

Nanoconfined NaAlH_4 as hydrogenation catalyst

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Abstract

Sodium alanate (NaAlH_4) is a metal hydride which has recently drawn more attention because it can be used as an efficient hydrogen storage material. One of the ways to efficiently use it as a hydrogen storage material is to use a carbon framework to confine the alanate particles on nanoscale. NaAlH_4 supported by a carbon framework can also be used as a catalyst for hydrogenation reactions. This research project focuses on the hydrogenation reaction of diphenylacetylene by NaAlH_4/C . The properties of the catalyst were studied and the influence of several reaction parameters was tested. Relations were found between the rate of the reaction and the solvent, hydrogen pressure and catalyst dehydrogenation. Cyclohexane performed better as solvent for the reaction than toluene, high hydrogen pressure in the reaction was very important for a high hydrogenation rate and catalysts which were dehydrogenated worked faster than the untreated catalysts. More complex features of the reaction were found when looking at the relation between the catalyst loading and the selectivity. Lower catalyst loadings showed an increase in the relative formation of *cis*-stilbene. Several complementary reactions have been performed to discover other external factors of influence, the reaction pathways and the mechanism in general. While some details regarding the reaction are still unknown, a large amount of information about the working of the NaAlH_4/C catalyst has been made evident. It was succeeded to speed up the reaction in several different ways and for the reaction intermediates ratios of *cis*-stilbene:*trans*-stilbene between 20:1 and 1:30 have been observed.

1 Introduction

This research project is focused on the catalysis of a hydrogenation reaction with nanoconfined sodium alanate or NaAlH_4/C . The sodium alanate on carbon catalyst used in this project is a form of sodium aluminium hydride on carbon aerogels. During the hydrogenation reaction the molecule diphenylacetylene, or DPA is hydrogenated by dissolved hydrogen gas. Starting from DPA, three different products can be obtained: *cis*-stilbene, *trans*-stilbene and bibenzyl. The first two products are hydrogenated once, the latter product is hydrogenated twice. This results in the reactions seen in Figure 1

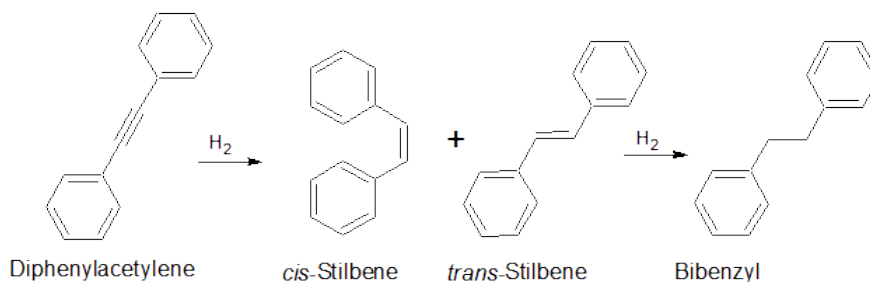


Figure 1: A simplified scheme of the hydrogenation of diphenylacetylene (DPA)

Sodium alanate has been known as a stoichiometric reaction agent for many years¹ but only recently has it been shown to be able to act as a useful catalytic reaction agent by using a hydrogen source for rehydrogenation.² This was discovered only after it was found that a titanium catalyst could be used to improve the release and uptake of hydrogen on the NaAlH_4 .³ Initially the focus on the research was done with the functionality of NaAlH_4 as a hydrogen storage material in mind. To improve the kinetic and thermodynamic properties of the material it was found that nanoconfinement could be used as well

instead of the titanium catalyst^{4,5} and it further improved the thermodynamics of using NaAlH₄ as a hydrogenation agent.

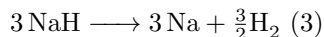
NaAlH₄/C can be seen as a new type of catalyst. Only recently in earlier research in the Inorganic Chemistry and Heterogeneous Catalysis group in Utrecht research has been done relating catalytic hydrogenation of organic molecules with this material. This project uses almost specifically NaAlH₄ on carbon aerogels as a type of NaAlH₄/C. Because this specific material is a very new material a number of basic reaction and blank experiments are included in the report. Furthermore this project aims to discover both the mechanism of the reaction and ways to improve properties of the reaction such as the rate and selectivity.

While there has been no earlier literature written specifically on the NaAlH₄/C catalyst it has been possible to collect a solid theoretical background on it by combining the collection of knowledge on NaAlH₄ as a hydrogen storage material, nanoconfinement and NaAlH₄ as a normal hydrogenation agent.

1.1 NaAlH₄, a metal hydride and hydrogen storage material

Central to this reaction is the material NaAlH₄. It is an inorganic compound and more specifically a metal hydride which consists of two different metals and four hydrogen atoms per molecule. Originally NaAlH₄ was created in a reaction between 4 units of NaH and AlCl₃.⁶ In this reaction NaCl was created as an unwanted side product. Not before long ways were found to create NaAlH₄ directly from the basic components Na, Al and H₂ in solution.^{7,8} Following this discovery the direct synthesis route in solution of another sodium aluminium hydride, Na₃AlH₆, was discovered.⁹ More interesting was the discovery of direct synthesis conditions from the basic components in the absence of solvents.¹⁰ With temperatures around 275°C and pressures around 175 bar nothing more than solid Na, solid Al and H₂ gas was needed. The creation of NaAlH₄ this way is a method to create a solid material containing hydrogen from the gas.

Once it is created NaAlH₄ can be heated outside of a hydrogen atmosphere to decomposition temperatures to dehydrogenate. This does not happen in a single step. It recombines to different materials before completely falling apart to Al(s), Na(s) and H₂(g). There are three distinct steps associated with the decomposition of metal hydrides like NaAlH₄.^{9,11} These three steps are described in equations 1,2 and 3. The first step is formation of the material Na₃AlH₆. The second step is the decomposition of Na₃AlH₆ to NaH. The last step is when NaH falls apart. The final products are Na(s), Al(s) and H₂(g). Decomposition of NaAlH₄ hydrogen desorption occurs at a negligible rate until the temperature reaches well over 200°C. The third step of the process is only reached at very high temperatures.¹² This makes the second step the final one in the many dehydrogenation steps and rehydrogenation steps of hydrogen storage and NaH is often considered as one of the final products.



By combination of hydrogenation and dehydrogenation NaAlH₄ can be used as hydrogen storage material. Hydrogen gas is stored as solid material decreasing the volume per hydrogen atom and dehydrogenation releases the gas for practical uses. Hydrogen storage in metal hydrides can be compared with the several other forms of storage like high pressure gas storage or liquid hydrogen. For it to compete with other types of storage a high gravimetric and volumetric density are needed. In the case of NaAlH₄ 7.4% of its weight consists of hydrogen. Of this 7.4% only 5.6% can be considered for dehydrogenation and rehydrogenation

in practice because of the high temperatures needed to decompose NaH.¹³ Even the kinetics for releasing the majority of the hydrogen of NaAlH₄ were less than ideal until it was found that with a titanium based catalysts the energy for the desorption of the majority of the hydrogen was lowered to around 150°C.³

There are several key properties expected of a metal hydride to use it as a hydrogen storage material. Next to high gravimetric and volumetric storage density the hydrogen equilibrium should be at a reasonable temperature as well.¹⁴ Figure 2 shows the decomposition temperature at 1 bar hydrogen pressure for many metal hydrides.¹⁵ A metal hydride like NaBH₄ has a decomposition equilibrium temperature around 600°C which makes the dehydrogenation conditions rather extreme. On the other side stand materials like LiAlH₄ with very low decomposition equilibria. Substituting Na with Li reduces the hydrogen affinity.¹⁶ This causes the material to dehydrogenate easily but it becomes much harder to hydrogenate it. Direct synthesis of LiAlH₄ is thus more difficult than its NaAlH₄ counterpart¹⁷ and very high pressures are needed to create the material from a direct synthesis.¹⁸

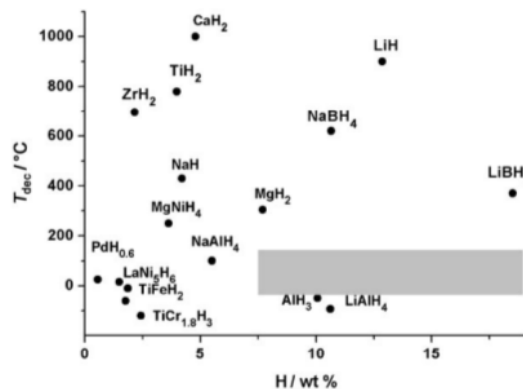


Figure 2: Thermodynamic and gravimetric properties of common metal hydrides.¹⁵

Even though the gravimetric properties for NaAlH₄ are below the targeted values its thermodynamic properties of NaAlH₄ as hydrogen storage material are within the desired range.^{3,15} NaAlH₄ doped with titanium releases hydrogen at temperatures between 100°C and 200°C. Figure 3 and 4 show a number of desorption profiles at different temperatures for NaAlH₄ and Na₃AlH₆ found by Bogdanovic et al. with and without Ti-doping in the form of 2 wt%TiCl₃. It can be seen that with this early catalyst the average temperature needed for quick dehydrogenation decreased by around 50°C. At the same time rehydrogenation under conditions with high pressure and temperature (150 bar, 170°C) is sped up dramatically.

Using the titanium catalyst as doping material did not come without disadvantages, one of the biggest disadvantages is that the time it takes to rehydrogenate the NaAlH₄ is extended with each cycle of dehydrogenation and rehydrogenation.¹⁹ This happens because, among other reasons, the titanium catalyst

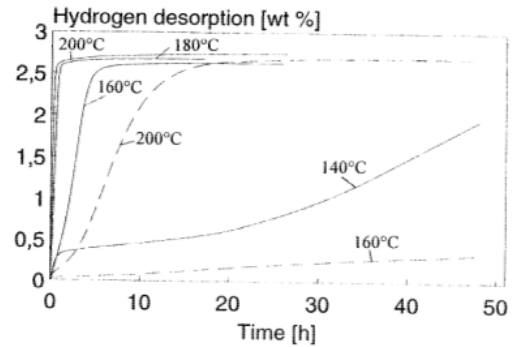
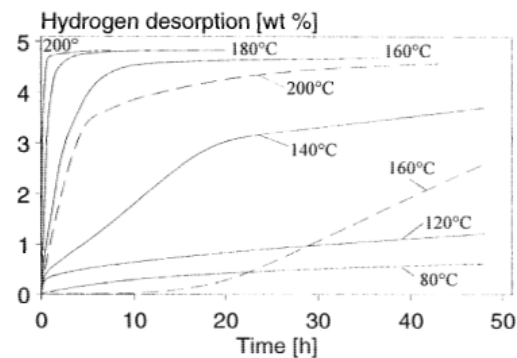


Figure 3: Hydrogen desorption rates of NaAlH₄¹⁹ Figure 4: Hydrogen desorption rates of Na₃AlH₆¹⁹

itself reacts with the NaAlH_4 and therefore deactivates.^{20,21} To solve these problems different methods of preparation and different additives were sought for. Both mechanical grinding and carbon additions were early solutions to improve the thermodynamics of the reaction without the titanium catalyst.²²

Since then, to improve the functionality of NaAlH_4 as hydrogen storage material, techniques like ball milling have been used,^{19,23} other molecular compositions of the titanium were used in experiments¹⁹ and additives like carbon nanotubes have been added.²⁴ As one of the later solutions nanosized sodium alanate particles has been researched as an alternative method to improve the desorption and resorption of hydrogen.^{4,5} By using nanosized sodium alanate some difficulties like the formation of a titanium aluminium alloy are prevented and the surface area is increased,⁵ benefiting the reaction in either case.

1.2 Nanoconfinement

In its purely crystalline form NaAlH_4 can be seen as a combination of Na^+ and AlH_4^- . The Na^+ ion can be replaced with other positive ions like Li^+ to form other alanates with slightly different properties. Replacing the aluminium creates other metal hydrides, which can also be used for similar reactions but have different properties.¹⁶ If NaAlH_4 can be considered as a crystal of Na^+ and AlH_4^- , Na_3AlH_6 could be considered as a combination of three Na^+ ions and AlH_6^{3-} as the counterion. Figure 5. shows the crystal structure of these materials.

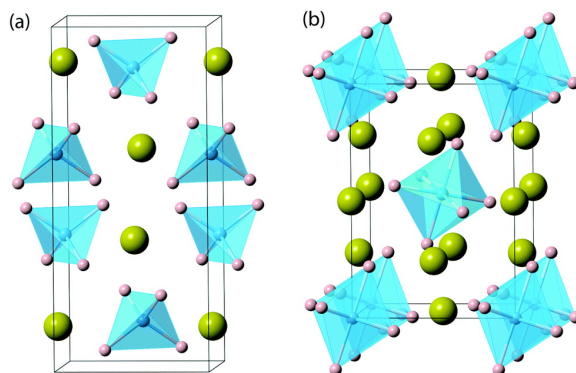


Figure 5: The crystal structures for NaAlH_4 and Na_3AlH_6 ²⁵

Because bulk NaAlH_4 is organized as a large solid crystal one of the barriers for hydrogen adsorption and desorption is transportation of the hydrogen. Figure 6 is a 2D representation of the adsorption of gaseous hydrogen (red) in a crystal structure (white). The hydrogen gas diffuses through solid material in the case of hydrogenation and dehydrogenation both. Reducing the particle size of the hydride can lead to a shorter diffusion time needed to reach the surface of the solid metal hydride.

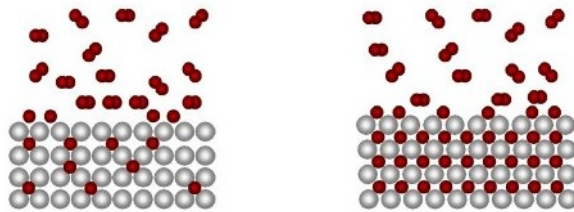


Figure 6: Adsorption of hydrogen in a solid material

The first trials to improve the decomposition of NaAlH_4 were focussed on kinetics and thermodynamics.²² Ball milling was used to increase the decomposition of NaAlH_4 at temperatures around 160°C . With the use of ball milling in the presence of carbon additives alloys were made. These alloys were discovered to improve both the desorption and absorption as well. At this point rehydrogenation at pressures below 100 bar became possible. The ideal situation was when 10 wt% carbon was added to the NaAlH_4 .²⁶ A very different situation from nanoconfinement where NaAlH_4 would be integrated in carbon frameworks.

To reduce this particle size nanoconfinement was used as an alternative solution.²⁷ Nanoconfinement on carbon aerogels was considered as a viable method to improve the thermodynamics for metal hydrides without using expensive or heavy materials. The earliest forms of nanoconfinement of NaAlH_4 were introduced a few years later. Impregnation of NaAlH_4 on carbon nanofibers showed to improve the thermodynamic properties for dehydrogenation and rehydrogenation.^{4,5} Following this a number of other materials were used to achieve the same or better results such as porous carbons and graphite.²⁹

Nanosizing the catalytic NaAlH_4 particles is more than just a replacement for titanium doping. The reaction profile is different from the original dehydrogenation. In contrast to the use of a titanium catalyst, nanoconfined sodium alanate does not show a difference between the first and second step of dehydrogenation.²⁹ This suggests that either the nanosizing or the interaction with the carbon support is affecting more than just a lowering of the energy barriers for the reaction. The sodium alanate completely loses its crystallinity when it adsorbs to the support by melt infiltration. This is supported by both X-ray and NMR measurements^{30,31} and also suggests that the properties and shape of the sodium alanate have been altered through interaction with the carbon support.

Theoretical studies of carbon supports show that the support will act as an electronegative substrate, which can compete with an AlH_4^- hydride for the electropositive Na^+ ion. In this way a framework assists in the creation of a relatively unstable hydride which can proceed to react further to hydrogen poorer species.³² The same study also proposed that there is a scale for the electronegativity of different carbon supports where a material like carbon nanotubes have more electron affinity than graphene sheets and thus lower the hydrogen removal energy by a larger amount.

The actual effect on the thermodynamics of the interaction between NaAlH_4 and the carbon support is best seen in the phase diagram in figure 7. The phase diagram consists of three parts, the light blue part where NaAlH_4/C is predominantly available, a yellow part in which the stable phase is NaH/C and an in between phase. This in between phase indicates the transition temperatures. Na_3AlH_6 would originally be expected at these temperatures but NMR measurements gave no indication of this.³¹ The black dots indicate points which were studied where originally Na_3AlH_6 would be the stable phase in bulk sodium alanate. At the same time pressure composition isotherms show that the loss of hydrogen is linear with the logarithm of the pressure.³³ This indicates that there is a steady distribution of temperatures at which hydrogen releases in contrast to the bulk sodium alanate where different steps of hydrogen loss can be clearly discerned.

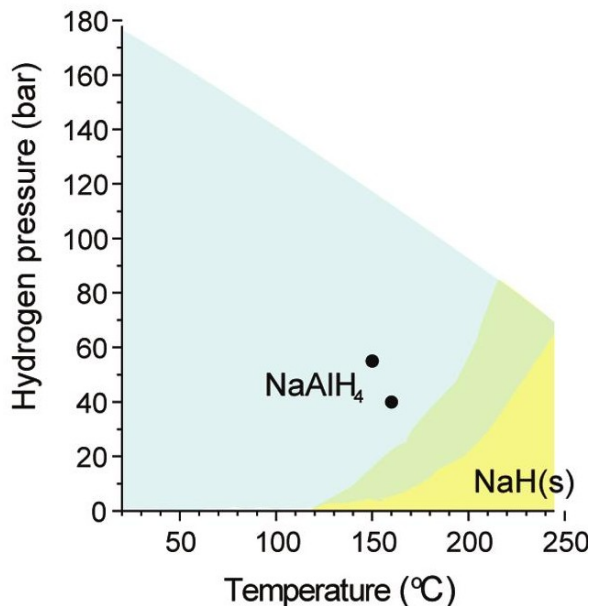


Figure 7: Indicative phase diagram for nanoconfined NaAlH_4 .²⁹

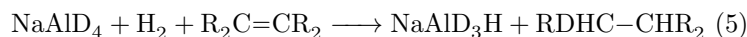
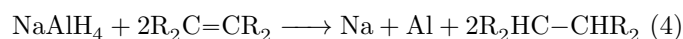
When the structure of NaAlH₄/C was studied by NMR it was discovered that the local environment of the NaAlH₄ did not change.³¹ This meant that the interaction with the support did not directly influence the local structure of the NaAlH₄. The NaAlH₄ clusters are intact, only the crystallinity of the material has decreased. When the catalyst is dehydrogenated and rehydrogenated the same NMR spectra are obtained showing that rehydrogenation is completely reversible. The peaks of aluminium and sodium broaden only slightly which is attributed to different contact orientations with the carbon support. In NMR results as well there is no discovery of the Na₃AlH₆ which does not seem to exist for the sodium alanate on carbon supports. The collection of research data on nanoconfined sodium alanate thus shows how a solid crystalline material is dispersed on the carbon which causes it to lose hydrogen more easily while causing the stepwise degradation to disappear.

