KU LEUVEN

FACULTEIT BIO-INGENIEURSWETENSCHAPPEN

Novel catalysts for the conversion of phenol to anilines

Promotor: Erasmus Dissertation

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It would be impossible to forget you, brave partner on the later hours. To you my best wishes, old radio of the laboratory.

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For all of you, just say it has been an honour staying at the KU Leuven with you in my final path of the chemistry bachelor; at last, now yes, it's over.

Summary

Anilines and its derivatives establish an important building blocks in pharmaceutical and polymer industry. The fountain of its obtainment are fossil resources and, due to someday they will come to an end, a more atom efficient and sustainable pathway towards these compounds must be found. Phenols, possibly obtainable from lignin, constitute a possible renewable feedstock.

In this thesis, the amination of phenols with primary amines was investigated. A hydrogenation - dehydrogenation pathway is followed in which cyclohexanone is a key intermediate that gets transformed into an imine and is subsequently either hydrogenated towards a N-aliphaticyclohexylamine or N-substituted aniline. In prior articles this is done by adding a reductant. However, in this thesis the reductant happens to be molecular hydrogen, a very comfortable working substance for industry. The goal is to procure N-alkylated anilines since phenol using an heterogeneous catalyst process. The catalyst allows the formation of the cyclohexanone, reactive specie which is attacked by the primary amine to form the N-substituted cyclohexylimine. Coming up next for this first step, the imine will evolve either towards the N-substituted aniline, in absence of molecular hydrogen, either towards the N-substituted cyclohexylamine in presence of the reductant. This theory was investigated using several Pd and Pt catalysts to perform the reaction between phenol and different primary amines.

First part of the research was dedicated to investigate the control that hydrogen pressure can perform on the possible hydrogenated/dehydrogenated ratio products. First work was developed with Pd/C catalyst. Later dehydrogenation step was studied on different catalysts and substrates, in order to precisely regard all the possible side paths of the step and find a suitable catalyst referring to selectivity and activity. After discover Pd supported on $CaCO_3$ was the most suitable catalyst to this end, some experiments with a amine were implemented at different low hydrogen pressures in order to regard not just the activity on the dehydrogenation step but on the complete reaction.

and Pt catalysts in order to find the one which accomplish the task of being efficient and selective towards the N-substituted aniline versus all the other possible species which can be obtained through the complex mechanism the reaction has.

This clearly shows that the hydrogen pressure can be used to control the product distribution, i.e. whether the hydrogenated or dehydrogenated product is obtained as main product. Further, this shows that the reaction at low hydrogen pressures is possible. These results are unprecedented in literature, as only cyclohexylamine was so far obtained with hydrogen as reductant

List of symbols and abbreviations

AN	Aniline
BZ	Benzene
CHA	Cyclohexylamine
CHO	Cyclohexanone
DCA	Dicyclohexylamine
ECN	Equivalent Carbon Numbers
FID	Flame Ionization Detector
GC	Gas cromatography
GC-MS	Gas cromatography-Mass Spectroscopy
i-pCHA	iso-propylcyclohexylamine
i-pAN	iso-propylaniline
PhAN	Phenylaniline
PhCHA	Phenylcyclohexylamine
PhOH	Phenol
2-EtHxNHCHA	2-ethyl-1-hexylcyclohexylamine
2- EtHxNHAN	2-ethyl-1-hexylcyclohexylaniline
IMINE DIMER	di-(2-ethyl-1-hexyl)-imine
DIMER	N,N-bis(2-ethyl-1-hexyl)amine

Content

Context and objectives

Since crude oil was first gained from the earth to produce petrol for supplying motors of cars and industry, technology has developed at an astonishing rate. Although technology has advanced way beyond key discoveries like the combustion engine, we still mainly rely on fossil resources for transportation and chemical industry. With depleting fossil resources and the requirement for more strict environmental rules, alternatives have to be found. If the technique humanity has developed see itself doomed to exhaust the fountain of its own energy, before developing of finding another, so much effort would have been in vain, due to this technique will became obsolete. Here is where chemical research plays an important role. Plants are among the most attractive alternative for carbon based chemicals and fuels. Lots of research have been made to obtain biodiesel, biogas and many other resources from a sustainable fountain. A problem is often that there is competition between growing plants for feeding the population and plants for fuel and chemical preparation, for example. An attractive pathway is the conversion of lignin, which can be found in large quantities in many plants in a non-edible fraction of the biomass. Lignin is a polymer of phenolic moieties. Although a variety of chemicals, above all phenols, can be obtained from lignin, there is still no access to others. Anilines are one example of molecules without a reasonably established method to be prepared straight from nature.

For this reason, the main objective of this Erasmus dissertation is to develop new methods for the conversion of phenols to anilines. The approach is to first hydrogenate phenol to cyclohexanone that can easily react with an amine to form a cyclohexylimine and then subsequently dehydrogenate the cyclohexylimine to form the aniline. To achieve this goal, two pathways will be followed.

1) The reaction in which a small hydrogen pressure will be employed, thus allowing for hydrogenation of the phenol and dehydrogenation of the cyclohexylimine at the same time.
2) A two-step-one-pot approach, in which the phenol is first reacted to the cyclohexylamine at a higher hydrogen pressure and is then dehydrogenated (after switching the gas atmosphere to nitrogen) at a different temperature. This method allows for optimization of conditions for each step individually, while remaining the simplicity of carrying out the reaction in one pot.

To find the best system conditions, different catalysts and key parameters, such as temperature and pressure, were tested and later investigated to gain an understanding of the system. From this it is possible to correlate the nature of the catalyst to the catalytic performance.

LITERATURE REVIEW

1 Phenols and anilines preparation and applications

1.1 Phenol

Hydroxybenzene and its derivates shape the phenol group. First used as disinfectant and later as intermediate for chemical industry, its currently most important field of usage appeared during the last century, i.e. phenolic resins and polymers, such as bakelites or polycarbonates. Its importance sets it among the first 50 most important chemicals in the world, and its worldwide demand is estimated to grow over 2.5% per year during the next three years.

It was first obtained from charcoal tar by Runge in 1834[3]. After this basic extraction from coal, different synthesis methods were developed as its demand was growing. First of them was the benzenosulfonateprocess[3]. Alkalyne hydrolysis of clorobenzene was discovered in 1872[3]. Direct oxidation of benzene methods have been studied, with O2 gas from air, hydroperoxyde and a catalyst, or directly with NO_2[3]. This last option is interesting due to the formation of NO_2 gas as by-product in adipic acid production, nevertheless a commercial solution hasn't been found yet[3]. It hasn't been commercialized yet as direct oxidation of benzene towards phenol[3]. Toluene oxidation was regarded during the 1950s, as it seemed to become cheaper than benzene[3]. A method which gave benzene and diphenylether as byproducts was developed[3]. Exxon Mobil patented a three steps reaction which involves generation of phenol and cyclohexane, which is important in nylon 6,6 production, since benzene[4-5]. In spite of all these mentioned methods, nowadays the most used method, withup to 95 % of the total phenol obtained is the cumene process.

Also known as the Hock Process, it starts transforming cumene into cumenehydroperoxide with oxygen. Second and last reaction step involves an strong mineral acid as catalyst in order to cleavage the cumenehydroperoxide into phenol and acetone, byproduct whose market importance maintains this method in the leading position of phenol production, with a 95% of the world produced phenol through the Hock Process.

1.2 Aniline

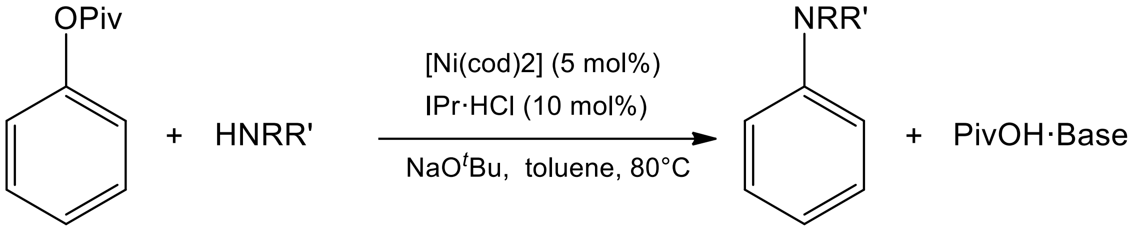
Aniline and its derivatives are very important building blocks for different fields, such as electronic materials, polymers and active pharmaceutical ingredients[7,6]. The majority of anilin is currently used for the production of methanylenedianline (MDA), i.e. the precursor for polyurethanes based on methylenediphenyldiisocyanate. The production is currently carried out by first nitrating benzene using sulphuric acid as catalyst. Nitrobenzene is then hydrogenated in the gas phase over a metal catalyst. In case of *N*-substituted anilines, a further alkylation step is required. This is often performed with alkylhalides, which form stoichiometric amounts of waste.

Alternative, established routes for the production of *N*-alkylated anilines include the amination of pre-activated arenes. Prominent examples are the Chan-Lam coupling, in which a pre-activated arylboronic acid is reacted with an amine using a copper catalyst and a base and the Buchwald-Hartwig reaction, in which most often Pd catalysts are employed to convert arylhalides to arylaminesin the presence of a base. The production of these pre-activated arenes often have non-ideal regioselectivity for substituted arenes and waste is generated during the formation of these molecules.

2 Phenol to aniline conversion

Given that phenol can be obtained from lignin in larger quantities in the future, the conversion of phenol to anilines is a more sustainable pathway towards anilines. Early reports focused on the conversion of phenol to a more activated arene, such as arylpivalates. Homogeneous Ni(0) catalysts with the NHC ligand derived from 1,3-bis(2,6-diisopropylphenyl)imidazoliumchloride(IPr·HCl) are known to be best for this C-O activation, in which pivalic acid is formally removed NaO^{t}Bu, which has to be added as a base (Scheme1).

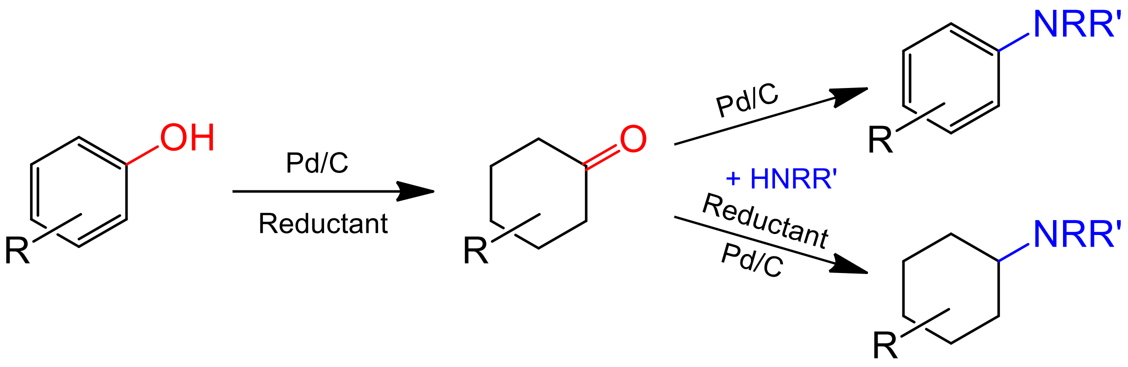
Scheme1. Conversion of phenylpivalates to anilines[8].



