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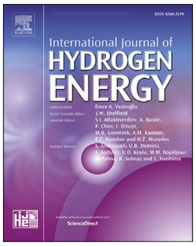

Syntheses of alkali-metal carbazolides for hydrogen storage

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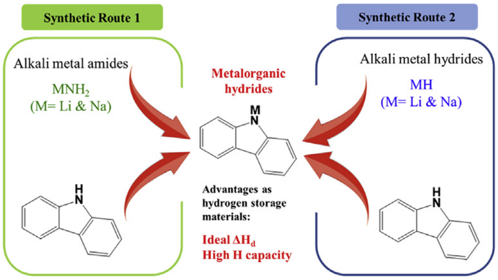
HIGHLIGHTS

- Na and Li carbazolides are synthesized via alkali metal hydrides and amides.
- Metal amides are able to synthesize metallo-carbazolides under milder conditions.
- The interaction involved in the synthesis of metallo-carbazolide was investigated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 February 2020
Received in revised form
21 May 2020
Accepted 3 June 2020
Available online xxx

Keywords:
Carbazole
Metallation
Hydrogen storage
Metalorganic hydride

ABSTRACT

Metalorganic hydrides are a new class of hydrogen storage materials. Replacing the H of N—H or O—H functional groups using metal hydrides have been recently reported, which substantially improved the dehydrogenation properties of heteroaromatic organic hydrides by lowering their enthalpies of dehydrogenation (ΔH_d), enabling dehydrogenation at much lower temperatures. Among the reported metalorganic hydrides, lithium carbazolide and sodium carbazolide appear to be the most attractive hydrogen storage/delivery material owing to its high hydrogen capacity (>6.0 wt%) and ideal ΔH_d. Nevertheless, the interaction of carbazole and corresponding metal hydride to form metallo-carbazolide is a multistep process involving intensive ball milling and high temperature treatment, where the interaction was not investigated in detail. In this paper, both alkali metal hydrides and amides were employed to react with carbazole to synthesize corresponding carbazolides, aiming to broaden and optimize the synthetic method and understand the reaction mechanism. Our experimental results showed that around one equivalent of H_2 or NH_3

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https://doi.org/10.1016/j.ijhydene.2020.06.024

Please cite this article as: Tan KC et al., Syntheses of alkali-metal carbazolides for hydrogen storage, International Journal of Hydrogen Energy, https://doi.org/10.1016/j.ijhydene.2020.06.024

could be released from the reactions of carbazole and corresponding hydrides or amides, respectively. Instrumental spectroscopic analyses proved that metallo-carbazolides were successfully synthesized from all precursors. It is found that the alkali metal amides (*i.e.*, $LiNH_2$ and $NaNH_2$) with stronger Lewis basicities as metal precursors could synthesize the metallo-carbazolides under milder conditions. Furthermore, *quasi in situ* nuclear magnetic resonance results revealed that alkali metal could replace H (H–N) gradually, donating more electrons to carbazole ring. Additionally, the solubilized alkali cation may unselectively interact with π-electron of aromatic systems of both carbazole molecules and carbazolide anions via electrostatic cation-π interactions.

Introduction

The ever-increasing reliance on the exhausting fossil fuel reserves has caused tremendous negative effects, both environmentally and economically to the society. Hydrogen, an alternative energy carrier, is poised to play critical role in dwindling such negative impacts if the application of hydrogen energy is made common. Nevertheless, widespread application of hydrogen as a fuel for energy supply in domestic, industry and transportation is limited largely due to the unsolved challenge in hydrogen storage. Among the hydrogen storage techniques available, *i.e.*, physical [1–3] and chemical storage [4–7] of hydrogen, chemical storage attracted intensive attention due to driving interest for vehicular application that emphasizes high volumetric and gravimetric capacities as the key prerequisites.