The weight percentage of hydrogen was significantly lowered in NaAlH₄/C because of the added carbon. In most cases no more than 25% of the material could be NaAlH₄, which meant that while the thermodynamic and kinetic properties became more favourable, the gravimetric hydrogen content became much lower.²⁹ This meant that as a hydrogen storage material NaAlH₄/C was less useful. Along with the use of NaAlH₄ as a hydrogen storage metal, the discoveries were also applied to other uses of metal hydrides and to catalysis in particular.²

1.3 Reactions with NaAlH₄

Before NaAlH₄ could be considered as a catalyst it was already known as a stoichiometric hydrogenation agent. A similar metal hydride, lithium alanate (LiAlH₄), was discovered in 1947.³⁴ This LiAlH₄ shows a lot of similarities with NaAlH₄ and some years later NaAlH₄ was created as well.⁶ At first the main use for NaAlH₄ was sought in organic reductions¹ much like the hydrogenation reaction of this research project.

Much of the earlier research on metal hydrides^{11,35} had been done on LiAlH₄ and it was even suggested as a homogeneous catalyst.³⁶ LiAlH₄ was considered a catalyst for *trans*-additions where both the alanate and the hydrogen gas donated one hydrogen atom to the reagent. Equation 4 shows the simplified scheme of the single reduction with NaAlH₄, equation 5 shows the reduction and hydrogenation in one step if the reagent was NaAlD₄. It is important to note that these reactions are done in tetrahydrofuran (THF) in which the LiAlH₄ and NaAlH₄ are dissolved. NaAlH₄/C and bulk NaAlH₄ are used as heterogeneous catalyst in contrast to this homogeneous catalysis.



Multiple studies towards the reactivity of metal hydrides have been performed. Early reactions with molecules with a stereospecific centre showed inversion of stereochemistry³⁷ and studies of reactivity rates showed patterns very similar to a S_N2 reaction profile.³⁸ However a number of reactive studies on benzylic halides^{39,41,42} and retentions of stereoselectivity⁴⁰ reported a radical single electron transfer mechanism instead. Even a multiple centre reaction has been suggested as a possible reaction intermediate.⁴³ A comparison between the two possibilities concludes that a number of methods of reduction are possible.⁴⁴

The conclusion which can be obtained from the studies on the reaction mechanism of reduction by metal hydrides is that the number of electrons the material can lose along with a proton core is not always consistent. This means that reactivity and selectivity towards certain materials might be very different under different circumstances. An interesting phenomena is as that the addition of transition metals speeds up the process of reduction. Many transition metals can catalyse the reduction of functional

groups which are inert to NaBH_4 or LiAlH_4 alone.⁴⁵ This effect is perhaps similar to the effect where addition of certain transition metals is shown to catalyse the loss of hydrogen of NaAlH_4 .³

A titanium catalyst was found in 1997 by Bogdanovic et al.³ which improved the conditions for metal hydrides to release hydrogen. This led to a lot of research in using NaAlH_4 as a hydrogen storage material and also a small part of the research was used in trying to add the titanium catalyst to a stoichiometric and homogeneous hydrogenation reaction of DPA.⁴⁶ This reaction was done at 55 degrees with dissolved NaAlH_4 in THF and used an additive of TiN nanoparticles. The results of this reaction were an increased reaction speed and a preference for the formation of *cis*-stilbene where without catalyst the reaction would prefer *trans*-stilbene. The results of this study were used to design a catalytic experiment, using only 0.75 mmol NaAlH_4 (1.5 mmol H_2) for 5 mmol DPA and 100 bar H_2 pressure.² Again these experiments were done in THF with the addition of a TiCl_3 catalyst. The result was a full hydrogenation in about 7 hours (80% bibenzyl) at 130 degrees for NaAlH_4 . This reaction can be seen in figure 8. The same reaction took only less than 2 hours and for the derivative NaAl_3H_6 under the same circumstances. Notable was that only *trans*-stilbene seemed to be formed as an intermediate in the reaction, in contrast with the earlier stoichiometric reaction. This *trans*-stilbene was only an intermediate as the full hydrogenation of the DPA to bibenzyl meant this was a successful homogeneous catalytic reaction.

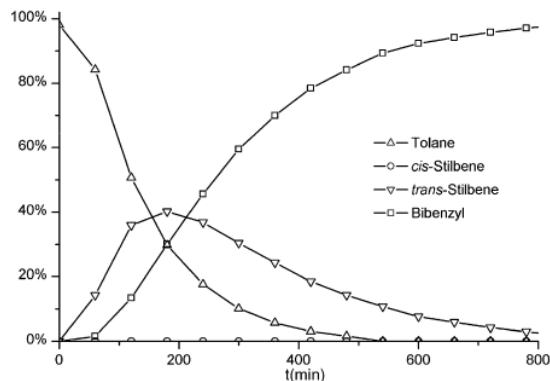


Figure 8: The reaction profile for Ti-doped NaAlH_4 as homogeneous hydrogenation catalyst²

Hydrogenation reactions with a heterogeneous NaAlH_4/C catalyst have significant differences from reactions with a homogeneous NaAlH_4 (in THF) catalyst. The research in the area of the NaAlH_4 heterogeneous catalyst is much younger and received more interest mostly because of the possibilities the material possessed for hydrogen storage. The larger part of the recent sodium alanate research has been focused on the direct release and uptake of hydrogen as gas. Yet a large amount of the research on NaAlH_4 as hydrogen storage material can be extrapolated to the hydrogenation reaction. Instead of using the sodium alanate as a hydrogen gas source it can be used in a similar way as a hydrogenation agent by adding the heterogeneous material as a catalyst to a solution with a reagent.

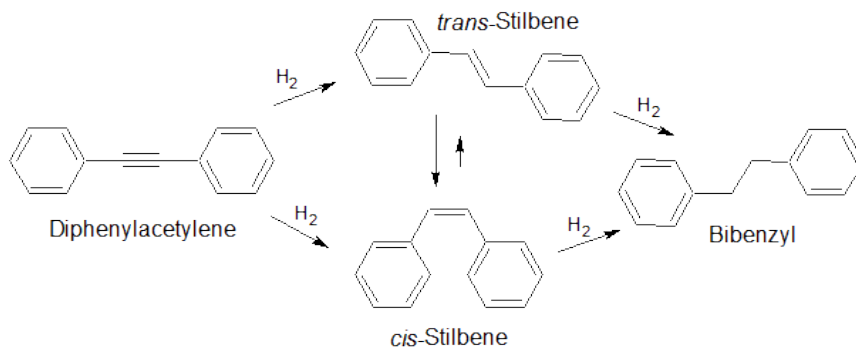


Figure 9: The reaction pathways of hydrogenation and isomerization

Diphenylacetylene or DPA is used for this project just as in the experiments with the homogeneous catalyst. DPA is a relatively simple molecule that can be hydrogenated by NaAlH_4/C . The molecule has a triple bond connecting two benzyl groups. The triple bond can be hydrogenated twice which could be seen earlier in figure 1. As the results of hydrogenation both *cis*- and *trans*-stilbene can be formed, depending on the selectivity of the reaction mechanism. Both these stilbenes can be even further reduced to bibenzyl and can be seen as intermediates of the reaction. At the same time isomerization is possible between these two intermediate products. The more complete reaction scheme can be seen in figure 9.

In this research project the catalyst is heterogeneous instead of homogeneous. At the same time the catalyst likely has a comparable structure on the single molecular level and the heterogeneous catalyst can do reductive hydrogenation as well without a hydrogen atmosphere because the material itself has hydrides. This is in contrast with other famous heterogeneous catalysts like Pd/C which is a commonly used hydrogenation catalyst. If the reaction profile of a heterogeneous catalytic reaction of NaAlH_4/C would be comparable with Pd/C it would adsorb H_2 onto its surface and cause a synchronous addition of both hydrogen atoms at once.⁴⁷ At the same time the heterogeneity makes a mechanism possible where a hydride on the solid reacts first with the catalyst after which the catalyst is then restored in shape by the external source of hydrogen. These types of mechanisms are known as a Mars and Van Krevelen mechanism where the product leaves with one or more constituents of the catalyst lattice^{48,49}

The NaAlH_4/C catalyst can be seen as a new catalyst which could possibly hydrogenate in various pathways. Hydride adsorption and radical transfer mechanisms like the homogeneous catalyst could be possible or syn-additions and Mars and Van Krevelen mechanisms as well. To find out how NaAlH_4/C works as a catalyst the results of the catalysis experiments will be used to compare with the results from these earlier studies of other partially different materials.

1.4 Catalysed hydrogenation by nanoconfined NaAlH_4

The research done on NaAlH_4 as a hydrogen storage material, nanoconfinement and catalysis with NaAlH_4 together are combined in one single NaAlH_4/C catalysis experiment. The set-up of the experiment is based on theory from the introduction but also on conclusions from a preliminary research project. A number of hypotheses were devised from the cumulation of the previous knowledge.

When NaAlH_4 was first reported as a hydrogenation catalyst it was still used in combination with the titanium additives.² The influence of the research on hydrogen storage materials directly influenced this choice for a catalyst. Using nanoconfinement of metal hydrides for hydrogen storage has also influenced the decision to use the nanoconfined material for hydrogenation as well.

This research project is among other things a continuation of a preliminary research project done by J.Gao at the research group for Inorganic Chemistry and Heterogeneous Catalysis from the University Utrecht. This earlier work was specifically focussing on the different support materials used as basis for the catalyst. The work not overlapping with the results from this research project are summarized in appendix A. Before the start of this research project it was already known that NaAlH_4 could be melt infiltrated on a number of supports, including carbon aerogels and high surface area graphite. The latter material was the material of choice for several other experiments. Using high surface area graphite has a big disadvantage, namely that there is almost no formation of *cis*-stilbene. This meant that selectivity could hardly be used as a method of description for the reaction.

Using carbon aerogels with different pore size distributions showed differences in selectivity. determining that aerogels with greater pore size produced relatively more *cis*-stilbene and aerogels with smaller pores produced relatively more *trans*-stilbene. It was also found that differences in selectivity between supports

were caused by different rates of isomerization. With this knowledge a carbon aerogel support with a pore size distribution around 20 nm was chosen.

The research project was about understanding how the catalyst worked and about being able to control the outcome of the reaction in terms of selectivity and reactivity. This project covered at first all the basics of the hydrogenation reaction. To further improve the reaction a set of standard reaction parameters was studied. After this several experiments went more in depth on the more interesting results of these parameters and it was attempted to modify the catalyst as well.

The preliminary research already showed that the rates of either hydrogenation or isomerization vastly differed depending on the circumstances. Simply breaking the reaction into pieces showed the balance between the possible reactions by using the stilbenes as starting materials. Comparisons between all the pieces were sought to give insight in the total reaction profile. The total reaction profile could be completed by a number of rate equations and experiments without the catalyst. During the course of this project the picture of what happened during the reaction was to be filled to completion as much as possible.

Some of the reaction experiments were performed with different solvents. While the solvent did not play a direct role in the reaction it can stabilize intermediates or restrict the movement of the substrates on the catalyst. The substrate may either interact directly with the catalyst or travel along the support until it reached the surface of the catalyst. In this process the adsorption would be hindered if the solvent would adsorb to the surface of the support or metal hydride as well.

NaAlH_4/C showed only two peaks of hydrogen release likely corresponding to NaAlH_4/C degrading to NaH/C and the degradation of NaH/C ²⁹ in contrast to the three steps observed in the degradation of bulk NaAlH_4 .⁹ At the same time partly degraded Na_3AlH_6 showed higher reaction rates for the hydrogenation reaction.² Even without detection of Na_3AlH_6 the use of a partly depleted catalyst may increase the reaction rate.

With the combination of these experiments this research project aims to create a solid basis of understanding of the hydrogenation reaction as well as creating a number of possibilities to control the outcome of the reaction in terms of rate and selectivity. At the end of this project it is sought to define the viability and possibilities of NaAlH_4/C as a hydrogenation catalyst.

1.5 Methods of Analysis

During the project four different methods of analysis were used. To identify the progress of the reaction gas chromatography was used. To characterise the catalyst temperature programmed desorption, X-ray diffraction and N₂-physisorption were used.

Gas Chromatography

Gas chromatography was used to discern DPA and the reaction products from each other by letting them pass a wax column in the gas phase. Gas chromatography was used to visualize the reaction profiles of every hydrogenation. The different molecules elute after different time intervals, depending on the strength of the interaction between the molecules in gaseous form and the liquid stationary phase. The method can both be used qualitatively and quantitatively. It discerned the organic molecules from each other and how much of each is present in the samples.

Temperature Programmed Desorption

To monitor the release of hydrogen Temperature Programmed Desorption (TPD) was used. In temperature programmed desorption a sample is heated in a controlled manner where the amount of molecules released from the sample is recorded. In this project the prepared catalysts differed in the amount of hydrogen they could adsorb and release and at which temperatures this hydrogen release occurred.

X-Ray Diffraction

Another method of characterisation was X-Ray Diffraction (XRD). Using XRD the crystallinity of the material was measured. Ordered materials, like solid state sodium alanate, show an XRD pattern depending on how regularly they are orientated. X-rays diffract on the atoms in the crystal. The signal that was produced was dependent on the wavelength of the rays, the orientation of the atoms and the interatomic distance. In the solid crystals, many atoms will have the same interatomic distance and a large signal can be obtained. When the sodium alanate was nanosized and melt infiltrated onto the carbon framework these distances changed and became irregular causing the large signals to be lost.

N₂-Physisorption

N₂-Physisorption measured the specific surface area of the material as well as pore volume and pore size distribution. The physisorption measured the extra amount of gas needed to reach a pressure equilibrium. A graph of adsorption vs pressure was used to define the size of nanopores. Next to characterisation of the materials a loss in pore volume implied nanoconfinement of NaAlH₄ within the pores. With N₂-Physisorption could also be determined what the surface area of the catalyst was and thus how much active sites there theoretically were.

2 Experimental

2.1 Preparation of the materials

Carbon aerogels

To create aerogel frameworks a mixture of resorcinol and formaldehyde was made. Resorcinol (Sigma Aldrich 99%, 8.65 g, 79 mmol), formaldehyde (Fisher chemical, analytical reagent 37-41%, stabilized by 12% methanol 12.89 g, 158 mmol) and sodium carbonate (Across organics, anhydrous pure, 0,01 g, 0.16 mmol) were dissolved in 12 mL deionized water. The organic weight fraction was 40% with this combination and was used to make aerogels with a pore size distribution aimed around 20 nm. The mixture was left to react for a day in a closed environment, heated to 60°C to stand for another day and finally heated to 90°C to react for three days.

Melt infiltration

NaAlH₄ was distributed onto the carbon aerogel surface by melt infiltration. NaAlH₄ was obtained as a powder from Sigma Aldrich (99%). 1 g of CA was mixed and ground with 0.25 mg of NaAlH₄ in a mortar, to create a 20 wt% NaAlH₄/C mixture. After preparation, all samples were hydrogenated in graphite sample holders inside a 50 mL stainless steel autoclave at 100 bar H₂, 150°C for 15 minutes 180°C for 15 minutes. After reaction the samples were cooled and transported to the glove-box under an argon atmosphere. All sample handling and storage was conducted in a glove-box under argon atmosphere.

Creation of the dehydrogenated catalyst

To create the dehydrogenated catalyst 0.5 g of catalyst was put in an empty autoclave. It was shown from the TPD analysis that the catalyst lost about half of its hydrogen after 35 minutes (167°C). Because the exact circumstances could not be simulated the sample was heated from room temperature to 150°C in half an hour and then the temperature was kept stable at 150°C for 15 minutes. To fully deplete the catalyst a new sample was heated to 250°C in 30 minutes and kept at that temperature for two hours. The catalyst was then cooled down to room temperature and stored under argon atmosphere.

Preparation of reactants and solvents

Cyclohexane (Sigma-Aldrich, anhydrous 99.5%) was stored under N₂ atmosphere and in a flask containing molecular sieves. Toluene was obtained from an on site distillation system. Both solvents were not further prepared before use.

DPA (Sigma-Aldrich, 98%), *trans*-stilbene (Acros, 99%) and bibenzyl(Sigma-Aldrich, 99%) were dried under running vacuum at room temperature for a minimum of a day. The materials were stored in the glovebox (N₂ atmosphere) before the reaction. *Cis*-stilbene (96%) and dodecane (Sigma-Aldrich, 99%) were prepared by bubbling nitrogen through the liquid in a Schlenk environment. *Cis*-stilbene (96%) was stored under N₂ atmosphere below freezing temperatures with molecular sieves. Dodecane was stored under N₂ atmosphere with molecular sieves at room temperature.

