Study of catalytic hydrogenation and dehydrogenation of 2,3-dimethylindole for hydrogen storage application

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2,3-Dimethylindole (2,3-DMID), a candidate with a hydrogen storage capacity of 5.23 wt%, was studied as a new liquid organic hydrogen carrier (LOHC) in detail in this report. Hydrogenation of 2,3-DMID was conducted over 5 wt% Ru/Al2O3 by investigating the influences of temperature and hydrogen pressure. 100% of fully hydrogenated product, BH-2,3-DMID can be achieved at 190 °C and 7 MPa in 4 h. Dehydrogenation of BH-2,3-DMID was performed over 5 wt% Pd/Al2O3 at 180–210 °C and 101 kPa. It is found that dehydrogenation of BH-2,3-DMID followed first order kinetics with an apparent activation energy of 39.6 kJ mol⁻¹. The structures of intermediates produced in the BH-2,3-DMID dehydrogenation process were analyzed by DFT calculations.

Introduction

Nowadays, the usage of renewable clean energy has become unavoidable, aiming to reduce greenhouse gas emissions and to compensate for declining fossil-fuel resources.1–3 A consensus has been reached that hydrogen energy is one of the most attractive choices.4–6 However, it is difficult to store hydrogen without bulky, heavy equipment due to the low density and high explosive risk.6–8 Apparently, the further transportation of hydrogen must be necessary depending on the method of hydrogen storage.7–9 Thus, the major challenge towards the large scale utilization of hydrogen is to develop a safe and practical method for the onboard storage.9–11 In the past decades, hydrogen was dominantly stored and transported in its elemental form as compressed hydrogen (200–700 bar) and liquefied hydrogen (−253 °C) for onboard applications, both of which require a large amount of energy in the storage process.9,12–14 Besides, the safety and cost are another concern for compressed hydrogen and liquefied hydrogen. Consequently, researchers are committed to search for materials which can store hydrogen more safely and efficiently.

Hydrogen can be stored in form of hydrogen molecule by physical adsorption on materials with a large specific surface area (e.g., carbon-based materials15–16 and metal organic frameworks17,18) and in form of hydrogen atoms by chemical adsorption which are bonded with the substrates by chemical bonding (e.g., organic liquid compounds19 and metal hydrides20). High hydrogen storage densities can be achieved at relatively low temperature (−196 °C) and high pressures (10–100 bar) for physical adsorption for the former. In comparison, elevated temperature is required to release hydrogen stored by chemical adsorption. LOHCs (liquid organic hydrogen carriers) have been considered as promising hydrogen storage substrates in recent years.21–26 Hydrogen was bonded to these compounds through catalytic hydrogenation and released through catalytic dehydrogenation. As early as 1970s, aromatic hydrocarbon compounds were initially proposed as hydrogen storage carriers such as benzene and toluene, which were mainly applied in industrial process (e.g., in oil refineries). However, with high enthalpy of dehydrogenation (>60 kJ mol⁻¹ H2), the operation temperatures of these hydrogenated cycloalkanes were required over 300 °C, which typically lead to the molecule cracking or coking.27–29 Hence, a large number of literatures concerning the catalysts development for dehydrogenation of cycloalkanes were reported in decades.30–37 In 2004, a series of heteroaromatic molecules with relatively low heat of hydrogenation screening as LOHCs were firstly studied through systematic experimental and theoretical by Pez et al.38,39 It is reported that incorporation of N heteroatom into the aromatic ring favored the dehydrogenation thermodynamics and kinetics. Carbazole-based compounds, such as N-ethylcarbazole (NECZ, mp: 70 °C) and N-propylcarbazole (NPCZ, mp: 48 °C), were investigated most widely as LOHCs by a lot of groups.40–45 With a hydrogen capacity of 5.79 wt%, NECZ can be completely hydrogenated over Ru/Al2O3 at the temperature of 150 °C with a hydrogen pressure of 5 MPa within 180 min. The fully reverse process, dehydrogenation of NECZ, can be realized below 200 °C over Pd/Al2O3 (ref. 46) and Pt/Al2O3.47 Wu et al. Reported a Co-based catalyst, which can achieve a reversible hydrogen uptake and
| Substrate | Melting point (°C) | Hydrogenated product | Hydrogen capacity (wt%) | Hydrogenation conditions from substrate to hydrogenated product | Dehydrogenation conditions from hydrogenated product to substrate |
|-----------|-------------------|----------------------|-------------------------|---------------------------------------------------------------|---------------------------------------------------------------|
| indole    | 51                | 2H-indoline          | 1.68                    | Pt/C, 3 MPa, 50 °C, 3 h, 100% conversion in H₂O with p-TSA.⁶⁶  | —                                                             |
| NMID      | -29               | 8H-NMID              | 5.76                    | Ru/Al₂O₃, 130 °C, 6 MPa, 2 h, 100% conversion in hexane solvent.⁵⁷ | Pd/Al₂O₃, 200 °C, 101 kPa, 3 h, 100% conversion.⁵⁷            |
| NEID      | -17.8             | 8H-NEID              | 5.23                    | Ru/Al₂O₃, 180 °C, 9 MPa, 2 h, 100% conversion in hexane solvent.⁶¹ | Pd/Al₂O₃, 190 °C, 101 kPa, 6 h, 100% conversion.⁶¹           |
| 7-EID     | -14.5             | 8H-7-EID             | 5.23                    | Ru/Al₂O₃, 160 °C, 7 MPa, 1.5 h, 100% conversion in hexane solvent.⁵⁹ | Pd/Al₂O₃, 190 °C, 101 kPa, 270 min, 100% conversion.⁵⁹       |
| 2-MID     | 57                | 2H-2-MID             | 1.43                    | Pt/C, 60 °C, 4 MPa, 4 h, 97% conversion in toluene with p-TSA.⁶⁴ | Cobalt pincer catalyst, 150 °C, 101 kPa, 4 d, 100% conversion in p-xylene solvent.⁶⁶ |
| 1,2-DMID  | 55                | 8H-1,2-DMID          | 5.23                    | Ru/Al₂O₃, 160 °C, 7 MPa, 0.7 h, 100% conversion in 1,4-dioxane solvent.⁶⁵ | Pd/Al₂O₃, 190 °C, 101 kPa, 4 h, 100% conversion in decalin solvent.⁶⁵ |