Despite the facts that chemical storage using inorganic hydrides including metal hydrides, complex hydrides and chemical hydrides were studied both intensively and extensively in the past two decades, copious obstacles such as reversibility, formation of by-products as well as high operational temperatures are still the main challenges that would need to overcome [4–10]. Adopting organic hydrides in the field of hydrogen storage is still rarely performed in the past few decades until the reversible hydrogenation and dehydrogenation of cycloalkanes had been reported [11]. Most of the organic hydrides are hydrogen rich but they typically suffer from imperfections including high dehydrogenation temperature, slow reaction kinetics and low selectivity which impede their applications in hydrogen storage. As the primary consideration of the practicability of the materials for application, a hydrogen rich material with reversible hydrogen storage at operating temperature in the range of −45 to 80 °C is highly favourable. In most cases of organic hydrides, high reaction temperature is a consequence of the collective effect of high reaction barrier and high reaction enthalpy [12,13]. Therefore, extensive research effort has been devoted to tune both the dehydrogenation thermodynamics and kinetics. Efforts such as incorporation of heteroatoms (N or O atom) into the carbon rings [14,15] or substitution of a more electron donating group outside the ring [14,16] have been proven to tune the thermodynamics of dehydrogenation efficiently. Emphasis on structural preferences that favour low temperatures dehydrogenation such as five-membered ring over six-membered ring system, extended pi-conjugated over pi-conjugated system, substituent N over ring N, as well as 1,3-arrangement over 1,2- and 1,4-arrangements of ring N, have been highlighted [15]. Carbazole is a well-known organic hydride which fulfils several of such structural preferences in a molecule, i.e., presence of extended pi-conjugated system with two six-membered of benzene rings being fused on either side of a five-membered nitrogen-containing ring, a ring N atom in five-membered ring and a substituent N atom in each of the benzene rings [14]. It has also been gaining significant attention in the field of hydrogen storage owing to its high hydrogen storage capacity (6.7 wt%). However, the high enthalpy of dehydrogenation ($\Delta H_d = 52$ kJ mol^{-1}-H_2) [15] is still not suitable for practical applications. Until recently, we proposed a new class of materials namely metalorganic hydrides [17,18] in which it involved the hybridization of organic and inorganic compounds via the replacement of the H of N–H (or O–H) of an organic compound with a more electron donating alkali or alkaline earth metal to tailor the ΔH_d of the compounds. Through this attempt, we found that the ΔH_d can be tuned with great significance. For instance, the ΔH_d of carbazole reduced drastically (from 52 kJ mol^{-1}-H_2 to a range of 26–40 kJ mol^{-1}-H_2 depending on different metals) upon metallation. Among the studied metal-substituted carbazolides, lithium and sodium carbazolides with H-capacity higher than 6.0 wt% and ideal ΔH_d (*ca.* 30–34 kJ mol^{-1}-H_2) are promising candidates for hydrogen storage. They were successfully synthesized by reacting carbazole with respective metal hydrides, where the basic $H^{\delta-}$ of metal hydride reacts with the acidic $H^{\delta+}$-N of carbazole, liberating one equivalent of H_2. However, it is worth noting that the synthesis of metal carbazolide was not straight forward. It required intensive ball milling followed by thermal treatment. Furthermore, the interaction of carbazole with metal hydrides was not well investigated. In this study, we mainly focus on the syntheses of sodium and lithium analogues of carbazolides using different lithium and sodium-based precursors, aiming to broaden and optimize

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the synthetic methods. More importantly, a comprehensive understanding of the formation of metallo-carbazolides was obtained from *quasi in situ* nuclear magnetic resonance (NMR) experiment.

Experimental

Sample preparation

Carbazole (95%, A11448.36), lithium hydride (97%, A17948.22) and lithium amide (95%, L16023.22) were purchased from Alfa Aesar whilst sodium hydride (90%, 223441) and sodium amide (98%, 208329) were obtained from Aldrich without further purification. Sample handling was conducted in a glovebox filled with purified argon to avoid contamination of metal hydrides and amides by air. The syntheses of sodium and lithium analogues of carbazolides using sodium and lithium hydride were described elsewhere [14]. However, using alkali metal amides ($LiNH_2$ and $NaNH_2$) to prepare the sodium and lithium carbazolides were conducted by ball-milling stoichiometric ratios of $LiNH_2$/$NaNH_2$ and carbazole (1:1) using Retsch Planetary Ball Mill PM400 at 200 rpm for 4 h followed by heat treatment.