2.2 Reactions

Main reactions

All the hydrogenation reactions were done in a 0.3 L Parr autoclave (200 bar, 350°C). 0.890 grams of DPA was collected inside the autoclave in a glovebox under N₂ atmosphere. 0.270 grams of catalyst was added as well as 0.200 grams DPA. Adding 180 mL of cyclohexane dissolved the DPA and dodecane and the autoclave was sealed. Appendix B contains the full table of reaction data and all the changes per experiment.

During the reaction the autoclave was pressurized to 100 bars of hydrogen pressure and heated to 150°C. Over the course of five and a half hours samples of around 1 mL were taken through an enclosed compartment extension on the autoclave. During the heating the pressure rose until around 120 bar. Taking the samples slowly took the pressure down to around 80 bar over time. The twelfth and last sample was taken after a night. All the samples were stored in the fridge until they were analysed by the GC.

Rate experiments

For the rate experiments smaller loadings of the catalyst were made. Loadings of 0.027, 0.054, 0.081 and 0.108 g were used. The rate experiments differed from the main experiments as well in the sampling times. Instead of every half hour samples were taken every ten minutes. For these experiments the first two hours of DPA depletion were taken as measurement point for the rate. Using these data points is to negate the effect of the initial delay in the reaction and the delay at lower DPA concentrations as well. The complete overview of the rate experiments is given in Appendix B.

Adsorption experiments

The adsorption experiments were done in a plastic reaction tube and inside a glovebox under N₂ atmosphere. For the adsorption of DPA on the catalyst a solution of DPA (0.027 g) and dodecane (0.02 g) in cyclohexane was made. The reaction was magnetically stirred and three samples of 1 mL were taken. After this the catalyst was added and the reaction mixture was again stirred for two minutes and a new sample was taken. The last two samples were taken after 15 and 30 minutes respectively. The same experiments have been done with *cis*- and *trans*-stilbene and bibenzyl as well instead of DPA. All of these experiments have been done with toluene as the solvent as well. Finally, instead of the catalyst, the reaction with DPA in cyclohexane was done with 0.022 g aerogels as well. All experiments were done twice and the second time all the GC analysis was done three times. The data on these experiments can be found in appendix B as well.

Hydrogen solvation

The hydrogen solvation experiments were done with 180 mL of solvent, both the cyclohexane and toluene solvation experiments were done in the same autoclave. The pressure was measured at set points in time at room temperature to measure the solvation over time. After one hour the solution was heated to 150°C and the solvation versus temperature was noted.

2.3 Experiment analysis

Gas Chromatography

All the GC experiments were done with a Shimadzu GC-2010 Gas Chromatograph. The column used was a CP-WAX 57 CB column. Samples were obtained over the course of 35 minutes. The first 5 minutes the temperature was kept at 60°C before the sample was heated to 210°C over the course of 15 minutes. The temperature was kept constant at 210°C for 15 minutes before cooling down. The total duration of the GC measurement time was 35 minutes.

Temperature Programmed Desorption

TPD experiments were done using a Micromeritics AutoChem II 2920 apparatus. Approximately 50 mg of the sample was weighted into glass tubes inside the glove-box. During loading of the sample holders in the apparatus, the sample was exposed to air for a minimum amount of time. After flushing 5 min with an Ar flow of 50 mL/min, the samples were heated to 450°C at 5°C/min in 25 mL/min Ar flow. After 20 minutes at 450°C the measurement stopped and the samples were cooled down.

X-Ray Diffraction

The XRD samples were prepared by spreading a thin layer of sample on the sample holder and a cover was used for keeping sample the stored under Ar atmosphere. XRD patterns were obtained at room temperature with angles from 20° to 80° with a Bruker-AXS D-8 Advance X-ray diffractometer set-up using $\text{CoK}\alpha$ 1,2 radiation with $\lambda = 1.79026$.

N₂-Physisorption

The carbon aerogels and NaAlH₄/C catalyst were characterized by N₂-physisorption to obtain information about the surface area and pore structure of the materials. The measurements were performed in airtight tubes at -196°C, using a Micromeritics Tristar apparatus. The pore size distributions of the samples were calculated from the desorption branch using BJH theory with the Carbon Black STSA equation. The surface area was calculated using the BET-equation and the micropore volume by using the T-plot method.

3 Results and Discussion

3.1 Preparation of the catalyst

The NaAlH_4/C catalyst consisted of two components. The NaAlH_4 was the working particle in the reaction but only attributed for 20 wt% of the catalyst. For almost every reaction in this project the catalyst was supported by carbon aerogels. The carbon aerogel were characterized by X-Ray Diffraction (XRD), which showed a profile with two bulges and without peaks, but more information about the structure and surface area of the aerogel was obtained with N_2 -physisorption. After melt infiltration the NaAlH_4/C catalyst was characterised just as the aerogels with XRD and N_2 -physisorption. Temperature programmed desorption (TPD) was used for the analysis of the catalyst as well. With these three methods a small array of characteristics of the catalyst could be defined.

The process of creating carbon aerogels caused a variety of pore size distributions. Figure 10 shows the nitrogen physisorption profile of the pore size distribution for the aerogel support before NaAlH_4 was melt infiltrated on it. All the aerogels were created in the same mixture of resorcinol and formaldehyde but were dried and pyrolyzed in three different batches. The method of preparation was aimed to create a pore size distribution averaging around 20 nm. The results showed that the aerogels had a distribution with the majority of pore sizes between between 5 and 25 nm and also a large amount of nanopores (<2nm). The figure also shows that the second and third batch were very similar but the first batch had a slightly different distribution of pores. The total pore volume of the first batch was also lower than the volumes of the second and third batch with 0.41, 0.64 and 0.57 $\text{m}^3/\text{g}\cdot\text{nm}$ respectively. The BET-surface area calculated was very similar for these three samples with area to weight ratios of 555, 551 and 564 m^2/g . To create the catalyst the aerogels from all three batches were mixed together before melt infiltration.

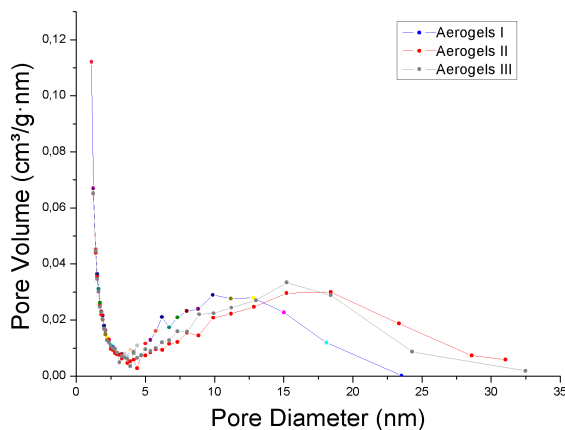


Figure 10: Nitrogen physisorption profiles of the aerogels

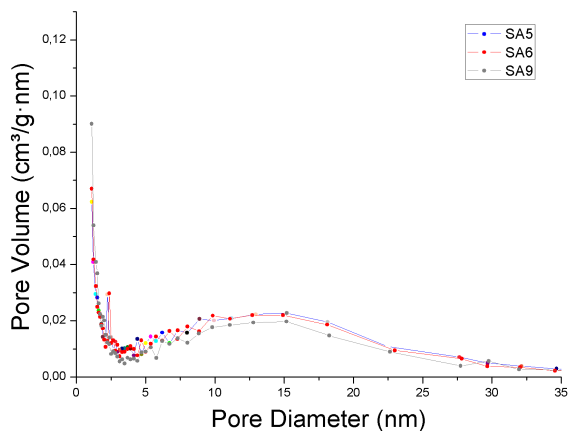


Figure 11: Nitrogen physisorption profiles of the catalyst

To distribute the NaAlH_4 inside the nanopores, the catalyst was melt infiltrated. This created a distribution of small NaAlH_4 particles inside the framework increasing the surface area for NaAlH_4 and at the same time formed interactions between the catalytically active material and the carbon support. Figure 11 show three different batches of catalyst. In the figure the total pore volume relative to the average pore size can be seen again. In total there was 0.47 $\text{m}^3/\text{g}\cdot\text{nm}$ of pore volume, 0.07 $\text{m}^3/\text{g}\cdot\text{nm}$ less than in the aerogels mixture. The surface area of the catalyst was 172 m^2/g lower as well. The loss of volume and surface area was explained by the filling of the pores with NaAlH_4 . The loss of the volume at almost every pore length showed that pores of various size were filled. This meant that

the aerogels filled with NaAlH_4 still had a size distribution along the same lines as the original aerogels.

The XRD diagram in figure 12 shows a number of diffraction peaks. The broad bulges represent the diffraction of the carbon aerogel support. The peaks can be explained with the help from the article of Adelhelm.²⁷ The first diffraction peak has an angle of 34° . This peak is the highest peak to indicate the presence of NaAlH_4 but it is only a very small peak compared to the height a bulk NaAlH_4 -peak would have at the same location. This indicates that most of the NaAlH_4 has lost its crystalline form and was in contact with the carbon. Of the four small peaks around an angle of 40° two also belongs to NaAlH_4 just as the peak at an angle of 57° . The other two very small peaks and a very small bulge at 64° might be an indication of NaH crystalline formation. There are three large peaks left with angles of 45° , 52° and 77° . These peaks belong to solid aluminium indicating that in the process of melt infiltration some NaAlH_4 is lost and Al and NaH are obtained. The more apparent Al -peaks in contrast to the NaH peaks could be attributed to the larger movability of Al -fragments which segregate from the carbon NaH and NaAlH_4 to form larger Al(s) -particles.²³ The larger Al(s) -particles are thus more strongly represented with XRD. From the XRD diagram the conclusion was made that most NaAlH_4 had become NaAlH_4/C and thus the crystallinity had been lost.

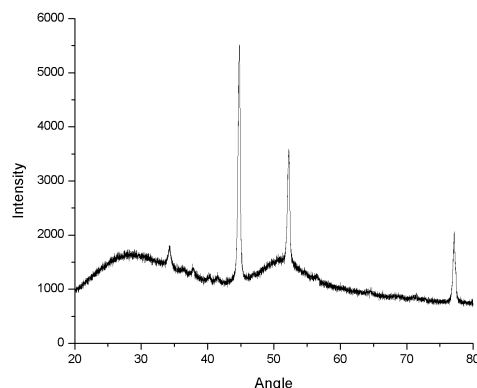


Figure 12: XRD diagram of the catalyst

The TPD results shown in figure 13 shows the loss of hydrogen over time. At a temperature of around 100°C hydrogen desorption from the NaAlH_4/C started and it peaked around 160°C . At this point hydrogen was lost at the highest rate and NaAlH_4/C became NaH/C , Al and H_2 . After this the hydrogen desorption rate started to decline until it peaked again at 320°C after which the rate of hydrogen desorption declined again. This was likely because the temperatures needed to deplete even NaH/C are reached. Almost the complete desorption happened between 100°C and 400°C .

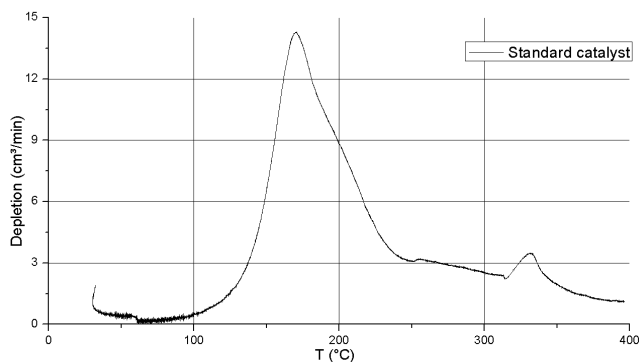


Figure 13: Temperature programmed desorption profile of the catalyst

The three methods of analysis showed no surprising results altogether. The NaAlH_4 was distributed on the carbon aerogel surface which caused it to lose its crystallinity and interact with the carbon forming NaAlH_4/C . The improvement in its thermodynamic properties was directly related to the easier hydrogen desorption.

3.2 Hydrogenation with a NaAlH₄/C catalyst

The basis of the project was a reaction where diphenylacetylene (DPA) is hydrogenated by sodium alanate on carbon (NaAlH₄/C). The standard reaction was used as a basis to compare with the other reactions. In most cases only one or two parameters were differentiated from the standard reaction. The standard reaction itself had been done a number of different times to discover how reproducible the results were. All the reproductions of this reaction were averaged to a single reaction profile. The reproducibility of this reaction profile is shown by the comparison of the DPA depletions of these standard reactions.

There were two initial products produced by the hydrogenation of DPA. *cis*-stilbene and *trans*-stilbene. Both of these products were intermediate products which could be hydrogenated again and form bibenzyl. To record what happened in the reactions, the profiles were expressed through the analysis of samples taken during different stages of the reaction. 5 mmol DPA and 1 mmol NaAlH₄/C were used as starting materials for the reaction. The reaction was tracked by sampling every half hour for five hours and a last sample was taken after a day to ensure that the reaction was completed. Figure 14 shows the reaction profile of this standard reaction. The graph represents the relative molecular quantity of DPA, *cis*-stilbene, *trans*-stilbene and bibenzyl. The reaction profile was normalised so that the sum of these materials is always 100%. The reaction has been performed seven times in total and the graph shows the average of all of these reaction profiles.

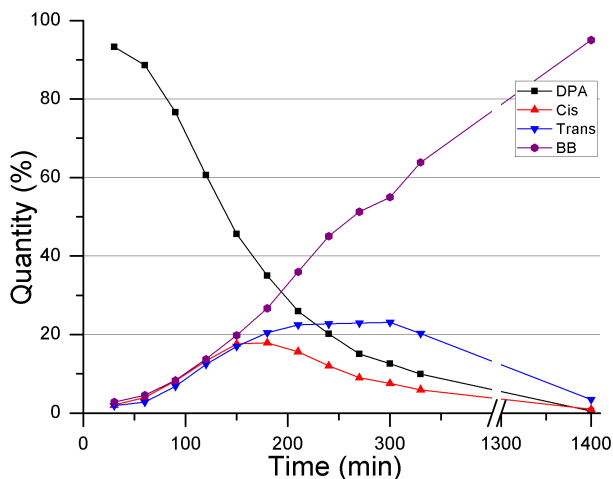


Figure 14: Average profile of seven reactions

In the figure it can be seen that at the start of the reaction only DPA was present. After a small induction period the concentration of DPA rapidly decreased and the products were formed. The amount of DPA dropped over the course of the reaction and from this both *cis*- and *trans*-stilbene were created, as well as bibenzyl. At one point in time the stilbenes were also hydrogenated and reacted to form bibenzyl. For *cis*-stilbene this diminishing in quantity started before the DPA was gone. The quantities of *trans*-stilbene however only started to diminish when both the quantity of DPA and of *cis*-stilbene was significantly lower.

In this standard reaction half of the DPA was depleted in 150 minutes. This means that under these circumstances the rate of this reaction was about 1 mmol DPA per hour. After another 150 minutes the amount of DPA was below 10%. The point at which DPA was completely gone fell beyond the time period which was sampled. The last sample, which was taken after a day shows that the DPA did completely hydrogenate, as well as the stilbenes. The profile of the reaction shows neither a linear nor an exponential rate of reaction, the fastest rate of depletion was only reached after around 100 minutes. In terms of selectivity this reaction showed almost no differences in the quantities of *cis*- or *trans*-stilbene for the first few hours. Only after a certain time, when the formation rate of both stilbenes was declining, a difference started to become apparent. An explanation for this change in selectivity could be that the *cis*-stilbene hydrogenation is favourable in comparison to the hydrogenation of *trans*-stilbene.

An interesting observation was the immediate formation of bibenzyl. This formation showed almost no dependency on concentrations of stilbene which would be expected if the hydrogenation of stilbene would proceed in a common way. For the formation of bibenzyl several factors were of importance. The composition of the reaction mixture was important and the rates of hydrogenation for DPA and the

stilbenes as well. While *cis*-stilbene and *trans*-stilbene are similar and produce the same product it might be that the hydrogenation of one stilbene proceeded at a higher rate than the hydrogenation of the other. In this reaction the almost linear formation rate of bibenzyl was remarkable because it suggest that at any time there were enough reagents to hydrogenate into bibenzyl. Yet at the start of the reaction there was almost no stilbene present. This phenomena suggested the possibility of a double hydrogenation of DPA.

The profile of DPA depletion was compared for seven standard reactions in figure 15. These experiments were all done with different catalyst batches and in several cases other minor factors changed. Two different autoclaves were used for the reactions and the amount of time between hydrogenation of the sample and heating the sample could be several minutes apart. None of these parameters was expected to have either a predictable or avoidable effect on the reaction. The catalyst batches were produced by repetition of a standard procedure but only a few reactions could be done with the exact same batch of catalyst.

In the comparison shown in figure 15 every line represents the DPA depletion profile of a single reaction. The thick line represents the average of these reactions. While no two reactions resulted in the same reaction profile, all reactions except one had lost 50% of DPA between two and three hours. The one exception, st8, was also the only reaction without a slow start in the DPA depletion and instead immediately dropped to 70% of the initial amount of DPA. If this reaction profile had been shifted with one hour in the graph it would have coincided well with the averaged reaction profile.

Batch	Rate	Selectivity
St1	30.8	0.600
St2	29.5	0.875
St4	30.3	2.810
St5	19.2	0.777
St6	25.0	0.201
St7	23.3	0.465
St8	22.9	1.297
AVG	25.9	1.004

Table 1: Comparison of rate and selectivity

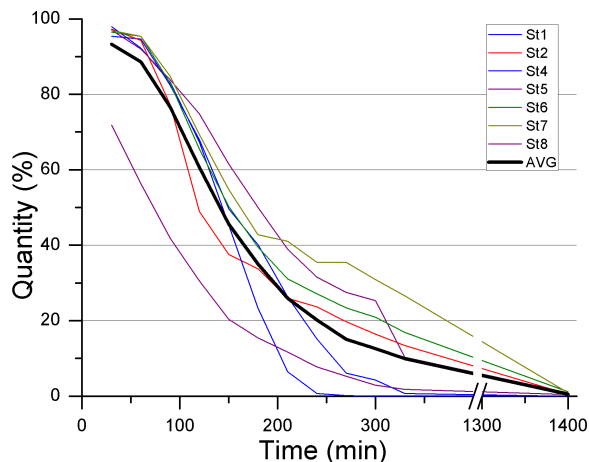


Figure 15: DPA depletion profile of seven standard reactions

There were many different ways in which the reactions could be compared. Table 1 gives the DPA depletion rates in %/hour and the selectivity average in *cis*:*trans* ratio. The depletion rate was determined by determining a trend line with the data from the first three hours. The selectivity was determined over the course of the complete reaction except for the last sample. The deviation from the average rate is within 7%/hour and the *cis*:*trans* ratio ranges between 0.2 and 3.0 and averages around 1. From these results was concluded that, while the reaction is reproducible, comparisons could only be made when differences were significant enough.