This method still produces significant amounts of waste, as a stoichiometric amount of base is required and further a rather large pivalic acid group is the leaving group. For the preparation of the phenylpivalate generally the pivaloyl chloride is employed, again adding negatively to the atom economy of this reaction.

An attractive alternative for phenol amination was recently described. In this reaction phenol is first reduced to the cyclohexanone, which easily undergoes a reaction with an amine to form the cyclohexylimine. The cyclohexylimine can afterwards be converted to either the cyclohexylamine by hydrogenation or to the corresponding aniline by dehydrogenation. (Scheme2).

Scheme2. Phenol amination with cyclohexanone as intermediate.



3 EXPERIMENTAL SECTION

3.1 Reactions

3.1.1 Reactions of phenol towards primary cyclohexylamines in autoclaves

Autoclaves with a volume of 11 mL were used for the reactions. To them was added, in sequentially order: the catalyst (always 5 mol % of the correspondent element, respective to phenol), then the crossed-stir bar, 1.4 eq of amine, 0.2 mmol Phenol, and later the solvent (always was used 1 mL Toluene). Then the autoclave is closed and purged three times with nitrogen (until 15 bar approximately before venting to 0 bar). After this, 4 bar nitrogen plus 2 bar hydrogen were added. As every experiment had their concrete hydrogen pressure, dilutions had to be made. Usually it was added nitrogen until 24 bar and then venting until 6 bar, for example, in order to portion the initial hydrogen pressure into four. Then the portions were made on desire: if it was needed 0.125 final hydrogen bar, the process started with two hydrogen bar and two portion cycles were made. The portions always started with, at least, 2 hydrogen bar due to the barometer minimum precise value is 2 bar. All the portions were finished with 6 final bar. The mixtures were stirred during all the reaction time. Four temperatures were studied, 140, 160, 180 and 200 ºC. Correspondent temperatures on the heating plate were, respectively, 151, 173, 216, and 195 ºC. After the reaction, the autoclaves were cooled down in a water bath and depressurized after. The samples were taken with a syringe and filtered with a hydrophobic fluoropore (PTFE) filter of 45 µm particle size. After they were placed on a GC-vial and analyzed with GC-FID.

3.1.2 Reactions of N-substituted cyclohexylamine towards N-substituted anilines (dehydrogenation step)

The process was the same as the expressed on the 1.1 section. Differences are: No phenol was used. After closing, filling and venting autoclave with nitrogen, in the same way as expressed in point 1.1, none hydrogen was pressurized. The temperature conditions were settled on the same way as in the point 1.1. Sampling and analysis follow the exactly same procedure as in 1.1.

3.2 Analysis and characterization

3.2.1 Gas chromatography- Flame Ionization Detector

All samples were analyzed using a Shimadzu 2010 gas chromatograph (GC) instrument. The instrument is equipped with an AOC-20s Autosampler and an AOC-20i Auto-injector. It is connected to the ShimadzuGCsolution Version 2.30.00 software. For all samples, the different molecular species are separated from the solvent background and among them on an Agilent CP-Sil 5 CB capillary column. The column length is 60.0 m, with an internal diameter of 0.32 mm and a film thickness of 0.25 µm. The separation is predominantly based on a difference in boiling point. This is due to the stationary phase, polydimethylsiloxane, which confers the column rather apolar properties. The volatilizable components from a sample volume of 1 µL need to be in the vapour phase. To achieve this goal split injection with a ratio of 1:30 at a temperature of 250ºC was used. A constant nitrogen flow of 2.30 mL/min carry the molecules through the column. This column is coupled to a FID (flame ionization detector), which measures the concentration of organic species in a gas stream. The molecules will be detected at 330 ºC. The temperature slope in the oven starts at 50ºC, this temperature is hold during a minute and then a 10ºC/min slope starts, until 330ºC. The oven stays at this temperature during 8 min. In total it summarizes a chromatogram of 37 minutes.

3.2.2 Gas chromatography - Mass Spectrometry Detector

In order to determine unknown compounds, gas chromatography coupled to an MS-detector (mass spectroscopy) was used. An Agilent 6890 gas chromatograph instrument, connected to a 5973 MSD mass spectrometer, was used to analyze the samples. The column which perform the peak separation is a HP-1 MS column with a length of 30 m, the internal diameter is 0.32 mm and the inner film thickness is 0.25 µm. The instrumental parameters for injection are identical than the described for the GC-FID, and temperature profile just varies on the starting temperature (70ºC instead of 50ºC in the GC-FID).The stationary phase is 100 % polydimethylsiloxane and the carrier gas is helium. The detection is based on the ionization of the components into radical cations, the instability of radicals leads to their fragmentation. The separation of these fragments is based on the difference in mass-to-charge (m/z) ratio, a quartz quadrupole mass spectrometer is used for this purpose. Every molecule has a characteristic mass spectrum, which is obtained plotting the relative abundance of the different fragments in function of the m/z ratio. The software coupled to the instrument is used for the identification of the products, a comparison is made between the obtained mass spectrum and data from the database NIST (National Institute of Standards and Technology). If this is giving no satisfactory result, manual fragmentation patterns of the possible products has to be made to find the right product, for example, "ChemDraw" software can be of assistance here.

3.2.3 Data Analysis

The analysis of the products, which were identified with GC-MS or by injecting reference compounds, is carried out by using the effective carbon numbers (ECN) concept. That means that every compound have a different response on the FID, depending on the effective carbon numbers of the compound. Obtained peak areas are divided by the effective carbon number and normalized to the initial phenol concentration.

Conversion, yield and selectivity (expressed in %) were calculated as follows:

Conversion= 100- concentration of phenol (in mol%)

Yield= concentration of the desired product (in mol%)

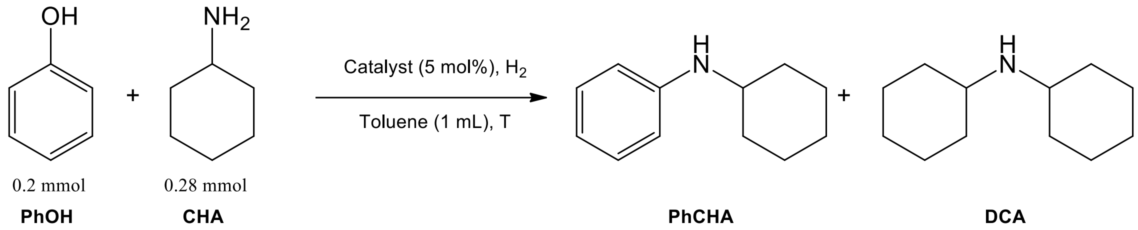
Selectivity= Yield/Conversion * 100

4 RESULTS AND DISCUSSION

4.1 Investigation of activity and selectivity towards ring-hydrogenated and dehydrogenated compounds

Initially, the reaction between phenol and cyclohexylamine with Pd on Carbon as catalyst, using H_2 gas as reductant was investigated (Scheme 3). In all of the reactions were 0.2 mmol phenol, 1.4 equivalents of cyclohexylamine were employed and different conditions combinations were investigated.

Scheme 3. General overview of the reaction of phenol with cyclohexylamine towards phenylcyclohexylamine and dicyclohexylamine.



Cyclohexylamine was used as reactant, because it forms symmetric amines, which are not prone to side-product formation. In this way the reactivity can be easily investigated without the problem of any selectivity issues regarding the amine.

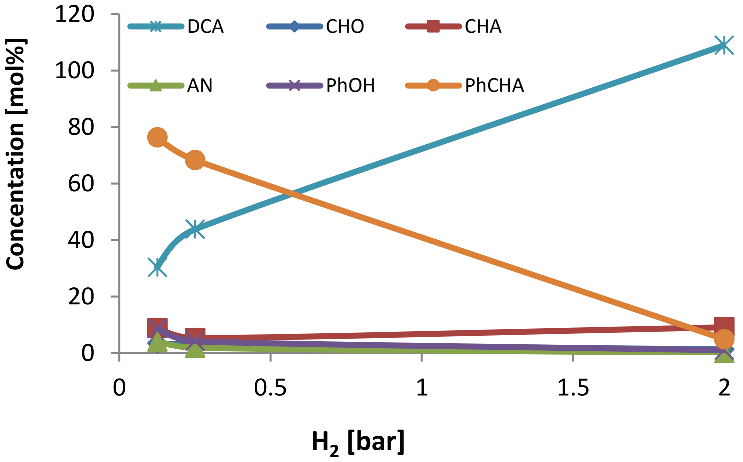
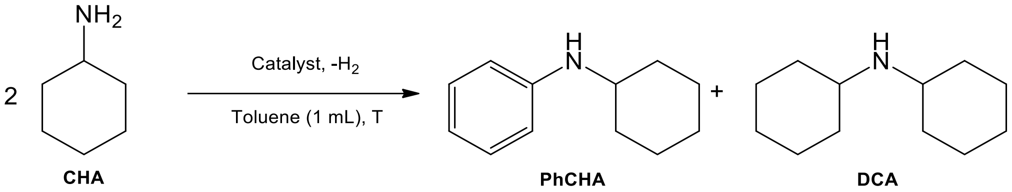


Figure 1. Concentrations of the reaction of phenol with cyclohexylamine in the presence of hydrogen after 240 minutes of reaction at different hydrogen pressures. The reaction was carried out at 140 °C. It can be clearly observed that at high pressures the hydrogenated Dicyclohexylamine product is obtained as main product.

The influence of the hydrogen pressure was tested for the reaction of phenol (PhOH) with cyclohexylamine (CHA, Figure 1).After 300 min one could observe a clear trend in the reaction outcome. At low hydrogen pressure (0.125 bar), phenylcyclohexylamine (PhCHA) was obtained as main product with a yield of 76 % and dicyclohexylamine (DCA) as most important side-product (30 %). Phenol was converted with 92 %. Notably, cyclohexylamine concentration was below 10 mol% over the whole investigated hydrogen pressure range. This, together with the high yield of PhCHA and DCA can be explained by the condensation of excessive cyclohexylamine to form PhCHA and DCA.[1] Aniline was found in small amounts (≤4 mol%). While increasing the pressure to 0.25 the yield of PhCHA decreased to 68 %, which was compensated by an increase of DCA to 44 %, PhOH conversion increased to 96 %. At 2 bar, however, DCA was obtained as main product with a yield of 109 % (relative to the initial phenol concentration). The theoretical maximum yield with 1.4 eq of CHA is 120 %, if all CHA is converted to the secondary amine (Scheme 4). PhCHA is only obtained in 5 % yield at a PhOH conversion of 99 %.

Scheme 4. Reaction of two CHA molecules towards PhCHA and DCA



This clearly shows that the hydrogen pressure can be used to control the product distribution, i.e. whether the hydrogenated or dehydrogenated product is obtained as main product. Further, this shows that the reaction at low hydrogen pressures is possible. These results are unprecedented in literature, as only cyclohexylamine was so far obtained with hydrogen as reductant.

