A transition-metal-free hydrogenation catalyst: Pore-confined sodium alanate for the hydrogenation of alkynes and alkenes

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Hydrogenation catalysis is dominated by transition metals, but interest in alternative catalysts has been growing over recent years. Herein, a transition-metal-free catalyst is discussed consisting of carbon supported $NaAlH_4$ as a selective catalyst for hydrogenation. This is illustrated using a range of substrates, and in more detail for the case of diphenylacetylene. Catalytic activity depends on the solvent utilized; in cyclohexane the activity is 2.3 mol (DPA) mol^{-1} ($NaAlH_4$) h^{-1} at 100 bar H_2, 150 °C with a slight preference for the formation of *trans*-stilbene. The catalyst selectivity is influenced by the loading, yielding a high selectivity toward the thermodynamically less stable *cis*-stilbene at low catalyst loadings. This proof of principle shows promise for using metal hydrides based on earth-abundant elements as effective hydrogenation catalysts.

1. Introduction

Hydrogenation of C-C multiple bonds is a key step in the synthesis of many important compounds [1–3]. As with many other fields of catalysis, transition metals dominate. For example, Pd is widely employed in hydrogenation of alkynes to alkenes [4–8], particularly in the case of the famous Lindlar catalyst [9]. Pd-based catalysts generally show very high activity (turnover frequencies, TOF, of 2500 h^{-1} at 22 °C) [10] under mild conditions but often relatively low selectivities [11,12].

In recent years a new family of transition-metal-free catalysts, frustrated Lewis pairs, has emerged which boast reasonably high activities (TOFs of 5–40 h^{-1} at 80 °C) [13] and selectivities toward *cis*-alkenes without utilizing transition metals [14,15]. Light metal hydrides such as $LiAlH_4$ and $NaBH_4$ are based on earth-abundant elements and are typically used in the stoichiometric reduction of polar groups such as carbonyls [16,17]. However, these materials so far have seldom been applied to the reduction of alkenes or alkynes and in such cases only as stoichiometric reagents, rather

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than as catalysts. There is one isolated example of $NaAlH_4$ being utilized as a hydrogenation catalyst where Ti and $NaAlH_4$ were milled together and tested in the hydrogenation of diphenylacetylene [18]. At 130 °C and 100 bar of hydrogen pressure the alkyne starting material was fully hydrogenated to the saturated product within three hours. Ti-doped sodium alanate is known to reversibly store and release hydrogen, which might explain its catalytic activity.

The preparation and characterization of confined light metal hydrides for the purpose of reversible uptake and release of hydrogen (hydrogen storage) at reasonably low temperatures with fast kinetics have been demonstrated in recent years [19–27]. Melt infiltration under hydrogen pressure (to prevent decomposition) can be utilized to prepare these materials. The metal hydride and support are mixed together and heated to the melting point of the hydride. The molten hydride infiltrates the pores and, upon cooling, produces solid metal hydride confined within the pores, which is referred to as nanoconfinement. The resulting material consists of a carbon matrix of which the pores are filled with metal hydride. This pore-confined metal hydride lacks long range crystallinity and demonstrates orders of magnitude faster kinetics of absorption and desorption compared to the corresponding macrocrystalline metal hydride material.

In the case of $NaAlH_4$ almost full reversibility of hydrogen release and uptake was achieved at 150 °C [21]. Reduction of the

particle size improves the kinetics of hydrogen sorption as bulk crystalline $NaAlH_4$ displays much slower uptake kinetics and requires temperatures above 180 °C to desorb hydrogen. Additionally, the presence of carbon alters the hydrogen release profile from a three-step pathway to a two-step pathway, bypassing the intermediate Na_3AlH_6 phase altogether [21]. Nanoconfinement promotes reversibility by preventing the macroscopic phase separation of NaH and Al. All of these factors allow the $NaAlH_4$/C nanocomposite to release and reabsorb hydrogen in a reversible manner at relatively low temperatures. This raises the interesting question of whether this material could also be used as a hydrogenation catalyst in the absence of any transition metals [18,28]. Hence we demonstrate carbon-confined $NaAlH_4$, previously developed for hydrogen storage purposes, as a transition-metal-free hydrogenation catalyst. We explore the hydrogenation of alkynes and alkenes, while studying in detail the recyclability, selectivity, and activity depending on solvent and catalyst loading in the case of DPA hydrogenation (Scheme 1).

2. Experimental section

All materials were stored in a nitrogen-filled glove box (Mbraun Labmaster I30, 1 ppm H_2O, <1 ppm O_2) prior to use, except for the catalyst which was stored in an argon-filled glove box (Mbraun Labmaster dp, 1 ppm H_2O, <1 ppm O_2) and transferred to the other glove box immediately before use. $NaAlH_4$ powder (hydrogen storage grade), DPA (98%), cyclohexane (anhydrous, 99.5%), dodecane (anhydrous, ⩾99%), 1-octyne (97%), 4-octyne (99%) and styrene (99%) were all obtained from Sigma-Aldrich. Toluene was dried in a distillation apparatus before storage. All liquid reagents and solvents were stored in the glove box over molecular sieves following degassing by bubbling nitrogen gas through the liquid for several hours. DPA was dried *in vacuo* overnight before storage in the glove box. The carbon aerogel was prepared by the sol-gel resorcinol procedure [26] and was analyzed by nitrogen physisorption (performed at −196 °C, Micromeritics TriStar) to determine the pore characteristics (BET surface area 564 $m^2\,g^{-1}$, pore volume 0.57 $cm^3\,g^{-1}$, broad pore size distribution with a maximum around 18–20 nm). The aerogel was dried at 600 °C under argon flow for 12 h before storing in the argon-filled glove box.