3.3 Experiment blanks

There are two defining properties of a catalyst. The first defining property is that it accelerates the reaction and the second defining property is that the catalyst itself is not consumed. To prove NaAlH_4/C actually works as a catalyst it has been compared with several blank experiments. This was done to prove that neither of the components, NaAlH_4 or carbon aerogel, alone was enough to catalyse the reaction. The catalytic reaction was also compared with the stoichiometric reaction to show what happened in the absence of a hydrogen atmosphere.

To show that the catalyst was actually necessary for the reaction a reaction was performed with every parameter the same as the standard reaction but the catalyst itself. Every increase in reaction speed, every difference in selectivity would then have to be caused by the catalyst. The reaction profile of a reaction without catalyst can be seen in figure 16. One immediate observation made from this figure is that the rate of hydrogenation was much lower in the reaction without NaAlH_4/C . This was the proof that the addition of this material catalyses the reaction. Combining this with the fact that 1 mmol of catalyst was enough to hydrogenate all the DPA made NaAlH_4/C a working catalyst. In figure 16 the DPA was hydrogenated partially as well leaving about 60%. A simple explanation for this would be that 100 bar H_2 and 150°C was enough for hydrogenation. A spontaneous reaction between H_2 gas and DPA seemed the most likely option. What the graph also shows is a higher selectivity towards *cis*-stilbene, there was almost no *trans*-stilbene or bibenzyl formation at all without catalyst.

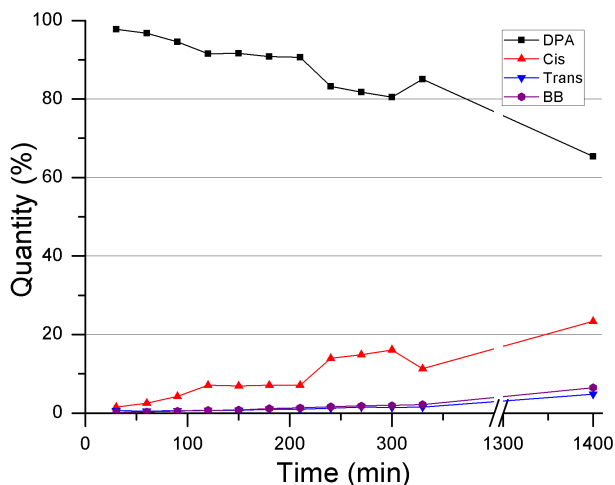


Figure 16: A reaction without catalyst

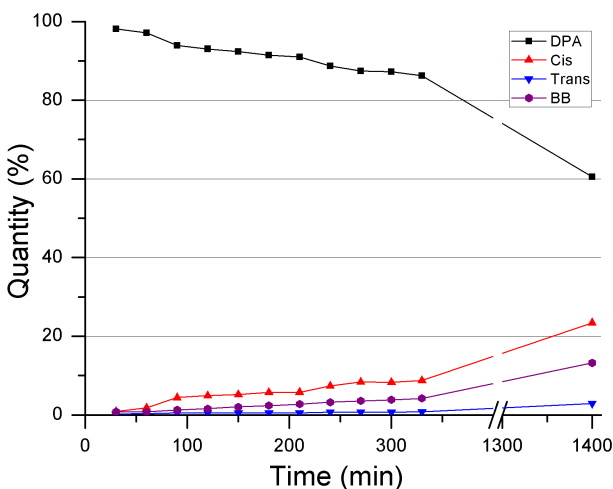


Figure 17: A reaction with only aerogels

Although taking the complete catalyst away had a severe effect on the reaction it did not prove yet that it was necessary to use specifically nanoconfined NaAlH_4 as a catalyst. There was still the possibility that either the aerogels or the NaAlH_4 by themselves would catalyse the hydrogenation. While it was not likely that this would have been the case for the aerogels a reaction was performed with only aerogels added instead of the catalyst. The result of this experiment is seen in figure 17. The reaction profile in this figure was very similar to that of figure 16. For this reason it could be concluded from this experiment that aerogels themselves did not increase the reaction rate. To conclude anything about the selectivity was more difficult. The only significant change seemed to be in the production of bibenzyl, although that could

not be excluded to be coincidental. The most important conclusion from this experiment with only aerogels was that the active part of the catalyst was, as suspected, the sodium alanate.

Without carbon the NaAlH_4/C catalyst would be just NaAlH_4 , a material which was already known as a hydrogenation material and known to react in catalytic reactions as well. The importance of the NaAlH_4 had already been proven in the former two reactions but they did not prove the importance of the carbon framework. For this reason an experiment with only NaAlH_4 as a pure solid material was done.

The results of the experiment with only solid NaAlH_4 can be seen in figure 18. The reaction profile was comparable with the previous two experiments but after a day the reaction had seemed to have proceeded a couple of times quicker than them. In terms of selectivity again a large amount of *cis*-stilbene was formed compared to *trans*-stilbene and, for the first five hours, bibenzyl. After a day the amount of bibenzyl was higher than the amount of *cis*-stilbene and DPA, which were both represented with a little over 20% in the reaction mixture. This reaction showed that NaAlH_4 did influence the reaction but that it was much less effective than the NaAlH_4/C catalyst, proving the influence of the carbon aerogel support as well. This supported the suspicion that NaAlH_4 would

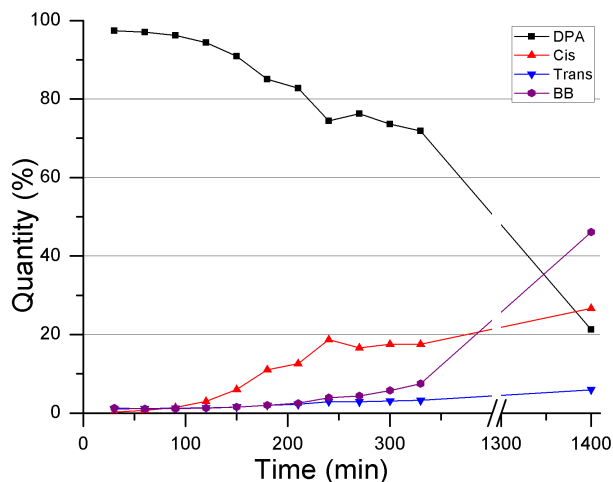


Figure 18: The bulk NaAlH_4 reaction

act as the active particle in NaAlH_4/C but that the carbon support caused the improved catalysis through interaction with the alanate. The three experiment blanks showed essentially the same thing: the reaction was not necessarily impossible without any part of the NaAlH_4/C catalyst, but hydrogenation happened at much lower rates and with a reaction more selective towards *cis*-stilbene. The combination of these experiments was the proof that the nanoconfined sodium alanate was a working catalyst.

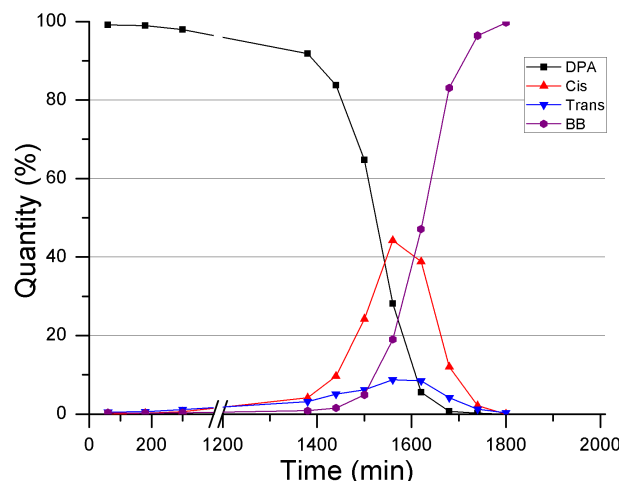


Figure 19: Delaying the introduction of external hydrogen

cis-stilbene did change. There was a couple of times more *cis*-stilbene than *trans*-stilbene in this reaction compared to the standard reactions, a results which could be reproduced. The reaction of figure 19 could be said to have had two different parts. A stoichiometric reaction part without external hydrogen thus using only NaAlH_4/C as hydrogenation reagent and a catalysis part where the material was rehydrogenated to act as a catalyst. Using the NaAlH_4/C as a stoichiometric reagent first did not seem to increase or decrease the eventual reaction rate. There was no sign that introducing the hydrogen pressure after a

There was still one essential factor for the catalysis. While the NaAlH_4/C catalysed the reaction the material could not be used without hydrogen. For the NaAlH_4/C to have been a working catalyst the catalyst itself had to use hydrogen from the atmosphere to hydrogenate the DPA. In these reactions there was never enough hydrogen available from the catalyst itself to fully hydrogenate the DPA. Figure 19 shows the profile of a reaction where only after a full day external hydrogen was supplied. There was almost no hydrogenation until after the moment the hydrogen was supplied. At this moment the rate of the reaction immediately increased, although there was still a slight delay before the highest reaction speeds were obtained. The long time before the reaction was put under pressure did not change much in terms of reaction speed, the reaction still took several hours to proceed. In contrast to that the selectivity towards

day, while the reaction was already at higher temperatures, shortened the delay before the catalyst had its highest activity. The change of selectivity however suggested that there was a change in the reaction. In this reaction the catalyst was already partly dehydrogenated before it could act as a catalyst which was a possible explanation for the changes in selectivity. How this changed the selectivity was a question which remained unanswered.

While the previous reaction already showed a bit of what happens with the reaction without hydrogen a week long stoichiometric reaction was performed as well. This was done both to see what the selectivity of the stoichiometric reaction would be and to see how much of the hydrogen on the catalyst could effectively be used for hydrogenation.

Figure 20 shows the reaction profile of the stoichiometric reaction. For this reaction the amount of catalyst was doubled to 2 mmol and the amount of DPA was slightly lowered to 4 mmol DPA. This meant that there was enough H_2 available for a single conversion of every DPA molecule. The reaction time was a full week. The reaction profile showed that without hydrogen around 65% of the DPA was hydrogenated. At the same time 10% of the stilbenes reacted further to form bibenzyl. Thus in total 75% of the catalyst was used. This percentage would have fit with the conversion of every $NaAlH_4/C$ to NaH/C . Even with the reaction time of a week there was no certainty that the reaction was completely finished. The reaction with stoichiometric reaction amounts was not much faster than hydrogenation without a catalyst.

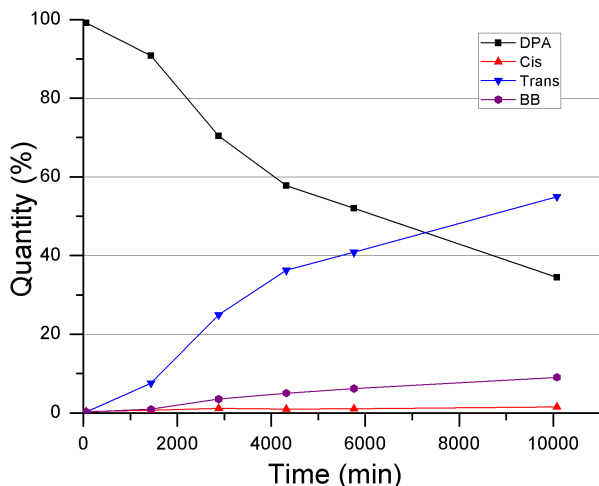


Figure 20: Stoichiometric hydrogenation

A different experiment with stoichiometric amounts was done where the samples were taken every hour for the first day. This stoichiometric reaction confirmed that there was no hydrogen on the $NaAlH_4/C$ which reacted faster than the rest. The rate of reaction, with only between 1 and 3% of DPA converted per hour, was very slow at the start as well. A conclusion from that observation was that it was unlikely that the catalyst worked just by a quick stoichiometric hydrogenation reaction and direct rehydrogenation.

Another observation was that the selectivity was primarily geared towards *trans*-stilbene. This showed that the reaction pathway was significantly different from hydrogenation without catalyst. It also proposed a reason for the discovery of both *cis*-stilbene and *trans*-stilbene in the reactions with both hydrogen and the catalyst but it must be noted that the formation of the *trans*-isomer was slower without hydrogen than with hydrogen. The formation of mainly *trans*-stilbene could suggest a hydrogenation in which hydrogen reacted in the form of single hydrides or hydrogen radicals where two hydrogen atoms reacted on opposing sides of the DPA. These methods would be consistent with the methods suggested for the homogeneous catalysis pathway.⁴⁴ Instead of a direct formation of *trans*-stilbene from DPA there was the possibility of forming *cis*-stilbene first and a following isomerization step to create *trans*-stilbene. Even in this reaction there were still both types of stilbene present.

3.4 The solvent

Next to the catalyst there were more factors which influenced the reaction but did not directly partake in it. The most important of these surrounding factors was the solvent. Although the solvent would normally be expected to take a passive role in the experiments there were several suspicions that it did still play a role in the reaction. To study the influence of the solvent experiments were done in toluene to compare with the experiments in cyclohexane. Toluene was chosen because it had a comparable size and constituents but there was one very important difference in the aromatic ring it carried.

Figure 21 shows almost the same reaction as the standard reaction but with toluene as a solvent. Compared to the reaction in cyclohexane, the reaction in toluene proceeded much slower. The selectivity on the other hand had not changed much. This indicated a process delaying both the hydrogenation and isomerization reactions. The fact that the selectivity did not seem to change drastically meant that the reaction process was slowed likely without changing the mechanism of the reaction. The aromatic ring of the toluene seemed to interact more strongly than cyclohexane with either the catalyst or the reactants, hindering the process of attachment of the reactant to the catalyst. One of the more likely possibilities was comparative adsorption where the solvent adsorbed on the surface of the catalyst and hindered the adsorption of other materials on the same place. To discover whether the competitive adsorption of the solvent on the would have been the problem adsorption experiments have been done with the materials on the catalyst in both toluene and cyclohexane.

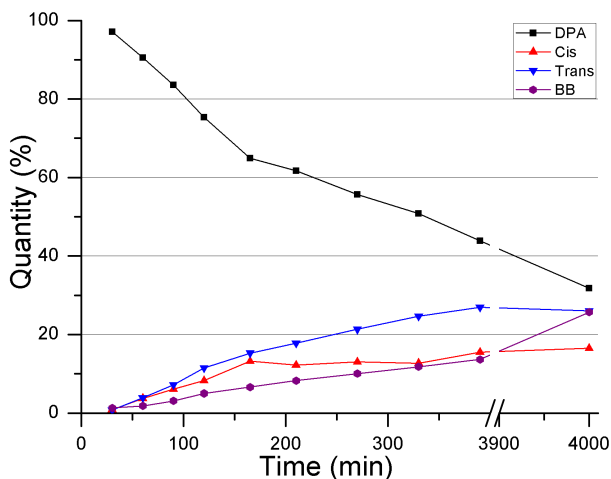


Figure 21: Reaction with toluene

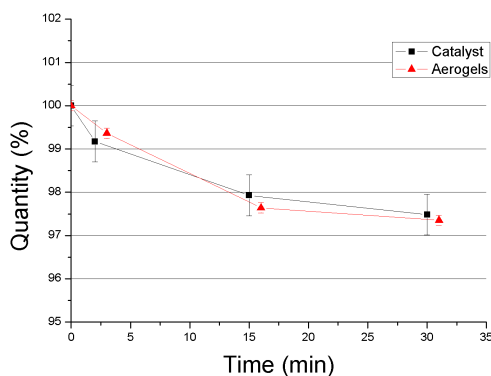


Figure 22: Adsorption on the catalyst and aerogels

adsorbing on the remnants of the aerogel surface of the catalyst support. This would have meant that the molecules might not adsorb the catalyst directly and only the aerogels would adsorb the reagents. In terms of numbers 80% of the catalyst was aerogels, but the catalyst itself had only 70% of the surface area of which more than a small part was suspected to be covered by NaAlH_4 . In terms of surface area it was suspected that the aerogels would adsorb more than the catalyst itself. The fact that there was almost no difference in adsorption between these materials showed that either DPA was adsorbed onto

Figure 22 shows the adsorption of DPA in cyclohexane on 0.270 grams of catalyst and 0.216 grams of purely aerogels. The first data point at $t=0$ was the reference point where DPA was dissolved in cyclohexane in absence of catalyst or aerogels. The catalyst was then added and after two minutes a sample was taken to measure what percentage of the DPA had been removed from the solution and was thus adsorbed. For both the addition of the catalyst and the aerogels a very small portion of the DPA was adsorbed. After 15 minutes this was 2% of the DPA and after half an hour it was around 2.5%. The experiment showed that DPA adsorbed on both the catalyst as well as the aerogels. This might have been the results of the molecules adsorbing

both the surface of the metal hydride and the aerogels or that the surface area of the catalyst existed mainly of aerogels. Only the conclusion that DPA is definitely adsorbed onto the catalyst as well as the aerogels could be made with certainty.

The adsorption experiments were done with 0.5 mmol of DPA and 0.1 mmol of catalyst, the aerogels however could not be expressed in a molar fraction. If 2% of the DPA was adsorbed it would be equivalent to 0.01 mmol of DPA. This meant that 1 molecule of DPA was adsorbed for every 10 molecules of NaAlH_4 . From the adsorption profile can be deduced that this took at least 10 minutes. This meant that the adsorption of DPA on the surface of the catalyst and the movement freedom were on the same time scale as the reaction itself. This implicated that competitive adsorption because of solvents could indeed have been the reason for different reaction rates in different solvents.

