Electronic Supplementary Information (ESI) for:

Sodium anilinide-cyclohexylamide pair: synthesis, characterization, and hydrogen storage properties

Zijun Jing,[ab] Yang Yu,[ab] Ruting Chen,[c] Khai Chen Tan,[d] Teng He,*[a] Anan Wu,*[c] Qijun Pei,[ab] Yongshen Chua,[d] Dewen Zheng,*[e] Xi Zhang,[e] Zhixin Ge,[e] Fudong Zhang,[e] and Ping Chen[a]

[a]. Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China.

[b]. University of Chinese Academy of Sciences, Beijing 100049, China.

[c]. Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China.

[d]. School of Chemical Sciences, Universiti Sains Malaysia, Pulau Pinang 11800, Malaysia.

[e]. New Energy Department, Research Institute of Petroleum Exploration & Development, China National Petroleum Corporation, China

*. Corresponding authors, e-mails: heteng@dicp.ac.cn (T.H.); ananwu@xmu.edu.cn (A.W.); zdw69@petrochina.com.cn (D.Z.)

Experimental section

Materials

Aniline (99.0%, Aladdin), cyclohexylamine (99.0%, Aladdin), sodium hydride (95%, Aldrich), TiO_2 (99.8%, Aladdin), $RuCl_3$ (47%Ru, Innochem) Na_2CO_3 (AR, Kermel) diethyl ether (AR, Kermel) were used without further purification. Water was removed for ether with molecular sieve prior to use. The commercial catalysts (5%Ru/Al_2O_3, Alfa Aesar; 5%Rh/ Al_2O_3, Acros; 5%Pt/C, Alfa Aesar; 5%Pd/C, Alfa Aesar) were used with pretreatment of reduction under H_2 atmosphere with a flow rate of 50 ml min^{-1} at 250 °C for 2h.

Synthesis of sodium anilinide and sodium cyclohexylamide

Sodium anilinide: In a 60 ml autoclave, 0.01 mol aniline and 0.01 mol sodium hydride were added in 20 ml diethyl ether and stirred at a rate of 500 rpm at room temperature. The reaction process was monitored by a pressure gauge. After 40 hours, around 1 equivalent of hydrogen can be released (Figure 2a). After the solvent was removed using a reduced pressure distillation at room temperature, a light gray solid powder was obtained. Upon charactering, it is found that some diethyl ether was still adducted in the sodium anilinide.

Ball milling method was conducted to synthesize solvent-free sodium anilinide. In a typical synthesis, 0.01 mol aniline and 0.01 mol sodium hydride were placed into a 180 ml stainless steel vessel and mechanically milled in a Retsch PM 400 planetary ball mill. The ball-milling was carried out at a rate of 200 rpm for 10 h, where around 1 equivalent hydrogen was released.

Sodium cyclohexylamide: 0.01 mol cyclohexylamine and 0.01 mol sodium hydride were placed into a 180 ml stainless steel vessel and mechanically milled in a Retsch PM 400 planetary ball mill. The ball-milling was carried out at a rate of 200 rpm for 160 h, where the hydrogen released was quantified by the pressure in the ball mill jar.

Synthesis of catalyst Na-Ru/TiO_2

Na-modified 1% Ru/TiO_2 (Na-Ru/TiO_2) was prepared through conventional impregnation method. In a typical synthetic procedure, 21.3 mg $RuCl_3$ and 1.0 g TiO_2 were added in 10 mL of deionized water and stirred for 6 hours followed by evaporated at 50 °C and dried in oven at 100 °C for 3h. The catalyst was calcinated at 300 °C for 4h. Then, Na_2CO_3 modified 1% Ru/TiO_2 catalyst was prepared by adding Na_2CO_3 and 1% Ru/TiO_2 (molar ration of Na to Ru is 10 to 1) in 10 mL of deionized water and was stirred for 6 hours. Then, the same drying procedures were performed. Finally, the catalyst was reduced under hydrogen flow at 300 °C for 2h.

