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# Study of hydrogenation and dehydrogenation of 1-methylindole for reversible onboard hydrogen storage application

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## ABSTRACTS

We report a new candidate of liquid organic hydrogen carrier, 1-methylindole, with a hydrogen content of 5.76 wt% and a low melting point of below  $-20\text{ }^{\circ}\text{C}$ . The hydrogenation of 1-methylindole and the dehydrogenation of octahydro-1-methylindole were investigated in details. Full hydrogenation of 1-methylindole was realized over a 5 wt% Ru/Al<sub>2</sub>O<sub>3</sub> catalyst at 130  $^{\circ}\text{C}$  and 6.0 MPa, and both conversion and selectivity of 100% towards octahydro-1-methylindole were achieved. The catalytic dehydrogenation of octahydro-1-methylindole was carried out over a 5 wt% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. By using a combined experimental and density functional theory approach, the mechanism of octahydro-1-methylindole dehydrogenation to 1-methylindole and the two stable isomers of octahydro-1-methylindole were analyzed. The effect of reaction temperature and dosage of catalyst on the hydrogen release content were systematically studied. In addition, the dehydrogenation of octahydro-1-methylindole at 160–190  $^{\circ}\text{C}$  on Pd/Al<sub>2</sub>O<sub>3</sub> was well described by a first-order stepwise dehydrogenation reaction with the apparent activation energy of 122.99 kJ/mol. The purity of released H<sub>2</sub> was higher than 99.99% with no detectable impurity.

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## Introduction

Hydrogen is a carbon-free fuel which oxidizes to water as a combustion product. Hydrogen can be generated from both fossil and renewable sources. Many recent studies have demonstrated that the potential applications of hydrogen technology in automotive industry and in stationary power generations are highly promising [1,2]. High capacity, safe hydrogen storage operated at near ambient conditions is one

of the grand challenges for large scale deployment of hydrogen technologies, which promises to make a profound impact on the current industrial and socioeconomic infrastructure [3–5]. Today, the state-of-the-art hydrogen technologies have been largely built upon compressed gas or liquefied storage technology up to 700 bar, which could potentially pose a serious safety risk to the public in case of explosion [6–9]. Despite over a decade of worldwide effort to develop hydrogen storage materials for vehicular, stationary and portable applications, few technologies have been

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successfully demonstrated to be commercially viable [10–13]. Virtually, almost all storage materials discovered to date have been in various solid forms with hydrogen adsorbed via either a physisorption or a chemisorption mechanism. While only a handful of materials have shown appreciable hydrogen uptake at room temperature via a physisorption process [14–16], a wide variety of compounds including metal hydrides [17,18] and chemical hydrides [19–21], with which hydrogen forms chemical bonds upon storage, have been discovered. Many of these chemical complexes with hydrogen exhibit various novel properties, such as high hydrogen capacity, good reversibility, low hydrogen release temperature, facile kinetics, etc. [22–24]. Unfortunately, for various practical reasons, none of these materials can satisfactorily meet all the necessary requirements for sustained fuel cell operations with competitive costs and longevity [5]. In particular, a detrimental deficiency associated with solid storage materials is the requirement to completely revamp the current gasoline infrastructure, should the storage technologies be deployed in commercial scale, which would be prohibitively expensive.

To minimize the impact with the radical infrastructural change, a novel concept of liquid organic hydrogen carriers (LOHCs), most prominently, N-ethylcarbazole (NECZ), was proposed [25–27], which enables hydrogen storage and release via catalytic hydrogenation and dehydrogenation to be realized entirely in a liquid form so that the current gasoline-based infrastructure can still be utilized. A series of heteroaromatic molecules with high boiling and melting points was firstly studied as a prototype for all-new generation of organic liquid hydrides through the experimental and theoretical work of Hansong Cheng et al. in their serious patents [28–33]. With a gravimetric density of 5.8 wt%, the hydrogenation of NECZ and dehydrogenation of dodecahydro-N-ethylcarbazole (12H-NECZ) has been well-studied on specific catalysts at a moderate temperature range of 130–200 °C [34–40]. Eblagon et al. [41] compare the catalytic hydrogenation of NECZ over noble metal (Ru, Pt, Pd, Ni, Rh), and found that Ru is the most active catalyst among all the metals studied for the hydrogenation of LOHCs. In our recent publication [38], we report a systematic study on dehydrogenation of perhydro-N-ethylcarbazole over several important supported noble metal catalysts to identify the optimal catalyst for dehydrogenation. The initial catalytic activity of the selected noble metal catalysts for the dehydrogenation process was found to follow the order of Pd > Pt > Ru > Rh.