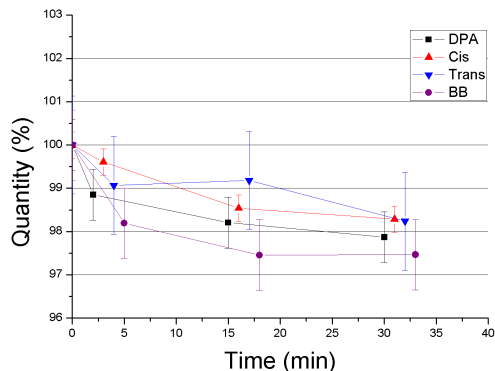


Figure 23: Adsorption in cyclohexane

Of course the best way to prove the influence of solvent effects on the adsorption was to do the adsorption experiments in different solvents. Figure 23 and figure 24 show the adsorption profiles in cyclohexane and toluene. At the same time these figures also represented the differences between the four substrates for the catalyst. DPA, *cis*-stilbene, *trans*-stilbene and bibenzyl.

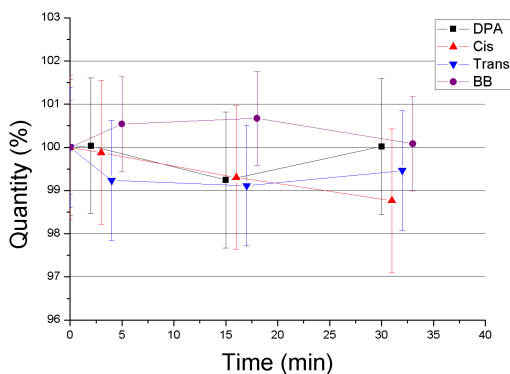


Figure 24: Adsorption in toluene

profiles in toluene could be seen as balancing around 100% this meant that there was less adsorption of the reagents on the catalyst. And a lack of adsorption would be a suitable explanation for the lower reaction rates in toluene.

Using figure 24 The relative adsorption of the four different substrates could be compared. All four materials adsorbed on the catalyst surface. While there were some evident differences between the amounts of different materials adsorbed, the inclusion of the standard errors show that the differences were not big enough for a significant comparison.

When comparing the two figures a significant difference in adsorption can be seen. The average adsorption after 30 minutes for cyclohexane for the four different substrates was around 2% while in toluene the adsorption was less than 0.5%. The error bars included in the figure show that the adsorptions seen in cyclohexane were relatively consistent while for toluene the measurements for the adsorption were less consistent. Individual measurements did also reach to values above 100%. In theory these results should not have been possible. GC measurement errors were on the same order of the inconsistencies for the experiments in toluene. But the inconsistency and the adsorption averages very near 100% were remarkable. If the adsorption

3.5 Partial reactions

Instead of regarding the hydrogenation of DPA to bibenzyl as a single reaction it was more logical to consider it as a collection of partial reactions. There were four different hydrogenation steps: from DPA to either intermediate, *cis*- and *trans*-stilbene and from both of these intermediates to bibenzyl. Besides the hydrogenation there was also the possibility of isomerization between *cis*-stilbene and *trans*-stilbene. This made the complete reaction schedule more than just a simple equation. To make studying of the reaction easier experiments had been set up with both stilbenes as starting material.

By using *cis*-stilbene or *trans*-stilbene as a starting material the first part of the reaction schedule was ignored and the combination of these partial reactions aided in studying the isomerization as well as the hydrogenation from stilbene to bibenzyl. The *cis*-stilbene experiment is shown in figure 25. With *cis*-stilbene as starting material 20% of the material had already isomerised to *trans*-stilbene. A small amount of bibenzyl was formed as well. The one hour mark was a turning point as within the time period of the second 30 minutes a little less than half of the original *cis*-stilbene was then either hydrogenated or isomerised. After this step decline the three materials were present in equal quantities. The relative quantity of both stilbenes then proceeded to decline. The amount of *cis*-stilbene present in the solution dropped faster than the amount of *trans*-stilbene. This could have been because of two reasons. Either the *cis*-isomer hydrogenated at a higher rate than the *trans*-stilbene or the hydrogenation of the *trans*-isomer only looked slower because at the same time the isomerization still depleted the *cis*-stilbene and created *trans*-stilbene. A comparison had to be made with an experiment starting with only *trans*-stilbene as the starting material.

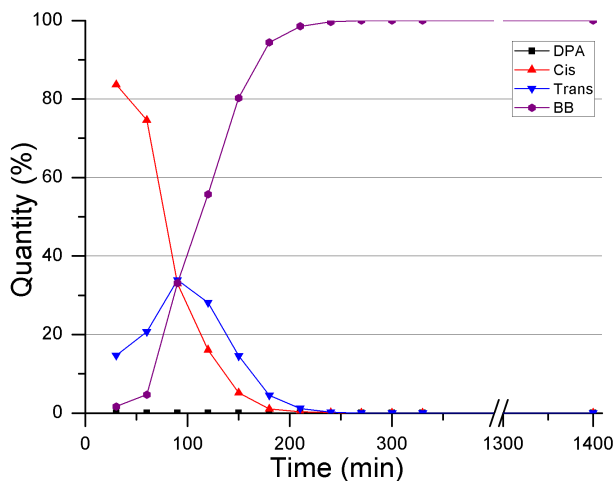


Figure 25: *Cis*-stilbene as starting material

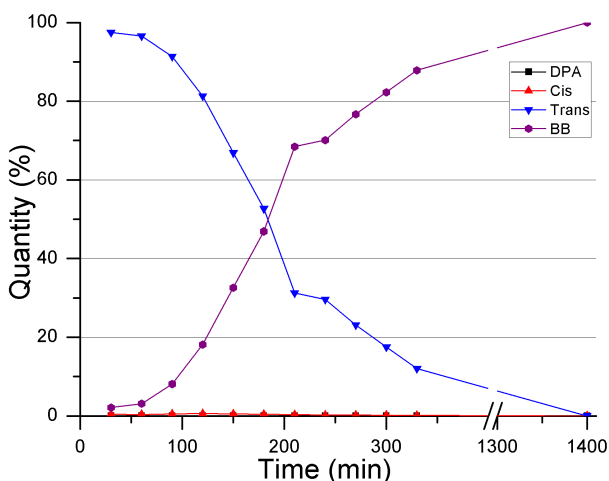


Figure 26: *Trans*-stilbene as starting material

The experiment with *trans*-stilbene is shown in figure 26. The reaction profile was different from the reaction with *cis*-stilbene. The balance between the stilbenes was much more in favour of the *trans*-isomer. During the five hours of the reaction the amount of *cis*-stilbene was never more than a hundredth of the amount of *trans*-stilbene. In terms of reaction speed there was a difference as well. It takes almost twice the time to reach 50% hydrogenation in the reaction with *trans*-stilbene. The formation of bibenzyl was expected to be at relatively the same rate in these reactions if *trans*-stilbene would hydrogenate at the same as *cis*-stilbene. This suggested that the assumption that *cis*-stilbene hydrogenates faster than *trans*-stilbene was correct. With the results from both figure 25 and 26 could be concluded as well that

hydrogenation of DPA forms at least *cis*-stilbene. It was not possible that the major contribution to the amount of *cis*-stilbene was isomerization from *trans*-stilbene. The reverse of this statement could not be made because of the possible fast isomerization of *cis*-stilbene to *trans*-stilbene. The hydrogenation of

DPA could, for example, be syn-addition to *cis*-stilbene only and the *trans*-stilbene would form by rapid isomerization. This led to the conclusion that the major hydrogenation pathway in the standard reaction with DPA was the hydrogenation of DPA to *cis*-stilbene.

From a comparison of reactions could be concluded that DPA and *cis*-stilbene both hydrogenated faster than *trans*-stilbene and that isomerization happened mostly from *cis*-stilbene to *trans*-stilbene and hardly the other way around. The comparison between the hydrogenation rate of DPA and the isomerization and hydrogenation rate had not been made yet. In the complete reaction all materials were present at once at some point and with the likely fact that these materials would all have been a substrate to the catalyst in the same manner the reactions also compete. In figure 27 DPA and *cis*-stilbene were both present as starting materials in the reaction. The comparison shows that the concentration of *cis*-stilbene actually increased for a period of time. Although it fell beyond the time frame of the graph it was possible to conclude that only after most DPA was depleted the quantity of *cis*-stilbene dropped. Thus hydrogenation of DPA to *cis*-stilbene was without doubt the dominating reaction to take place early on in the reaction. The loss of *cis*-stilbene, neither from hydrogenation or isomerization depletes the intermediate at a higher rate than it is created.

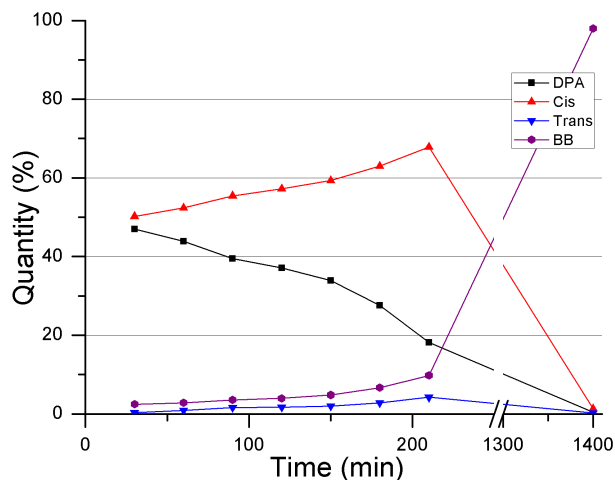


Figure 27: Reaction with both DPA and *cis*-stilbene as starting materials

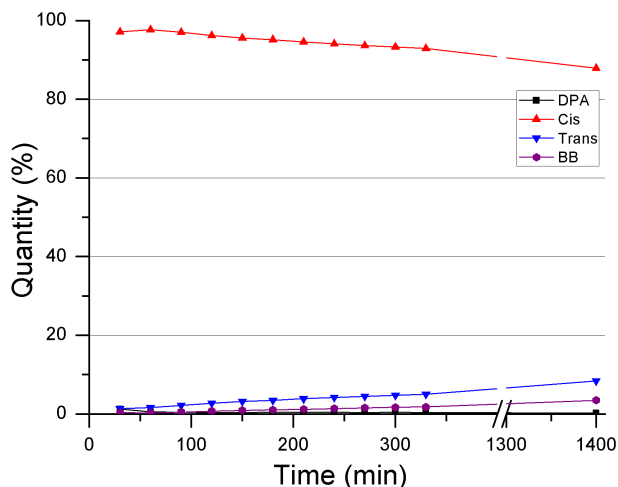


Figure 28: Isomerization of *cis*-stilbene without catalyst

A short but interesting question was whether the isomerization came from the NaAlH_4/C catalyst or whether or another constituent in the reaction was responsible for this. To answer this question again an experiment was done where the catalyst was replaced with purely aerogels but this time with *cis*-stilbene as the starting material. In this reaction, shown by figure 28, only a low amount of isomerization was discovered. This proved that the isomerization was dependent on the catalyst like the hydrogenation. In this reaction some hydrogenation was apparent shown by the formation of bibenzyl, proving *cis*-stilbene was hydrogenated without catalyst as well. The fact that both the hydrogenation and the isomerization were dependent on the catalyst exposed new problems. The balance between hydrogenation and isomerization was further investigated with the results of the experiments where the rates of hydrogenation and isomerization were studied.

periments where the rates of hydrogenation and isomerization were studied.

3.6 Rate

Catalysis itself is the process of lowering activation barriers and speeding up a process. Thus one of the most important factors to determine was the rate of reaction. It already became apparent that the solvent influenced the rate of reaction. Another factor determining the rate of the reaction was the amount of catalyst used in the process. By using several different catalyst loadings the rate of the reaction per amount of catalyst was given.

The relation between the amount of catalyst and both the rate and selectivity were studied by executing reactions with different amounts of catalyst. Experiments were performed with 27, 54, 81 and 108 mg of catalyst. The rate of hydrogenation was determined by the depletion rate of just DPA in the solution for the first two hours. This relation proved to be close to a linear rate of depletion. In figure 29 the rates of depletion for cyclohexane are shown. These rates are normalised in respect to the fastest rate in cyclohexane for quantitative comparison. The same experiments have been performed in both cyclohexane and toluene as both these reactions showed different reaction rates earlier. The figure shows that by reducing the catalyst loading in DPA the rate of the reaction was almost linear to the catalyst loading. This was in agreement with intuition that using twice as much catalyst would substitute for a reaction twice as fast. For toluene the relation was also linear but it seemed to have an base value. At higher loadings the reaction in toluene was slower than the reaction in cyclohexane but at lower loadings there was no difference. If these lines were extended in a linear fashion to even lower catalyst loadings the reaction in toluene would be faster than in cyclohexane. It would also mean that there would be no reaction in cyclohexane without catalyst but there would be a reaction in toluene. It was suspected that neither is the case and that for both toluene and cyclohexane the reaction rate will move towards the same point at lower loadings. It was already proven that there was a slight hydrogenation in experiments without catalyst but no further experiments to find the progression of the rate at lower catalyst loadings had been done.

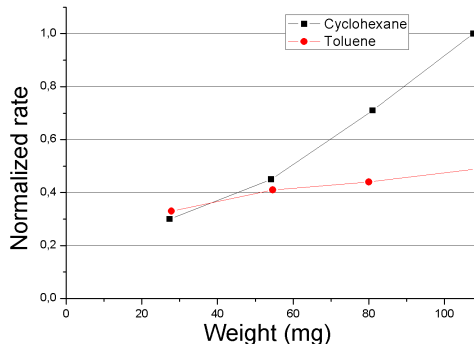


Figure 29: Rates of DPA depletion in toluene and cyclohexane

In figure 29 the rate of DPA depletion was taken as the reaction rate for the catalyst. This reaction rate did only describe the first hydrogenation step. The hydrogenation of the stilbenes and the isomerization were not described in this figure. Because these reactions were simultaneous and competing with each other it was not possible to directly relate the rate equations for the intermediates and products. The amounts of each stilbene and bibenzyl could only be used to express relative trends between the rates of these reactions. The amount of these reaction products after 60 minutes of the reaction was shown in figures 30 and 31 in cyclohexane and toluene respectively. The 60 minute mark was chosen because this would ensure that the amount of *cis*-stilbene was not already dropping. The production can thus be seen as production rate per hour for the first hour.

The production rates of cyclohexane were higher in almost every case. Only at the lowest catalyst loading the production of *cis*-stilbene was higher in toluene. What can be seen in figure 30 especially was that at low catalyst loadings the production of *cis*-stilbene was already significant, but that only at higher catalyst loadings *trans*-stilbene and bibenzyl were formed. For toluene this effect seemed even stronger. Only at the highest loadings more than a few % of the reaction mixture consisted of *trans*-stilbene or bibenzyl after an hour. There could be two logical explanations for this effect. The first explanation

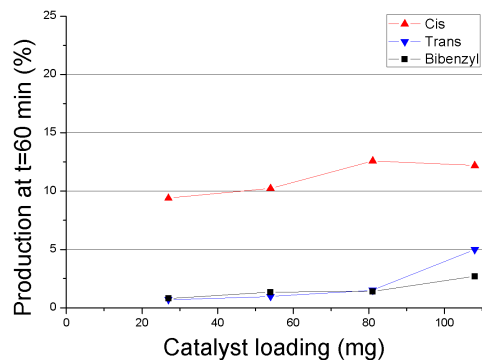
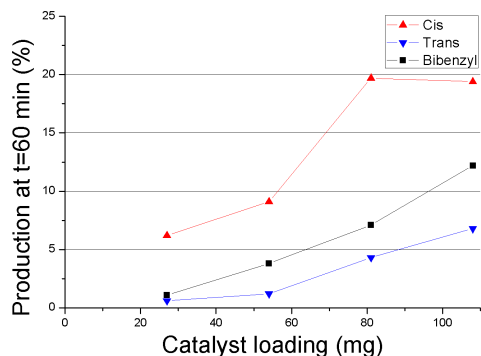


Figure 30: Rate of product formation in cyclohexane Figure 31: rate of product formation in toluene

was that taking a point after an hour with different catalyst loadings only resulted in samples taken at a different stage in the reaction. *Cis*-stilbene was first to form and then reacted to *trans*-stilbene and eventually bibenzyl. This would indicate that the linear progression of the formation of these products was overestimated. The other explanation was a true shift in selectivity. This would mean that it did not matter at what stage the reaction was in, but the selectivity would be dependent on the catalyst loading. This could be proved for example by showing that when 50% of the DPA was converted the ratio between the products had actually changed. This will be discussed in the next subchapter about selectivity.

To put the catalyst to practical use it would be most useful if the turnover per catalyst particle was high. From graph of the average of standard experiments could be seen that after two hours 40% of the DPA had reacted. This corresponds to 1 mmol per hour, per 1 mmol of NaAlH_4 . The turnover per hour of this catalyst was thus 1. To put this into perspective an experiment has been performed with the common hydrogenation catalyst palladium on carbon or Pd/C.

In theory, the NaAlH_4/C catalyst would be a cheap replacement of catalysts like Pd/C with more expensive components. In practice there was a gap in the reaction rate between which would likely never be overcome. Figure 32 shows the reaction with Pd/C. The time scale was set at two hours like the rate experiments and 27 mg of catalyst was used. Two new intermediates/reaction products were attained by using this catalyst. This was because bibenzyl could actually react twice more. There are two aromatic ring with several double bonds which could be hydrogenated as well. After 60 minutes there was at least 400 times more conversion if the energy needed to break an aromatic ring was seen as equal to the energy needed to hydrogenate a triple bond to a double bond. Thus putting the hydrogenation with the NaAlH_4/C catalyst on a completely different time scale and limiting the usefulness of the catalyst.