Characterizations

X-ray diffraction (XRD) patterns were collected on a PANalytical X'Pert diffractometer equipped with Cu Kα radiation at 40 kV and 40 mA. Liquid-state nuclear magnetic resonance (NMR) spectroscopies were collected on a Bruker AVANCE 500 MHz NMR spectrometer (11.7 T) at room temperature. DMSO-d_6 and benzene-d_6 were used as deuterated reagents. Thermogravimetric-differential thermal analysis (TG-DTA) were collected on a synchronous thermal analysis STA 449 F3, made by NETZSCH.

Hydrogenation of sodium anilinide

The hydrogenation of sodium anilinide catalyzed with different catalysts were carried out in a high-pressure reactor. A grinding mixture of sodium anilinide and catalysts by hand at a certain molar ratio was loaded into a stainless-steel reactor, then the argon gas was removed by vacuum pump followed by heated up to the desired temperature (heating rate: 2 °C/min). After that, 70 bar of hydrogen was charged into the reactor and the reaction was monitored using a pressure gauge. The final products were analyzed and quantified via ^1H NMR and ^{13}C NMR.

Dehydrogenation of sodium cyclohexylamide

The dehydrogenation behavior of the catalyzed sodium cyclohexylamine was monitored on a homemade temperature-programmed desorption system equipped with a mass spectrometer (HPR20, Hiden) (TPD-MS). A grinding mixture of sodium cyclohexylamide (30 mg) and Rh/Al_2O_3 by hand at a molar ratio of 10:1 (reactant to metal) was put into a stainless-steel reactor followed by heated up to 300 °C at a ramping rate of 2 °C/min under argon flow of 50 mL min^{-1}.

For the close system, the dehydrogenation of sodium cyclohexylamide was carried out in the stainless-steel reactor. The reactant with commercial catalyst was heated up to the desired temperature at a heating rate of 1 °C/min, and then kept for a certain time. The final products were analyzed and quantified by ^1H NMR and ^{13}C NMR.

All the sample loadings were carried out in a glove box filled with purified argon.

Computational Method

For the geometry optimization, B3LYP hybrid function was employed in connection with the all-electron basis set of 6-311+G (D, P). Analytical frequencies were calculated to confirm that a local minimum has no imaginary frequencies. Natural population analysis was performed to obtain the NBO charges. All calculations in the present study were carried out using the Gaussian09 package.

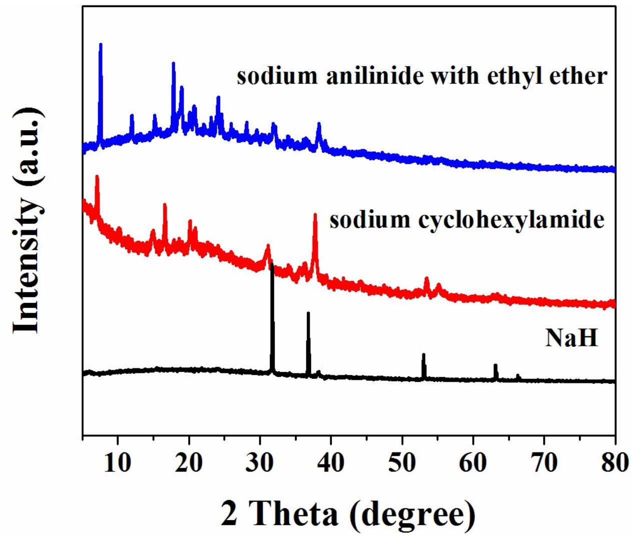


Figure S1. XRD patterns of synthesized sodium anilinide (from diethyl ether) and sodium cyclohexylamide compared with sodium hydride.

