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## Short Communication

# Catalytic hydrogenation and dehydrogenation of N-ethylindole as a new heteroaromatic liquid organic hydrogen carrier

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## ABSTRACT

Hydrogenation of N-ethylindole was investigated over a 5 wt% Ru/Al<sub>2</sub>O<sub>3</sub> catalyst in the temperature range of 160–190 °C at 9 MPa. The process was found to undergo the sequential steps of N-ethylindole → 2H-N-ethylindole → 4H-N-ethylindole → 8H-N-ethylindole with rapid consumption of all intermediate species. The reverse process, dehydrogenation of octahydro-N-ethylindole, was subsequently conducted for tests over a 5 wt % Pd/Al<sub>2</sub>O<sub>3</sub> catalyst in the same temperature range. Full dehydrogenation can be achieved with a moderate reaction rate. The released H<sub>2</sub> gas was found to be of a high purity. Our results indicate that N-ethylindole is a promising new member of liquid organic hydrogen carrier family.

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## Introduction

Hydrogen is one of the most efficient energy carriers, capable of offering a stable source of power for energy converting devices. Safe and efficient utilization of hydrogen power provides a convenient way to help combat the pressing challenge of global greenhouse gas emissions [1,2]. Central to the potential mass deployment of hydrogen technologies in the market place is the development of large scale, high density and safe storage and transport of hydrogen, which

unfortunately has remained to be one of the grand challenges for the incipient hydrogen economy today [3–5]. The low boiling point (–253 °C) and high flammability of hydrogen have significantly limited the broad applicability of hydrogen technologies. Despite the recent effort to utilize high pressured tanks (up to 700 bars) to contain hydrogen for onboard vehicular applications [6], the associated high cost, the need to radically change the current gasoline-based infrastructure and the potential safety risks have raised legitimate concerns on the suitability of the approach for consumer market [7]. Obviously, efficient hydrogen storage technologies that are

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compatible with the current energy infrastructure, offer high storage density and operate at near ambient conditions are essential for widespread applications.

The concept of liquid organic hydrogen carriers (LOHCs), in which hydrogen is covalently bonded with an organic molecule of liquid substance, was proposed in 1970s [8] and a variety of organic molecules has been discovered to date [9–16]. Technologies based on LOHCs are deemed to be advantageous over the conventional solid storage materials for the excellent compatibility with the current gasoline based energy infrastructure and the high scalability for potential mass adoption in market place [17]. One of the most prominent and well-studied LOHCs is N-ethylcarbazole, which exhibits a high volumetric density of 55 g/L and a high gravimetric density of 5.8 wt% [18–20]. Hydrogen can be stored via catalytic hydrogenation in a stationary filling station and then transport at ambient conditions. The gas can be liberated on demand via catalytic dehydrogenation under well controlled conditions onboard. The process has been shown to be highly reversible [17,21–23]. With the design of off-board hydrogenation and onboard dehydrogenation in mind, the LOHC technologies are well suited for vehicular applications. Hydrogen delivery can be made with the conventional energy infrastructure. Using the existing gasoline filling station, the fully hydrogen loaded LOHC can be safely pumped into a vehicular tank, which is divided into two parts via a movable separator, in the same way as how a gasoline tank is filled [7,14,21]. For onboard hydrogen release, the dehydrogenation kinetics must be sufficiently fast with no side reactions. Thermodynamically, the heat of reaction should also be relatively moderate to ensure that the reaction takes place in a temperature range appropriate for fuel cell operation. However, dehydrogenation reactions of many cycloalkene or aromatic based compounds have been reported relatively slow, which is thus not appropriate to serve as storage carriers [15,24]. The high heats of reaction and the high activation barriers of dehydrogenation with these LOHCs make the reactions to occur only at significantly elevated temperatures, potentially resulting in side reactions that could be detrimental to fuel cell devices [1,25–27]. In contrast, the LOHC based on N-ethylcarbazole enables nearly a full release of hydrogen under 200 °C with virtually no side reaction [28,29]. Unfortunately, in spite of the fact that the perhydrogenated N-ethylcarbazole is a liquid, the fully dehydrogenated product is in a solid form below 70 °C. This makes practical applications of the LOHC material inconvenient because of the poor compatibility with the existing energy infrastructure.