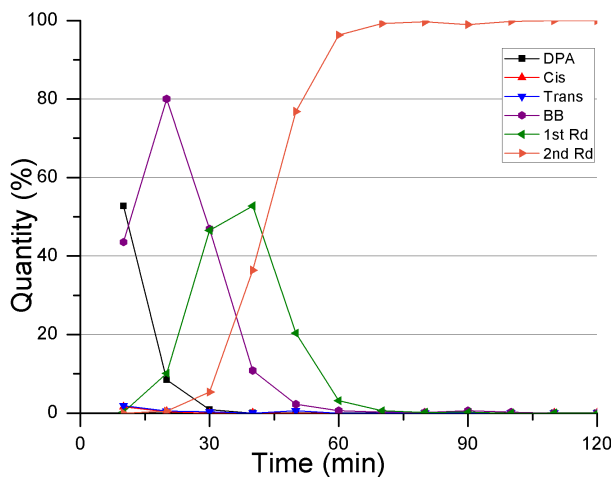


Figure 32: A reaction with a Pd/C catalyst

3.7 Selectivity

While the experiments with catalyst loading were originally performed to determine the reaction rate they also showed an effect on the selectivity of the reaction. The rate of the reaction showed to be very low compared to currently used catalysts but to influence the selectivity of the reaction product would be a useful feature as well. With very selective catalysts a desired *cis*- or *trans*-product could easily be obtained in large quantities.

Figure 33 shows the *cis*-stilbene:*trans*-stilbene ratios for the experiments with different catalyst loadings. An immediate observation is that the catalyst loading has a very large influence on the selectivity. Something which was already suspected from the production graphs of figure 30 and 31. The determination of the selectivity however was this time not done at a single point but by taking the average of the five largest *cis*-stilbene:*trans*-stilbene ratios. In most cases this was a consecutive row of numbers between the first and second hour.

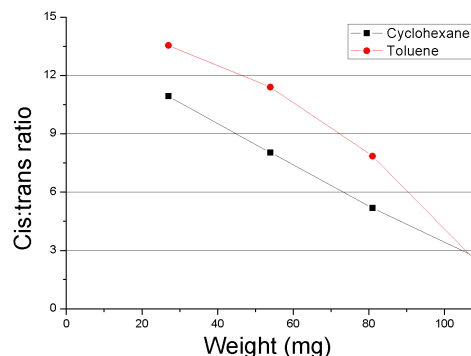


Figure 33: The *cis:trans* ratio at different catalyst loadings

The selectivity decreases for higher catalyst loadings were the results of the relative increase in the formation of *trans*-stilbene compared to *cis*-stilbene. In cyclohexane the formation of *cis*-stilbene was increased from 7% to 19%/hour when the catalyst loading was increased from 27mg to 108mg. The formation of *trans*-stilbene only increased with 8%/hour but this increase was from 1% to 9%/hour which made the relative increase of *trans*-stilbene production much higher. In toluene this effect was even stronger because even the absolute increase in production of *trans*-stilbene was higher at higher catalyst loadings.

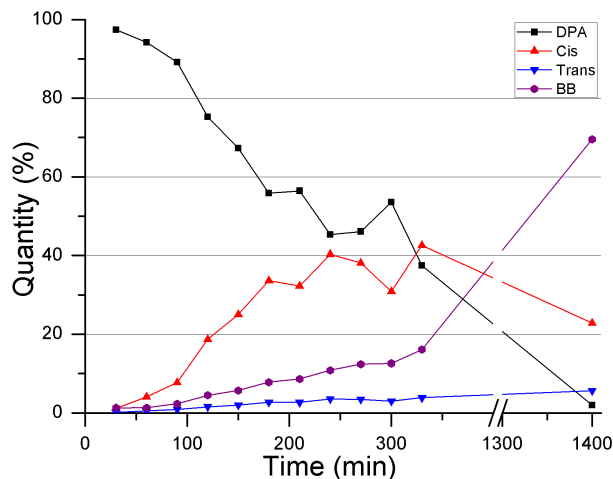


Figure 34: Low catalyst loading experiment and isomerization both seem to depend on the NaAlH_4/C catalyst, they depended on it in a different way.

Figure 34 answered the very important question whether this selectivity increase would have also been true for complete reactions and was not only caused by determining the selectivity with only a part of the reaction. The reaction reached 40% conversion into *cis*-stilbene with ten times less *trans*-stilbene. While the reaction was definitely slower than the standard reactions, the formation of *cis*-stilbene in the first few hours was comparable to the same formation rate with ten times more catalyst. The formation rate for bibenzyl was a few times lower and the formation of *trans*-stilbene was very low. This suggested that isomerization from *cis*- to *trans*-stilbene was very low with lower catalyst loadings while hydrogenation still occurred at a reasonable rate. Not only did the hydrogenation

The evident effect on the selectivity of the reaction by lower catalyst loadings could have been caused by either the fact that the relative or absolute amount of NaAlH_4/C was lowered. This meant that the same effect might or might not appear in a solution with both ten times less DPA and NaAlH_4/C . When the amount of both DPA and NaAlH_4/C is lowered ten times there is essentially no change in the amount of catalyst relative to the reactant. In a theoretical case, no change in reaction profile would be noted unless the behaviour in the solvent played a role in the reaction process.

Figure 35 shows a reaction pattern different from the reaction with normal amounts of NaAlH_4/C and DPA. It is not entirely comparable with figure 34, this reaction was faster in terms of relative hydrogenation and slower in terms of absolute hydrogenation. The reaction stabilised after four hours. In terms of selectivity between the stilbenes there was not much difference, there was only more formation of bibenzyl. The reaction profile showed a very steady formation of bibenzyl starting at $t=0$. This was even a clearer example of how the concentration of *cis*-stilbene in the reaction mixture did not seem to influence the rate of formation for bibenzyl. In terms of rate the DPA depletion was faster than with the low catalyst loadings yet these reaction rates were very comparable with the standard reaction. This showed the definite proof that lowering the absolute amount of catalyst raised the selectivity of the reaction. There could be several reasons for the changes in selectivity. One of the possibilities was that the solvent played a role in this selectivity. There was already a difference in selectivity visible for the rate experiments but using single reference points this could have been misrepresented. Another possibility would have been that a large part of the NaAlH_4/C catalyst was not used for hydrogenation and that catalyst not used for hydrogenation could cause isomerization.

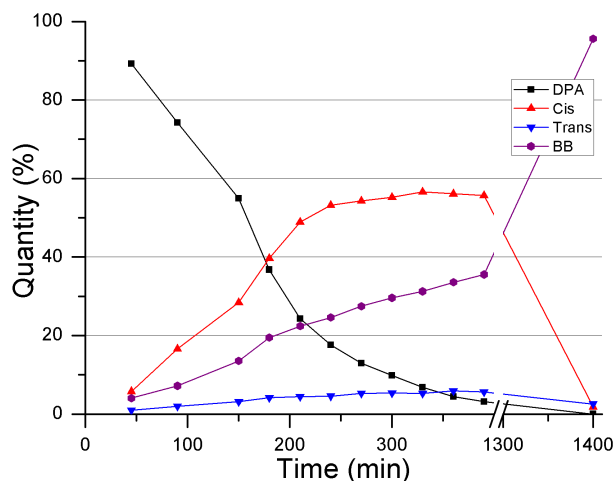


Figure 35: Lowered amounts of DPA and NaAlH_4/C

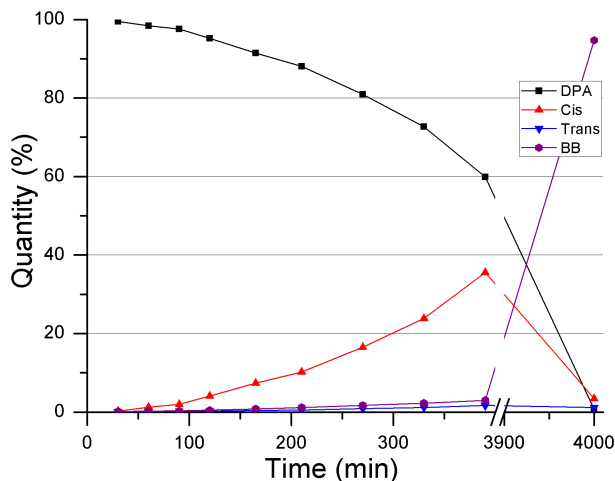


Figure 36: Low Catalyst Loading reaction in toluene

not have been possible if the hydrogenation of DPA and the hydrogenation of *cis*-stilbene were dependent on only the catalyst.

The influence of the solvent on a complete reaction with lower catalyst loadings can be seen in figure 36. There was only one significant product in this reaction after six hours, namely *cis*-stilbene. After these six hours the reaction was still in full progress thus how much *cis*-stilbene would be formed and how fast the formation of bibenzyl would be after this could not be observed. The reaction did suggest that selectivity was also dependent on the solvents with low catalyst loadings. This effect was not obviously seen with higher catalyst loadings. The selectivity comparisons from the rate experiments however already showed that the selectivity at higher catalyst loadings became the same for each solvent. The most interesting observation found in figure 36 was likely the absence of bibenzyl production. This was something which would

To prove that the absence of isomerization was the direct cause for the increased selectivity an experiment was performed with *cis*-stilbene as starting material. Figure 37 shows that with only a low catalyst loading *trans*-stilbene and bibenzyl were formed at a steady but very low rate. The profile of the bibenzyl formed in this reaction was very comparable with the reaction where DPA was used as starting material. This again contributed to the idea that DPA could immediately hydrogenate twice at the same time after certain prerequisites would be met. Interestingly enough the amount of *trans*-isomer was comparable to the low catalyst loading reaction with DPA as well. In earlier reactions with normal amounts of catalyst there was definitely a large amount of *trans*-stilbene which was created through isomerization of the *cis*-stilbene. This reaction raised the question whether the formation of *trans*-stilbene could also come directly from DPA through two consecutive reaction steps as well. Instead of a double hydrogenation step to form bibenzyl, DPA would hydrogenate once to *cis*-stilbene and consecutively isomerize without ever leaving the surface of the catalyst.

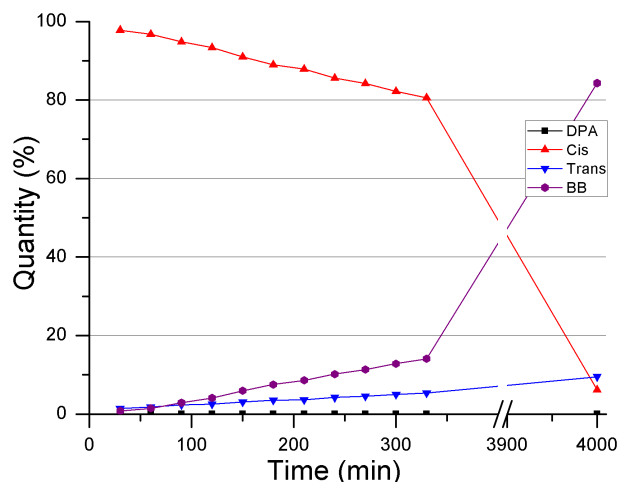


Figure 37: *Cis*-stilbene reaction with lower catalyst loadings

3.8 Hydrogen and hydrogenation

While in this project the focus was mostly on the reaction between the catalyst and DPA, the hydrogen needed for the reaction to happen was provided through an external supply of gaseous hydrogen. Although a volume of around 100 mL hydrogen gas with a pressure of 100 bar H_2 gas at room temperature meant there was hydrogen available in abundance (450 mmol), the gas still had to reach the surface of the catalyst to react.

The first step for hydrogen to partake in the reaction was to dissolve into the solution. The large volume of H_2 gas was only found above the solution and did not come into direct contact with the catalyst which was submerged in solvent. The gas had to dissolve into the solution before it could act in the reaction.

Having the solution present complicated the situation. Differences in pressure were due to the solvation of hydrogen. What made it more complicated was that there were four equilibria which in equilibrium depending on either temperature or time. The first of these equilibria was the simple relation between the pressure and the temperature, as the temperature rose so did the pressure. The second was how much hydrogen dissolved over a period of time. The third equilibrium was the extra solvation as a rise of pressure, because a higher gas pressure meant there was more hydrogen dissolved in the solution. The fourth was the amount of hydrogen which left the solution at higher temperatures. While seeming counter-intuitively at first, the amount of gas which could dissolve in the solution at high temperatures would be less than at lower temperatures. The latter solvation effects two are opposing forces. Raising the temperature with already a fully saturated solution of hydrogen could cause either a decline or an increase in the solvation of hydrogen. This would cause an extra increase or decrease in pressure on top

of the normal relation between temperature and pressure.

Because of the multiple complications with the process of hydrogen solvation and because it was not the primary focus of the research, these experiments were more qualitative than quantitative and aimed to copy only these specific reaction circumstances. One of the complicating factors was that while hydrogen was supplied it dissolved at the same time. The choice had been made to shut off the hydrogen supply immediately after it reached the maximum pressure. Which meant that for about five seconds the hydrogen had already had the chance to dissolve in the solution, although this was without stirring which significantly delayed the process. This course of action was consistent with the usual process of the hydrogenation reactions. Other complications were the inaccuracy of the measuring equipment and the fact that the heating was not completely consistent.

The solvation in relation to time is shown in figure 38. In any experiment the pressure would already have dropped significantly before the temperature could rise. In cyclohexane, where the pressure started at 98 bar the pressure was only 83 bar after just two minutes. This meant that 15% of the hydrogen was now found dissolved in the solution. For toluene the adsorption rate was slower, it took almost an hour to reach the pressure limit. This difference in hydrogen solvation could be another explanation of the influence of the solvent in the reaction. Even in toluene though, the pressure dropped near 10 bar within minutes. There would always be more hydrogen gas in the solution than either catalyst or DPA.

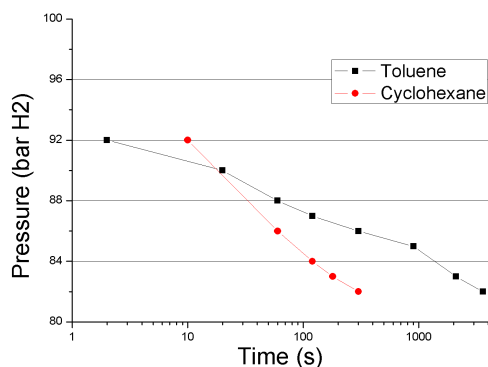


Figure 38: Solvation profiles over time

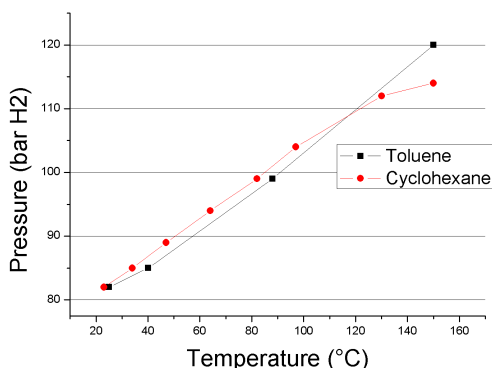


Figure 39: Solvation profiles over temperature

this ideal gas law estimate was comparable with the actual final temperature. In cyclohexane the pressure reached 114 at a temperature of 150 degrees and in toluene the increase was somewhat stronger and the pressure reaches 120 bar.

Although the concentration of hydrogen was important, a significant amount would always be present. It would be more likely that the adsorption on the catalyst was slower and determining the concentration of usable hydrogen for the catalysis. The adsorption may be dependent on pressure or it could be that the surface of the catalyst would be saturated at all times. To study this the relation between reaction rate and pressure was measured directly and not through hydrogen concentration in the solution.

If the supply of hydrogen was fast and the rate of the reaction would be determined by other reaction steps determining the exact amount of hydrogen would not matter much. 10% of the hydrogen was dissolved within a minute in cyclohexane which meant that around 50 mmol of hydrogen was present in the reaction. If the adsorption step to the catalyst surface or other determining steps would be fast as well the rate of the reaction would not be dependent on the pressure. At the same time higher pressures could have actually prevented the reaction from continuing at a decent rate. If it was needed to partially remove the hydrogen on NaAlH_4/C to activate the catalyst this process would be hindered by a strong pressure and stay completely hydrogenated. Both of these hypotheses provided a reason to perform experiments with lowered hydrogen pressure.

Figure 40 shows a reaction rate significantly slower than the standard reaction and a depletion in linear fashion rather than a curve. This shows that the relation between hydrogen pressure and hydrogenation was very strong. This reaction was done with 50 bar of hydrogen as well and this produced a similar linear reaction profile with a DPA depletion rate about twice as fast. The relatively slow rate at 50 bar could mean that instead of a purely linear relation between pressure and the reaction rate there could be a certain pressure from which the reaction became much faster.

The large pressure dependency was not unexpected but could explain several phenomena in previous reaction. The sampling system used meant that there was always a loss of several bars of pressure when starting with high pressures and temperatures. This meant that the reaction was always slower at later time periods even if it would be completely linear otherwise. There was little means to control this loss of pressure and so this could potentially cause large differences between different reactions. A decrease in the accuracy of the reproductions may definitely be attributed to this reason.

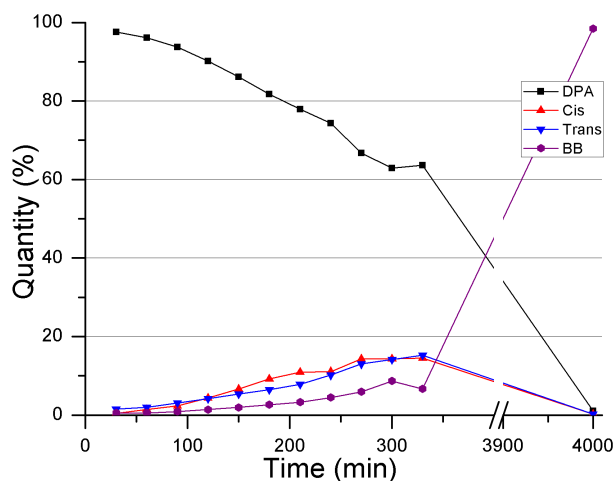


Figure 40: Low hydrogen pressure reaction

3.9 Dehydrogenation of the catalyst

When NaAlH_4 became nanoconfined on carbon the first step of dehydrogenation seemed to disappear.²⁹ In the work by Streukens et al.² however it was discovered that the reaction for Na_3AlH_6 was faster than for NaAlH_4 . With this in mind the catalyst was prepared by depleting the hydrogen of the catalyst first.