A home-made temperature-programmed desorption-mass spectroscopy (TPD-MS) combined system was employed to detect the gaseous products of the post-milled samples. In this measurement, a ramping rate of 2 °C min^{-1} was set and purified argon gas was utilized as a carrier gas for the dynamic flow mode of this system. The formation of gaseous products were eluted from the reacting system. Quantitative measurements of the gas elution from the samples were performed on a home-made volumetric release reactor. Initially, *ca.* 300 mg of the post-milled samples were heated up to ~250 °C, except that $NaNH_2$-carbazole mixture was only treated up to 150 °C, with a ramping rate of 1 °C min^{-1}. The vessel was connected to a pressure gauge for pressure monitoring. In the syntheses using NaH and LiH, *ca.* 1 equivalent H_2 was released after heat treatment, forming sodium and lithium-substituted carbazolide via the Reaction (1) whereas the formation of metal-substituted carbazolides employing $NaNH_2$ and $LiNH_2$ were indicated via the Reaction (2), where M resembles the alkali metals used.

Quasi in-situ NMR

The samples for *quasi in situ* NMR were prepared by gradually increasing the molar percent of sodium hydride (20%, 40%, 60%, 80% and 100%) into a NMR tube containing pristine carbazole, 450 μL of tetrahydrofuran (THF, Macklin, HPLC grade, ≥ 99.9%) and 100 μL of deuterated DMSO solvent (99.9% + 0.03% TMS, Cambridge Isotope Laboratories Inc.). After the sodium hydride was added, the reaction was allowed to run for 1 h first, followed by collecting the results at room temperature.

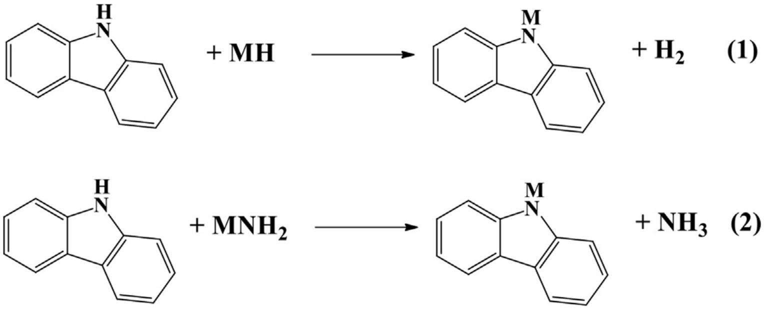
Characterizations

Liquid ^{1}H, ^{13}C, ^{7}Li and ^{23}Na NMR spectroscopy were conducted on a Bruker AVANCE 500 MHz NMR spectrometer (11.7 T) at ambient temperature with DMSO -d_6 as the deuterated solvent (99.9% + 0.03% TMS, Cambridge Isotope Laboratories Inc.). X-ray diffraction (XRD) measurements were carried out on a PANalytical X'pert diffractometer (Cu-Kα radiation, λ = 0.154 nm; 40 kV; 40 mA). Thermogravimetric and differential thermal analysis (TG-DTA) measurements were conducted on a Netzsch TG-DTA apparatus (Netzsch, Germany). Approximate 10 mg of samples were placed in Al_2O_3 crucibles at 2 °C min^{-1}.

Results and discussion

Structures and characterization

To synthesize carbazolides of sodium and lithium, the sodium and lithium-based precursors including hydrides and amides were ball milled with carbazole in a molar ratio of 1:1, respectively. Because no gaseous product was released from the mixtures of carbazole and metal precursors during the mechanical ball-milling treatment, the post-milled mixtures were subsequently subjected for TPD-MS measurement to investigate the interaction between precursors and carbazole during heating. As shown in Fig. 1a and c when metal hydrides were used as metal precursors, two hydrogen signals were detected. The first signal in a lower temperature range of 200–260 °C may be resulted from the interaction of M-$H^{\delta-}\cdots H^{\delta+}$-N (carbazole) to form corresponding metallo-



