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Sodium anilinide-cyclohexylamide pair: synthesis,

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characterization, and hydrogen storage properties

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The lack of efficient hydrogen storage material is one of the bottlenecks for the large-scale implementation of hydrogen energy. Here, a series of new hydrogen storage materials, i.e., anilinidecyclohexylamide pairs, are proposed via the metallation of anilinecyclohexylamine pair. DFT calculations show that the enthalpy change of hydrogen desorption (ΔH_d) can be significantly tuned from 60.0 kJ/mol-H₂ of pristine aniline-cyclohexylamine pair to 42.2 kJ/mol-H₂ for sodium anilinide-cyclohexylamide and 38.7 kJ/mol-H₂ for potassium anilinide-cyclohexylamide, where an interesting correlation between the electronegaticity of the metal and the ΔH_d was observed. Experimentally, sodium anilinide-cyclohexylamide pair was successfully synthesised with a theroritical hydrogen capaicty of 4.9wt%, and the hydrogenation and dehydrogenation cycle can be achieved at a relatively low temperature of 150 °C in the presence of commercial catalysts, in clear contrast to the pristine aniline-cyclohexylamine which pair undergoes dehydrogenation at elevated temperatures.

The development of advanced materials for both on-board and large-scale hydrogen storage/transportation is regarded as a key prerequisite for the widespread implementation of hydrogen energy^{1, 2}. Tremendous efforts have been devoted to solid-state hydrogen carriers, including metal hydrides³, complex hydrides⁴⁻⁶ and chemical hydrides⁷⁻⁹, and liquid organic hydrogen carriers (LOHCs)^{10, 11}. Among them, LOHCs have the great potential to meet the applications for on-board hydrogen storage and large-scale hydrogen contents, reversibility in absorbing and desorbing hydrogen and the ease of widespread

implementation at minimal modification on the existing fuelling infrastructure¹². However, the dehydrogenation of LOHCs, such as benzene-cyclohexane pair (ca. ΔH_d =73.6 kJ/mol-H₂), occurs at relatively high temperatures due to the unfavourable dehydrogenation enthalpy change, leading to a low round-trip energy efficiency. It was demonstrated theoretically and experimentally that incorporation of heteroatoms (such as N) into aromatic ring reduced the ΔH_d effectively^{13, 14}. Nethylcarbazole/perhydro-N-ethylcarbazole pair (NEC/12H-NEC) with ΔH_d = 53.2 kJ/mol-H₂ was developed and well-investigated recently^{15, 16}. Jessop and co-workers also demonstrated that the dehydrogenation thermodynamics (ΔH_d) can be reduced through attaching an electron donating group outside the aromatic ring¹⁷. As matter of fact, phenol-cyclohexanol pair has a ΔH_d that is ca. 64.5 kJ/mol-H₂ lower than benzenecyclohexane pair due to electron donation nature of -OH group. Very recently, we introduced sodium to phenol-cyclohexanol pair, forming sodium phenoxide-cyclohexanolate pair, which can further tune ΔH_d to 50.4 kJ/mol-H₂ and undergoes reversible hydrogenation and dehydrogenation under mild condition¹⁸. The continuous reduction in ΔH_d from benzene to phenol and to phenoxide correlates to the electron donating capability of -H, -OH and -ONa to the benzene ring. To further develop materials that have the optimal ΔH_d (ca. 30-40 kJ/mol-H₂), a substituent having stronger electron donation should be attached to the benzene ring. A straightforward strategy is to couple the effects of both metal (alkali or alkaline earth metal) and organic substituent which possess a stronger electron donating ability. Herein, aniline-cyclohexylamine pair was chosen as the pristine organic pair because the electron donating ability of -NH₂ is stronger than -OH. We then employed metallation strategy developed by us recently to modify the -NH₂ groups and synthesized the sodium anilinide and cyclohexylamide for the first time. To our delight, Both DFT calculations and experimental results show that the ΔH_d of alkali anilinide-cyclohexylamide pairs can be reduced to the optimal region, and hydrogen absorption/desorption cycle can be realized at a temperature as low as 150°C.