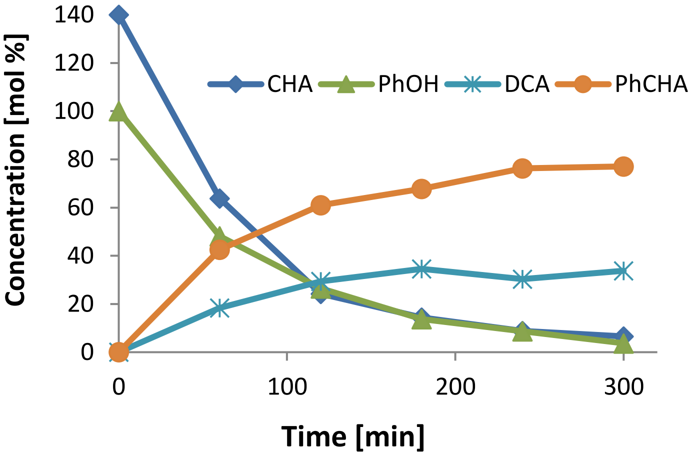


Figure 2. Amination of phenol with CHA at 0.125 H_2 bar and 140 ºC (left) and the same reaction at 2 bar H_2 (right).

As it can be seen, the low pressures hydrogenation kinetics graph has been obtained. The tendency is very clear; The reaction between the CHA and the CHO is very fast, yielding towards goods amounts of DCA (18.3 %) and PhCHA (42.6 %) in the first hour already, with a consumption of PhOH of 51.8 %. As initially, CHA equivalents are 1.4, its consumption has reached the amount of 76.2 %. This shows the reaction works really well with little hydrogen (H_2) pressure. After two hours of reaction every compound behave the same, proportions are as follows: 115.7 % and 73.6% consumptions of CHA and PhOH, respectively, towards 29.4 %

of DCA and 60.9 % of PhCHA. CHO and AN amounts hasn't overcome the 3.5 % yet. As the reaction mechanism is well known[9], from this could be interpreted that the formation of CHO since PhOH is slower than the reaction with the amine on the working conditions. On the contrary, accumulation of CHO will be recorded. Or, said with other words, CHO is a very reactive specie, again, on the working conditions. Third and fourth point (180 and 240 min) follows the same tendency as before, but the proportions on the different substances amounts doesn't suffer high changes. Respectively in time, amounts are: 14.4 % and 8.8 % for CHA, 13.8% and 8.6 % for PhOH, 67.7 % and 76.3% for PhCHA and 34.6 % and 30.3 % for DCA. This last compound shows a decrease. This is due to the experimental mistake. It is possible that at this point the equilibrium has been reached, mainly because there is almost none PhOH in comparison with the first points. After 300 min of reaction, the amounts are as follow: 6.6 % of CHA, 3.3 % of CHO , 2.9 % of AN, 3.7 of PhOH, 33.8 % of DCA, and 77.1 % of PhCHA.

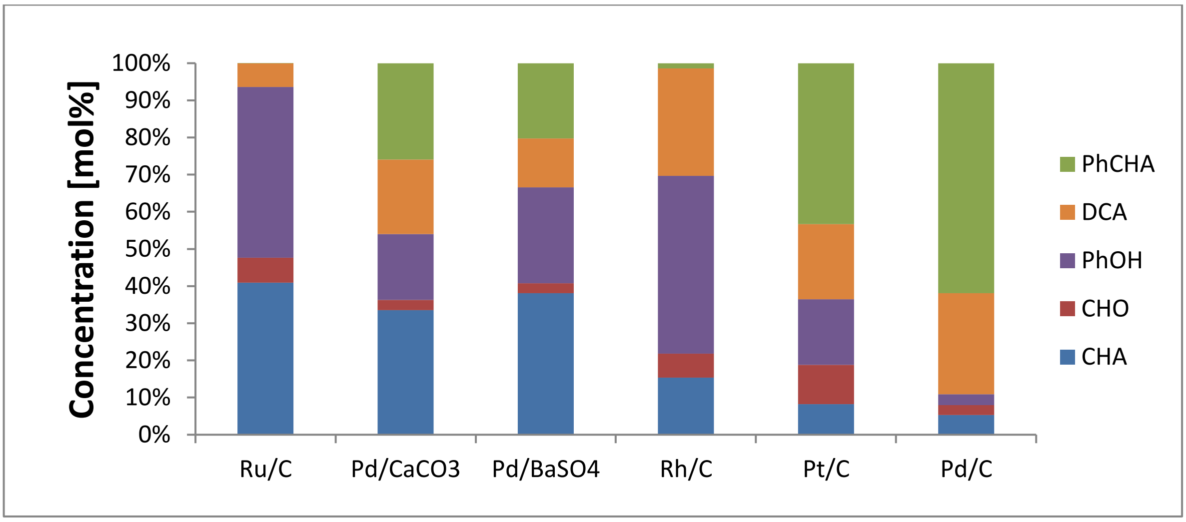


Figure 3.Normalized concentration of the different products after reaction at low hydrogen pressures (0.125 bar) for 300 min at 140 ºC.

Next, different catalysts were investigated at 0.125 and 2 bar H_2 under otherwise identical conditions to see whether there are more suitable catalysts for this conversion.

At 0.125 bar Pd/C was the most active catalyst with a phenol conversion of 96%. This transformation was directed towards PhCHA (yield=77%) and DCA (34 %). At the working temperature (140ºC), the second most active catalystwas Pd/$CaCO_3$, with a PhOH conversion of88% , mainly towards CHA (final concentration=23 %). PhCHA was obtained in a 1 %, and DCA was obtained in a 14 %. Pd/$BaSO_4$ was the third most active catalyst with more PhOH transformation (81.1 %) mainly towards CHA (32 %), and some amount of PhCHA (15 %) and DCA (10 %). These results show that although Pd/C shows the highest activity, results in terms of final CHA concentration differ significantly. This clearly indicates that the reaction of two CHA molecules towards the secondary amines (as shown in Scheme 4) is less favoured over these catalysts compared to Pd/C.

Rh/C showed low PhOH conversion (17.8 %), towards cyclohexanone (CHO) (14.5 %) and DCA (13.9 %). This indicates that Rh/C is not overly active nor selective under these conditions. Ru/C showed some transformation of PhOH (17.8 %) mainly towards DCA (49.7 %) and a little of CHO (11 %), while CHA non transformed conformed a 26.5 %.

Pt/C showed a PhOH conversion of (76%), giving PhCHA as main product (60%) and DCA as most abundant side-product (28%), but also some CHO (15 %) is formed. Thus, the performance is somewhat similar, yet worse than Pd/C.

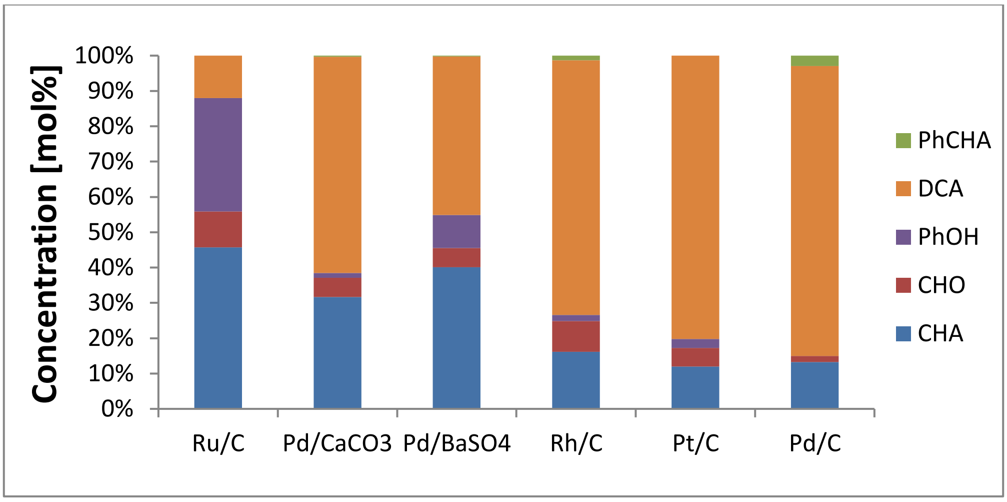
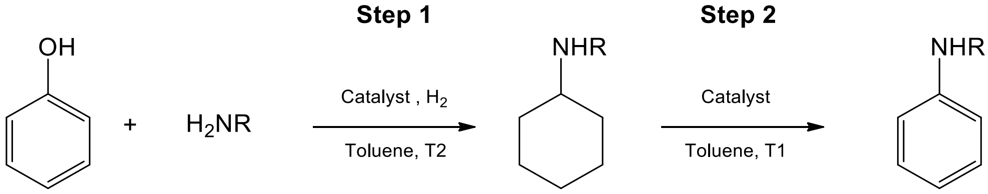


Figure 4. Normalized concentration of the different products after reaction at high hydrogen pressures (2 bar) for 60 min at 140 ºC.

At high hydrogen pressure (2 bar), almost all PhOH (<10%) was transformed (except for Ru/C with a conversion of 23.7 %). In all cases the main product is the DCA, with a transformation of, at least 28.4 % for all the catalysts. This low transformation was achieved by Ru/C. It reached a CHA conversion of 31.5 % (from a 140% of total initial), while it produced the highest amount of CHO (24.2 %) in comparison with the other catalysts. It also was the catalyst which less DCA produced (28.4%). DCA were obtained on a similar way for Pd/$CaCO_3$ (144.7%) and Pd/$BaSO_4$ (105.6%). Both of them had similar CHA amount remaining (74.8 % and 94.3 %, respectively), nor for PhOH, where the second one left some amount without react (22 %). Rh/C, Pt/C and Pd/C behaved very similar on this experiments, with around a 100% yield towards DCA and less than 5% PhOH remaining. Respectively, they had 31.7 %, 28.4% and 31.7 % of CHA remaining. Pd/C had 7.1 % of PhCHA.

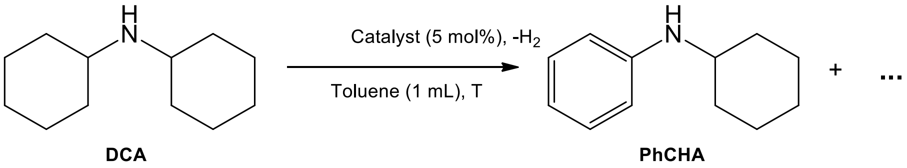
The most noticeable effects of the H_2 pressure regarding PhOH conversion are observed in the case of Rh/C, where can be observed no PhOH conversion (It is supposed the % of PhOH couldn't overcome in any case the 100 %, but it does, which probably means that some water got into the reaction mixture or, more improbable, the PhOH solution had a bigger molarity than supposed) at 0.125 bar, whereas at 2 hydrogen bar can be regarded a PhOH conversion of 96.1%. This clearly shows that this catalysts require higher pressures (or eventually longer times to drive the conversion further) to allow PhOH activation into cyclohexanone (CHO). Pd-based catalysts already showed a higher conversion at low pressures, yet they are still improved. Also in this case it can again be seen that the dehydrogenated PhCHA is obtained preferentially at lower pressures, yet the hydrogenated DCA rather at higher pressures. Further, it can be seen that only Pd and Pt catalysts seem to catalyze the reaction towards the dehydrogenated PhCHA in rather high yield.

Scheme 5. Schematic of the two-step-one-pot approach.



As the dehydrogenation of the amine seems to be a challenging step, this is next investigated separately to quantify the extent of dehydrogenation for different catalysts. This step in the mechanism requires as littleH_2 as possible, but some H_2 pressure is needed in order to transform the phenol into cyclohexanone. It is, however, possible to follow a two-step-one-pot method, in which the phenol is first reacted towards the cyclohexylamine at a higher hydrogen pressure (e.g. 2 bar), which can then be dehydrogenated in a second step under optimized conditions after switching the hydrogen atmosphere (Scheme 5).