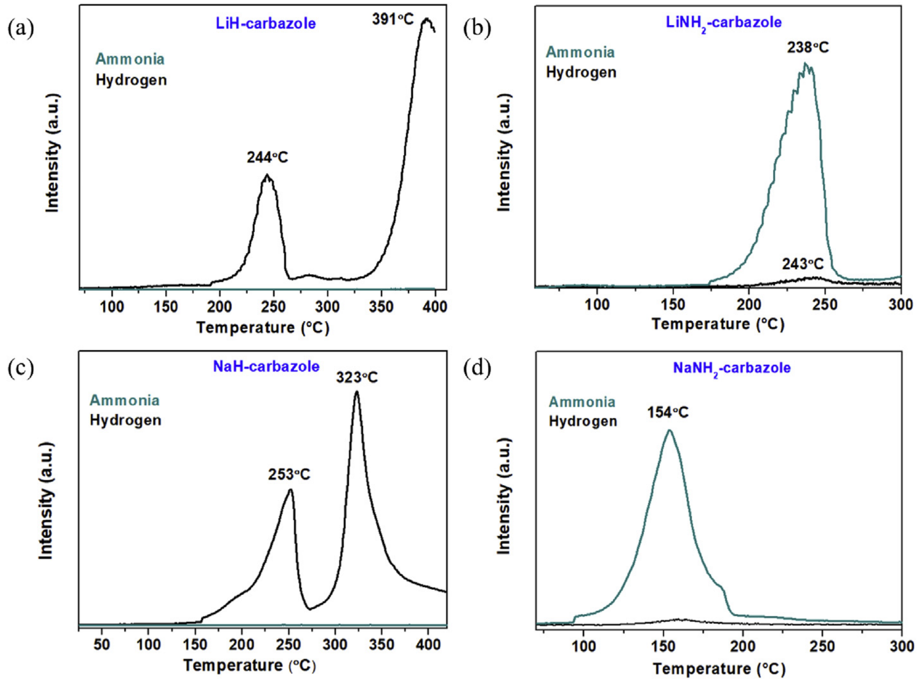


Fig. 1 – TPD-MS of the syntheses of metallo-carbazolides using (a) lithium hydride, (b) lithium amide, (c) sodium hydride and (d) sodium amide.

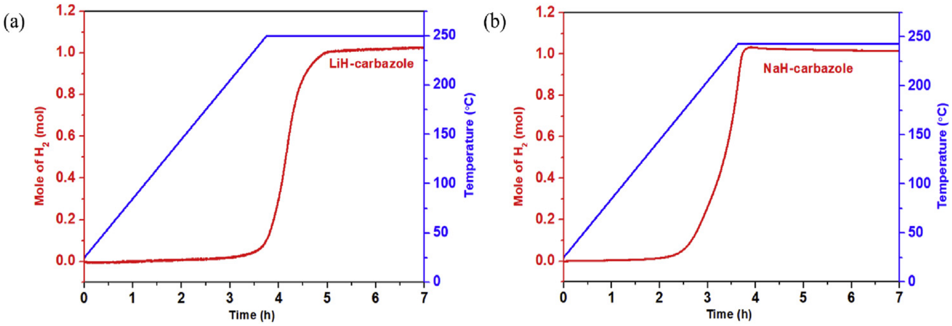


Fig. 2 – Hydrogen release upon the heat treatment of ball milled (a) LiH-carbazole and (b) NaH-carbazole at 250 °C and 243 °C, respectively.

carbazolides and the other signal in a higher temperature range of 320–400 °C could be attributed to the decomposition of metal hydrides. Since carbazole melts at ~243 °C, under an open flow mode, evaporation of molten carbazole might occur in parallel with the first step dehydrogenation, resulting in the remains of metal hydrides which contributes to the second step dehydrogenation. This is further proven by thermogravimetric analysis (TGA, Fig. S1b and S1c) where the weight loss at temperature corresponds to the first step dehydrogenation was significantly higher than the theoretical value of ~1 wt%.

To avoid evaporation of carbazole during thermal treatments, quantitative measurements of the amount of H_2 release in a close system are employed as shown in Fig. 2a and b. It is noticeable that *ca.* 1 equivalent of hydrogen was released from LiH-carbazole and NaH-carbazole at 250 °C and 243 °C, indicating the formation of lithium and sodium carbazolides, respectively (Reaction 1). When alkali-metal amides were used as metal precursors, NH_3 instead of H_2 were released predominantly as evidenced from TPD-MS (Fig. 1b and d). To verify the occurrence of Reaction 2, the amount of released NH_3 was quantified using TGA and exemplified using $NaNH_2$-carbazole. From the result obtained (Fig. S1d), at temperature ~150 °C, the solid-solid interaction of the mixture started and approximately 17% of weight loss was observed in two steps. By matching with TPD-MS results in Fig. 1d, the first step which peaked at 151 °C as shown in the derivative thermogravimetry (DTG) result corresponds to the NH_3 release. However, the second step which peaked at 195 °C could not be matched with any gas release. Therefore, it is plausible to ascribe the excess weight loss to the evaporation of carbazole, similar to those observed in the TGA of hydride-carbazole (Fig. S1b and S1c). However, in a closed system thermal treatment which evaporation of molten carbazole can be effectively avoided, we envisage that complete reaction between metal amide and carbazole can be achieved via formation of 1 equivalent NH_3. It is shown that the reaction