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X1s method¹⁹ was employed to calculate the heats of formation of alkali and alkaline earth metal anilinides and cyclohexylamides, respectively. The corresponding heats of hydrogen desorption (ΔH_d) from the anilinide-cyclohexylamide pairs can be derived which are shown in Figure 1. We also calculated ΔH_d of the parent anilinecyclohexylamine pair and obtained a value of 60.0 kJ/mol-H₂, which agrees well with that determined experimentally $(59.7 \text{ kJ/mol-H}_2)^{20}$. Because $-NH_2$ is more electron donating than -OH, the ΔH_d of anilinecyclohexylamine pair is lower than that of the phenol-cyclohexanol pair (64.5 kJ/mol-H₂). The metallation of aniline-cyclohexylamine pair leads substantial decrease in ΔH_d as shown in Figure 1. For instance, the ΔH_d of sodium and potassium anilinidecyclohexylamide pairs decreases to 42.2 and 38.7 kJ/mol-H₂, respectively, and are within or close to the ideal ΔH_d region for reversible hydrogen storage. Our previous results on phenoxidecyclohexanolate system showed that both phenoxides and cyclohexanolates were stabilized upon metallation. However, the phenoxides were more stabilized than the cyclohexanolates due to the magnitude of conjugation effect in phenoxide is significantly greater than that of the hyper-conjugation effect in cyclohexanolate. Similarly, in the present study, electrons on the N atom of the metallo anilinide generate a delocalized resonance with benzene ring forming a p- π conjugation and consequently stabilizing the aniline. In the cyclohexylamide cases, however, the electrons on N are hard to be delocalized. Therefore, the substantial decrease in ΔH_d is resulted in metallo anilinide-cyclohexylamide system. Since the ΔH_d of metallo anilinide-cyclohexylamide pair is related to the electron donation from the metals, we refer to the Pauling electronegativity of metal as an indication of the metallation effect. Interestingly, a nearly linear relationship between ΔH_d and the electronegativity can be obtained as shown in Figure 1, suggesting that the ΔH_d can be rationally tuned by selecting different metals. It was reported that the ΔH_d of cycloalkane scales with the Hammett parameter (σ) of substitute group¹³, where the Hammett parameter is a measure of the electron-donating ability of the substituent group. The electronegativity also reflects the ability of an atom in a molecule to attract or donate electrons. Therefore, a correlation between the ΔH_d and the electronegativity of cation will be reasonable. Because the sodium anilinide-cyclohexylamide pair has relatively smaller ΔH_d , high hydrogen capacity (ca. 4.9wt%) as well as the ease of synthesis, it was chosen as an example for experimental investigation.



Figure 1. Theoretical calculation results of ΔH_d for alkali and alkaline earth metal anilinide-cyclohexylamide pairs in gaseous phase as a function of Pauling electronegativity of metal. For the ease of illustration in the insert equation, M is in monovalent. In case of divalent, it is understandable that twice as much anions (anilinide and cyclohexylamide) will be needed.

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Sodium anilinide and cyclohexylamide were synthesized via reacting sodium hydride and aniline/cyclohexylamine through wet chemical method and ball-milling method (see Supporting Information), respectively. Around 1 equiv. H₂ was released from both reactions (Figure 2a), indicating the formation of sodium anilinide and cyclohexylamide following the reactions 1 and 2. Powder X-ray diffraction (XRD) patterns of the as-prepared samples emerged several new peaks which cannot match with any Na-, C-, N-, H-containing compound in database (Figure and S1). Thermogravimetric-differential thermal analysis (TG-DTA) and temperature-programmed desorption system equipped with a mass spectrometer (TPD-MS) results (Figure S2 and S3) show that around 10 mol% diethyl ether is released from the as-prepared samples during heating process, indicating adduction of the solvent molecules to sodium anilinide. However, the removal of diethyl ether from sodium anilinide at 90 °C would lead to an amorphous product. Structure determination is still in process. It is worth mentioning that hydrolysis of these two compounds may occur in humid air.



Figure 2. (a) Hydrogen evolution from sodium hydride and aniline in diethyl ether solution. (b) ¹H, (c) ¹³C and (d) ²³Na NMR spectra of synthesized sodium anilinide and cyclohexylamide compared with those of aniline and cyclohexylamine in DMSO-d₆.



Scheme 1. The reversible reaction of sodium anilinide and cyclohexylamide.

