

Metallo-N-Heterocycles - A new family of hydrogen storage material

Khai Chen Tan^{a,b,1}, Yang Yu^{a,c,1}, Ruteng Chen^{d,1}, Teng He^{a,*}, Zijun Jing^{a,c}, Qijun Pei^{a,c}, Jintao Wang^{a,c}, Yong Shen Chua^{b,**}, Anan Wu^{d,***}, Wei Zhou^e, Hui Wu^{e,****}, Ping Chen^a

^a Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China

^b School of Chemical Sciences, Universiti Sains Malaysia, 11800, Minden, Penang, Malaysia

^c University of Chinese Academy of Sciences, Beijing, 100049, China

^d Fujian Provincial Key Laboratory of Theoretical and Computational Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China

^e NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD, 20899-6102, USA



ARTICLE INFO

Dedicated to the Dalian Institute of Chemical Physics, Chinese Academy of Sciences on the occasion of its 70th anniversary.

Keywords:

Metallo-N-Heterocycle
Thermodynamic alteration
Reversible hydrogen storage

ABSTRACT

Storing hydrogen efficiently in condensed materials is a key technical challenge. Tremendous efforts have been given to inorganic hydrides containing B–H, Al–H and/or N–H bonds, while organic compounds with a great variety and rich chemistry in manipulating C–H and unsaturated bonds, however, are undervalued mainly because of their unfavourable thermodynamics and selectivity in dehydrogenation. Here, we developed a new family of hydrogen storage material spanning across the domain of inorganic and organic hydrogenous compounds, namely metallo-N-heterocycles, utilizing the electron donating nature of alkali or alkaline earth metals to tune the electron densities of N-heterocyclic molecules to be suitable for hydrogen storage in terms of thermodynamic properties. Theoretical calculations reveal that the enthalpies of dehydrogenation (ΔH_d) of these metallo-N-heterocycles are dependent on the electronegativity of the metals. In line with our calculation results, sodium and lithium analogues of pyrrolides, imidazolides and carbazolides of distinct structures were synthesized and characterized for the first time, where the cation- π interaction was identified. More importantly, a reversible hydrogen absorption and desorption can be achieved over lithium carbazole which has a hydrogen capacity as high as 6.5 wt% and a suitable enthalpy of dehydrogenation of $34.2 \text{ kJ mol}^{-1}\text{-H}_2$ for on-board hydrogen storage.

1. Introduction

Finding a practical hydrogen storage material possesses a daunting challenge in the implementation of hydrogen economy [1–3]. Storing hydrogen chemically in condensed materials provides a safe and efficient way to solve this problem [4,5]. Tremendous research efforts have been made on the development of inorganic hydrides such as alanates [6], amide-hydride composites [7], borohydrides [8], etc. in the past two decades. Comparatively less attention was given to organic hydrides [9, 10], undervaluing the potential of the large family of organic compounds. This is probably due to the difficulties in manipulating the thermodynamic properties and the selectivity in the dehydrogenation of organic hydrides. Given that no materials developed to date could fully

meet the practical requirements for hydrogen storage in terms of thermodynamic/kinetic properties, reversibility, hydrogen capacity, safety and cost etc., a breakthrough in the development of novel material systems is highly needed. The idea we discuss in the present work is the hybridization of inorganic and organic hydrides [11–14], in particular N-heterocycles, to form a new family of hydrogen storage material namely metalorganic hydrides. Actually, in chemistry, a hydride is a compound having negatively-charged hydrogen anion [15]. However, nowadays, hydrogenous compounds having hydrogen bonded to metals or non-metal in ionic, metallic or covalent manner are collectively referred as hydrides [1,16]. Therefore, we use the term metalorganic hydrides here. We demonstrated that three N-heterocycles (pyrrole, imidazole, carbazole) can be transformed into novel metallated

* Corresponding author.

