclohexane	Decalin
1.	Melting point (°C)	6.5	–126.6	–30.4
2.	Boiling point (°C)	80.74	100.9	185.5
3.	Density (g/ml)	0.779	0.77	0.896
4.	Standard formation enthalpy in dehydrogenation of cyclic hydrocarbons (101.3 kPa) $\Delta H$ (kJ mol <sup>-1</sup> )	+205.9	+204.8	+319.5
5.	Theoretical hydrogen storage- weight basis (%)	7.2	6.2	7.3
6.	Theoretical hydrogen storage –volume basis (10 <sup>28</sup> mol/m <sup>3</sup> )	3.3	2.8	3.8
8.	Product of dehydrogenation	Benzene	Toluene	Naphthalene

hydrogen atoms via pi-bond formation [3]. Dehydrogenation results in formation of hydrogen and aromatic. The reaction is highly selective over Pt catalysts and there have been reports for formation of no by-products or partially dehydrogenated products. Dehydrogenation and its subsequent hydrogenation of aromatics are easily reversible [1, 2, and 4]. A typical concept of transportation of hydrogen from hydrogen production facility to fueling station using methylcyclohexane is depicted in Fig. 1.

Thus, in view of this researchers are trying to demonstrate hydrogen storage and supply using liquid organic hydrides mainly cycloalkanes such as cyclohexane, methylcyclohexane and decalin. Hodoshima and co-workers reported that the decalin should be considered as a potential candidate for fuel cell vehicles [5]. The advantages related to decalin are investigated by Lazaro and group as negligible evaporation loss, low toxicity, no parallel reactions, low cost and low dehydrogenation energy which allows reaction to perform at relatively low temperatures [6]. The methylcyclohexane exhibits similar advantages as a candidate medium. The advantages explained by Oda and group include relatively high boiling point and no carcinogenic products are formed [7]. Hodoshima and co-workers also reported that the tetralin can be a potential option over decalin due to 4–5 times higher reaction rate under superheated liquid film condition [8].

In an earlier article we have given an account of chemical hydrides in general and LOH in particular for hydrogen storage and supply [2]. This article covers the state-of-art development on several other aspects such as kinetics, thermodynamics, patent-review regarding LOH technology.

## 2. Dehydrogenation catalysts

Several catalysts are reported for dehydrogenation of cycloalkanes. Coughlan et al. in 1990 reported that the dehydrogenation of cyclohexane on nickel exchanged Y-zeolites proceeded via

series of consecutive dehydrogenation steps [9]. Kobayashi et al. reported Pt/Al<sub>2</sub>O<sub>3</sub> as an efficient catalyst for dehydrogenation of iso-propanol [10]. In an early work related to this reaction, 3.82 wt % Pt/PCC (Pt supported on petroleum coke carbon) catalyst was studied for dehydrogenation of methylcyclohexane and decalin by Kariya et al. [4]. They concluded that the major properties such as hydrogen spillover and hydrogen-recombination to be taken into consideration while selecting the catalysts. The same group in 2003 reported methylcyclohexane dehydrogenation over 10 wt % Pt/ACC (Pt supported on activated carbon cloth) wherein the hydrogen evolution rate was reported as 0.52 mmol/g<sub>mev</sub>/min at 298 °C [1]. They proved that the particle size of catalyst have profound effect on dehydrogenation reaction. Hodoshima and group in one of the report concluded shorter Pt distance with its neighbor can affect dehydrogenation of decalin. They even proposed to modify catalyst and study the effect of alkali reagents on catalytic activity and fine structure of Pt species [11].

Bi-metallic catalysts have shown considerably higher activity for dehydrogenation than monometallic catalysts as has been reported by Ichikawa and group [4]. They concluded that Pt–Mo/PCC, Pt–W/PCC and Pt–Re/PCC exhibit comparatively better hydrogen evolution rate than monometallic Pt/PCC for cyclohexane dehydrogenation. They also suggested that physical mixing of Pd/PCC and Pt/PCC improves catalytic activity, since Pd helps in suppressing reverse reaction and Pt helps in hydrogen-recombination ability. These conclusions are based on the hydrogen evolution activity and there is no evidence of arrangement of metal presence on support. Hodoshima and co-workers explained catalyst selection is based on its ability to C–H dissociation for alkane and investigated Pt–Re/AC (Pt–Re supported on activated carbon) to have excellent activity for dehydrogenation of decalin with nearly 100% conversion [12]. In the same year 2005, Hodoshima et al. have reported dehydrogenation of tetralin over carbon supported on Ni–Ru and suggested that this can be alternate catalyst to costly Pt. Biniwale et al. have reported an

**Table 2 – Comparison of properties of methylcyclohexane with gasoline and diesel.**

Sr. No.	Properties	Diesel	Gasoline	Methylcyclohexane
1.	Reid vapor pressure (psi)	0.2	8–15	1.61
2.	Auto ignition temperature (°F)	446	572	482
3.	Flash point (°F)	165	–45	25
4.	Peak flame temperature (°F)	3729	3591	
5.	Density (g/cc)	0.83	0.75	0.81
6.	Flammable limit in air LEL–UEL	1.3–6.0%	1.4–7.4%	1.1–6.7%

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