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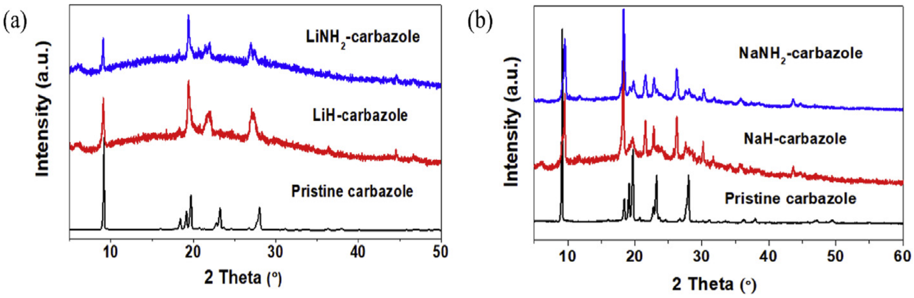

Fig. 3 – XRD patterns of (a) lithium carbazolide and (b) sodium carbazolide using different metal-based compounds as metal precursors.

temperature of amide (especially for sodium amide) with carbazole is much lower than that of hydride, which may be due to the stronger basicity of NH_2^- that abstracts the acidic $H^{\delta+}$-N to form NH_3 [19,20]. Furthermore, we also compared the TGA of pristine carbazole (Fig. S1a) with all the metallo-carbazolides. Obviously, without adding any metal-based precursors, pristine carbazole started to melt and evaporate at higher temperature (>230 °C). Eventually at 289 °C, all the starting materials have been fully evaporated. The lower melting point of carbazole observed in MH-carbazole and MNH_2-carbazole could be attributed to the additive effects of the reduced particle size and intermolecular disruption by MH or MNH_2 via $M\text{-}H^{\delta-}\cdots H^{\delta+}\text{-}NC_{12}H_8$ or $M\text{-}(NH_2)^{\delta-}\cdots H^{\delta+}\text{-}NC_{12}H_8$ upon ball milling.

All the end-products were characterized using XRD and NMR. XRD measurements on the metallated compounds show that the end products from LiH and $LiNH_2$ precursors exhibited identical diffraction patterns, an indication of formation of same products which is different from that of pristine carbazole (Fig. 3a).

Moreover, XRD measurements on the metallated compounds using sodium hydride and sodium amide also exhibited a new set of diffraction peaks (Fig. 3b) but demonstrated better crystallinity than lithium-based compounds as aforementioned. Derived from such observation, several new peaks were detected at 18.2°, 21.6°, 22.9°, 26.3°, 27.6°, 30.2°, 35.8° and 43.6° as compared to pristine carbazole and these peaks do not match with any known compound containing sodium, hydrogen, nitrogen and oxygen. The structural determination is still ongoing.

^1H NMR spectroscopic analysis reveals the absence of H resonance of N–H from metallo-carbazolides (Fig. 4a), suggesting the H of N–H has been replaced successfully by the alkali metals. When both LiH and $LiNH_2$ were used as lithium precursors, clearly resolved two triplets and two doublets at 6.7 ppm, 7.1 ppm, 7.4 ppm, and 7.9 ppm were observed,