** Corresponding author.

*** Corresponding author.

**** Corresponding author.

E-mail addresses: heteng@dicp.ac.cn (T. He), yschua@usm.my (Y.S. Chua), ananwu@xmu.edu.cn (A. Wu), huiwu@nist.gov (H. Wu).

¹ These authors contributed equally.

derivatives via facile reaction with hydrides of alkali or alkaline earth metals (Li, Na, K, Mg, and Ca). Two new structures were resolved. The hydrogen storage thermodynamic properties of the newly developed materials depend strongly on electronegativity of the metal as indicated by our DFT calculations. Our experimental results further proved that lithium carbazolide, as a representing metalorganic hydride, exhibits attractive properties in terms of hydrogen capacity (6.5 wt%) and reversibility (enthalpy of dehydrogenation, $\Delta H_d = 34.2 \text{ kJ mol}^{-1}\text{-H}_2$).

2. Results and discussion

2.1. Thermodynamic calculations

The common feature of N-heterocycles (pyrrole, imidazole and carbazole) investigated hereinafter is that they have N–H bond where the electropositive $\text{H}^{\delta+}$ may be replaced by alkali and alkaline earth metal cations ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Mg}, \text{Ca}$) to form metallo-N-heterocycles. It was reported that the reactions between alkali or alkaline earth metal hydrides and organics with active $\text{H}^{\delta+}$ (such as N–H or O–H) are thermodynamically favourable and experimentally feasible [11–13]. Consequently, the metallations investigated in the present study could be feasible as shown in the reactions 1 to 3 in the experimental section. We then focus on the effect of metallation on the heat flow of hydrogen absorption and desorption over the tetrahydropyrrolide/pyrrolide (M-H-PY/M-PY for short), tetrahydroimidazole/imidazole (M-H-IMD/M-IMD for short), and dodecahydrocarbazole/carbazole (M-H-CZ/M-CZ for short) pairs as shown in Fig. 1a using X1s method [17] which combines the DFT method with a neural network correction for a more accurate prediction of heat of formation of large molecules than normal DFT method.

To verify the accuracy of X1s method in determining the thermodynamic properties of N-heterocycles, we firstly calculated the

dehydrogenation enthalpy (ΔH_d) of tetrahydropyrrole (H-PY), tetrahydroimidazole (H-IMD) and dodecahydrocarbazole (H-CZ) and found that the ΔH_d of H-PY is in agreement with the value from experiment [10,18]. Since we used an improved method to calculate ΔH_d , the results are slightly different from the calculated values from other methods [10,19]. We then performed the gas-phase calculations on the metallo-N-heterocycles and reveal significant decreases of ΔH_d of the metallated systems compared to those of the pristine systems (Fig. 1b and Tables S1–S5). Noticeably the ΔH_d decreases with Pauling electronegativity, Z , of the metals (Fig. 1b and Tables S2–S5). We further quantified the amount of charge transfer from metal to aromatic ring, and considered it as a descriptor of the metallation effect (Fig. 1c and Tables S2–S5). Nearly linear relationships between ΔH_d and the charge transferred were obtained, agreeing well with the electronegativity effect of metals and manifesting that the ΔH_d could be manipulated via adjusting metals. Although both H-lean and H-rich metallo-N-heterocycles can be stabilized, the conjugation effect is significantly greater than hyperconjugation effect of the same type, i.e., the electrons transferred from metal to aromatic ring in H-lean compounds are more easily delocalized than that of H-rich compounds, resulting in more stabilized H-lean counterparts as well as substantial decrease in ΔH_d upon metallation. This could be the reason to the linear relationship between ΔH_d and charge transfer from metal to aromatic ring (Fig. 1c and Tables S2–S5). It is also shown that ΔH_d of M-H-PY and M-H-IMD decrease more significantly than that of M-H-CZ, which could be ascribed to the fact that the donated electrons from metal in M-CZ can be delocalized in 3 rings of the carbazole, averaging the metallation effect. Theoretical investigations by Jessop et al. disclosed nicely that electron donating substituents such as $-\text{OH}$, $-\text{NH}_2$ etc. can decrease the ΔH_d of cyclohexane from ca. 68 to 65 and 62 $\text{kJ mol}^{-1}\text{-H}_2$, respectively, where the extent of variation is less than 10% [10,18]. The change in ΔH_d is also insignificant when a methyl group is substituted on imidazole (39.7 $\text{kJ mol}^{-1}\text{-H}_2$) to form

