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Hydrogenation of Nitrobenzene over a Pd/Al₂O₃ Catalyst – Mechanism and Effect of the Main Operating Conditions

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The catalytic hydrogenation of nitrobenzene (NB) was studied in a three-phase basket reactor with a commercial Pd/Al₂O₃ sample as catalyst. The kinetic experiments allowed a better understanding of the mechanism behind the formation of aniline (ANL) and by-products, a topic not yet well comprehended. The effect of some operating conditions was studied and the existence of more by-products than mentioned in the literature was stated; specifically, benzene formation was verified. Both the reaction kinetics and selectivity were found to be strongly dependent on the temperature, while the effect of total pressure is not that pronounced. Moreover, the high selectivity of the catalyst used in the present work was proved, and as such the deep hydrogenation of ANL to form by-products only occurs in considerable extension when the NB concentration in the reaction mixture becomes negligible.

Introduction

The catalytic hydrogenation of nitrobenzene (NB) is an important industrial reaction used in the commercial production of aniline (ANL) that is in turn a major intermediate in the polyurethane industry. ANL is mainly consumed in the production of methylene diphenyldiisocyanate (MDI) [1].

ANL production can be carried out in gaseous or in liquid phase [2]. For the vapor phase reaction, fluidized- and fixed- bed reactors are used, typically at temperatures of 200 °C to 400 °C and pressures in the range of 1–10 bar, whereas for the liquid phase the common reactor used is a slurry reactor operating in the temperature range of 100–300 °C and at pressures between 1.5 and 22 bar [3–8]. The choice of the catalyst to be used will depend on the type of reactor and also on the possibility of being poisoned by nitro compounds. For instance, it was detected that in the case of Ni-based catalysts the presence of a large excess of NB may cause some kind of inhibition since NB will be adsorbed preferentially on the most active sites and consequently only a few sites remain available to promote the hydrogenation reaction [2].

At industrial scale, for the reaction in liquid phase the main catalysts reported are based on

noble metals like Pd, Pt, and Ru [5, 6]. Nevertheless, many studies have already been made, in order to obtain the best catalyst for this reaction (Tab. 1).

Although there is a large volume of literature available describing this reaction, there is not much information about the reaction mechanism itself. This mechanism is complex and can be divided into two main steps: the first one is the formation of ANL and the second one is the production of secondary products from the deep hydrogenation of ANL.

The first step was explained by the mechanism for ANL formation through NB hydrogenation that was first proposed by Haber in 1898 [20]. However, this mechanism does not fully explain all the experimental results. Consequently, more studies were done, and another mechanism was proposed by Wisniak and Klein [21] that is slightly more complicated than the Haber's one. Some years later, Gelder et al. [22] suggested that the number of steps involved in ANL formation was higher and substantially different from those previously reported.

There is more information available for the mechanism of ANL production than for the formation of secondary products in the second step. Nagata et al. [23] proposed a mechanism to explain the formation of some of these compounds (Fig. 1 a). However, this mechanism does not include the formation of cyclohexanol (CHOL) and dicyclohexylamine (DICHA) that are observed in experimental tests carried out by several authors and also in those performed in the present work.

In 1995, Narayanan et al. [10] identified the following reaction products: cyclohexane (CH), cyclohexylamine (CHA), DICHA, and *N*-phenylcyclohexylamine (NPCHA). They observed that in the case of supported nickel catalysts, depending upon the conditions of the experiment and catalyst metal content, products such as CHA and DICHA are formed. In a latter article, Narayanan and Unnikrishnan [24] compared the catalytic properties of Co/Al₂O₃ and Ni/Al₂O₃ materials. It was concluded that by increasing the contact time of ANL, the conversion increased and CHA and NPCHA were the two major products. CHA formation was slightly favored at short contact time and NPCHA was formed in roughly similar amounts at all contact times. However, under long contact times, DICHA (DCHA in their notation) and CH were also formed. Based on these results they proposed the mechanism for the formation of secondary products as indicated in Fig. 1 b.