HFIP: hexafluoroisopropanol; p-TSA = p-toluenesulfonic acid.
release of NECZ in high efficiency. Fully dehydrogenated N-propylcarbazole can be obtained at 200 °C in 240 min with applied Pd/Al₂O₃ catalyst. Arlt et al. investigated the thermochemical properties of N-alkylcarbazoles (N-isopropylcarbazole, N-propylcarbazole, and N-butylcarbazole) and found the melting point of eutectic systems composed of N-alkylcarbazoles can be lowered dramatically to 24 °C, which are suitable for large scale and long distance storage and delivery at ambient conditions with existing infrastructures. In addition, Wersscheid et al. proposed benzyltoluene (BT) and dibenzyltoluene (DBT) as promising LOHCs. Although dehydrogenation of these hydrocarbon molecules was required at temperatures above 250 °C, these mixtures were still regarded as attractive LOHCs as the result of their low melting point (−34–36 °C), high boiling point (390 °C), low flammability and low costs. Recently, indole-based compounds were also suggested as LOHCs, such as indole, N-methylindole (NMID), 1,2-dimethylindole and 7-ethylindole (7-EID). Table 1 gives an overview of properties and reaction conditions for indole derivatives hydrogenation and dehydrogenation which have been reported in relative literatures. It is indicated that indole derivatives with different alkyl chains substituted in different positions exhibit markedly difference in hydrogenation and dehydrogenation kinetics.

In fact, we have published a number of hydrogen storage molecular articles, including carbazole series, indole series, etc. The purpose of this work is to build a database of organic hydrogen storage molecules and to obtain a certain construction rule by studying the influence of molecular structure (such as the number of side groups, types and number of aromatic rings) on the dehydrogenation performance of organic molecules. In this work, the disubstituted 2,3-dimethylindole (2,3-DMID) was well studied as a new LOHC candidate. The influences of temperature and hydrogen pressure on the hydrogen uptake rate of 2,3-DMID were investigated. Complete hydrogenation of 2,3-DMID can be realized at the temperature of 190 °C within 240 min. The dehydrogenation reaction rate of 8H-DMID was first order for 8H-DMID concentration. The apparent activation barrier of 8H-DMID consumption was 39.6 kJ mol⁻¹ at temperature in the range of 180–210 °C. The dehydrogenation process of 8H-2,3-DMID was analysed by experimental and DFT calculations.

## Results and discussion

### The physicochemical properties of 2,3-DMID and 8H-2,3-DMID

As shown in Table 2, both of 2,3-DMID and 8H-2,3-DMID keep high stability at ambient conditions and no severe hazard to people health and environment. The melting point of 2,3-DMID is 105 °C, which can be decreased by mixing with other LOHCs to form eutectic mixtures. The hydrogenated product, 8H-2,3-DMID, was liquid at room temperature, which can be conveniently delivered by using existing gasoline-based infrastructures.