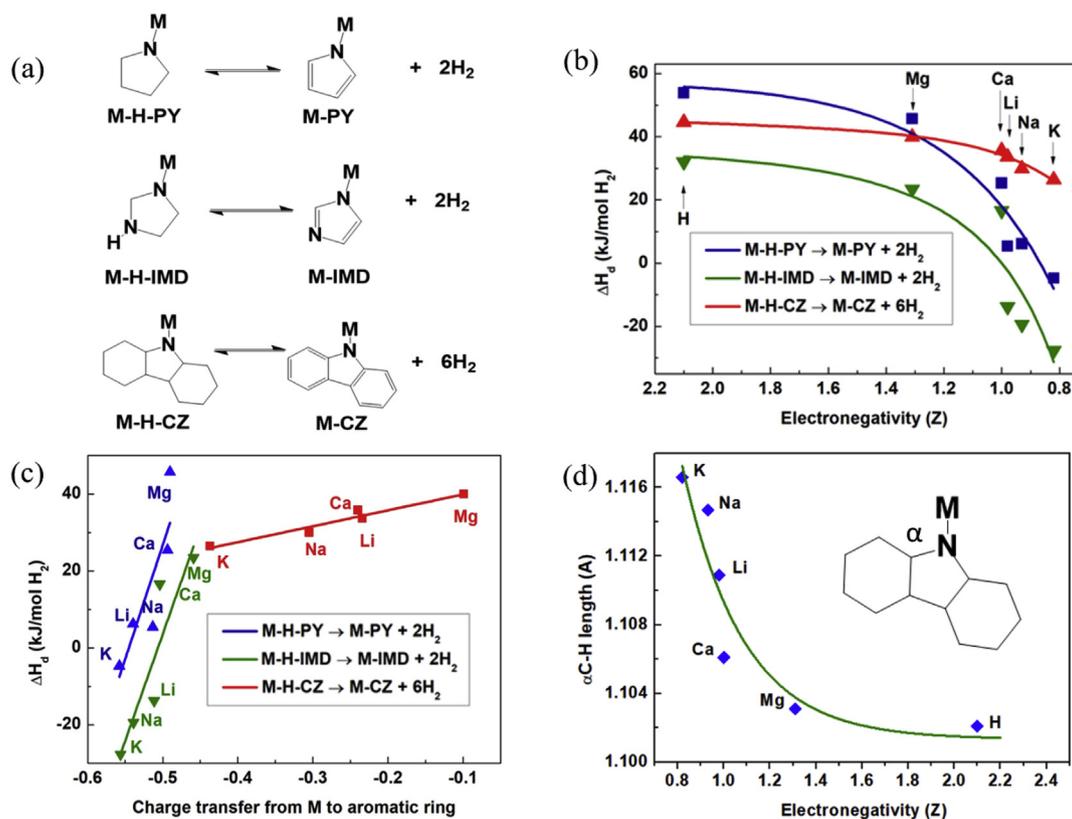


Fig. 1. (a) Proposed reactions for reversible hydrogen storage using metallo-N-heterocycles. (b) ΔH_d of different metallo-N-heterocycles versus electronegativities of H and metals. (c) ΔH_d versus the charge transfer from metal to aromatic rings. (d) The length of C–H at α site of M-H-CZ versus electronegativities of H and metals. *For the ease of illustration, M in (a) is mono-valent.

