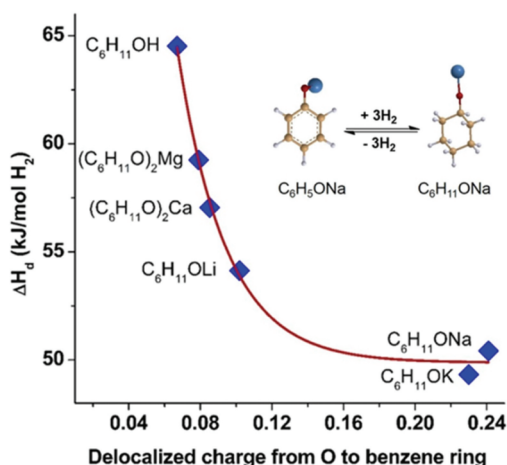
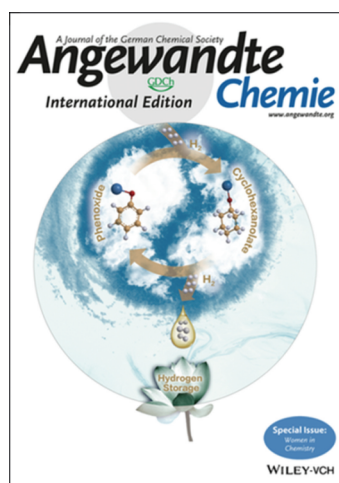


Metallated organic hydrides for hydrogen storage

With the support by the National Natural Science Foundation of China, Ministry of Science and Technology of China, and Chinese Academy of Sciences, the research team led by Prof. Chen Ping (陈萍) and Prof. He Teng (何腾) at Dalian Institute of Chemical Physics, Chinese Academy of Sciences demonstrated a new strategy for development of hydrogen storage materials, which was published in *Angew Chem Int Ed* (2019, 58: 3102–3107) as a back cover. This work was conducted through collaboration with Dr. Wu AnAn (吴安安) from Xiamen University.



The development of cost-effective, stable, and efficient energy carriers to store and transport energy, especially those generated from intermittent and distributed renewable resources, is vitally important. Hydrogen has long been viewed as an ideal energy carrier; however, storing hydrogen effectively is a grand challenge. Hydrogen uptake and release in arene-cycloalkane pairs provide an attractive opportunity for on-board and off-board hydrogen storage. However, those hydrocarbons suffer in part from low round trip storage efficiencies; that is, the large enthalpy changes of dehydrogenation require high temperatures to release hydrogen.

In this investigation, the researchers proposed a strategy for optimizing the thermodynamics of cyclohexanol-phenol pair by replacing H in the -OH group with alkali or alkaline earth metals to form phenoxide-cyclohexanolate pair. The enthalpy change of dehydrogenation decreases substantially, i. e., from 64.5 kJ/mol- H_2 for cyclohexanol to 50.4 kJ/mol- H_2 for sodium cyclohexanolate, as disclosed theoretically and experimentally. Such an enthalpy change correlates with the electron delocalized from oxygen to the benzene ring in phenoxides. Theoretical calculations reveal that the replacement of H with alkali or alkaline earth metal leads to a reduction in the energy gap of HOMO and LOMO, and the elongation of the C-H bond in the α site in cyclohexanolate, which indicates the cyclohexanol is activated upon metal replacement. Experimental results demonstrated that the sodium phenoxide-cyclohexanolate pair with the hydrogen capacity ca. 4.9wt% can absorb and desorb hydrogen reversibly at ca. 423K and 413K in solid state in the presence of commercial catalysts, respectively. To further improve the kinetic behavior, the hydrogenation and dehydrogenation were conducted in aqueous phase. It was shown that the hydrogenation and dehydrogenation can be accomplished at the temperatures as low as 303 and 373 K, respectively. It should be noted that the thermal dehydrogenation temperatures for cycloalkanes, and N-heterocycles are generally higher than 573 and 443 K, respectively. This is the first report on the metallation of the cycloalkane-arene pair forming metalorganics to achieve reversible hydrogen storage under moderate conditions.