The catalyst was prepared by melt infiltration according to previously reported literature [21] with a loading of 20 wt% $NaAlH_4$. The result was analyzed by X-ray Diffraction (Bruker AXS D8 advance 120 machine, Co-K$_\alpha$ radiation, air-tight sample holder used), Temperature Programmed Desorption (Micromeritics Auto-Chem II, equipped with a TCD detector, Ar flow of 25 mL min^{-1})

and nitrogen physisorption before use in catalytic tests. Multiple batches of the catalyst were prepared using the above procedure and their full characterization can be found in Section S1 of the supporting information.

All hydrogenation reactions were carried out in a Parr 300 mL autoclave at 150 °C, 100 bar hydrogen pressure and constant stirring. The autoclave was loaded in the nitrogen glove box. 270 mg of catalyst (1 mmol $NaAlH_4$) and 890 mg of DPA (5 mmol) were added to 180 mL of solvent. Dodecane was added as an internal standard. Aliquots of reaction mixture were taken for analysis at regular intervals using a sampling arm which was flushed with a small amount of reaction mixture before the taking of each sample (roughly 2 mL of reaction mixture per sample). Samples were then analyzed by Gas Chromatography (GC-2010 Shimadzu gas chromatograph equipped with a Shimadzu AOC-20i Auto injector) using a CP-Wax column to separate the reaction mixture by boiling points; Boiling points: DPA (300 °C), *cis*-stilbene (307 °C), *trans*-stilbene (305 °C), bibenzyl (284 °C).

The following blank and reference measurements were performed, the results of which can be found in Sections S2–S3 in the supporting information. The influence of the carbon support on the activity was tested by performing the above catalysis experiments using only 215 mg of the carbon support in the absence of $NaAlH_4$. To rule out the effect of the metals in the autoclave walls catalytic tests were performed using a Teflon lining in the autoclave. As the Teflon liner reduced the volume of the reaction vessel the reaction was scaled down by 15%. The catalytic tests were repeated to demonstrate reproducibility. The recyclability of the catalyst was tested by recovering the catalyst at the end of the hydrogenation reaction and re-using in another test. Since 150 mg of the $NaAlH_4$/C catalyst was recovered (due to losses through filtering and removing the catalyst from the reactor) the catalytic loading in the second reaction was 150 mg instead of 270 mg. Isomerization studies were carried out by performing the reaction in the same manner as above but instead of adding DPA either *trans*-stilbene or *cis*-stilbene was added.

For the experiments on the adsorption of each substrate on the catalyst in different solvents the following procedure was applied. All experiments were performed at room temperature to ensure no hydrogenation reaction occurred. In each experiment a substrate, either DPA, *cis*-stilbene, *trans*-stilbene or bibenzyl, was dissolved in 9 mL of the solvent and stirred for 5 min. This was then analyzed by gas chromatography to determine the substrate concentration at 100%. Then 100 mg of catalyst was added (with a volumetric liquid:solid ratio of 203) to the solution and a sample was taken at 60 min for gas chromatography (GC) analysis. The decrease in
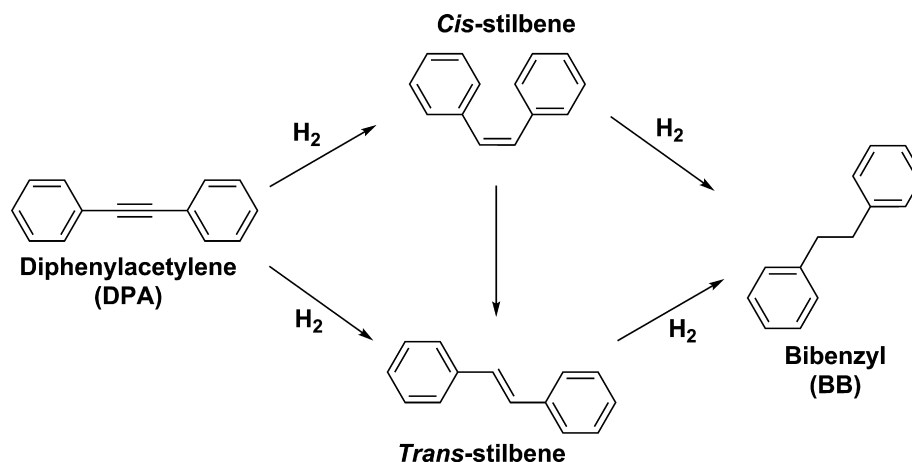
Scheme 1. Reaction scheme showing the hydrogenation of diphenylacetylene to bibenzyl.