Scheme 6. Dehydrogenation of dicyclohexylamine



The activity of the catalysts for dehydrogenation was first established for dicyclohexylamine (Scheme 6). In this case few side-reactions are expected, as the exchange of the *N*-substitutent does not result in the formation of a product with a different connectivity.

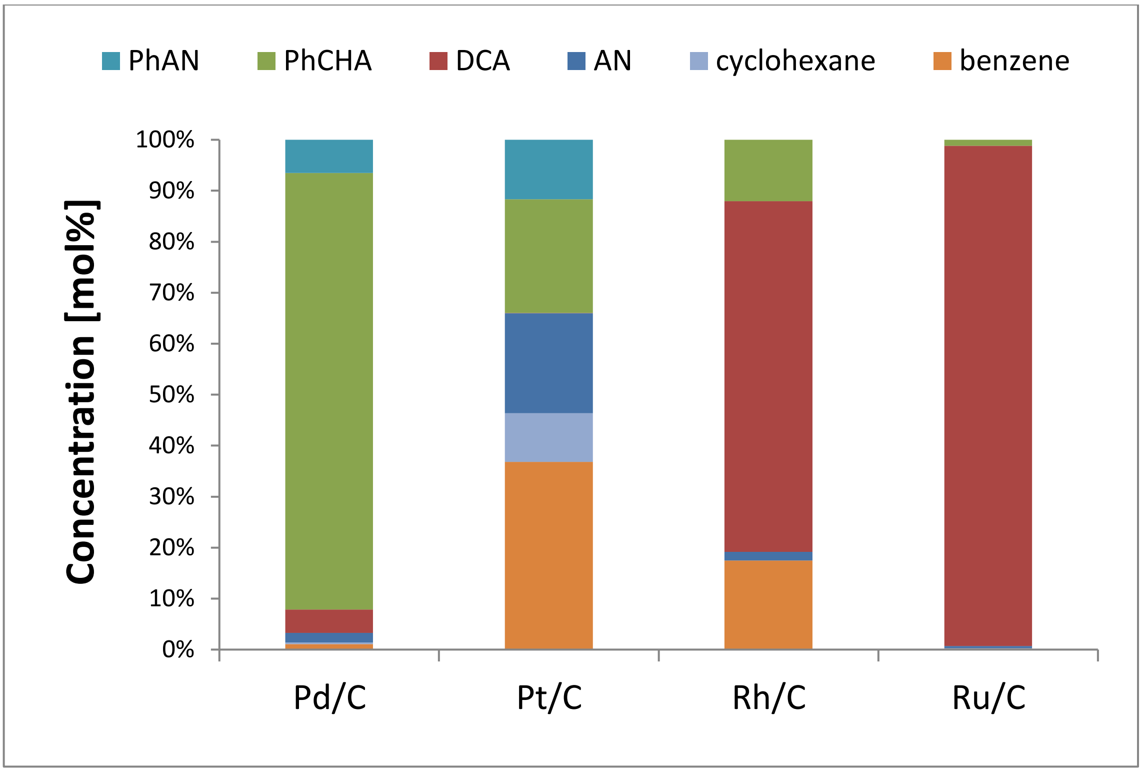


Figure 5. Concentration of the different products of the dehydrogenation of DCA and DCA itself after 180 min. Reactions were carried out at 180 ºC using different carbon supported catalysts.

The different activity of the dehydrogenation step was tested on different catalysts (Figure 5). At the reaction temperature (180 ºC) Ru/C didn't catalyze any dehydrogenation. Rh/C performed some dehydrogenation (yield of 8.5 % of PhCHA), but more pronounced was the cleavage of the secondary amine towards benzene (BZ), which obviously also included a dehydrogenative step (19.6 %) and AN (1.9 %). Pt/C converted DCA entirely, but mainly towards the products that include dehydrogenation, i.e. BZ (39.2%) followed by aniline (20.9%) and some CHA (10.1 %). Therefore, its selectivity towards PhCHA (18.5 %) plus PhAN (9.7 %) is not comparable to Pd/C, which gave remainder amounts of the undesired cleavage products (<10 %). This catalyst perform the higher amount of PhCHA of the four of them (78.2 %), and a little amount of PhAN (5.9 %). Conclusively, Ru/C and Rh/C seem to be rather inactive in the conversion, while Pd/C shows the highest yield of the dehydrogenated PhCHA. Pt/C showed the highest activity and the presence of benzene shows high dehydrogenation activity, yet under these conditions, the hydrogenolysis seems most significant. Not that hydrogen is generated during the dehydrogenation of the compounds

4.2 Deep research in selectivity towards the dehydrogenated product: Dehydrogenation step

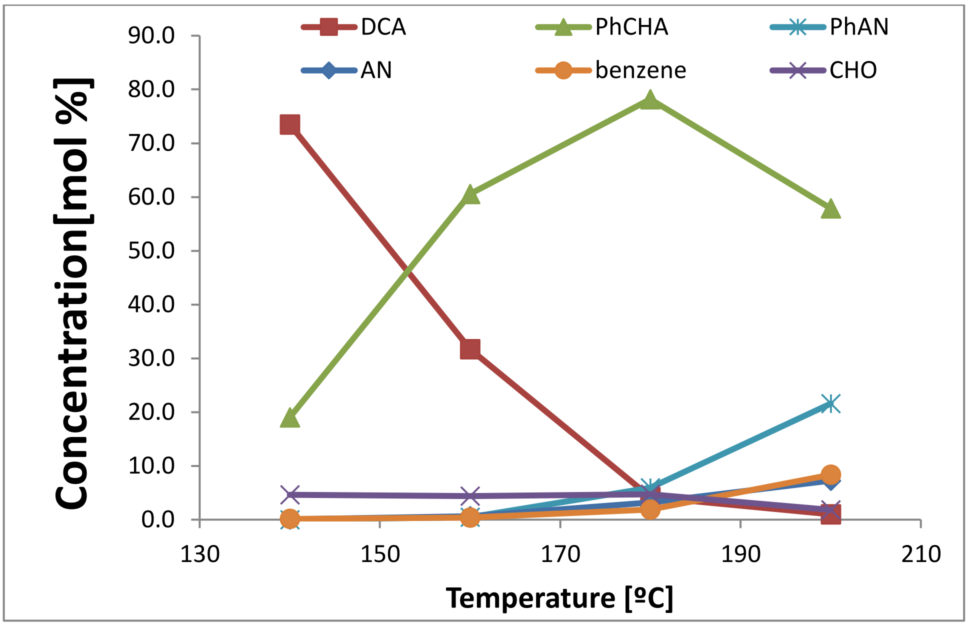


Figure 6. Dehydrogenation of DCA after 180 min of reaction using Pd/C as catalyst. CHA isn't displayed due to its small concentration in all the experiments.

The influence of temperature was tested for the dehydrogenation of DCA on Pd/C (Figure 6). Reaction was carried out for 180 min. At 140 ºC little DCA was converted (27 %) giving PhCHA (19.3 %) and CHA (2.4 %) as products, while also some cyclohexanone and cyclohexanol was formed in these reactions, which can come from residual water in the reaction mixture (4.3 %). At 160º C the products proportion changes markedly. PhCHA becomes the main product (61 %), yet DCA was not transformed completely (68 % conversion). At 180 ºC the proportion evolves following the previous tendency. DCA is almost completely converted (96 %) and PhCHA is obtained with a yield of 78 %, while the other compounds remained below 10 % yield. At 200ºC, the yield of PhCHA amounts to 58 %, thus lower than at 180 °C, the undesired cleavage products, benzene and aniline were obtained in 8 % and 7 % yield. Notably, the concentration of phenylaniline (PhAN) increased at 180 °C (6 mol%) and especially at 200 °C (22 mol%). Thus, at 180 °C there is a maximum of PhCHA, since the reaction drives towards complete dehydrogenation of the molecule, i.e. PhAN and cleaved side-products. This shows that Pd/C dehydrogenation is a rather good catalyst: It can be directed on a level where little side-products are obtained, with high yield towards the desired dehydrogenated product.

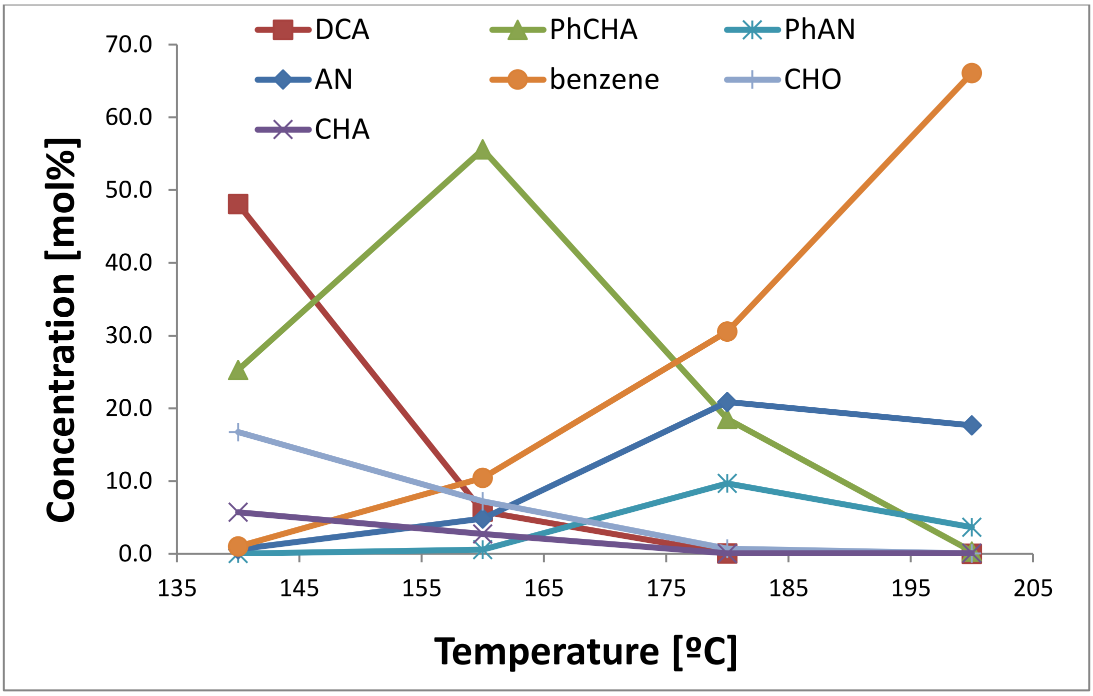


Figure 7. Dehydrogenation of DCA after 180 min of reaction using Pt/C as catalyst. CHA isn't displayed due to its small concentration in all the experiments.