1-methylimidazole ($38.9 \text{ kJ mol}^{-1}\text{-H}_2$). Comparatively, metallation exerts a much stronger effect owing to a stronger electron donating ability of alkali or alkaline earth metal (see Fig. 1b and Tables S2–S5). For instance, hydrogen desorption from lithium imidazolidate ($-13.8 \text{ kJ mol}^{-1}\text{-H}_2$) is even exothermic! Another interesting finding is that the lengths of C–H bond at the α -site of H-rich CZ increase upon metallation as shown in Fig. 1d and Table S6, manifesting the C–H bond can be activated to certain extent and likely to dissociate firstly upon dehydrogenation. Considering the hydrogen storage capacity and ΔH_d of these metalorganic hydrides predicted in Fig. 1, we synthesized lithium and sodium analogues of pyrrolide, imidazolidate and carbazolidate to verify these conceptual materials.

2.2. Syntheses and crystal structures of metalorganic hydrides

As shown in Table S2, lithium and sodium analogues of metallo-N-heterocycles are more appealing in terms of hydrogen storage capacity, enthalpy of dehydrogenation and ease of synthesis. Therefore, we attempted to synthesize lithium and sodium analogues of metallo-N-heterocycles using LiH and NaH as the metal precursors to react with pyrrole, imidazole and carbazole, respectively, in a molar ratio of 1:1 according to equations 1–3 in experimental part. One equivalent of H_2 was released in the mechanical milling process of LiH/NaH with pyrrole and imidazole, suggesting a complete conversion to metallo-pyrrolides and imidazolides, respectively. New phases were detected by X-ray diffraction (XRD, Fig. 2a). However, the reactions between hydrides and carbazole can only take place at elevated temperatures ($\sim 250 \text{ }^\circ\text{C}$) giving rise to metallo-carbazolides (see XRD patterns in Fig. 2a). The metallated

products were characterized using liquid state nuclear magnetic resonance (NMR). However, no proper solvent was found for imidazolides of sodium and lithium, other metallated products clearly show the disappearance of the protons of N–H group of pyrrole and carbazole at 10.7 ppm and 11.3 ppm, respectively. The ^1H resonances of pyrrolides and carbazolides are shifted upfield, indicating more shielding effect upon metallation (Fig. 2b). In addition, strong ^7Li and ^{23}Na signals were detected in the pyrrolide and carbazolidate samples (Figs. S1 and S2) further evidence the substitution of H by Li or Na. ^{13}C NMR spectra also reveal the impact of metallation: the C atom closes to the N atom has a downfield shift, while the C atom further to N atom has an upfield shift (Fig. 2c), which is consistent with our simulation on ^{13}C NMR signals of sodium carbazolidate and pyrrolide (Figs. S3 and S4).

All the metallated samples present distinct XRD patterns from the parent pyrrole, imidazole and carbazole (Fig. 2a). The structures of some of the aromatic metallo-N-heterocycles are difficult to be resolved due to their poor crystallinity or interference of impurity phases. Fortunately, the structures of sodium analogues of pyrrolide and imidazolidate were successfully identified by direct space methods. DFT calculations were then performed to optimize the atomic positions (see supporting information, Tables S7 and S8) and the fully relaxed structures are used in the bond length discussion below. Rietveld refinements with rigid body constraints on organic anions based on the DFT optimized structure models were conducted using the synchrotron and laboratory XRD data (Figs. S5 and S6). Sodium pyrrolide and imidazolidate possess monoclinic (Cc (No. 9)), and orthorhombic (Pna $_2$ 1 (No. 33)) structures, respectively (Tables S7–S11). As shown in Fig. 2d and e, in the two structures, Na^+ forms ionic bonds with the $\text{N}^{\delta-}$ of the aromatic N-heterocycles via