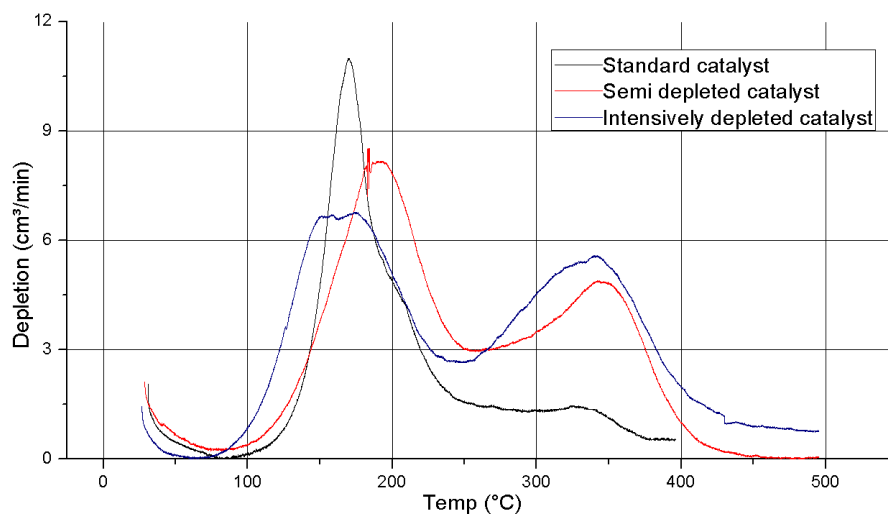


Figure 41: Comparisons of the depleted catalysts

The depletion was done by heating the catalyst in an empty autoclave before the reaction. The amount of time the catalyst was heated was based on the TPD data from figure 41. This figure shows the TPD profiles of the standard catalyst compared with a sample that had been depleted for a small period of time and an intensively depleted catalyst which was depleted of hydrogen at higher temperatures for longer periods of time.

From the TPD data could be read that within half an hour almost half of the hydrogen was depleted. For this reason the catalyst was prepared by heating the sample steadily for half an hour and stagnating the temperature for 15 minutes. This was done to aim for a loss of hydrogen comparable where half of the total hydrogen would be lost and hopefully leaving the hydrogen which would deplete only at higher temperatures still on the catalyst. Figure 42 shows the reaction profile for this partially depleted catalyst. Although the concentrations of *cis*-stilbene and *trans*-stilbene in the solution seemed to be more stable this effects seemed hard to attribute only to the catalyst depletion itself. Repeating the experiment did show the same stability but with reversed concentrations for the stilbenes. Thus the catalyst was depleted for longer times at higher temperatures to find whether this observations would stand or whether this was an artefact.

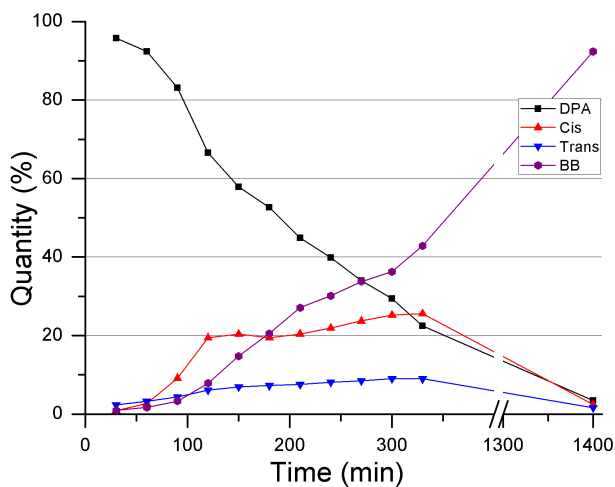


Figure 42: Semi dehydrogenated catalyst reaction

For the full depletion the catalyst was heated to a temperature of 250° over the course of two hours. This temperature would normally deplete most of the hydrogen from NaAlH_4/C and form NaH/C which would still be stable. The TPD diagram showed this effect only to a small extent. The peak after 250° was only a little higher on a normalized scale compared with the semi depleted samples. In the reaction profile of figure 43 can be seen that while the TPD shows little change, the reaction itself changed a lot in terms of speed. Repeating this experiment resulted in a comparable rate increase. A reasonable conclusion was that the depletion of hydrogen caused a structural change in the material where more sites appear where hydrogen could easily be adsorbed onto the catalyst and react. This might have had less to do with the loss of hydrogen and more with restructuring of the compound when taken into account that the effect was not visible with the catalyst depleted only at reaction temperatures.

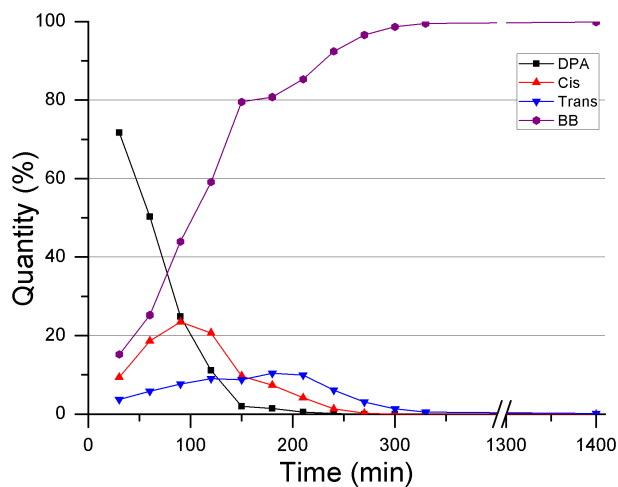


Figure 43: Intensively dehydrogenated catalyst reaction

To conclude the collection of performed experiments figure 44 shows the final stage of the catalyst. After the reaction the catalyst was retrieved and analysed using TPD. What it showed was that the only hydrogen left on the catalyst would desorb at higher temperatures. It was very likely that all NaAlH_4/C was at least decomposed to NaH/C or even further. After the reaction most hydrogen had left the catalyst. Thus whether or not hydrogen was used from external sources or how the catalyst was prepared eventually it was likely that no NaAlH_4/C would be left until rehydrogenation would bring the catalyst back.

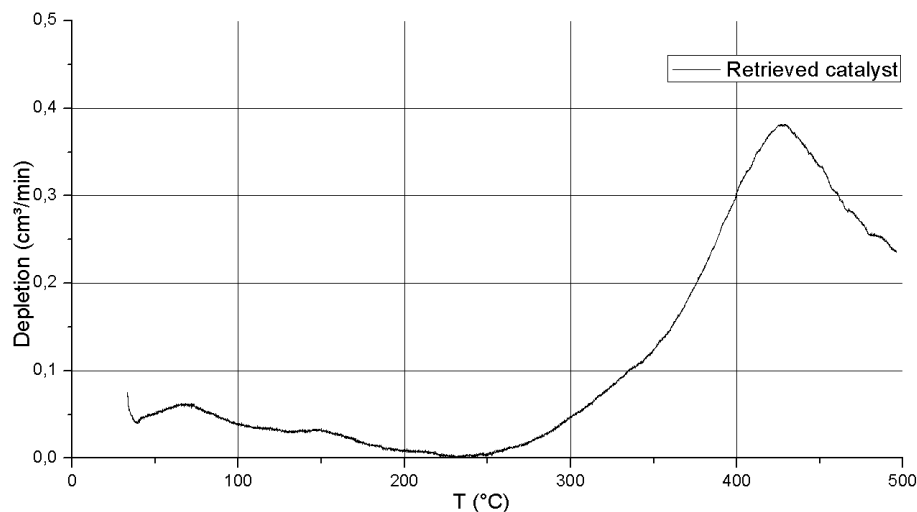


Figure 44: TPD of a used and retrieved catalyst

3.10 The complete reaction profile

During the course of this project many of the reaction reaction steps have been researched to get a picture as complete as possible. While this last subchapter of the discussion shows no new data it collects the conclusions from the previous single topic parts to show what pieces of the puzzle that is the hydrogenation reaction catalysed by NaAlH_4/C are known and which are not.

The hydrogenation of DPA did not seem to start as a hydrogenation from the catalyst itself. While a stoichiometric reaction followed by an immediate rehydrogenation could be considered as a reasonable pathway for the reaction, the reaction acted at a decent rate only after hydrogen was added. Even this way it could be that there were hydrogen sites very quick to react but the reaction with stoichiometric amounts showed a relatively stable progress for the reaction, not a initially fast reaction which was then slowed significantly after. The initial delay seen in most reactions would also not be a logical results from a simple two step hydrogenation and rehydrogenation process, especially not when considering that depletion of the catalyst actually sped up the process.

Altogether it was more likely that the interaction between dissolved hydrogen and the catalyst is the start of the actual catalysed reaction. The real start of the reaction could be said to be the solvation of hydrogen in the solution. The solvation experiments showed that at lower temperatures there was hardly any problem for the gas to dissolve when the reaction mixture was stirred. For toluene this solvation was slower than in cyclohexane and restriction of the movement of hydrogen might actually have been one of the reasons for the slower reactions in toluene. After considering that within seconds a couple of bars of hydrogen was taken into the solution it seemed unlikely in either case though that the resupplying of hydrogen would have been a problem in the catalysis. The concentration of dissolved hydrogen could likely be considered as stable depending for the biggest part only on the pressure equilibrium in the autoclave.

When the substrate and hydrogen were in the solution the reaction could take place at the surface of the heterogeneous catalyst. This meant that there was an equation for both the hydrogen and the substrate to reach the surface of the catalyst. This equation depended on the concentration of both of them in the solution and the energy barrier needed to be overcome to adsorb on the catalytic surface. The concentration of both materials in the solution was not so difficult to estimate. For hydrogen this could be deduced from the pressure and the concentration of substrate was measured by the GC. The energy barriers to reach the surface however was a different story.

The adsorption experiments showed that the substrate adsorbed onto the surface of the support. From there it could likely move along the surface and reach the catalytic surface of the metal hydride. In toluene the adsorption was lower and this gave a likely explanation how the reaction was delayed in this different solvent. For hydrogen however the method of adsorption was unknown and could not be tested easily. It could not be said that the hydrogen adsorbed in the same manner or whether this would limit the rate of reaction. From the reactions with *cis*- and *trans*-stilbene could be deduced that there was a *syn*-addition of two hydrogen atoms at the same time. A *syn*-addition seemed the most likely way to explain how *cis*-stilbene was selectively formed by hydrogenation. The large dependency on hydrogen pressure and the lower dependency on substrate concentration lead to the conclusion that the supply of hydrogen adsorbed on the catalyst might actually have been a slower step than the adsorption of the substrate on the support.

When all prerequisites were met the substrate and hydrogen could react. The products formed in this reaction were not very predictable. The standard reaction showed an increase in DPA hydrogenation rate for the first 90 minutes and the steepest fall was found between 90 and 150 minutes. During this complete period the formation of *cis*-stilbene, *trans*-stilbene and even bibenzyl was almost the exact same. This meant that the double hydrogenation proceeded with the same rate as a single hydrogenation without

isomerization (*cis*-stilbene), which went at the same rate as a single hydrogenation with isomerization (*trans*-stilbene). Even after the initial delay the formation of bibenzyl seemed to proceed in a nearly linear fashion, independent on the concentration of either *cis*-, *trans*-stilbene or DPA.

To elaborate on this interesting phenomena the conclusions from the lower concentrations reactions and lower catalyst loading reactions could be used to complement these observations. From these experiments could be concluded that lowering the catalyst loading increased the selectivity for *cis*-stilbene and also lowered the hydrogenation rate of *cis*-stilbene. Another conclusion was that a decrease of DPA as well did not increase the selectivity towards *trans*-stilbene much but did cause an increase in the further hydrogenation towards bibenzyl. From the rate experiments it could be seen that this effect was mostly because of the relatively stable rate of *cis*-stilbene formation at lower catalyst loadings. This suggested that with low catalyst loadings the reaction which predominated was the single *syn*-addition of hydrogen to *cis*-stilbene while at higher catalyst loadings other reactions started to take place at the same time as well.

Interestingly enough the amount of substrate did not seem to play a large role in the increased selectivity at lower catalyst loadings. The two things which played a role in the reaction and did change relatively to the amount of catalyst were the amount of solvent and the amount of available hydrogen in the solution. The same experiment in toluene always showed an even larger preference for a selective single hydrogenation from DPA to *cis*-stilbene. This effect was not very large as the average selectivity was 1.3 times more in toluene than in cyclohexane for the rate experiments but significant nonetheless. Because the role of hydrogen was still hard to examine and the solvent did actually influence the uptake of hydrogen in the solution as well, the effect of hydrogen on the selectivity can not be attributed with certainty. The hydrogenation of DPA was believed to use the same mechanism as the further hydrogenation of stilbene. This meant that a lower supply of hydrogen would mean more single hydrogenations and thus more *cis*-stilbene than bibenzyl in experiments at lower hydrogen pressures. While there is relatively more single hydrogenation than double hydrogenations in the lower pressure experiments it was still on a different scale compared to the lower catalyst loadings. Thus the exact reason for this phenomena remained inconclusive.

Next to the hydrogenation there was also the fact that isomerization could be completely independent of hydrogen. The most conclusive experiments on isomerization vs. hydrogenation were the experiments starting with *cis*-stilbene. Three different experiments showed large differences between the rates of isomerization. A normal hydrogenation showed a large amount of isomerization at first and showed that the majority of the *trans*-stilbene in the reactions was likely produced by isomerizing *cis*-stilbene. This was supported by the fact that the high surface area graphite supports (appendix A) showed almost only *trans*-stilbene in the reaction mixture and showed how the isomerization of *cis*-stilben with this support was very strong relatively to aerogels. The low hydrogenation rate and even lower isomerization rates for *cis*-stilbene with low catalyst concentrations supported a similar conclusion. The selectivity and hydrogenation rates were very dependent on what happened after the first reaction of DPA hydrogenation.

Thus this research project concludes with several questions besides the answers we obtained earlier. Figure 45 is a graphical representation of the reaction where the hydrogen dissolved and adsorbed on the catalyst. The DPA gets adsorbed on the support and along the surface of the support it reached the catalytic particles. The DPA and hydrogen were then brought together at the edge of the catalyst surface and the DPA was hydrogenated. The intermediate reaction product, *cis*-stilbene, then left the spot or stuck to the catalyst. Through hydride/radical exchange or another way the catalyst then isomerised the *cis*-stilbene to *trans*-stilbene. After this the question was again whether the stilbene would leave or stay and be hydrogenated again. At the same time the earlier formed stilbenes could adsorb again from the solution to the support and hydrogenate or isomerize. The final result was in every reaction a complex mixture of DPA, the stilbenes and bibenzyl.

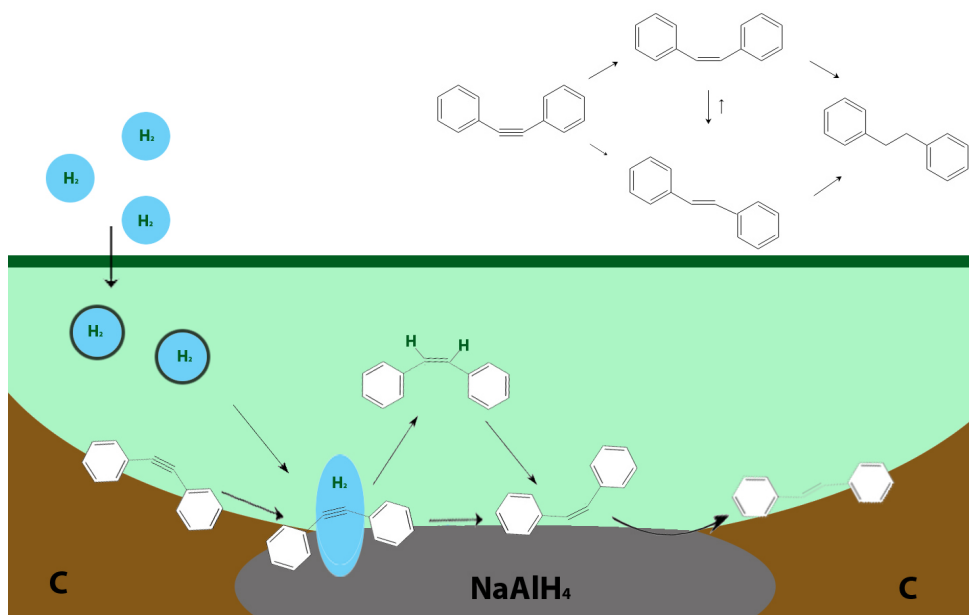


Figure 45: The simplified reaction as image

4 Conclusion

In this research project it was first shown that a NaAlH₄ catalyst supported on carbon aerogels was a capable hydrogenation catalyst. To prove this experiment blanks were performed without the aerogel support, without the NaAlH₄ and without either of them to show that this catalyst played an important role in the reaction when both metal hydride and support were present. The catalytic process worked by continuous hydrogenation of DPA and rehydrogenation of the catalyst itself when the reaction mixture was pressurized and brought to higher temperatures. This meant that NaAlH₄/C catalyst could also work in a stoichiometric fashion at larger quantities and the actual source of hydrogen could be from the original catalyst and the atmosphere both.

Next to hydrogenation, isomerization was possible between the *cis*- and *trans*-isomer. This was proven by using the intermediate products *cis*-stilbene and *trans*-stilbene as starting materials. Using *cis*-stilbene a large amount of *trans*-stilbene formed as well. In reverse, starting with *trans*-stilbene only a small amount of *cis*-stilbene was formed. This proved that the *cis*-stilbene formed in the reaction of hydrogenation with DPA and was not a product of the isomerization of *trans*-stilbene the reverse however could not be said with certainty.