### Hydrogenation of 2,3-DMID

The hydrogenation reaction of 2,3-DMID was performed at 160–200 °C and 7 MPa. The hydrogen absorption curves at the selected temperatures have been displayed in Fig. 1. The hydrogenation uptake rate accelerates as the reaction temperature was increased from 160 °C to 190 °C. After reaction for 1 h, the hydrogen storage gravimetric density reaches 0.57 wt% at 160 °C, 2.91 wt% at 170 °C, 3.21 wt% at 180 °C and 4.67 wt% at 190 °C, respectively. Specially, the hydrogen uptake rate increases notably with temperature rising from 160 °C to 170 °C, which can be explained that most reactant molecules can be activated to overcome the hydrogenation reaction barrier as the temperature exceeded 160 °C. The theoretical hydrogen capacity

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**Table 2** Physicochemical properties of 2,3-DMID and 8H-2,3-DMID

| Name | 2,3-DMID | 8H-2,3-2MID |
|------|----------|-------------|
| CAS number | 91-55-4 | N/A |
| Molecule formula | C₁₀H₁₁N | C₁₉H₂₄N |
| Molecular weight | 145.20 | 153.20 |
| Structural formula | ![2,3-DMID Structure](image) | ![8H-2,3-2MID Structure](image) |
| Melting point/°C | 105 | ≤−10 |
| Boiling point/°C | 285 | ≥285 |
| State | Yellow solid at room temperature | Transparent liquid at room temperature |
| Storage and stability | Store in cool, dry and well-ventilated areas; stable under ambient conditions, but light sensitive | Store in cool, dry and well-ventilated areas; stable under ambient conditions, light sensitive |
| Safety | May cause irritation of skin and eyes. The toxicity of this substance has not been investigated completely | May cause irritation of skin and eyes. The toxicity of this substance has not been investigated completely |
of 2,3-DMID (5.23 wt%) can be reached at 190 °C after 4 h. However, the reaction rate decreased when the temperature was further raised to 200 °C. The reasons for the decrease may be its exothermic nature of hydrogenation reaction, which causes the equilibrium to be shifted towards the reactants with increasing temperature. In addition, high temperature led to the difficulty in dissolving more hydrogen in the liquid though the pressure was increased, which limited the hydrogen transfer at the surface of the catalyst.

Fig. 2 shows the evolution of product distribution with reaction time during 2,3-DMID hydrogenation over Ru/Al₂O₃. Only 4H-2,3-DMID was detected as the intermediate along with the fully hydrogenated product, 8H-2,3-DMID. The consumption rate of 2,3-DMID increased significantly in 170–200 °C compared with that in 160 °C, which explained the obvious decrease of the hydrogen uptake rate (Fig. 2) in 160 °C at the beginning of the reaction. The concentration of 4H-2,3-DMID rapidly reached maximum in the initial 30 minutes at 170–200 °C. Almost 100% hydrogenation of 2,3-DMID was realized in 240 min at 190 °C, 540 min at 180 °C and 660 min at 170 °C. Increase temperature to 200 °C, the consumption of 4H-2,3-DMID become sluggish which lead to the decrease of hydrogen uptake rate compared with that of at 190 °C. No 2H- and 6H- intermediates were detected. It is likely that they were kinetic unstable and immediately further converted to the final product upon formation.

Fig. 3 displays the hydrogen adsorption curves of 2,3-DMID under different hydrogen pressures at 190 °C over 5 wt% Ru/
Al$_2$O$_3$. It is found that the increase of pressure is in favor of accelerating hydrogenation rates, which can be attributed to the improvement in hydrogen solubility and the shift in the direction of hydrogenation of the chemical equilibrium.

**Dehydrogenation of 8H-2,3-DMID**

The dehydrogenation reactions were carried out at the temperature of 180–210 °C over 5 wt% Pd/Al$_2$O$_3$. The hydrogen release curves of 8H-2,3-DMID at different temperatures were shown in Fig. 4. The dehydrogenation rate accelerates obviously with the temperature raised from 180 °C to 200 °C. 96% dehydrogenation was obtained after 600 min at 200 °C. Further increase temperature to 210 °C, the time for achieving the theoretical hydrogen storage gravimetric density (5.23 wt%) was shortened to be 480 min.