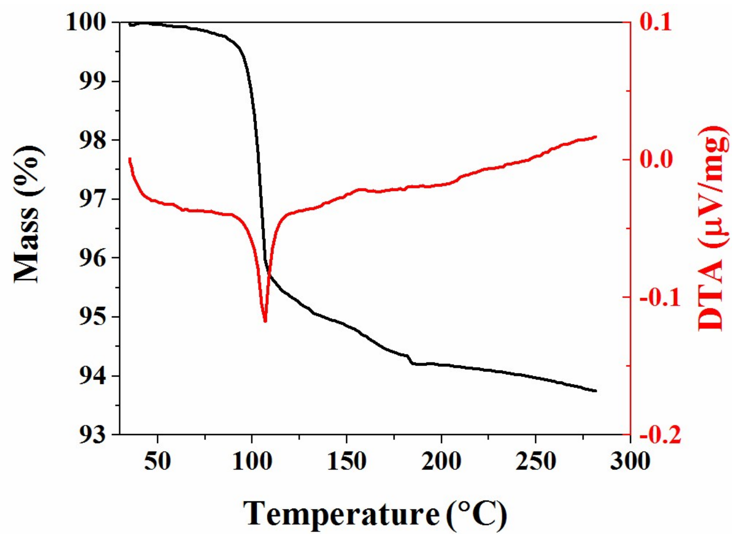


Figure S2. TG-DTA of synthesized sodium anilinide from diethyl ether.

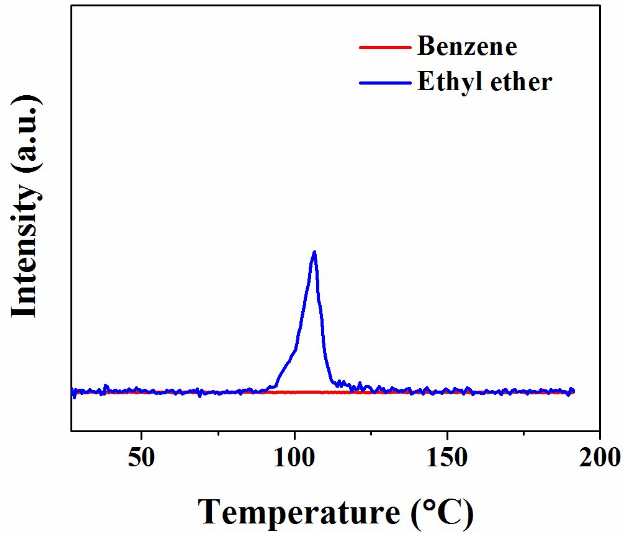


Figure S3. TPD-MS of synthesized sodium anilinide from diethyl ether, which indicates some diethyl ether is still adducted on sodium anilinide.

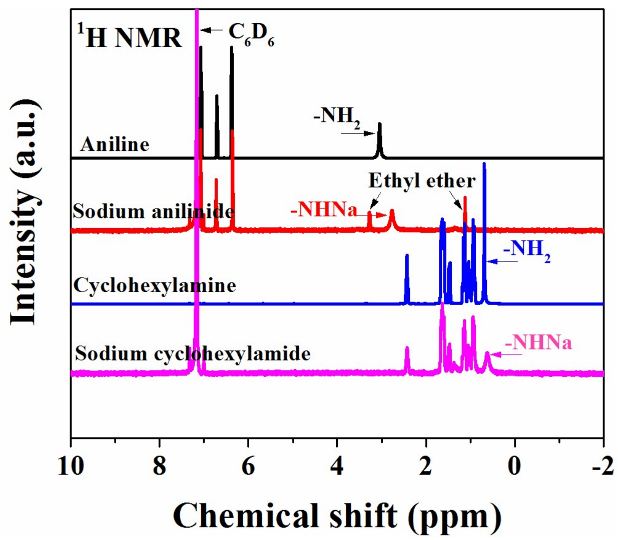


Figure S4. ^{1}H NMR spectra of sodium anilinide and sodium cyclohexylamide compared with those of aniline and cyclohexylamine in C_6D_6.