Nevertheless, NECZ is a solid at ambient conditions with a melting point of 68–70 °C, which of course severely limits the applicability of LOHCs to practical energy converting devices such as fuel cells and hydrogen internal combustion engines.

Several new heterocyclic LOHC candidates with high hydrogen content and lower melting point has been developed, such as N-propylcarbazole (NPCZ) [42], 2-methylindole (2-MID) [43] and N-ethylindole (NEID) [44] reported in our recent studies with a relatively low melting point of 48 °C, 57 °C and –17.8 °C respectively. Their theoretical gravimetric hydrogen contents (5.43 wt% for NPCZ, 5.76 wt% for 2-MID and 5.23 wt% for NEID) are modestly lower than NECZ. With a high hydrogen content of 6.2 wt%, dibenzyltoluene (DBT) was proposed as one of the most attractive LOHC candidate with favorable toxicological profiles, low flammability and

outstanding thermal stability [45], however the high dehydrogenation temperature (above 250 °C) of perhydrodibenzyltoluene (18H-DBT) limits its automotive onboard applications [46].

In this paper, we report a new promising LOHC candidate, 1-methylindole (NMID), which remains in a liquid state above –20 °C before and after hydrogenation. The gravimetric and volumetric density of NMID are 5.76 wt% and 59.10 g/L respectively, surpassing the U.S. DOE target for onboard application. Full hydrogenation can be carried out at 130 °C and 6.0 MPa over a 5 wt% Ru/Al<sub>2</sub>O<sub>3</sub> catalyst; hydrogen can be completely released via dehydrogenation of octahydro-1-methylindole (8H-NMID) on a 5 wt% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst starting from 160 to 190 °C with higher than 99.99% purity and no detectable impurity. The material exhibits a low vapor pressure with no more health and environmental hazards than gasoline and is thus well-suited for large scale utilization as a hydrogen carrier at near ambient conditions. Because both the hydrogenated and the dehydrogenated forms are in liquid states over a wide temperature range of practical interest with excellent reversibility, a storage technology built upon the new hydrogen carrier could potentially pave the way for commercial scale deployment of hydrogen technologies.

## Experimental

### General

1-Methylindole was of analytical grade and was purchased from Energy Chemical company. Sichuan Ally High-Tech company supplied ultra-high purity hydrogen (99.999%) and argon (99.999%). The commercially available 5 wt% Ru/Al<sub>2</sub>O<sub>3</sub> and 5 wt% Pd/Al<sub>2</sub>O<sub>3</sub> catalysts were purchased from Shanxi Kaida Chemical Engineering Company Limited. The reaction mixtures were analyzed by Agilent 7890/5975C GC-MSD. The generated gas was analyzed using the Dynamic Sampling Mass Spectrum (DSMS, HPR-20) attached to the gas outlet from the reactor.

### Hydrogenation of NMID

The catalytic hydrogenation of 7-MID was carried out at 130 °C and 6.0 MPa over a 5 wt % Ru/Al<sub>2</sub>O<sub>3</sub> catalyst in batch reactor. 20 g of 1-methylindole, and 2 g of 5 wt% Ru/Al<sub>2</sub>O<sub>3</sub> catalyst were added to a 600 mL stainless autoclave batch reactor (Parr Instrument Company 4568) with magnetic stirring. The reactor was pressurized with H<sub>2</sub> and vented 3 times to purge the system of oxygen. The reactor was then pressurized again with 6 MPa H<sub>2</sub> pressure and the autoclave was heated to 130 °C under the heating mantle. The reaction mixture was stirred with a stirring speed of 600 rpm/min over 240 min. The autoclave was cooled to room temperature and the pressure was released. The GC/MSD analysis showed that this procedure produces >99% 8H-NMID in nearly quantitative yield.

### Dehydrogenation of 8H-NMID

The catalytic dehydrogenation of 8H-NMID was carried out in a 50 mL three-neck flask with a stir bar and an integrated

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