In 2008, Relvas [25], using a Ni catalyst, proposed another mechanism based on the one of Nagata et al. [23]. For this proposal, several laboratorial tests were made to study operating condition effects. DICHA and CHOL (through cyclohexanone (CHONA) hydrogenation) were included in the proposed mechanism (Fig. 1 c) since they were detected in the experimental tests, as well as *N*-cyclohexylaniline (CHANIL) and cyclohexyldeneaniline (CHENO). Nevertheless, as recognized by Relvas [25], this mechanism does not fully explain the formation of all secondary products in NB hydrogenation. So, further work in this topic is still required.

Summarizing, the information available in the literature about the overall reaction mechanism involved in the NB hydrogenation is not sufficient. It is important to mention that the knowledge and understanding of this mechanism has implications for both catalyst and reactor design. Consequently, the present study has the objective of trying to determine all the compounds obtained from this reaction, and also the overall mechanism that may explain both the formation of ANL and secondary products during NB hydrogenation. The experiments were performed using a Pd-based catalyst and under different experimental

conditions.

2 Materials and Methods

Hydrogenation of NB in liquid phase was carried out in a 1-L Parr batch reactor provided with an air-impelled stirrer to promote appropriate mixing and gas distribution during the experiments. The stirrer was equipped with a basket, where the catalyst was placed. The catalyst used was a commercial 1 wt % Pd/Al₂O₃ material in spherical form with a diameter of 2–4 mm.

A known amount of Pd/Al₂O₃ catalyst was loaded into the reactor. The material was pretreated in situ as described in the Supporting Information. NB was charged in a vessel connected to the reactor and subsequently pushed into the reactor by using a high-pressure hydrogen stream; cf. Fig. S1 in the Supporting Information. The procedures used in the catalytic studies and in the analyses along the reaction time were the same as described by Relvas et al. [2] and are summarized in the Supporting Information. The reference values for temperature, pressure, and NB concentration during the parametric study are $T = 150\text{ }^{\circ}\text{C}$, $P = 14\text{ barg}$, and $C_{\text{ref}} = 10\text{ wt\% NB}$ (100 000 ppm), respectively. The experiments performed and the conditions used are given in Tab. 2. Test B12 was carried out only with ANL in order to study the formation of secondary products. The catalyst-to-liquid volume ratio was in all cases 80.0 g L^{-1} .

The concentration of all compounds is presented as a relative dimensionless value that was calculated as follows:

$$C_i = \frac{C_{i,t} \text{ (ppm)}}{C_{\text{ref}} \text{ (ppm)}} \quad (1)$$

where C_i is the dimensionless concentration of component i , $C_{i,t}$ is the concentration of component i at time t , and C_{ref} stands for the NB reference concentration.

3 Results and Discussion

In order to better understand the mechanism for the formation of aniline and secondary products in the reaction of NB hydrogenation, experiments were done in batch mode where the influence of NB initial concentration, temperature, and pressure was studied in detail. The liquid phase analysis confirmed the presence of the following products: NB, ANL, CHA, CHOL, CHONA, CHANIL, DICHA, CHENO, and benzene (Bz); cf. nomenclature list at the end of the paper. Relatively to the carbon mass balance, all the compounds identified allowed to close the balance within the analytical uncertainty ($\pm 6\%$).

Some tests were performed under the same operating conditions, namely, 10 wt % NB, 14 barg, and $150\text{ }^{\circ}\text{C}$, which allowed for confirming the reproducibility of the experiments (data not shown). It was also concluded that the catalyst is stable during the runs made and within the conditions studied.

A comparison between tests B4 and B12 as indicated in Fig. S2 of the Supporting Information, clearly confirms that the formation of secondary products, i.e., sum of all species other than ANL, only begins to occur in a considerable extension after the significant

decrease of NB concentration in the reaction mixture, ca. 90–100 min, although both NB and ANL were initially loaded into the reactor (run B4). On the other hand, if there is initially only ANL (run B12) in the reactor, the formation of secondary products starts from the beginning of the reaction. So, when the NB is also present in the reactor, this formation will be delayed and only happens when the NB concentration becomes very small, which means that this catalyst is very selective for NB hydrogenation.