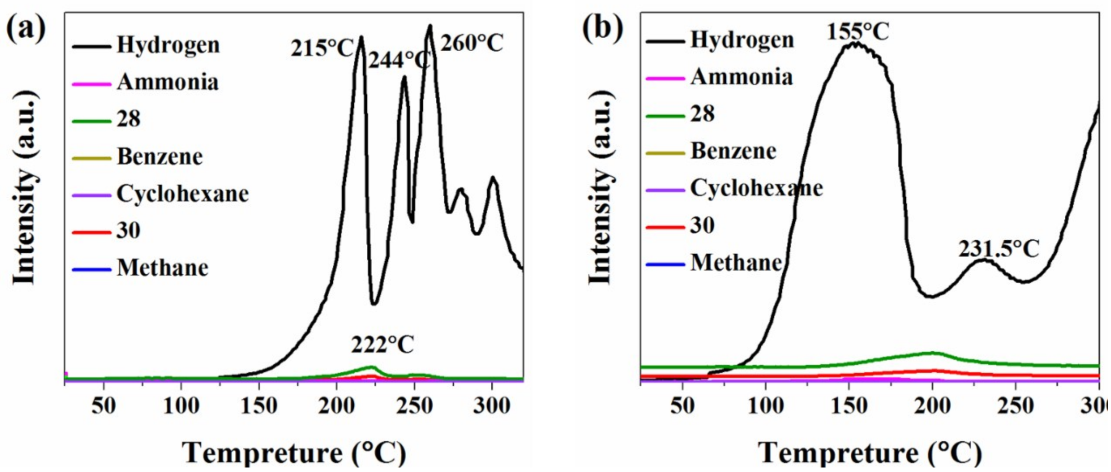


Figure S5. (a) TPD-MS of sodium cyclohexylamide (b) TPD-MS of sodium cyclohexylamide catalyzed by Rh/Al_2O_3 (m/z=28 and 30 are the fragments of by-products, which may be due to the partial decomposition of sodium cyclohexylamide or other products. No other impurity was observed. The molar ratio of Rh to sodium cyclohexylamide is 1:10.).

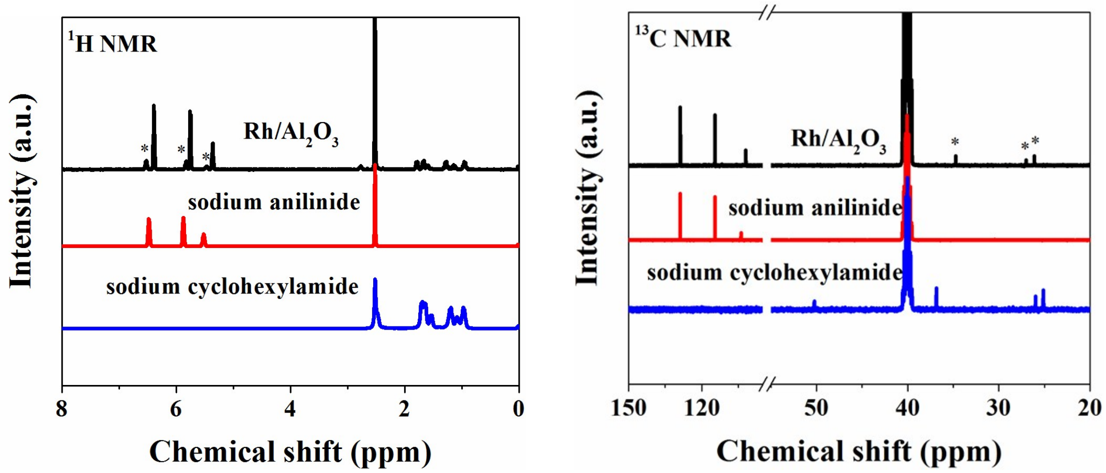


Figure S6. ^{1}H NMR and ^{13}C NMR spectra of dehydrogenated sodium cyclohexylamide catalyzed by 5%Rh/Al$_2$O$_3$ in DMSO-d$_6$. (* N-cyclohexylbenzenamine)