The influence of temperature was tested for the dehydrogenation of DCA on Pt/C (.). Reactions were carried out for 180 mins. At 140 ºC 48 % of the DCA was converted towards PhCHA (25 %). Some CHA was obtained (6 %) as well as cyclohexanone and cyclohexanol (together 17 %). At 160º C PhCHA becomes the major product (56 %) and some DCA remains (6 %). BZ becomes a significant product (17 %) as a consequence of C-N cleavage, not so to a lesser extent AN was formed (5 %). At 180ºC the proportion evolves following the previous tendency. All DCA reacted. BZ rises to 30.6 %, and AN concentration grows till21 %, clearly a consequence of a considerable increase on the cleavage activity of the Pt/C catalyst. Some PhAN appears (9.7 %), which means the catalyst dehydrogenate the secondary amine towards PhCHA (18.5 %) before dehydrogenating it towards PhAN. At 200ºC the cleavage activity of the Pt/C catalyst is more than clear. No DCA remains, neither any PhCHA. They have been transformed towards BZ (69 %), AN (18 %) and some PhAN remainders(3.6 %). Since this, it can be understood the cleaving mechanism towards BZ can run through AN, PhCHA or PhAN indistinctly.

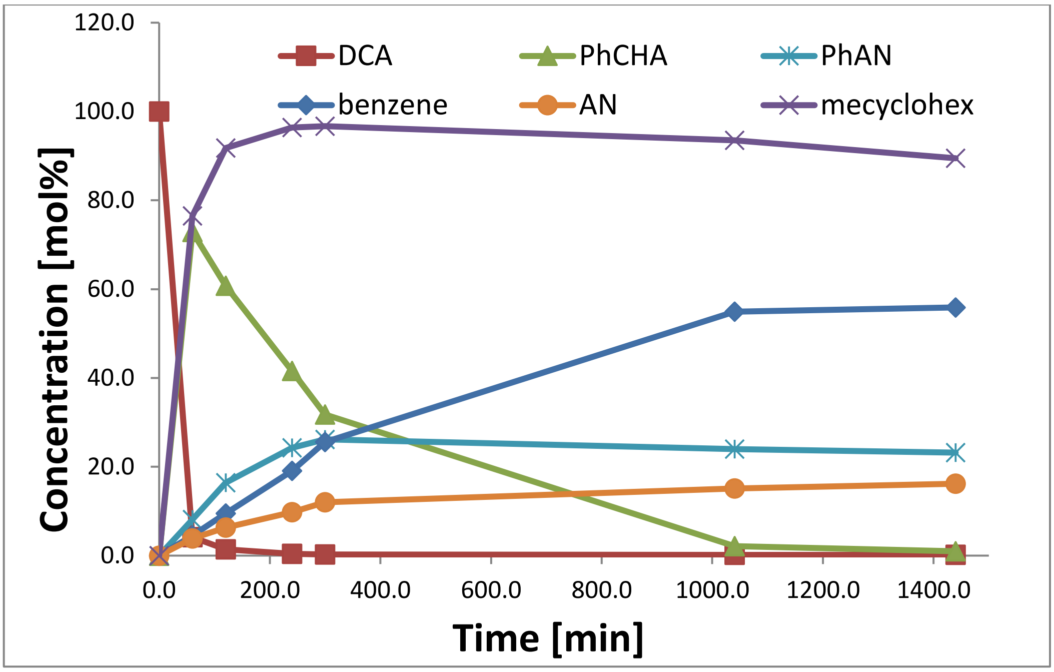
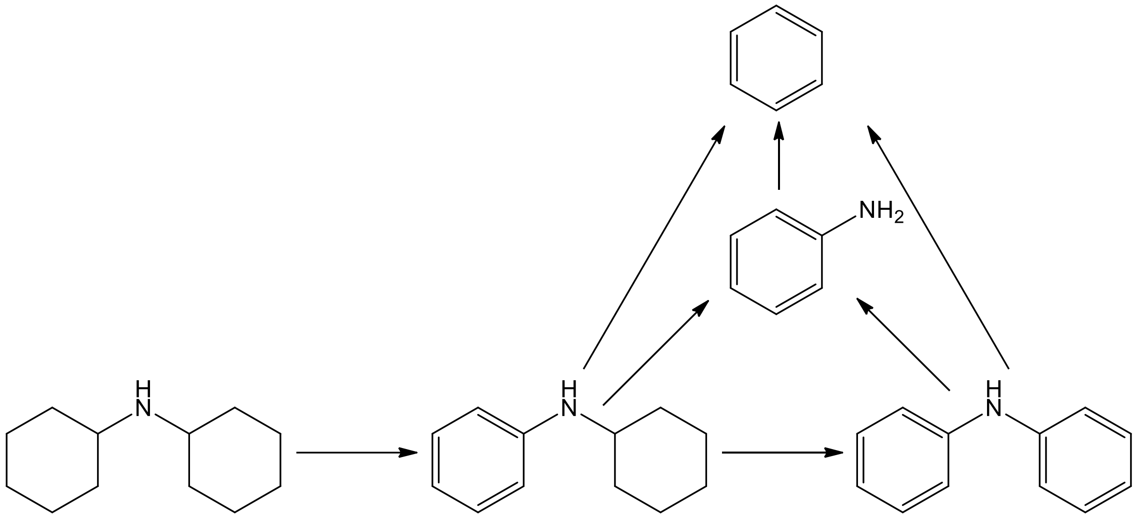


Figure 8. Dehydrogenation of DCA on Pd/C at different times. Reaction was carried out at 200ºC on different times. That allow us to regard the kinetic aspect of the dehydrogenation step on the reference catalyst. Species concentrations relatives to mol %. It can be observed that in the first hour almost all the DCA has been transformed into PhCHA. At five hours PhAN reaches a maximum since where its concentration starts to decrease. Finally, Pd/C also cleavages the substrate into aniline and benzene, but in much less quantity than Pt/C (.). It can be appreciate the third order kinetics DCA PhCHA BZ+PhAN+AN. As an anecdote methylcyclohexane concentration has been included, showing somehow the solvent bias the activity on the catalyst surface.

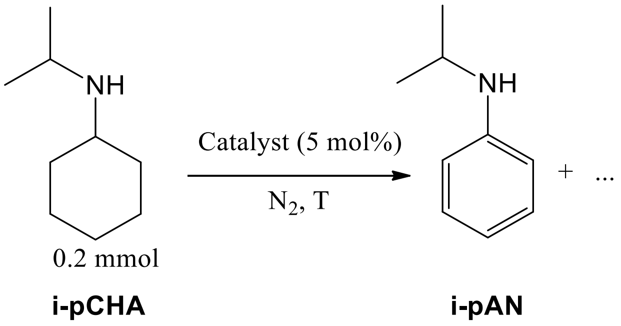
To understand the reactivity of the system towards the side-products, kinetic measurements were performed for Pd/C at 200 °C (**Error! Reference source not found.**). This will further show, whether a shorter time might allow for higher selectivity. Within the first hour of reaction, DCA is almost fully converted (96 %) and PhCHA is obtained at a yield of 73 %, with small amounts of BZ(4 %), AN (3.8 %) and PhAN (8.15 %) being formed. The further development of the graphs shows the kinetic trend of a cascade reaction, where DCA is the starting materials which gets transformed into PhCHA, the second species. After 240 min DCA is fully converted. This second one gets finally transformed into BZ, AN and/or PhAN. As PhAN concentration doesn't stay constant on a maximum, but lightly decreases, this means PhAN also gets transformed into BZ and AN, but at a much lower rate than PhCHA does. After 1440 min of reaction (24 h) the intermediate PhCHA is fully converted (99%) to BZ (55.9 %), PhAN (23.2%), AN (16.2 %) . The fact that the BZ concentration is higher than the AN concentration shows that also AN is converted to BZ(Scheme 7). Further it could be seen that toluene was transformed to methylcyclohexane mainly in the initial 120 min of the reaction. Thus, at least for the first dehydrogenation, it seems to fulfill the effect of being a hydrogen scavenger. The fact, that it reacts also shows that it reacts on the catalyst surface. Thus, it is possible that it somewhat decreases the activity because of competitive adsorption.

Scheme 7. Shematic for the reaction network for the side-product formation from DCA dehydrogenation



Different catalysts were employed for the dehydrogenation of DCA. As explained before, DCA does not form distinguishable side-products, if the *N*-substituent exchange. Asymmetric *N*-substituted secondary amines are valuable chemicals. Thus, to extend this methodology to asymmetric secondary amines and asymmetric *N*-substituted cyclohexylamine will next be investigated to discover the selectivity in the dehydrogenation reaction, which is as seen before the more challenging part in the mechanism.

Scheme 8. Schematic for the dehydrogenation of iso-propylcyclohexylamine.



In this sense, iso-propylcyclohexylamine (i-pCHA) was chosen as for the dehydrogenation (Scheme 8), in which more side-products can be formed. Several catalysts that were previously synthesized in this laboratory (of Pd and Pt) were tested to investigate which characteristics of the catalysts is important in the reaction. It is supposed that with different supports the activity and selectivity of the metal catalyst will vary, and therefore, the yields of the different possible products as well. Nevertheless, the dehydrogenation was first investigated using reference catalysts (Pd/C and Pt/C), to have a reference point of a generally very active carbon supported catalyst.

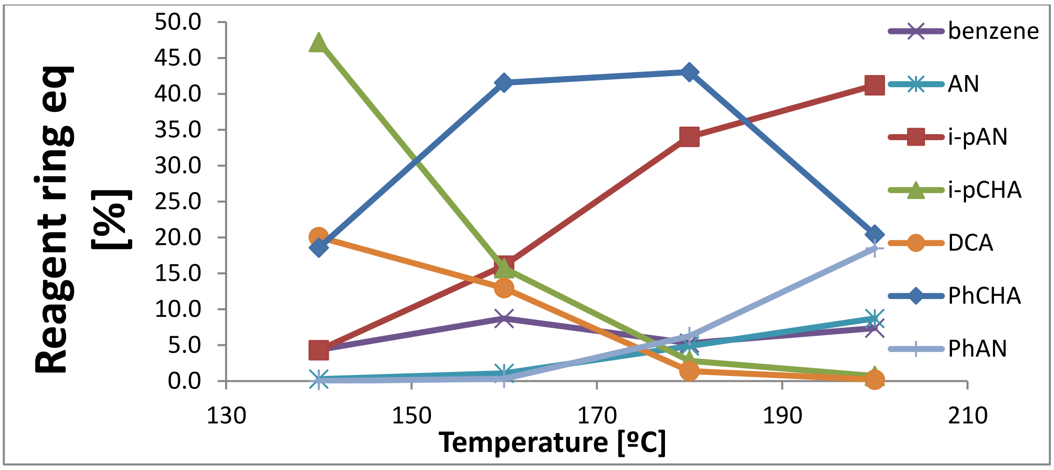


Figure 9. Percentages of the different obtained products are expressed toward rings equivalent of the initial i-pCHA.Pd/C is the catalyst. Reactions have a duration of 180 min. The graph shows similarities with the DCA dehydrogenation (Figure 6). It can be regarded that higher temperatures present the better selectivity, but from the hand of a crescent cleavaging activity.