3.1 Influence of Initial Nitrobenzene Concentration

Tests B4 (10 wt % NB), B7 (30 wt % NB), and B11 (3 wt % NB) were realized under the same operating conditions, 150 °C and 14 barg, and only the NB concentration was varied, cf. Tab. 2 and Fig. 2. Comparing the three tests, it is observed especially in the case of CHONA (Fig. 2 d) that in the beginning of the reaction the concentration is higher when the NB concentration is 30 wt %, unlike what is observed for the other compounds where the concentration is very similar even for high NB concentrations.

According to the mechanism illustrated in Fig. 1 c, CHA, CHANIL, and DICHA are formed from ANL hydrogenation, which was also observed by Nagata et al. [23], although they did not identify the formation of DICHA. The results obtained are thus in agreement with Relvas's mechanism; for short reaction times, their concentration is small but when the NB concentration starts to decrease along each experiment, which means an increase of ANL concentration and high NB conversion (see also Fig. 1 c), their concentration also becomes higher; this is particularly noticeable for CHA and CHANIL, as demonstrated in Fig. 2 because DICHA is a final hydrogenation product. CHENO shows a similar trend but its formation is anticipated by another route; cf. Fig. 1 c.

As indicated in Fig. 3 a, at the beginning of the reaction the ANL concentration decreases due to the entrance of NB in the reactor. Then, NB starts to convert mainly into ANL and consequently its concentration increases steadily, the hydrogenation of NB being the preferential reaction, thus confirming the selectivity of the catalyst used in this reaction. In fact, ANL hydrogenation is verified mostly when the NB concentration inside the reactor is quite low. Although this is not very clear in these tests because the runs were stopped before the hydrogenation of ANL becomes the preferential reaction, in other tests a subsequent decrease of ANL concentration is clearly seen, e.g., in Fig. 8 e, at higher temperatures.

Narayanan and Unnikrishnan [24] observed under vapor phase conditions the formation of cyclohexane (CH) and ammonia (NH₃) through hydrogenolysis of CHA at 250 °C. In the current case, CHA conversion was not observed in some additional studies that were done (data not shown for brevity), and CH was not detected. This could mean that CH and DICHA are not formed from CHA conversion as it was proposed by those authors, but from ANL hydrogenation as it is proposed by Nagata *et al.* [23] and Relvas [25]. Nevertheless, Bz was herein identified and quantified. To the authors' knowledge, the quantification of Bz obtained as a by-product is not referred nor presented in any other previous studies. The presence of Bz and also of NH₃, which was detected during sample collection, could be related to the hydrodenitrogenation of ANL.

Fig. 4 demonstrates the time evolution of the total of secondary products formed, i.e.,

excluding ANL, for the three runs as well as the NB concentration. Analyzing this figure, it is observed that the total of secondary products exhibits in general a greater increase when the NB concentration starts decreasing significantly, and so it can be concluded that their formation is mostly due to the ANL hydrogenation reaction. This can be also related with the adsorption affinity because NB adsorbs much easier on the catalyst surface than ANL. Moreover, it is seen that in general the higher the initial concentration of NB, the higher is the formation of secondary products, although the maximum in their concentration is shifted towards longer reaction times. The reason is that a longer reaction time is required to reduce the NB to a low level for increasingly initial loads of this reactant in the reactor.

In the results of NB consumption, illustrated in Fig. 4 and as will be shown below, it is noteworthy that the maximum expectable value of its concentration is never reached because the compound is not inside the reactor at the initial instant as detailed in the experimental/ Supporting Information section. Consequently, when it is loaded into the reactor, there is immediately a consumption of NB and so the maximum expectable concentration is not achieved, e.g., C_{NB}/C_{ref} of 3 for run B7 is not reached, neither C_{NB}/C_{ref} of 1 for run B4, etc.