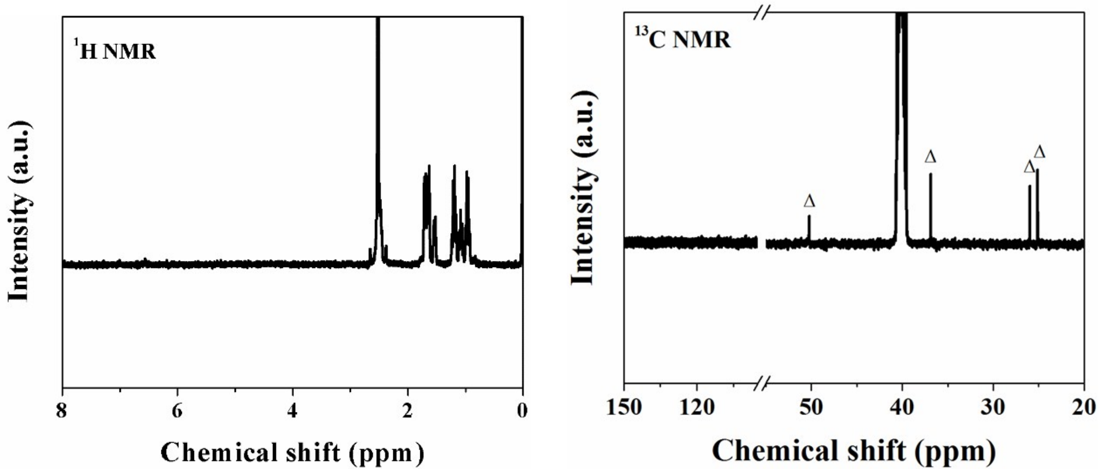
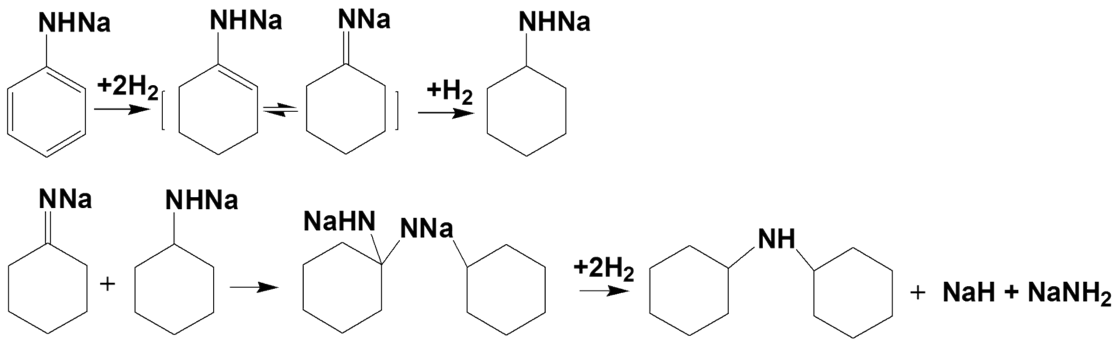
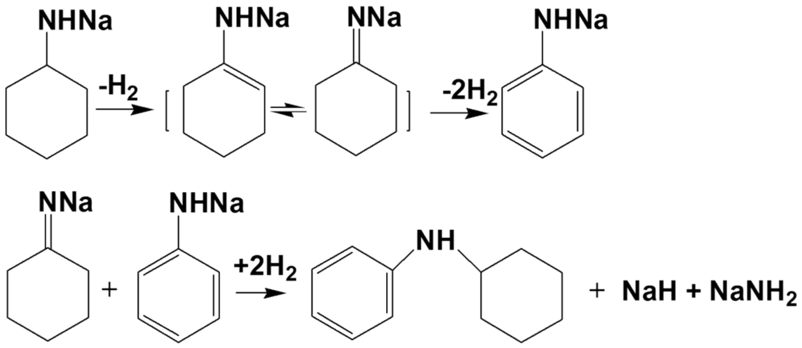


Figure S7. ^{1}H NMR and ^{13}C NMR spectra of hydrogenated sodium anilinide in DMSO-d$_6$. (Δ sodium cyclohexylamide) Hydrogenation conditions: Na-1%Ru/TiO$_2$ as a catalyst (the molar ratio of Ru to sodium anilinide is 1:10) at temperature 150 °C under the pressure of 70 bar of hydrogen.



Scheme S1. Proposed hydrogenation pathways of sodium anilinide.



Scheme S2. Proposed dehydrogenation pathways of sodium cyclohexylamide.