In this Communication, we report a new LOHC molecule, N-ethylindole (NEID), for full liquid phase hydrogen storage and delivery. The carrier itself and its hydrogenated form are all in liquid forms at near ambient conditions. The melting point, boiling point and flashing point of NEID are  $-17.8$  °C,  $253.5$  °C and  $107.1$  °C, respectively. The material has a theoretical gravimetric density of 5.23 wt%, modestly lower than the value of N-ethylcarbazole. Hydrogenation of NEID was carried out over a 5 wt% Ru/Al<sub>2</sub>O<sub>3</sub> catalyst and dehydrogenation of octahydro-N-ethylindole (8H-NEID) was conducted over a 5 wt% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. We demonstrate that with a melting point of  $-17.8$  °C, NEID is potentially well suited for on-board automotive applications.

## Experimental

### Catalytic hydrogenation of N-ethylindole

Hydrogenation of N-ethylindole was carried out over a 5 wt% Ru–Al<sub>2</sub>O<sub>3</sub> catalyst at temperatures in the range of 160–190 °C and a H<sub>2</sub> pressure of 9 MPa, in a 600 ml Parr autoclave batch reactor (Parr 4568) with magnetic stirring. The reactor was loaded with 3 g of N-ethylindole in a 30 ml of hexane and 0.3 g of 5 wt% Ru/Al<sub>2</sub>O<sub>3</sub> before being sealed. As the reaction proceeds, a small volume of the liquid sample was removed periodically for analysis using gas chromatography and mass spectrometry (Agilent 7890/5975C GC-MS).

### Catalytic dehydrogenation of octahydro-N-ethylindole

The final product of the hydrogenation was used as the reactant in dehydrogenation. The reaction was conducted in a 50 ml flask using 0.2 g of 5 wt% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst added to 2 g of octahydro-N-ethylindole in the temperature range of 160–190 °C at 101 kPa. A constant flow of Ar gas was used for removal of hydrogen in the reaction process. Analysis of the liquid samples was done with GCMS and the exit gas composition was detected using Dynamic Sampling Mass Spectrum (DSMS) attached to the intelligent gravimetric analyzer (IGA100).

## Results and discussions

A N-ethylindole molecule is capable of storing four H<sub>2</sub> molecules with the theoretical gravimetric density of 5.23 wt%. Hydrogenation of the compound over a 5 wt% Ru–Al<sub>2</sub>O<sub>3</sub> catalyst was conducted in the temperature range of 160–190 °C and at 9 MPa. The hydrogen storage capacity as a function of time was recorded with GCMS and the results are displayed in Fig. 1. Clearly, the reaction temperature exerts a significant influence on the rate of storage capacity. As the temperature increases, the reaction rate rises sharply. 100% hydrogenation of NEID was achieved within 80 min at 190 °C. In contrast, at 160 °C, full hydrogenation takes as long as

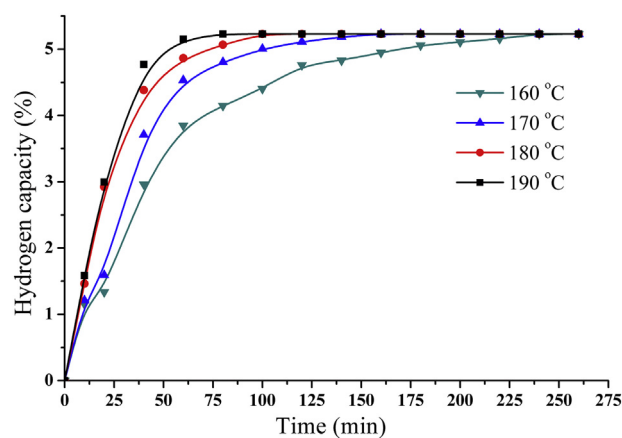


Fig. 1 – Evolution of hydrogen capacity at various temperatures.

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