Fig. 5 presents the same results as the ones in Fig. 2, but in this case the species concentrations are represented as a function of the dimensionless NB concentration. Thus, it is possible to confirm and better understand the discussion above and also to compare the results at the same level of NB concentration. The results should be analyzed taking into account that the evolution of the reaction time is done from the right to the left, which corresponds to the decrease of NB concentration. Consequently, it is observed that the secondary products are formed in greater quantities when the NB concentration is very low. Because ANL is also initially loaded into the reactor (see Supporting Information), this means that the Pd/Al₂O₃ catalyst is selective towards NB hydrogenation, but the undesired reactions become more significant when the NB concentration is very low. Moreover, it is noted that some of the compounds are already present in the reactor at the start of the reaction, which is due to the fact that the ANL used, namely, industrial-grade ANL, contains already traces of secondary products. It is finally noted that, in general, the amount of secondary products formed is increased for higher initial NB concentrations: run B7 30 wt % NB > run B4 10 wt % NB > run B11 3 wt % NB.

3.2 Influence of Pressure

The tests in this section were performed at the same temperature, 150 °C, and with the same initial concentration of nitro- benzene, 10 wt % NB. The total pressure in the reactor was increased from 14 barg (run B4) by 6 barg (20 barg in run B2) and 16 barg (30 barg in run B3). Pressure variation is due to the increase of hydrogen pressure; so there will be more hydrogen in the gas phase and also solubilized in the reaction mixture. Fig. 6 presents the results obtained as a function of the reaction time. It is noticed that Bz formation is almost independent of the total pressure (Fig. 6 a). For the other secondary products, it seems that for higher pressures higher quantities of these compounds are obtained, although this effect varies from product to product. Even so, the effect of pressure on the total formation of secondary products is not very pronounced (Fig. 7 b).

Since these by-products are mostly formed after ANL formation/NB complete consumption (Fig. 7), it is concluded that the results obtained are in agreement with Relvas' [25] mechanism. Moreover, at the same reaction time and when the pressure is higher, the NB concentration is lower and, consequently, the ANL concentration rises. Therefore, ANL hydrogenation will be favored and the concentration of the secondary products will increase sooner, as indicated in Fig. 7. Although for higher pressures it seems that more secondary products are formed, the effect of an increase in pressure from 20 to 30 barg is less significant.

The influence of pressure is also visible in the reaction rate. When the total pressure in the reactor rises, there is also an increase in the reaction rate and consequently, NB is consumed in a shorter period of time and the ANL concentration will increase more rapidly.

Fig. S3 of the Supporting Information presents the same data but as a function of the dimensionless NB concentration.

3.3 Influence of Temperature

The influence of temperature – runs B4 (150 °C), B9 (180 °C), B10 (210 °C), and B5 (240 °C) – was also studied at the same pressure, 14 barg, and initial NB concentration, 10 wt %. It was concluded that temperature is the parameter with greater influence in the production of secondary products, as shown below (Fig. 8 and Fig. S4 of the Supporting Information).

Fig. 8 presents the results obtained in these experiments, showing the concentration of by-products and ANL as a function of the reaction time. Concentration profiles show the same trend for all the tests; indeed, it is possible to see that for higher temperatures the concentration of secondary products increases in the order 240 °C > 210 °C > 180 °C > 150 °C.

Bz belongs to the compounds that seem to be more influenced by temperature variation. In the temperature range of 150–210 °C, the concentration profiles obtained are similar to those shown above. While at lower temperatures Bz is detected only in small amounts, at 240 °C, when the dimensionless NB concentration is < 0.012 (after ca. 1 h), its concentration starts to increase considerably (Fig. 8 a) which had not been observed before. Some tests of ANL hydrogenation, which were performed at different operational conditions (data not shown), confirmed the Bz formation from ANL and that its concentration is higher when the conditions are more severe, namely the temperature; see also Fig. S4 of the Supporting Information.

In the case of CHA, DICHA, and CHANIL, it is shown that when the temperature rises, there is an increase in their concentration when the NB concentration is low (high conversion). As it was observed in the tests with pressure variation, in the first hour of reaction the concentration profile is described by a plateau. This plateau corresponds to the period when NB is present in high quantities and when the conversion of NB into ANL mainly takes place. After that period, although the NB conversion still proceeds, ANL hydrogenation becomes more pronounced and, consequently, the concentration of secondary products increases. This reaction, ANL hydrogenation, starts to be more important with higher temperature.