Liquid-state ¹H and ¹³C nuclear magnetic resonance (NMR) spectra of the as-prepared samples in DMSO-d₆ are shown in Figure 2b and 2c. Obvious upfield shifts are observed in the ¹H NMR spectrum of the synthesized sodium anilinide compared with that of pristine aniline, indicating more shielding effect upon metallation, which is Published on 14 January 2020. Downloaded by Queen Mary, University of London on 1/14/2020 12:04:27 PM

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Table 1. Hydrogenation of sodium anilinide catalyzed by different commercial catal	ysts
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Entry	Catalysts	Μ%	T /°C	P /bar	t /h	C ª /%	Selectivity a /%		
							СНА	DCHA	Aniline
1	_	—	150	70	48	2	100	0	0
2	5%Ru/Al ₂ O ₃	1:10	150	70	90	85	67	33	0
3	5%Rh/Al ₂ O ₃	1:10	150	70	24	50	84	16	0
4	5%Pt/C	1:10	150	70	8	>99	39	56	5
5	5%Pt/C	1:15	140	70	10	>99	59	36	5
6	5%Pt/C	1:19	140	70	20	>99	46	40	14
7	5%Pt/C	1:30	140	70	10	78	83	17	0
8	Na-1%Ru/TiO ₂	1:10	150	70	15	>99	100	0	0

M%: molar ratio of catalyst to anilinide (metal:anilinide). T: temperature. P: pressure of H₂. t: time. C: conversion. CHA: cyclohexylamide. DCHA: dicyclohexylamine. ^a: Conversion and selectivity were quantified by ¹H NMR.

consistent with the electron donating effect of the metal. However, only slight shifts of ¹H NMR of sodium cyclohexylamide to upfield are detected compared with pristine cyclohexylamine, which may be due to the absence of conjugation effect of cyclohexylamine. However, it is noticeable that the signals of proton which bonded to nitrogen are disappeared in the synthesized sodium anilinide and sodium cyclohexylamide. This could be due to the overlapping of this N-H peak with other peaks or the influence of the deuterated DMSO-d₆ reagent used. The peaks of N-H of sodium anilinide and sodium cyclohexylamide re-appear in deuterated benzene-d₆ reagent (Figure S4). Therefore, the disappearance of N-H resonance could be attributed to the hydrogen-deuterium exchange between DMSO-d₆ and sodium anilinide or cyclohexylamide. ¹³C NMR spectra in Figure 2c show similar results to ¹H NMR spectra in which electron state of anilinide is obviously changed via metallation. However, the impacts on the ¹³C resonances in metallo anilinide and cyclohexylamide are more complicated. The C atoms close to N and at para-position show obvious chemical shifts in sodium anilinide. Meanwhile, the strong ²³Na NMR signals in sodium anilinide and sodium cyclohexylamide in Figure 2d suggest the replacement of H in -NH₂ by Na. Combining the quantity of hydrogen evolution during syntheses, XRD, and NMR results, it is confirmed that the sodium anilinide and sodium cyclohexylamide were successfully obtained. Considering the decrease in $\Delta H_d,$ hydrogen absorption and desorption of sodium anilinide-cyclohexylamide pair are investigated in the following studies (Scheme 1).

As sodium anilinide and cyclohexylamide are both solids, different commercial catalysts were hand-milled with these two materials to promote hydrogenation and dehydrogenation. Hydrogenation of sodium anilinide was carried out in the absence/presence of commercial catalysts (Pt/C, Ru/Al₂O₃ and Rh/Al₂O₃) under different conditions as shown in Table 1. Although the selectivity to the desired product (CHA) is high without catalyst (entry 1), the conversion of sodium anilinide is quite low (ca. 2%) even for 48 h. Among these catalysts, Pt/C catalyst exhibits the best activity (entry 2 to 4), i.e., a conversion of 99% of sodium anilinide can be obtained in less than 8 hours. In contrast, conversions of 85% and 50% can only be reached for Ru/Al₂O₃ and Rh/Al₂O₃ catalysts even with longer reaction time, respectively. However, the selectivity to the desired product (cyclohexylamide, CHA) on Pt/C is much lower than that of Ru/Al_2O_3 and Rh/Al_2O_3 . In order to enhance the selectivity to the desired product, the amount of catalyst, temperature and the reaction time were further optimized. Although lowering the amount of catalyst would sacrifice the conversion under the same condition (entry 5 to 7), a higher selectivity to the desirable product could be retained. Delightfully, it was found that a selectivity as high as 83% to cyclohexylamide with a conversion of 78% for anilinide was obtained at 140 °C in the presence of Pt/C catalyst with the molar ratio of catalyst to anilinide at 1:30. Furthermore, the formation of dicyclohexylamine (DCHA) suggests the breaking of N-Na bond in anilinide or cyclohexylamide. Comparing the entries 5 to 7, it looks like that longer reaction time would lead to lower selectivity to cvclohexvlamide. which indicates the formation of dicyclohexylamine may be from the dimerization of cyclohexylamide. To further suppress the formation of dimer, efficient catalyst is needed. Here, a sodium modified-Ru/TiO₂ catalyst (Na-1%Ru/TiO₂) was developed in our group very recently, which exhibited superior performance for hydrogenation of aromatics²¹ and was employed in the hydrogenation of sodium anilinide in this study. As shown in Table 1 and Figure S7, >99% conversion of sodium anilinide and selectivity to sodium cyclohexylamide were obtained. It is shown that different catalysts exhibit different functions. For example, Na-1%Ru/TiO₂ catalyst could enhance the reaction rate significantly. While, the other catalysts not only enhanced the activity, but also changed the selectivity.