Dependence on the temperature for the dehydrogenation step of i-pCHA on Pd/C (Figure 9). Percentages are expressed toward rings equivalent of the initial i-pCHA. Several temperatures were tested at the constant time reaction of 180 min. At 140ºC the reaction drives towards some cleavage (4.4 % BZ, 4.0 % CHA) and condensation products (DCA 10 %, PhCHA 9.3 %). Almost none i-pAN has been obtained, just 4.3 %. Half (47.2 %) of the i-pCHA has been transformed. The reaction starts working towards the desired product at 160ºC, but without more selectivity: 84.3 % of the i-pCHA has been transformed mostly towards PhCHA (41.5 %) and DCA (12.9 %), but also towards i-pAN (16.1 %), BZ (8.7 %) and CHA (2.1 %). AN makes it first appearance with a 1.1 mol %. At 180ºC the situation changes following the previous tendency, except for PhCHA, which concentration remains similar than before (43 %). Almost all the reagent has been consumed (97.2 %), yielding a 34 % of i-pAN, 1.4 % of DCA, 6.3 % of PhAN, 4.9 % of AN, 0.7 % of CHA and 5.3 % of BZ. At 200ºC the most concentration of i-pAN is obtained (41.2 %). Reagent consumption has been achieved (99.3 %). Condensation products amount has diminished (0.2 % of DCA, 20.4 % of PhCHA) towards their most dehydrogenated version, PhAN (18.5 %). Cleavage products distribution is as follows: 7.4 % of BZ, 0.3 % of CHA and 8.7 % of AN. It seems that at higher temperatures, dehydrogenation (for all the possible rings) predominates for Pd/C. Then, at 200ºC it is obtained the most dehydrogenated products, either for the cleavage products, either for the condensation ones (Scheme 5). At 180ºC, the competence between the dehydrogenation and the other possible reaction paths is maintained on a similar level., Therefore, it is obtained some PhCHA but some PhAN and any DCA. At 160ºC, condensation process have the most weight, nevertheless there is some yield towards i-pAN. At 140ºC cleavage (hydrogenolysis) and condensation processes are the most important comparing it with dehydrogenation, but not with high yield regarding the reagent concentration.. Two options can be handled. 180ºC is not going to give the best results in terms of pure yield, but it probably will avoid the cleavage products which will appear working at 200ºC.

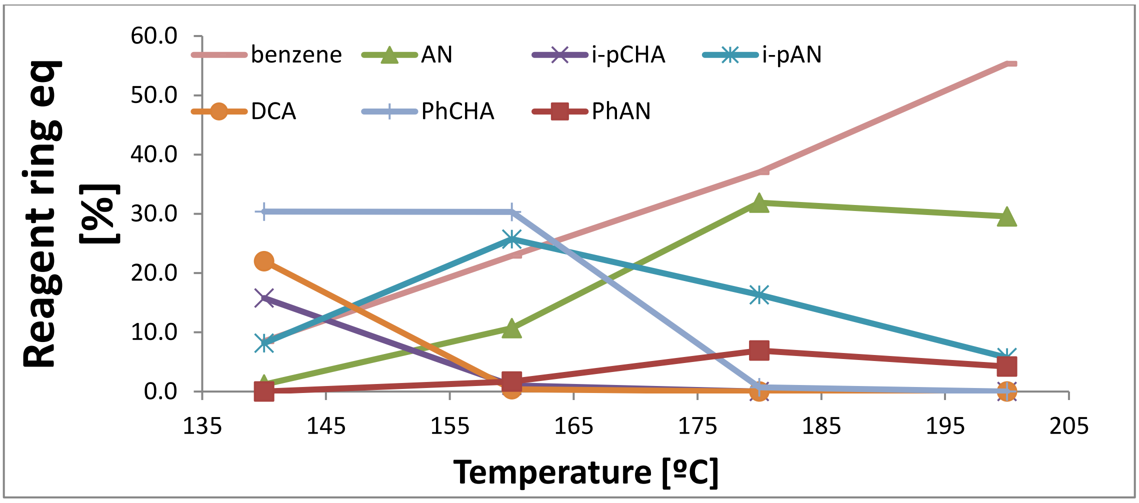


Figure 10. Reagent ring equivalents (%)of the different obtained products on the dehydrogenation of i-pCHA with Pt/C as a catalyst. Reactions were stopped after a course of 180 min. Graph is very similar to the DCA dehydrogenation (Figure 7). It can clearly be seen the high cleavage activity in every temperature, but the highest yield towards the dehydrogenated product was found at 160ºC.

Dependence on the temperature for the dehydrogenation step of i-pCHA on Pt/C (Figure 10). Several temperatures were tested at the constant time reaction of 180 min. At 140ºC cleavage process has more importance than for Pd/C (8.5 % BZ, 4.7 % CHA), and similar weight for condensation process (DCA 22 %, PhCHA 30.4 %). Some i-pAN has been obtained, 8.2 %. An important (84.2 %) amount of the i-pCHA has been transformed. The reaction shows some desired product at 160ºC, but with less selectivity: 98.9 % of the i-pCHA has been transformed mostly towards i-pAN (25.7 %), but cleavage path gains importance: BZ (22.9 %) and AN (10.7 %) amounts grow. PhCHA amount remains constant (30.3 %). At 180ºC the situation boost the cleavage path: BZ (37 %) and AN (31.9 %) lead the different species concentration. All the reagent has been consumed (100 %), yielding just a 16.3 % of i-pAN, 0.4 % of DCA, 6.9 % of PhAN and 0.8 % of PhCHA. At 200ºC the less concentration of i-pAN is obtained (5.7 %). Reagent consumption has been achieved (100 %). Condensation products amount has diminished (0 % of DCA, 0 % of PhCHA, 4.2 % of PhAN). Cleavage products distribution has given most of the weight onto BZ (55.3 %), since AN amount has diminished in comparison (29.5 %) with the 180ºC. As the temperature grows, cleavage path leads the different possible ways for Pt/C. Then, at 200ºC it is obtained mainly cleavage products. At 180ºC, cleavage is still the most important path of the reaction, but there is still some dehydrogenation products. At 160ºC, cleavage and dehydrogenation process are more or less equilibrated, which is traduced in some yield towards i-pAN, BZ and AN. It is obtained some PhCHA, but in not so big amount as the others. At 140ºC none of the process seems to be the main one, but all of them have some representation. Then, as the best temperature for the dehydrogenation process is 160ºC, this is the temperature which will be tested for the different Pd catalysts.

Once it is clear what working temperatures are the best for the two different elements, several reactions should be made to have a global vision of the possibilities all the catalyst can give

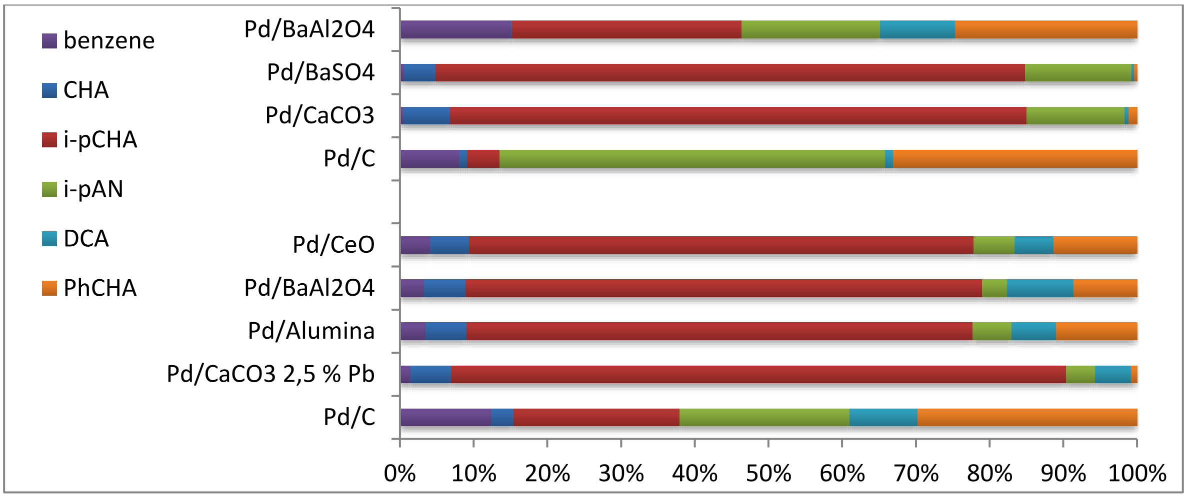


Figure 11. Concentration of iso-propylcyclohexylamine (i-pCHA) dehydrogenation products. Reaction was carried out with different Palladium catalysts during 180 min. First group of reaction was performed at 180ºC. The reactions in the lower block were performed at 160ºC

First, different Pd catalysts were study in order to investigate the selectivity of the dehydrogenation step (Figure 11). Several Pd catalysts were investigated towards the dehydrogenation step, in order to find selectivity towards dehydrogenation avoiding as much as possible side reactions. Some of the catalysts of the first block show good selectivity but low conversion, i.e.Pd/$CaCO_3$ and Pd/$BaSO_4$, which achieved 25.3% and 22.5% of i-pCHA transformation and12.7 % and 14 % yield towards i-pAN, respectively. They also showed some transformation towards CHA (6.1% and 4.2%, respectively). For the other two catalysts in the first data set there can be regarded more variety on compounds: Pd/C achieved higher converison (97.2 % of i-pCHA was transformed)and a higher yield of i-pAN (34 %) was obtained than for Pd/$CaCO_3$ and Pd/$BaSO_4$. Nevertheless, the selectivity was lower, as a yield of 22 % PhCHA and 5 % BZwere obtained. The Pd/BaAl2O4 catalyst obtained a conversion of 78 %, but with high yields towards the side products PhCHA (17.7 %), BZ (10.8 %) and DCA (7.3 %). I-pAN was obtained in 13.5 % yield only, showing the undesired path has more relevance if this catalyst is used. Second row shows not much improvements. Besides, the reactiontemperature is 160 ºC this time, where less activity will be found. Pd/CeO, Pd/BaAl2O4 and Pd/Alumina show very similar results: Around 42 % of the reagent have been transformed towards BZ (APROX 3%), CHA (4.6%),PhCHA and DCA (aprox 14 % of the double ring product derivates), and just an approximate 3-5 % of the desired product was obtained. Pd/CaCO3 poisoned with Pb (2.5 %) catalyst showed worst results if possible, with a 4.6 % of DCA, 5.2 % of CHA and 1.3 % of BZ obtained, straight from a total 22.4 % of i-pCHA converted, to just yield a final 3.6 % i-pAN) (%). Pd/C catalyzed reaction offers a good transformation of the reagent (84.3 % conversion), but with low selectivity (16.1 % towards i-pAN). PhCHA was the most product obtained (20.8 %), followed by BZ (8.7 %), DCA (6.5 %) and a little of CHA (2.1 %). This last data, plus the Pd/BaAl2O4, both at 160ºC, compared with the information of the results for both catalysts, from the same reaction at 180ºC, show that temperature plays an important role on the selectivity of the dehydrogenation of the amine. If the contrasted on the two studied temperatures information of Pd/C and Pd/BaAl2O4are extrapolated towards the CeO and Alumina catalysts, it could be said they will give us not enough selectivity. Therefore, the best catalysts to carry on with the research are, quite clearly, the Pd/CaCO3 and Pd/BaSO4. Albeit the conversion is rather low, but the high selectivity combined with the possibility of performing the reaction for longer times and higher temperatures to increase the conversion is promising.