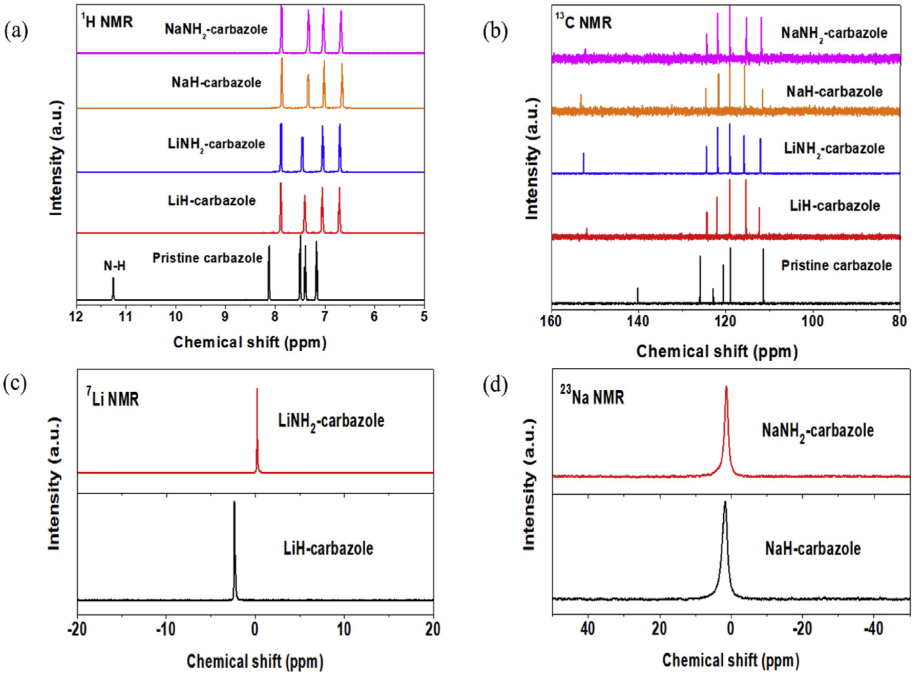

Fig. 4 – (a) ^1H and (b) ^{13}C NMR of metallo-carbazolides as compared to pristine carbazole in DMSO-d_6. (c) ^7Li and (d) ^{23}Na NMR of lithium and sodium carbazolide, respectively.

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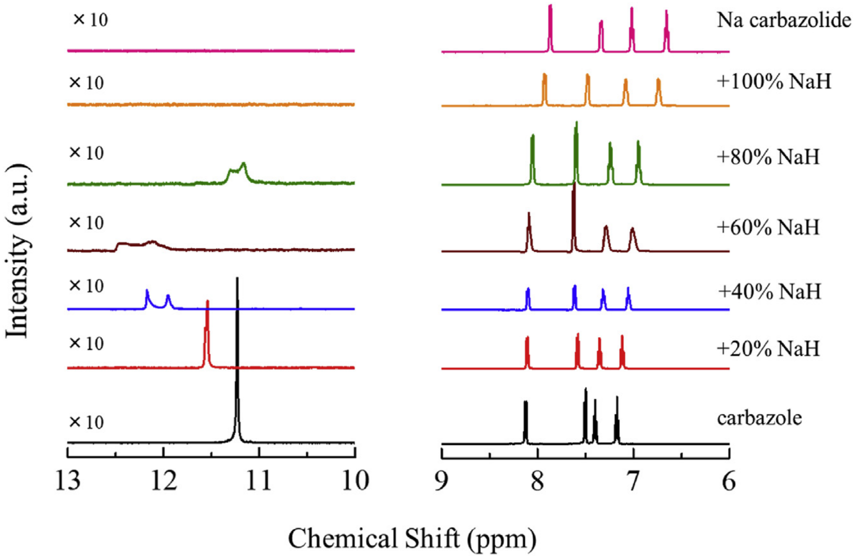

Fig. 5 — Quasi in situ ^{1}H NMR of sodium carbazolide by gradually increasing the percentage of using sodium hydride as compared to pristine carbazole in DMSO-d_6.

respectively. Careful inspection on the ^{1}H NMR of sodium carbazolide also shows similar splitting of the peaks and disappearance of N–H resonance after the reaction (Fig. 4a). Moreover, all the ^{1}H resonances of carbazolides are shifted upfield, which are due to the replacement of H of N–H with a more electron donating substituent group (in this case, Li or Na cation), thus creating a more shielding environment upon metallation.

Other than that, the ^{13}C NMR studies of the metallo-carbazolides demonstrated obvious shifting in comparison to pristine carbazole (Fig. 4b). Our earlier calculations suggested that the C atom which locates near to the N atom shows a downfield shift whereas the C atom situates far from N atom has an upfield shift upon the metallation effect [14]. As can be seen, when sodium and lithium amide were used as metal precursors, the ^{13}C NMR signals were in good agreement with the results using sodium and lithium hydride. We also further proved the successful formation of lithium and sodium-substituted carbazolides through ^{7}Li and ^{23}Na NMR spectroscopic analysis. Undoubtedly, strong signals are seen in both ^{7}Li and ^{23}Na NMR, respectively (Fig. 4c and d), showing the formation of soluble lithium and sodium salts. However, a slightly shift in ^{7}Li resonance can be observed between LiH- and $LiNH_2$-produced carbazolides, which may be due to the adduct of NH_3 molecules to Li^+ in $LiNH_2$-carbazole system. Careful inspection on the ^{1}H NMR spectra of LiH-carbazole and $LiNH_2$-carbazole in Fig. 4a also finds minute differences, which may be ascribed to the presence of NH_3.