Both CHONA and CHENO generally present concentration profiles similar to the compounds discussed above, but at the end of the reaction their concentration seems to start to stabilize,

reaching a plateau as indicated in Figs. 8 d and 8 g. For CHOL, similar profiles are anticipated; however, longer reaction times are probably required to observe such a pattern.

In relation to NB, there is, effectively, an important growth of the rate of the hydrogenation reaction with the temperature increase, which means that for higher temperatures the same NB conversion is achieved in much less time, as shown in Fig. 9.

Once more it is noticed that the concentration of secondary products is strongly dependent on the temperature of the reaction (Fig. 9 b). Indeed, the formation of secondary products is tremendously accelerated as a consequence of the exponential temperature effect in the kinetics according to the Arrhenius law. The different activation energies for each reaction in the complex reaction scheme also explain the various effects of temperature in each product formed. For those steps with higher activation energies, reaction rates are more favored for the same increase in the temperature.

Narayanan and Unnikrishnan [24] also studied the influence of temperature on a Co/Al₂O₃ and a Ni/Al₂O₃ catalyst and concluded that with higher temperature the ANL conversion increases over Co/Al₂O₃ but over Ni/Al₂O₃ the increase in temperature reduced the conversion, due to the decrease of the hydrogen adsorption. Besides, they also observed that above a certain temperature, hydrodenitrogenation is favored leading to the formation of CH. In the current case, instead of CH formation, the formation of Bz was observed and the same tendency was noticed, namely, a higher temperature favors the Bz formation; see Fig. 8 a. Relatively to the catalyst herein used, its behavior was similar to the Co/Al₂O₃ one; with higher temperatures the ANL conversion increased.

Analyzing all the results obtained, it can be stated that the obtained data are in general agreement with the results described by Relvas [25], and all compounds mentioned were identified in our experiments. Furthermore, even using a different type of catalyst, Pd in this work vs. Ni in Relvas' work, and different experimental conditions, the mechanism was found to be very similar. Another important issue which is worth mentioning in the results herein presented, is the formation of Bz, which is not considered by Relvas nor by any other authors in the literature, except by Králik et al. [26]; however, the authors did not quantify Bz. Consequently, and reflecting the results obtained, the Bz formation should be considered in the mechanism through the reaction of ANL hydrodenitrogenation, as detailed in Fig. 10.

4 Conclusions

The hydrogenation of NB to ANL over a Pd catalyst was studied. A parametric study was performed in which the effects of the initial NB concentration, temperature, and pressure were tested. It was found that temperature is the parameter with greater influence in the production of secondary products, for the ranges analyzed.

It was also observed that the formation of secondary products is strongly dependent on the concentration of NB in the reaction mixture: their concentration rises more when the NB concentration starts decreasing significantly, or becomes almost negligible, and consequently it can be concluded that the formation of secondary compounds is mostly due to the ANL hydrogenation. This highlights the high selectivity of the used Pd-based catalyst.

Some mechanisms were already proposed in the literature; nevertheless, the one proposed by Relvas, using a Ni/SiO₂ catalyst, is the one that better describes the majority of the experimental results herein obtained for both ANL and formation of secondary products, despite the fact that

a Pd-based catalyst was now used. Furthermore, the formation of Bz was also identified, which was not considered in a quantitative manner by any previous authors in the literature.

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The authors have declared no conflict of interest.