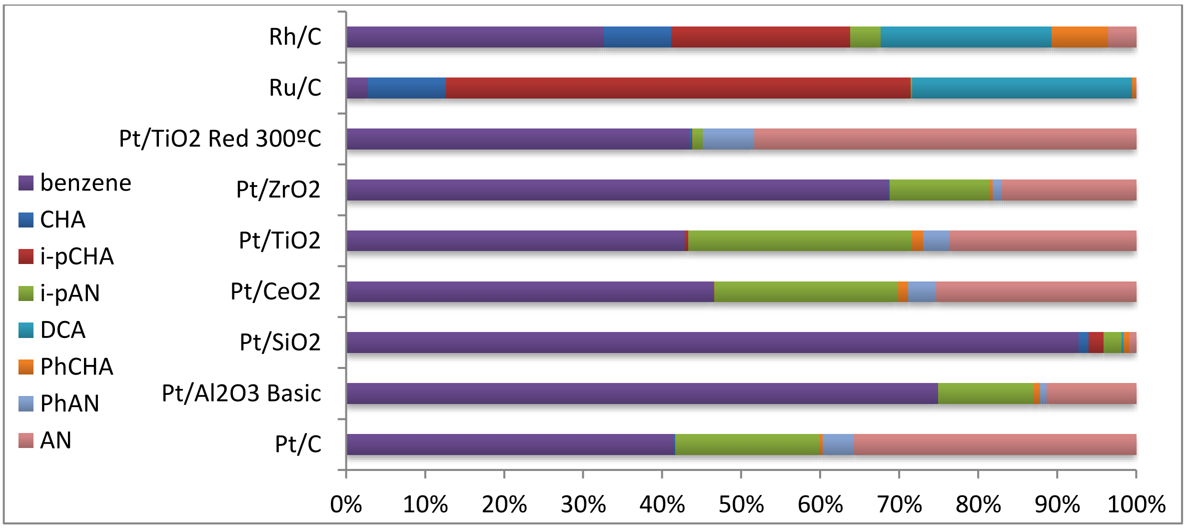


Figure 12. Rh/C, Ru/C and several Pt catalysts dehydrogenation of i-pCHA. Normalized concentrations. All the reactions were carried on at 180 ºC during 180 mins. Rh/C and Ru/C are not very active, neither selective. Rh/C seem to be a very good catalyst towards the DCA formation. Pt catalysts show high activity, but not selectivity on the working conditions. CeO or TiO_2 showed some activity towards the dehydrogenated product but also towards aniline and benzene formation, information which says us some i-propylamine has been also formed. Pt/SiO_2 will turn into an important catalysts in case some N-substituted aniline became the fountain of benzene all around the world. Pt/C presented some activity towards the dehydrogenated product, but mostly catalyzes the cleavage of the amine, something to be avoided.

Different selectivity of Rh/C, Ru/C and different Pt catalysts for dehydrogenation step was catched sight (Figure 12). The less active is Ru/C, with a reagent transformation of 58.5 %. It transformed the i-pCHA mainly in DCA (19.6 %), some CHA (6.3 %) and a little of BZ (2 %). After it, Rh/C was the catalyst with less reagent transformation achieved (83.3 %), mainly towards cleavage products, vice BZ (24.1 %), some CHA (6.3 %) and a little of AN (2.6 %) . It was also observed side reaction products: 15.9 % of DCA plus 5.3 % of PhCHA. I-pAN amount obtained was derisory (2.8 %). Regarding Pt catalysts, all of them present high activity (The catalyst with less i-pCHAwas Pt/SiO2, with a 98.2 % of transformation), with low selectivity. On decreasing order of i-pAN yield: Pt/TiO2 (25.4 %), Pt/CeO2 (21.1 %), Pt/C (16.3 %), Pt/ZrO2 (11.8 %), Pt/Al2O3 (11.3 %), Pt /SiO2 (2.1 %) and Pt/TiO2 Red 300ºC (1.1 %). All of them had important cleavage activity, mainly towards BZ (38.4 %, 42.1 %, 37 %, 63.8 %, 70.3 %, 85.7 % and 36.1 %, respectively) and AN (21.2 %, 22.9 %, 31.9 %, 15.8 %, 10.6 %, 0.8 % and 40 % respectively). Just in three of them Cyclohexane concentration wasn't >3.5 %, vice Pt/C (4.9 %), Pt /SiO2 (5.8 %) and Pt/TiO2 Red 300ºC (9.7 %). Remarkable is the Pt/SiO2 example. It has mainly transformed all the reagent into BZ, property which would turn it into an worldly important catalyst if some day N-aliphatic substituted anilines became the only BZ fountain. As it is also the catalyst which most cyclohexane has yield, could be two options for the mechanism: First happens the cleavage of the amine towards cyclohexane plus then the cyclohexane dehydrogenation towards BZ or first happens the dehydrogenation of the secondary amine which will be cleaved later. As there is much more cyclohexane than i-pAN, I would say first option is most important. Also Pt/TiO2 Red 300ºC had an interesting little yield towards PhAN (5.4 %) and a similar yield towards BZ and AN (36.1 % and 40 % respectively). It could be interpreted that the mechanism in this catalyst works as it follows: First it forms the diaromatic compound, releasing either the propane, the iso-propylamine, or the di-iso-propylamine, for then later divide them almost stoichiometrically. Nevertheless, this is jus an hypothesis.

Therefore, some of this catalysts could be tested on lower temperatures in order to regard if the cleavage activity is being reduced towards more selective paths. Also research cannot avoid testing higher temperatures for the Pd catalyst, whose high selectivity at lower temperatures seem promising.

Therefore, none of this lasts catalysts are important to the goal to be achieved. Research has to continue testing higher temperatures on the Pd high selective catalysts, vice Pd/CaCO3 and Pd/BaSO4

Once observed general properties, research was carried on specific catalysts at less temperature in some of the Pt catalysts, to regard if the cleavage was diminished, and higher temperatures for the palladium chosen, to regard if the selectivity its maintained with higher transformation, but with the same reaction times.

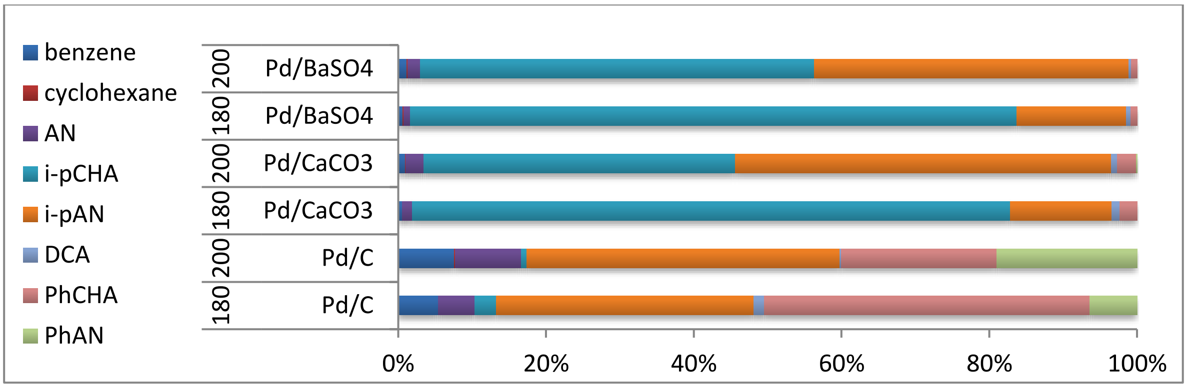


Figure 13. Dehydrogenation of i-pCHA carried out by Pd catalysts. Reaction time was fixed on 180 min. A new temperature was tested (200ºC) in order to compare the reaction yield with previous obtained data of the same reaction at lower temperature (Figure 11). Correspondent temperature is written down in the column to the left of the catalyst name. As it can be seen, the selectivity has been maintained on a satisfactory way rising the temperature, also the transformation has been increased. Pd/CaCO3 and Pd/BaSO4 raised it activity towards the desired product with the temperature, which means that with longer times, higher dehydrogenation will be achieved (Figure 14)(Figure 15).

Tested Pd catalysts showed a good behaviour in selectivity towards i-pAN with not enough yield (Figure 11) towards the desired N-substituted aniline, and it was thought higher temperatures could improve it. In this way, dehydrogenation of i-pCHA on more appropriate conditions were studied (Figure 13) due to the comparisons obtained with some of the previous experiments with DCA (Figure 6). Figure 13 shows that the Pd/C experiment (Figure 9) was extrapolable towards the other two Pd catalysts. Thus, i-pAN concentration arose with the temperature on an important proportion. Results for Pd/BaSO4 were not as promising for Pd/CaCO3. The i-pCHA consumption grew since 22.5 % towards 47.5 % and since 25.3 % towards 58.6 % respectively. Due to the selectivity for these two catalyst are really effective, this reagent consumption is almost directly traduced on an upgrowth of the i-pAN concentration. For Pd/$BaSO_4$ it grew since 14 % towards 41.9 %, and for Pd/$CaCO_3$ it grew since 12.7 % towards 49.9 %, data respectively expressed for the 180ºC and 200ºC experiments. None of the other compounds showed overpassed 2.5 % for these remarked catalysts and temperatures, except for CHA in the 180ºC experiments, with 6.1 % in the Pd/CaCO3 catalyzed reaction, and 4.2 % in the Pd/$BaSO_4$ one. Pd/C catalyzed experiments also showed an increase in the dehydrogenated product concentration proportional to temperature, since 34 % in the 180ºC experiment, towards 41.2 % in the 200ºC experiment. Nevertheless, this increase was also regarded for the cleavaging and side reactions activity: Increments on different products are enumerated: 5.3 % to 7.4 %(BZ), 6.3 % to 18.5 %(PhAN), 4.9 to 8.7% (AN). The only side product which concentration diminished was PhCHA, since 43.8 % to 20.4 %. Reagent consumption was higher in the 200ºC experiment : 99.3 % versus 97.2 %.

With these data, it is manifest the study must continue with the Pd selective catalysts. Next variable to be explored on the dehydrogenation step of the i-pCHA was time, in order to regard if yield towards a selective dehydrogenation could be achieved. The experiments will be performed on the best temperatures and catalysts that previous experiment showed. (Figure 14)(Figure 15)(**Figure** 16)

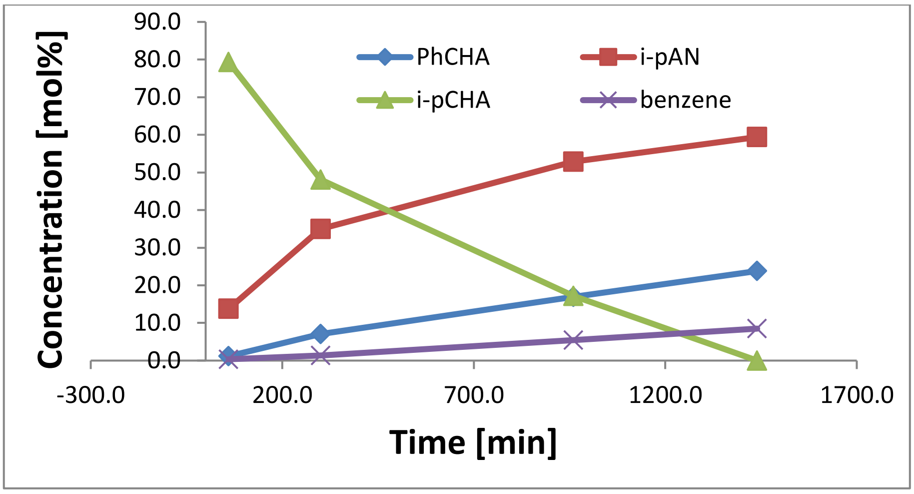


Figure 14. Kinetics of the dehydrogenation of i-pCHA at 200ºC on Pd/CaCO$_3$. As it can be seen, the longer the time of reaction, the more products are obtained, predominantly the dehydrogenation one. Rest of the compounds haven't been showed because they weren't superior to 3 % in any case.