Fig. 5 shows the evolution of product distributions with reaction time at selected temperatures during the process of 8H-2,3-DMID dehydrogenation. 8H-2,3-DMID was consumed as soon as the reaction was started. However, the conversion of 8H-2,3-DMID was sluggish and the complete conversion of 8H-2,3-DMID was not obtained until the reaction proceeded in 8 h at 210 °C. Three intermediates, 6H-, 4H- and 2H- were detected and no other side products were found. The accumulation of 6H-2,3-DMID from 8H-2,3-DMID was converted rapidly to form 4H-2,3-DMID and 2H-2,3-DMID, resulting in the maximum concentration of 6H-2,3-DMID to be reached quickly. Obviously, the dehydrogenation of 8H-2,3-DMID was a consecutive four step reaction, sequentially forming 6H-2,3-DMID, 4H-2,3-DMID, 2H-2,3-DMID and the fully dehydrogenated product, 2,3-DMID. The conversion of 8H-2,3-DMID and selectivity to 2,3-DMID after 5 h were presented in Table 3, which were calculated by the eqn (1) and (2) bellow, respectively.

$$\text{Conversion} = \frac{\text{Reactant converted}[\text{mol}]}{\text{Sum of reactants [mol]}} \times 100\% \quad (1)$$

$$\text{Selectivity} = \frac{\text{Specific product [mol]}}{\text{Sum of products [mol]}} \times 100\% \quad (2)$$

In fact, a disubstituted indole derivative, 1,2-DMID has been studied in detail previously. Only 4H-1,2-DMID was identified as the intermediate in the dehydrogenation reaction of 8H-1,2-DMID and completely dehydrogenated product can be obtained in 60 min at 200 °C with applied Pd/Al$_2$O$_3$. In comparison, three intermediates, 6H-, 4H- and 2H- were detected and the consumption of these intermediates were sluggish under designed conditions in 8H-2,3-DMID dehydrogenation. The reason may be that the steric hindrance produced by the methyl connected to the N atom in 1,2-DMID benefits the sorption of 1,2-DMID on the catalyst, which leads to a faster dehydrogenation rate.

The dehydrogenation kinetics of 8H-2,3-DMID were also investigated. Previous investigations on dehydrogenation of several LOHCs such as N-ethylcarbazole, 1,2-dimethylindole and 2-methylindole have shown that the reaction follows first order kinetics. Hence, the dehydrogenation of 8H-2,3-DMID was assumed to follow first order kinetics. Fig. 6(a) presents the plots of $\ln(C_0/C_{8H-2,3-DMID})$ versus reaction time $t$ at 180–210 °C, which indicates that the experimental points can be readily fitted to the first order reaction kinetics model. The rate constant derived from the slope of the fitting lines increases from 0.0050 mol L$^{-1}$ at 180 °C to 0.0090 mol L$^{-1}$ at 210 °C. Particularly, the dehydrogenation rate constants increase obviously from 180 °C to 200 °C due to its endothermic nature. Further increase temperature to 210 °C, the rate constant only

![Fig. 5](image-url) Time-dependent product distribution for 8H-2,3-DMID dehydrogenation at different temperatures. (a) 180 °C, (b) 190 °C, (c) 200 °C, (d) 210 °C.

![Fig. 6](image-url) (a) First-order kinetic model fitted to the experimental data obtained for dehydrogenation of 8H-2,3-DMID. (b) Arrhenius plot obtained from 8H-2,3-DMID dehydrogenation reactions at 180–210 °C.

| Temperature (°C) | Conversion (%) | Selectivity (%) | Hydrogen release content (wt%) |
|-----------------|---------------|----------------|-------------------------------|
| 180             | 81.5          | 62.3           | 3.71                          |
| 190             | 89.2          | 75.6           | 4.27                          |
| 200             | 94.1          | 85.2           | 4.67                          |
| 210             | 93.6          | 88.7           | 4.75                          |

Table 3 The conversion, selectivity and hydrogen release content under different dehydrogenation temperatures in 5 h.
increases slightly. The reason may be that the high temperature is beneficial for dehydrogenation kinetics meanwhile causes carbon deposition on the catalyst which decreases the catalytic activity. As shown in Fig. 6(b), the ln k was plotted verse the 1/T.

The estimated reaction activation barrier for 8H-2,3-DMID dehydrogenation based on the Arrhenius equation is 39.6 kJ mol$^{-1}$, which is significantly lower than that of 8H-1,2-DMID dehydrogenation (111.9 kJ mol$^{-1}$). Notably, the reaction activation energy obtained from the experiments was influenced by kinds of factors, such as reaction conditions, mass transfer and so on.$^{68}$

In addition, the purity of released hydrogen was tested by DSMS (Dynamic Sampling Mass Spectrometer), which can dynamically monitor the pressure of the released gas during dehydrogenation. As shown in Fig. 7, the water vapor may come from the atmosphere when the liquid was added to the dehydrogenation reactor. The result indicated that no side reactions occurred under designed dehydrogenation conditions and the hydrogen gas was in a high purity (>99%).