When the reaction with *cis*-stilbene as starting material was performed with only aerogels only a small amount of *trans*-stilbene could be detected. This meant that the isomerization was also dependent on the NaAlH₄/C catalyst and thus hydrogenation and isomerization seemed to be a competing processes. The hydrogenation of DPA was the major reaction. Even if there are equal amounts of DPA and *cis*-stilbene the amount of the latter still rose, indicating that it was formed faster through hydrogenation of DPA than it depleted through either isomerization or hydrogenation.

There were several factors determining the rate of the reaction. The solvent had an important influence on the reaction. Solvents like toluene could interfere through π -interactions of the aromatic ring with the

rings in the aerogels or the catalyst itself. This could be seen by comparing toluene and cyclohexane in adsorption experiments. The concentration of the substrate in a solution of cyclohexane declined when catalyst was added but stayed relatively stable when the same experiment was done in toluene. From this could be concluded that the DPA and the products adsorbed onto the catalyst in the solution of cyclohexane but were hindered by competitive adsorption in toluene.

Another factor important in determining the speed of the reaction was the hydrogen pressure. The catalyst needed hydrogen to rehydrogenate and experiments with lower pressures showed that the reaction proceeded much slower at these pressures. Depleting the hydrogen of the catalyst itself however did not have this effect. Instead, depleting the catalyst for several hours at 250°C resulted in faster reaction rates.

Perhaps the most intriguing discovery lay in the experiments with different catalyst loadings. Looking to the rates relative to the catalyst loading, for cyclohexane the rate seemed almost to relate directly to the amount of catalyst added but for toluene the rate was slower, as would be expected from earlier results. At lower loadings this difference in rate seemed to decrease and this difference had almost disappeared with loadings a tenth of the normal reaction loading. More interesting however were not the rate but the selectivity changes. The selectivity dropped consistently with higher catalyst loadings. This was the result of more *cis*-stilbene formation at lower loadings and more *trans*-stilbene formation at higher loadings. This went for reactions starting with *cis*-stilbene as well so the effect had likely more to do with the isomerization step than the hydrogenation itself. The same effect was seen when both the amount of DPA and catalyst were lowered so the conclusion could be made that a large ratio of solvent to catalyst was the cause of this effect and not a substrate to catalyst ratio. What was interesting to note was that the solvent itself had less effect on the selectivity, the rate experiments with different loadings in toluene showed only a little more selectivity than the same experiments in cyclohexane. The reason for this phenomena of this was perhaps the biggest mystery this research project left.

5 Recommendations

Using NaAlH₄/C catalysts for hydrogenation reagents is a very cheap option and the catalyst is very versatile. The problem is to get control over the versatility of the reaction. The easiest way to produce *trans*-isomers is to use other supports like high surface area graphites, where the isomerization is highly favoured over the hydrogenation. To create *cis*-isomers several tricks can be used like lower catalyst loading and also changes in the aerogel support. One of the disadvantages of this reaction is that the stilbenes are just intermediate products and bibenzyl is formed as the final product. Using another starting material may yield interesting results and answer some different questions. Of special interest may be stereoselective hydrogenations of double bonds.

To find out more about the hydrogenation process it would be interesting to do experiments with NaAlD₄ to find out whether the *trans*-isomer can also directly be formed. If this is not the case and only a *syn*-addition is possible it would mean that to prevent the formation of *trans*stilbene only the isomerization step needs to be halted.

Alterations to the catalyst can be made in many ways. One of the more important alterations to try is to oxidise the catalyst a little. Some of the samples were likely contaminated with oxygen and actually showed higher reaction rates than non contaminated ones. Addition of titanium particles used in homogeneous reactions might cause a cumulative effect. Reusing a retrieved catalyst in a new reaction is another way of using an already depleted catalyst for the experiments. It will be of interest to see if the effect of this type of depletion yields the same results or whether the dehydrogenated catalyst was shaped in a different way. To examine the resulting catalyst after any type of alteration with spectroscopy will also be of value.

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6 Appendices

6.1 Appendix A: Catalyst design (J.Gao)

As an appendix to this project the results are included of an earlier study by Jinbao Gao from the Utrecht University department of Inorganic chemistry and catalysis. In this project a number of different support materials had been used to study the effect of the support on the reaction. These results were summarized to support the discussion in the report and to give the reasons of the selection of the aerogel catalyst. High surface area graphite was used in combination and *cis*-stilbene as the starting material. An important note for these reactions is that all of them were done in toluene.

The importance of the aerogel pore size

The carbon aerogels made to study the influence of the support material were made of formaldehyde and resorcinol and water. The pore size of the carbon aerogels can be influenced by the production process, by tuning the fraction of organic material versus the fraction of water. A pore size distribution of around 6 nm and around 100 nm had been used in these experiments. The results of figure 46 and figure 47 show reactions with these aerogels. In figure 46 more water had been used which led to the formation of larger pores. Figure 47 shows the opposite, where the organic fraction was greater. What can be seen is that in the former figure with larger pores more *cis*-stilbene was formed, while in the latter figure more *trans*-stilbene was formed. This immediately lead to the suggestion that pore size was related to isomerization.

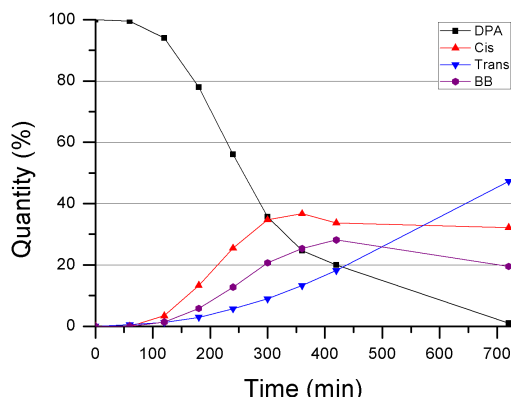


Figure 46: Reaction with aerogels with larger pores

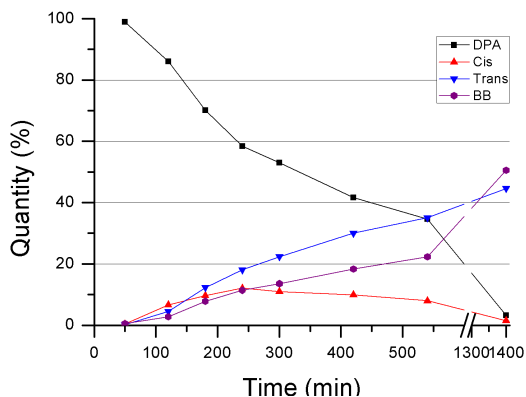


Figure 47: Reaction with aerogels with smaller pores

A pore size distribution around 100 nm showed the most *cis*-formation, but also showed a fast reaction rate given that the reactions were performed in toluene. This again showed that the reaction rate and selectivity were not necessarily related. The most likely explanation for this would be that the smaller cavities stimulated isomerization and not hydrogenation. These results led to the decision to make 20 nm catalysts which theoretically would have a distribution with comparable *cis*- to *trans*-ratios. When we look at the results of the standard experiments this seemed to have been a reasonable deduction. Although individual results have differed the average selectivity was very balanced. After two hours *cis*-stilbene:*trans*-stilbene ratio reached a value of 1.013567199.

Different carbon support materials

While carbon aerogels were easily created supports with a comparable *cis*- to *trans*-ratio, a number of other materials had been tested as support for the NaAlH_4 . Other materials that had been used as a support were: High Surface Area Graphite (HSAG), SBA16 and R2030H. Although the support did not catalyse the reaction directly, it was found to have a large influence on the catalyst. A reaction with a HSAG support was comparable to the aerogels reaction in rate. The results of this reaction can be found in figure 48. Although the reaction started to run slower after a certain period of time. The ratio between *cis*- and *trans*-stilbene however was very different from the aerogels. Significant amounts of *cis*-stilbene were only seen in the first three hours of the reaction, until the DPA was about half depleted. After this moment the DPA declined with a slower rate and the stilbene depletion started to take over. There could be two reasons for the very selective formation of *trans*-stilbene. Either more *trans*-stilbene was formed directly on the surface of NaAlH_4 /HSAG or almost any *cis*-stilbene in the solution was immediately transformed into the other isomer.

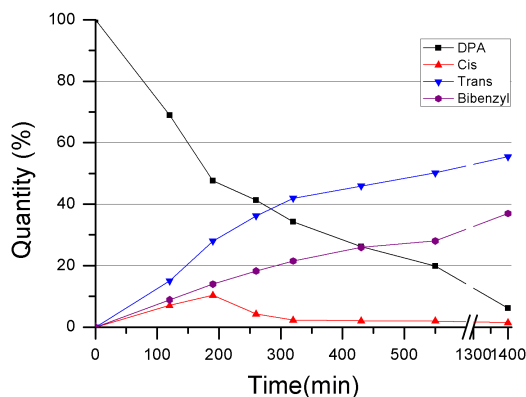


Figure 48: Reaction with HSAG as the support

After this moment the DPA declined with a slower rate and the stilbene depletion started to take over. There could be two reasons for the very selective formation of *trans*-stilbene. Either more *trans*-stilbene was formed directly on the surface of NaAlH_4 /HSAG or almost any *cis*-stilbene in the solution was immediately transformed into the other isomer.

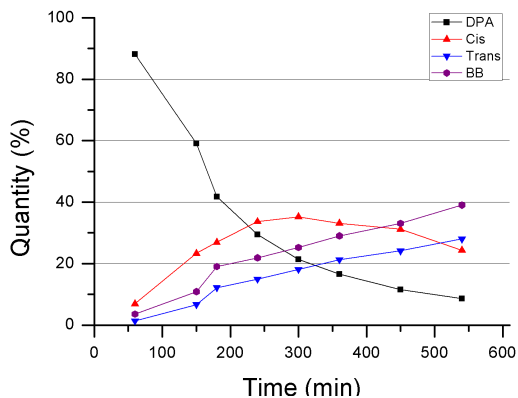


Figure 49: Reaction with R2030H as the support
Because the reaction profile of the R2030 looked more like the carbon aerogels, a division purely by pore size could be excluded.

A different support material which had been used was R2030. The results of the reaction are shown in figure 49. R2030 was a steam activated extruded carbon with only micropores. When R2030H was used instead of carbon aerogels and showed a reaction profile comparable with the larger aerogels. More *cis*-stilbene was produced than *trans*-stilbene. The bibenzyl production was also higher in this case. The fact that R2030 only contained micropores and created more *cis*-stilbene was an interesting result. If pore size would be the only factor in determining the selectivity, the reaction profile would be suspected to look more like the profile of 6 nm diameter carbon aerogels, which also had mostly cavities with very small pore diameters.

The last of the different materials used was CSBA-16, which was a carbon replica of the mesoporous SBA-16. This mesoporous carbon material had only a small pore size distribution around 3.7 and did not have the micropores. In figure 50 it can be seen that the CSBA showed a reaction profile most similar to the high surface area graphite. Compared to HSAG the amount of *cis*-stilbene formed was even lower and at the same time the rate of DPA loss was faster. The aerogels also showed that the aerogel sample with the smaller mesopores showed higher *trans*-stilbene formation. A reason could be that isomerization of *cis*-stilbene could be very effective with cavities of this size. Why these sizes would be so effective in isomerization would however still be a question unanswered.

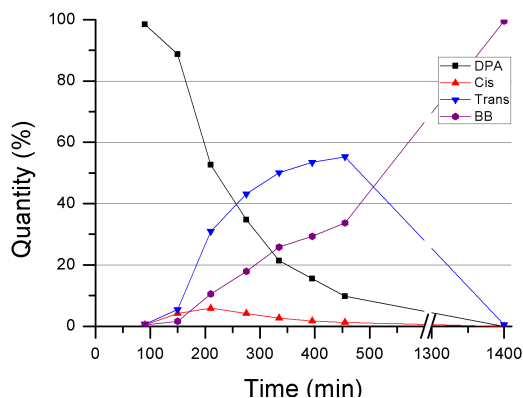


Figure 50: Reaction with SBA16 as the support

Isomerization between carbon aerogels and HSAG

The presence of pores between 2 and 10 nm seemed to bring about isomerization from *cis*- to *trans*-stilbene. An important question raised was whether the strong presence of *trans*-stilbene in reactions with different support materials was because of isomerization or a direct hydrogenation reaction from DPA. To discover why the selectivity was so different between HSAG and carbon aerogels the reactions were done with *cis*-stilbene as starting material. Figure 51 shows the reaction with the NaAlH₄ supported on aerogels and figure 52 shows the same reaction on HSAG.

What can be seen in this reaction is the quick depletion of *cis*-stilbene on HSAG, while on carbon aerogels the decline is much slower. It shows that the main contribution to the formation of *trans*-stilbene was the isomerization with the HSAG support. It also showed that hydrogenation from *trans*-stilbene seemed to be a linear process in this case as well, independent of reagent concentration. Concluding the results of this project support materials were shown to be a very important influence of the reaction, especially in the case of isomerization.

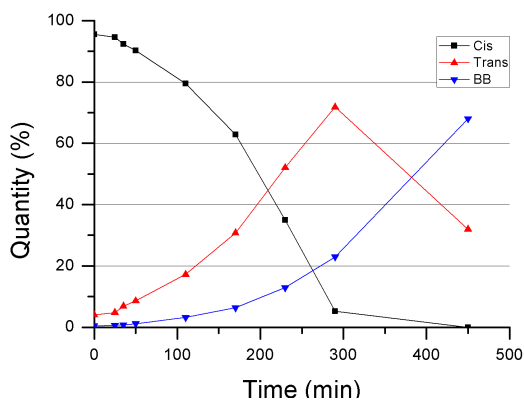


Figure 51: Rate of product formation in cyclohexane

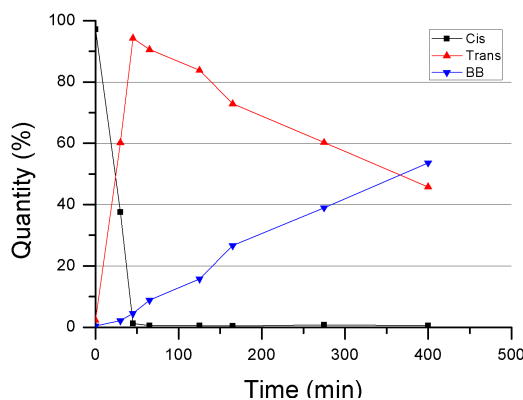


Figure 52: Rate of product formation in toluene

6.2 Appendix B: Research data tables

Sample name	DPA (mg)	Stilbene (mg)	Catalyst (mg)	Dodecane (mg)
Standard 1	891	0	269	216
Standard 2	890	0	270	211
Standard 3	890	0	270	192
Standard 4	890	0	270	189
Standard 5	890	0	270	198
Standard 6	894	0	273	232
Standard 7	891	0	272	193
Standard 8	889	0	270	210
Standard S	845	0	265	191
Standard L	819	0	267	213
Teflon Lining	740	0	223	166
Teflon Lining Blank	742	0	0	162
Without Catalyst	890	0	0	198
Aerogels Blank	890	0	215 (aero)	223
Aerogels Blank Cis	0	900 (cis)	216 (aero)	191
Aerogels Blank DPA & Cis	445	454 (cis)	216 (aero)	202
NaAlH ₄ Blank	889	0	54 (bulk)	200
NaAlH ₄ Blank 2	888	0	54 (bulk)	192
Paladium on Carbon	445	0	27 (Pd/C)	210
Stoichiometric Amounts	711	0	538	201
Stoichiometric Amounts Week	712	0	541	199
Delayed reaction	890	0	270	204
Delayed reaction 2	890	0	272	227
Cis	0	903 (cis)	269	199
Trans	0	900 (trans)	270	198
DPA and Cis	495	506 (cis)	269	199
Toluene	890	0	263	214
Medium Catalyst Loading	890	0	135	227
Low Catalyst Loading	890	0	54	214
Low Catalyst Loading 2	893	0	55	198
Low Catalyst Loadings Cis	0	935(cis)	54	214
Low Catalyst Loadings Toluene	890	0	54	247
Low Concentrations	92	0	29	219
Hydrogen Pressure 10 bar	890	0	266	236
Hydrogen Pressure 50 bar	889	0	270	205
Semi Depleted	890	0	270	197
Semi Depleted 2	890	0	270	205
Fully Depleted	891	0	136	204
Fully Depleted 2	891	0	271	210

Table 2: Starting materials of the main experiments

Sample	DPA (mg)	Catalyst (mg)	Dodecane (mg)
108 mg Cyclohexane	445	108	224
81 mg Cyclohexane	445	81	195
54 mg Cyclohexane	445	54	192
27 mg Cyclohexane	446	27	221
108 mg Toluene	445	109	196
81 mg Toluene	445	80	234
54 mg Toluene	446	55	194
27 mg Toluene	446	28	197

Table 3: Starting materials of the rate experiments

Sample	DPA (mg)	Catalyst (mg)	Dodecane (mg)
Aerogels 1	89	22	26
Aerogels 2	89	22	24
DPA cyclohexane 1	89	27	18
DPA cyclohexane 2	89	27	23
Cis cyclohexane 1	88	27	20
Cis cyclohexane 2	86	27	17
Trans cyclohexane 1	90	27	17
Trans cyclohexane 2	89	26	18
Bibenzyl cyclohexane 1	93	27	23
Bibenzyl cyclohexane 2	93	27	25
DPA toluene 1	90	27	18
DPA toluene 2	88	27	19
Cis toluene 1	87	27	28
Cis toluene 2	92	27	20
Trans toluene 1	90	27	17
Trans toluene 2	89	27	19
Bibenzyl toluene 1	91	27	25
Bibenzyl toluene 2	91	26	20

Table 4: Starting materials of the adsorption experiments