Quasi in situ NMR

As NMR plays a pivotal role to study the transformation of organic compounds in chemistry, *quasi in situ* NMR was employed to get an in-depth understanding about the transformations from carbazole to carbazolide. As described in the experimental section, *quasi in situ* NMR was performed by gradually increasing the molar percent of sodium hydride into the NMR tube containing pristine carbazole in solvent THF and DMSO-d_6. Referring to Fig. 5, before mixing the pristine carbazole with sodium hydride, apparently, the chemical shift at 11.3 ppm can be assigned to the acidic N–H group of carbazole precursor. When 20% of sodium hydride was added, the N–H resonance became asymmetric with clear shoulder and it shifted 0.2 ppm downfield relative to that of pristine carbazole, suggesting that the N–H of the unreacted carbazole was strongly deshielded. In additions, two of the C–H resonances from the carbazole rings were also shifted upfield and hence, it clearly evidences that when sodium carbazolide was formed, the electron donating Na^+, even present in small amount, is sufficient to trigger changes in the electronic properties of the neutral carbazole ring system. As the amount of NaH increased, the N–H resonance decreased in intensity, split doubly and shifted further downfield. Interestingly, the associated C–H resonances were also slightly downfield shifted. These downfield shifts of C–H and N–H may be due to the cation-π interaction between sodium and neutral carbazole molecule, which is consistent with our calculation results in Fig. S2. However, when sodium hydride reached 80% in the reaction mixture, the N–H groups were strongly shielded instead and the C–H resonances were slightly shielded concomitantly, evidencing an increased electron density in the carbazolide ring upon mass conversion, which are in agreement with calculated chemical shifts observed in fully converted carbazolide anion as shown in Fig. S2. Eventually, when both reactants are in equivalent molar percent, the NMR spectrum indicates the complete conversion of pristine carbazole to sodium carbazolide and this result matches well with those obtained from thermal activated synthetic route.

Despite of the marginal shifts observed, in all cases only one set of C–H resonances corresponding to carbazole ring system can be detected regardless of the amount of NaH added, indicating an identical C–H environment in both unreacted carbazole molecules and sodium carbazolide. Since sodium carbazolide is soluble in organic solvents, the solubilized Na^+ is likely to interact unselectively with the π-electron of carbazole ring system in both carbazole molecules and carbazolide anions via electrostatic cation-π interactions. Due to the small ionic size of Na^+, Na^+ is likely to reside in between the planar carbazole ring systems. In contrary to the marginal influence observed in the C–H resonances, the amount of NaH added greatly affect the N–H of carbazole with more than one N–H resonances were detected in the process of metallation. This result reveals that other than cation-pi interaction, NH-pi and $N\cdots Na^+$ interactions might also take place in the metallation process, thus resulting in deshielding and shielding of N–H groups at different stages of the reaction.

Conclusions

In short, lithium and sodium carbazolides as potential candidates for hydrogen storage materials can be synthesized by reacting amides or hydrides with carbazole in the present study. *Quasi in situ* NMR provided a comprehensive understanding of the formation of metallo-carbazolides. The synthesis strategy investigated in this study can be further expanded to synthesize myriad oxygen and nitrogen bearing metalorganic hydrides. Moreover, both lithium and sodium carbazolides are highly potential candidates not only as hydrogen storage materials, but also as materials for organic light-emitting diodes (OLEDs), pharmaceutical and so on.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

The authors acknowledge the supports provided by National Key R&D Program of China (2018YFB1502101, 2019YFE0103600), the National Natural Science Foundation of China (51671178, 21875246), DICP (DICP DCLS201701), LiaoNing Revitalization Talents Program (XLYC1807157), and K. C. Wong Education Foundation (GJTD-2018-06). K. C. Tan would like to acknowledge the financial support from Universiti Sains Malaysia (USM) Fellowship and Dalian Institute of Chemical Physics throughout the study of this project. Y. S. Chua would like to acknowledge the financial support from Universiti Sains Malaysia RU Grant (1001/PKIMIA/8011011).

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.ijhydene.2020.06.024.

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