The catalyst stability was also tested in 2,3-DIMID hydrogenation and dehydrogenation. The same Ru/Al$_2$O$_3$ catalyst was used to hydrogenate 2,3-DIMID under 190°C and 7 MPa for 3 times. It is found almost 100% 8H-2,3-DIMID was achieved within 240 min in 3 cycles, indicating the high stability of Ru/Al$_2$O$_3$ catalyst in hydrogenation of 2,3-DIMID. Similarly, the same Pd/Al$_2$O$_3$ was used to dehydrogenate 8H-2,3-DIMID for 3 times. The obvious catalytic activity degradation of Pd/Al$_2$O$_3$ was observed. This may be because the carbon formation on the surface of the catalyst and the metal agglomeration after dehydrogenation for a long time. The study on design and preparation high activity and stability catalyst is under way (Fig. 8).

During 8H-2,3-DIMID dehydrogenation, three intermediates, 2H-, 4H- and 6H-, were detected. The possible structures of the isomers were designed and the corresponding energy for each species has been displayed in Fig. 9.

**Scheme 1** The reaction pathway of 8H-2,3-DIMID dehydrogenation. (Unit of Er: kJ mol$^{-1}$).

### Experimental

**Materials**

2,3-dimethylindole (AR) and Mesitylene (AR) were provided by Energy Chemical Company and Sinopharm Chemical Reagent Company Limited, respectively. 5 wt% Ru/Al$_2$O$_3$ and 5 wt% Pd/Al$_2$O$_3$ catalysts were purchased from Shanxi Kaida Chemical Engineering Company Limited. The BET surface areas and pore sizes of the Ru/Al$_2$O$_3$ and Pd/Al$_2$O$_3$ are 85.24 m$^2$ g$^{-1}$, 13.41 nm
and 68.35 m² g⁻¹, 11.89 nm, which are measured by ASAP 2020. Ultra-high purity H₂ gas was obtained from Sichuan Ally HighTech Company. Gas chromatography and mass spectrometry (Agilent 7890/5975C GC-MS) was used to analyse the reaction liquid samples regularly. The test method was same as described in ref. 59.

Hydrogenation reaction of 2,3-dimethylindole

The hydrogenation reaction was performed in a 250 ml autoclave batch reactor (Shanghai LABE Instrument LB250) over 5 wt% Ru/Al₂O₃ by controlling the reaction temperatures and hydrogen pressures. The reactor was loaded with 1 g of 2,3-dimethylindole and 0.1 g of Ru/Al₂O₃ in a 40 ml of mesitylene and heated to the designed temperature. As the reaction started, small amount of the mixture liquid sample was collected and analysed regularly by GC-MS.

Dehydrogenation reaction of 8H-2,3-dimethylindole

The 8H-2,3-DMID produced by complete hydrogenation was used as initial reactant in dehydrogenation. The reaction was performed at 180–210 °C in a 50 ml three-necked flask reactor which was connected with a condenser. 5 g of 8H-2,3-DMID was injected into the reactor. Then the reactor was heated to the required temperature following by adding 1 g of 5 wt% Pd/Al₂O₃ catalyst. The reaction time was recorded as soon as stirring was started. Liquid mixtures were taken out regularly and analysed with GC-MS. The hydrogenation and dehydrogenation experiment process for 2,3-DMID was described as below (Fig. 10).

DFT calculations

The binding energies of all structural isomers were calculated by DFT (density functional theory), which were conducted by Material Studio DMol³. The detailed calculation method was the same as mentioned in ref. 58.

Conclusions

Indole-based derivatives have been selected as attractive LOHCs recently. These indole-based compounds exhibit different hydrogenation and dehydrogenation kinetics, which can be strongly influenced by the steric hindrance which were created by the different substituted alkin chains. 2,3-DMID was studied as another new LOHC in detail in this report. Fully hydrogenated product can be obtained within 4 h at 190 °C and 7 MPa. Dehydrogenation of 8H-2,3-DMID fits first order kinetics model. The apparent activation barrier of 8H-DMID dehydrogenation was estimated to be 39.6 kJ mol⁻¹ at 180–210 °C. The dehydrogenation process can be written as: 8H-2,3-DMID → 6H-2,3-DMID → 4H-2,3-DMID → 2H-2,3-DMID → 2,3-DMID.

Conflicts of interest

There are no conflicts to declare.

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