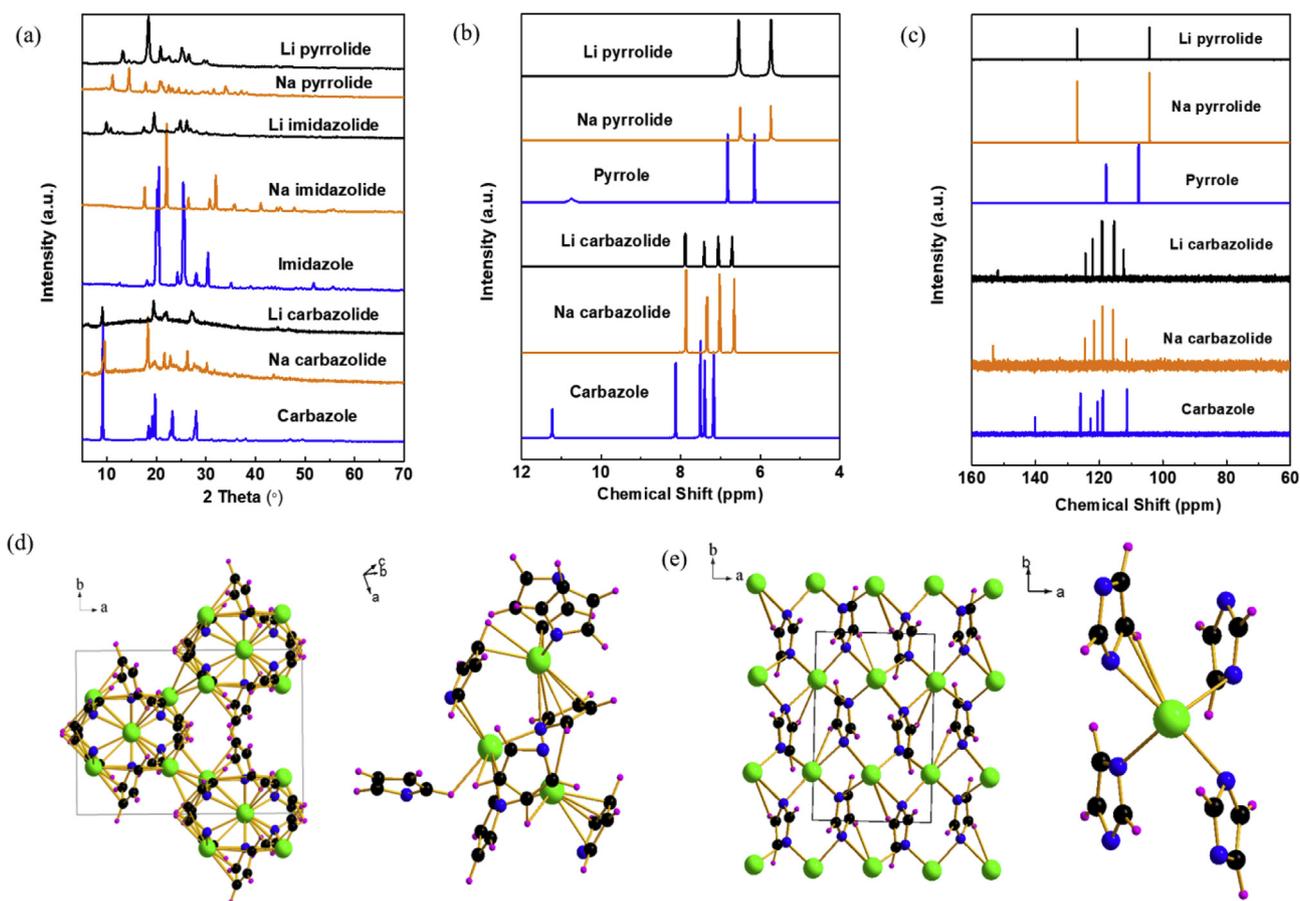


Fig. 2. (a) XRD patterns of sodium and lithium analogues of pyrrolides, imidazolides and carbazolides. (b) ^1H NMR spectra of synthesized metallo-pyrrolides and -carbazolides as compared to their molecular counterparts in *d*-DMSO. (c) ^{13}C NMR spectra of synthesized metallo-pyrrolides and -carbazolides as compared to their molecular counterparts in *d*-DMSO. Crystal structures (left) and local coordination of Na^+ cation (right) of (d) sodium pyrrolide and (e) sodium imidazolidate. Blue sphere: nitrogen, green sphere: sodium, black sphere: carbon and pink sphere: hydrogen.

electrostatic attraction. In sodium imidazolidine, each Na^+ cation binds to the N of four neighboring imidazolidine anions, forming a distorted tetrahedral coordination with Na–N bond distances ranging from 2.4196 to 2.4455 Å to 2.5031–2.5174 Å. The imidazolidine anions are closely linked by such Na–N interactions assembling a strongly bonded three-dimensional network. At the same time, a weak cation- π interaction between sodium and the adjacent aromatic ring was observed. While in the cases of sodium pyrrolidine, besides Na–N bonding, Na^+ cation also interacts with the face of an adjacent aromatic ring via cation- π interaction. The pyrrolidine anions are chained together through both Na–N bondings (2.3927–2.3979 Å and 2.4776–2.6814 Å) and the cation- π interaction with the Na^+ on top of π face of the pyrrolidine rings, creating a 3-D arrangement (Fig. 2d). The determined crystal structures provide insightful details about cation-anion arrangement configurations and interactions, which will conversely help hone the DFT calculations on their thermodynamic parameters.

2.3. Hydrogen absorption and desorption