I-pCHA dehydrogenation kinetics. The reaction was carried out with Pd/CaCO$_3$ as catalyst (Figure 14). First point was obtained after 60 min of reaction. There, low amount of reagent had been consumed (just 20.6 %) towards its dehydrogenated analogue (13.7 % of i-pAN), a tiny amount of BZ (0.4 %) and PhCHA (1.2 %). In the second kinetic point (300 min) the reaction has advanced: Half of the i-pCHA (51.9 %) has reacted mainly towards i-pAN (35 %). BZ amount grows shyly (1.4%) than the condensation product PhCHA (7 %). Third kinetic point (960 min) shows an advanced state of the reaction. A good amount of the i-pCHA (82.8 %) has been converted into i-pAN (52.8 %). BZ amount grows slowly (5.4 %), not as PhCHA, which reaches an amount of 16.9 %. In the last point, taken at 1440 min, thermodynamic equilibrium could be aproximated. All the i-pCHA has been consumed (100 %), with a high yield towards i-pAN (59.4 %). BZ continues impasive with its slow growth and achieves an amount of 8.5 %. Last, PhCHA has reached an amount of 23.8 %. The difference between this and the point before shows that condensation in comparison with dehydrogenation has been favoured in relative terms. I-pAN amount has increased in 6.8 % points, and PhCHA 6.9 % points, but as PhCHA starts since a more little position, in relative terms its amount has been more increased. Said in other words, if a process want to purify the dehydrogenated product, and the condensate one is hard to remove from the mixture, it will be worthier to stop the reaction at 960 min and purify our product in easier conditions than try to achieve a major amount , because this little difference is not enough as if to invest more effort into the almost twofold purifying problem. Anyways, this is not the case.

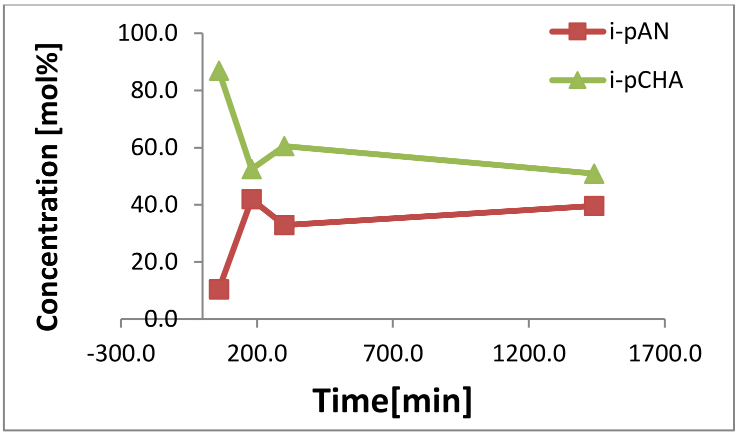


Figure 15. Kinetics of the dehydrogenation of i-pCHA at 200ºC on Pd/BaSO$_4$. It can be seen an strange slope for the second and third point, consequence of the experimental mistake. Anyways, the last point shows the thermodynamic of the reaction, and can be interpreted that the catalyst get poisoned at some point. The other compounds haven't been showed due to they don't get over 2.2% in any case.

I-pCHA dehydrogenation kinetics. The reaction was carried out with Pd/BaSO$_4$ as catalyst (Figure 15). First point was obtained after 60 min of reaction. There, low amount of reagent had been consumed (just 13.2 %) towards its dehydrogenated analogue (10.5 % of i-pAN), and derisory amounts of BZ (0.3 %), cyclohexane (0.2 %), AN (0.6 %) and PhCHA (0.3 %). In the second kinetic point (180 min) the reaction has advanced: Half of the i-pCHA (47.5 %) has reacted mainly towards i-pAN (41.9 %). BZ amount grows shyly (1.1%) than the condensation product PhCHA (0.8 %). Third kinetic point (300 min) is contradictory with the one before. It can't be certainly know who of them are wrong. This is due to the experimental error. Anyways, it could be said that is approximately the same. I-pCHA (39.5 %) has been converted into i-pAN (32.9 %). In the last point, taken at 1440 min, thermodynamic equilibrium could be aproximated. Half of the i-pCHA has been consumed (49.1 %), with most of the yield towards i-pAN (39.7 %). BZ continues impasive with its slow growth and achieves an amount of 2.1 %. Last, PhCHA has reached an amount of 2 %. The little amounts of any side reaction products (from cleavage or condensation) shows that Pd/BaSO$_4$ is quite selective towards dehydrogenation only. Nevertheless, it gets poisoned, at least, after three hours of reaction, which in the end limits its activity towards the dehydrogenation until approximately 40 % of yield. If we compare both catalysts it is evident that Pd/BaSO$_4$ reaches quickly a high conversion, also it doesn't present any side products. Nevertheless, at some point it gets poisoned, avoiding the reaction to continue until higher yields, problem that Pd/CaCO$_3$ doesn't present. The main problem of Pd/CaCO$_3$ is that, as it doesn't become poisoned, also doesn't avoid side reaction paths. In this way, the dehydrogenation product concentration grows with time, but also accompanied by side reaction products. Now it is know how do these catalysts behave in the specific step of dehydrogenation. Few more experiments on these two catalyst for the complete reaction have to be improved, in order to have more information in which be based to decide which of the two present better properties.

4.3 Application of the obtained knowledge towards the higher yields

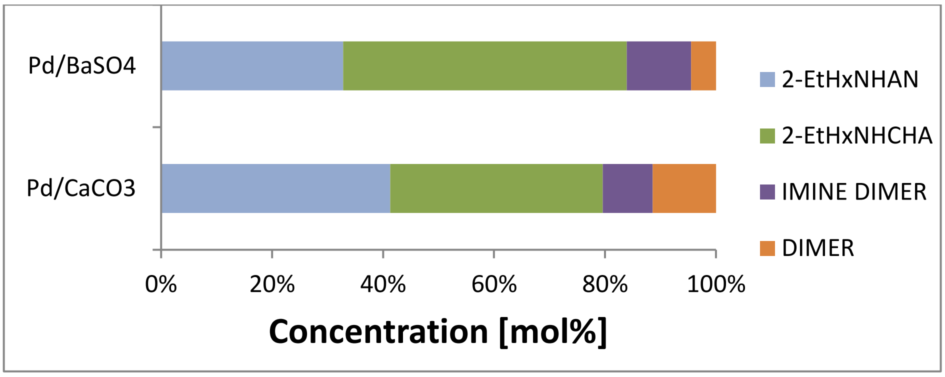


Figure 16. Relative concentrations of the products obtained the reaction between 1 eq. of PhOH and 1.4 eq. of 2-ethyl-1-hexylamine (2-EtHxNH). The percentages of the reagents have been taken into account as 100 % for the PhOH and an additional 140 % for the amine. The reaction was catalyzed with Pd/BaSO$_4$ and Pd/CaCO$_3$ respectively. H$_2$ was used as reductant at the pressure of 0.125 bar. Reactions were carried out at 140ºC during 300 mins. It hasn't been showed respective reagents concentration in the graph in order to make more visible the different products proportion, due to not much transformation was achieved: 25.6 % and 40.6 % (from 100%) transformation was reached for phenol, respectively, whereas 25.8 % and 46.4 % (from 140 %) transformation was reached for the amine.

Comparison of the Pd/BaSO$_4$ and Pd/CaCO$_3$ activities on the reaction between 1 eq. of PhOH and 1.4 eq. of 2-ethyl-1-hexylamine (2-EtHxNH) towards N-(2-ethyl-1-hexyl)-aniline (2-EtHxNHAN) and/or N-(2-ethyl-1-hexyl)-cyclohexylamine (2-EtHxNHCHA) . As the important information to be shown was the products concentration, reagents hasn't been included in the (Figure 16), just because the transformation hasn't been really high. If they would have been included, the graph would have been coloured just by the reagents counterfactual colours. Nevertheless, it has been enough transformation to have meaningful information: 25.6 % and 40.6 % (from 100%) transformation was reached for phenol, respectively, whereas 25.8 % and 46.4 % (from 140 %) transformation was reached for the 2-EtHxNH amine. That first data, not showed in the graph, confirms that Pd/CaCO$_3$ catalyst have more activity. Regarding the products concentration for Pd/BaSO$_4$ in decreasing order: 2-EtHxNHCHA (14.3 %), 2-EtHxNHAN (9.2 %), IMINE DIMER (3.2 %) and DIMER (1.2 %). Compared with the concentrations obtained in the Pd/CaCO$_3$ catalyzed reaction [2-EtHxNHCHA (17.7 %), 2-EtHxNHAN (19.1 %), IMINE DIMER (4.2 %) and DIMER (5.3 %)] it is evident that this last catalyst presents quite more better yields, the same for the desired products (aliphatic cyclohexylamine/aniline) as for the no desired ones (dimer/ imine dimer).

A couple of experiments (2 H2 bar, 60 min, 140ºC, same catalysts and reagents proportions as in (Figure 16) didn't show any reagent transformation (almost 2-3 %), so it didn't make sense to plot them but just comment them, in order to know that in such conditions almost none reaction occurs

5 GENERAL CONCLUSION

According to the objectives outlined in the beginning of the thesis, the reaction of phenol with primary amines was investigated. Using a one pot hydrogenation, dehydrogenation strategy, where cyclohexanone was formed as intermediate, it is possible to successfully realize the synthesis of N-substituted anilines.

It was found that the dehydrogenated/hydrogenated products ratio could be controlled with the hydrogen pressure. Also it was investigated the activity of different catalyst supported on carbon towards the dehydrogenation of dicyclohexylamine. Just Pd/C and Pt/C showed high activity, first mainly towards dehydrogenation, the second mainly towards hydrogenolysis. Any activity was found for Rh/C and Ru/C. After this, it was studied the temperature effect for first two named catalysts. Pt showed anincreasingtendency to hydrogenolysis with temperature, and Pd/C showed aincreasing selectivity towards dehydrogenation with temperature, either towards PhCHA or PhAN. Effect on time was studied for Pd/C, and it was observed a kinetics in cascade for the mechanism step. First DCA was quickly transformed into PhCHA, which was transformed into PhAN, mainly, but also into hydrogenolysis products.

After this, research on the selectivity of the dehydrogenation step was studied. For this, a few catalysts were investigated.i-pCHA was used as reagent, due to its easy hydrogenolysis towards benzene and/or aniline. First, several temperatures were studied using reference catalysts (Pd/C and Pt/C) togain a general understanding of the effect of temperature for the different catalysts and investigate at which side-reactions are prevalent at which temperature. It was found high temperatures for Pd/C, and low temperatures for Pt/C were most suitable. Then, several dehydrogenation reactions were tested for different catalysts. Results showed that using Pt catalysts, hydrogenolysis was the predominant path, whereas for Pd ones high selectivity was achieved on the working conditions. The best Palladium catalysts were Pd/$CaCO_3$ and Pd/$BaSO_4$.

Last, these two catalysts were used to study the complete reaction between phenol and 2-ethyl-1-hexylamine, instead of cyclohexylamine in the beginning. With two reactions it was observed that Pd/$CaCO_3$showed higher activity towards the formation of the N-substituted aniline/cyclohexylamine.

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