Table 2. Dehydrogenation of sodium cyclohexylamide catalyzed by Rh/Al_2O_3 catalysts.

Cotolucto	+ /h	C a /o/	Selectivity ^a /%		
Catalysis	t/n	C //	Anilinide	NCHBA	
5%Rh/Al ₂ O ₃	11	>99	80	20	

The molar ratio of Rhodium to cyclohexylamide is 1:10. The reaction temperature is 150°C and the pressure is 0 bar. t: time; C: conversion; NCHBA: N-cyclohexylbenzenamine; ^{*a*}: Conversion and selectivity were quantified by ¹H NMR.

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For dehydrogenation, TPD-MS results (Figure S5a) show that the as-prepared sodium cyclohexylamide dehydrogenates at the temperature higher than 130 °C. Meanwhile, small amounts of byproducts are detected during heating, indicating that side reactions occurred. Then, a commercial 5% Rh/Al₂O₃ catalyst was employed to catalyse the dehydrogenation of sodium cyclohexylamide. Interestingly, the Rh-catalyzed sodium cyclohexylamide sample starts to evolve H_2 at about 80 °C and gives a broad desorption peak centered at ca. 155 °C as shown in Figure S5b, which is much lower than that of the pristine sodium cyclohexylamide. Further increasing the temperature to 300 °C, more hydrogen can be released, which may be due to the decomposition of the reactant. In order to suppress the side reaction, catalytic dehydrogenation was conducted at 150 °C which is below the temperature for producing those byproducts. As shown in Table 2, the conversion of sodium cyclohexylamide dehydrogenation can be achieved as high as 99% in 11 hours. The selectivity to the desired product of sodium anilinide was determined as 80%, whereas, 20% of by-product, Ncyclohexylbenzenamine (NCHBA) was also observed (Figure S6). Catalytic dehydrogenation is always a challenging task in organic hydrogen carriers. Design and fabrication of novel catalyst will be beneficial to the conversion and selectivity. Therefore, development of efficient catalysts is highly demanded in the following investigations.

Nevertheless, the hydrogen uptake and release can be achieved through the sodium anilinide-cyclohexylamide pair at the temperature as low as 150 °C. It should be noted that the dimer by-products (dicyclohexylamine or N-cyclohexylbenzenamine) were always been observed during hydrogenation or dehydrogenation (Table 1 and 2). Usually, the dimers were detected in the catalytic hydrogenation of aniline²². Therefore, the formation of dimers in our case may undergo a similar pathway to that of catalytic hydrogenation of aniline (Scheme S1 and S2).

In summary, the thermodynamics of aniline-cyclohexylamine pair for hydrogen storage can be manipulated via metallation strategy, i.e., the ΔH_d of cyclohexylamides correlates well with the electronegativity of metals. Specifically, sodium anilinidecyclohexylamide pair with ΔH_d of 42.2 kJ/mol-H₂ was successfully synthesized. The hydrogenation and dehydrogenation can be realized at the temperature as low as 150 °C in the presence of commercial catalysts. More importantly, because of the large diversity of organic compounds, it could be easily broadening the current scope of amine-based materials thus providing vast opportunities for the further exploration.

Conflicts of interest

There are no conflicts to declare.

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Metallo anilinide-cyclohexylamide pairs with promising thermodynamic properties for reversible hydrogen storage were successfully developed for the first time.