As shown in Fig. 1c, the dehydrogenation thermodynamics can be manipulated by varying metals. For instance, the ΔH_{d} of H-CZ/CZ pair can be significantly reduced upon metallation to a suitable range of 26.4–40.0 $\text{kJ mol}^{-1}\text{-H}_2$. Of all the studied pairs, the Li–H-CZ/Li-CZ pair with ΔH_{d} of 33.7 $\text{kJ mol}^{-1}\text{-H}_2$ and the theoretical hydrogen storage capacity of 6.5 wt% appears to be attractive. Therefore, Li–H-CZ/Li-CZ pair was investigated for the demonstration of the reversible hydrogen storage. Because the hydrogenation (including the activation of H–H and C=C bonds) would need to overcome certain kinetic barrier, we introduced fresh-made Pt, Pd, Rh and Ru particles to catalyse the hydrogen absorption over lithium carbazolidine (Figs. S7 and S8), and found that Ru outperforms others, i.e., a complete hydrogenation can be achieved even under 100 °C and 70 bar of H_2 as evidenced by the amount of hydrogen absorbed (Fig. 3a) and the NMR observation of Li–H-CZ as the only product (Fig. 3b and Fig. S9).

Because of the high selectivity towards Li–H-CZ, we employed C80 to measure the heat of hydrogenation of Li-CZ to Li–H-CZ. As shown in

Fig. 3c, an exothermic feature is observed, from which a ΔH of ca. -34.2 $\text{kJ mol}^{-1}\text{-H}_2$ for hydrogenation can be derived (see supporting information) that is in excellent agreement with the DFT prediction (33.7 $\text{kJ mol}^{-1}\text{-H}_2$ for dehydrogenation, Fig. 1).

Catalytic dehydrogenation is always a challenging task in organic hydrogen carriers [20–24]. In the dehydrogenation of Li–H-CZ, Ru particles, however, is not effective. We, therefore, tried commercial 5 wt% Pd/C and 5 wt% Rh/ Al_2O_3 to improve the kinetics of hydrogen desorption process. Fortunately, both catalysts were capable of selectively converting Li–H-CZ back to Li-CZ at 200 °C, recorded a conversion yield of 72% and 44%, respectively. (Fig. 3d and Table S12). Because the mixture of the reactant and catalyst are in slurry form, we suppose higher conversion can be achieved upon sufficient contact between the Li–H-CZ and the catalysts. It is noteworthy that neat dodecahydrocarbazole shows no conversion for dehydrogenation under the same conditions, which may be due to the unfavourable dehydrogenation thermodynamics (Table S12).

Development of efficient catalysts is highly demanded for both dehydrogenation and hydrogenation of these metallo-N-heterocycles. Although no report was found on the catalyst development for these newly developed materials, the concept and knowledge on the cycloalkanes and N-heterocycles will definitely shine light on the fabrication of suitable catalysts for metallo-N-heterocycles. Furthermore, it is scientific interests to explore other forms of energy, such as light, to drive the hydrogenation and dehydrogenation under the help of catalyst, which are hot topics in the hydrogenation/dehydrogenation of organics recently [25,26].

3. Conclusion

As demonstrated in this study, alkali or alkaline earth metals can be utilized as strong electron donating substituents for N-heterocycles, creating a new family of hydrogen storage materials with tunable thermodynamic properties. Three types of metallo-N-heterocycles were studied in the present study. The Li-CZ pair serves as an example demonstrating the capability of the metalorganic hydride for hydrogen

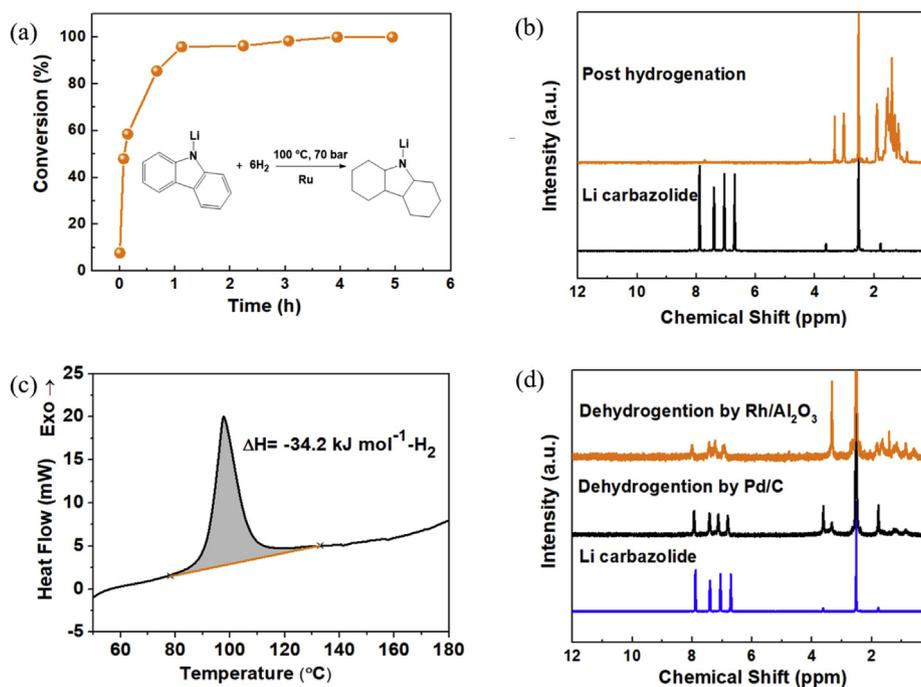


Fig. 3. (a) Conversion of lithium carbazolidine catalyzed by Ru particles. (b) ^1H NMR spectra of the neat and hydrogenated lithium carbazolidine in *d*-DMSO. (c) Measurement on the heat of hydrogenation of lithium carbazolidine using C80. (d) ^1H NMR spectra of the neat lithium carbazolidine and the dehydrogenated lithium dodecahydrocarbazolidines catalyzed by Pd/C and Rh/ Al_2O_3 at 200 °C.