Abbreviations

ANL	aniline
Bz	benzene
CH	cyclohexane
CHA	cyclohexylamine
CHENO	cyclohexyldeneaniline
CHOL	cyclohexanol
CHONA	cyclohexanone
DICHA / DCHA	dicyclohexylamine
MDI	methylenediphenyldiisocyanate
NB	nitrobenzene
NPCHA	<i>N</i> -phenylcyclohexylamine

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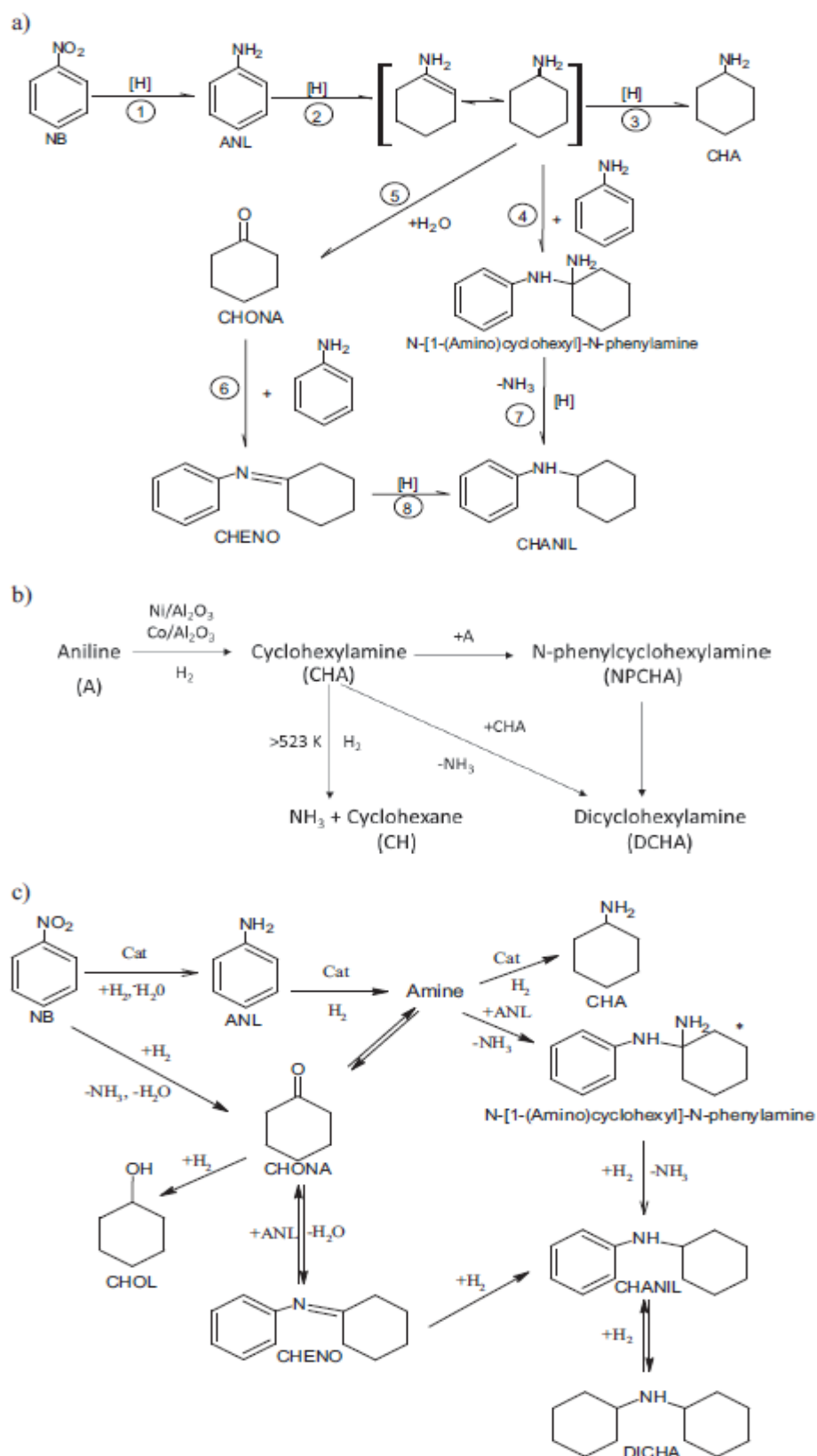


Figure 1. Reaction network for the formation of ANL and secondary products as proposed by (a) Nagata et al. [23]; (b) Narayanan and Unnikrishnan [24]; (c) Relvas [25].

*Very reactive and unstable compound

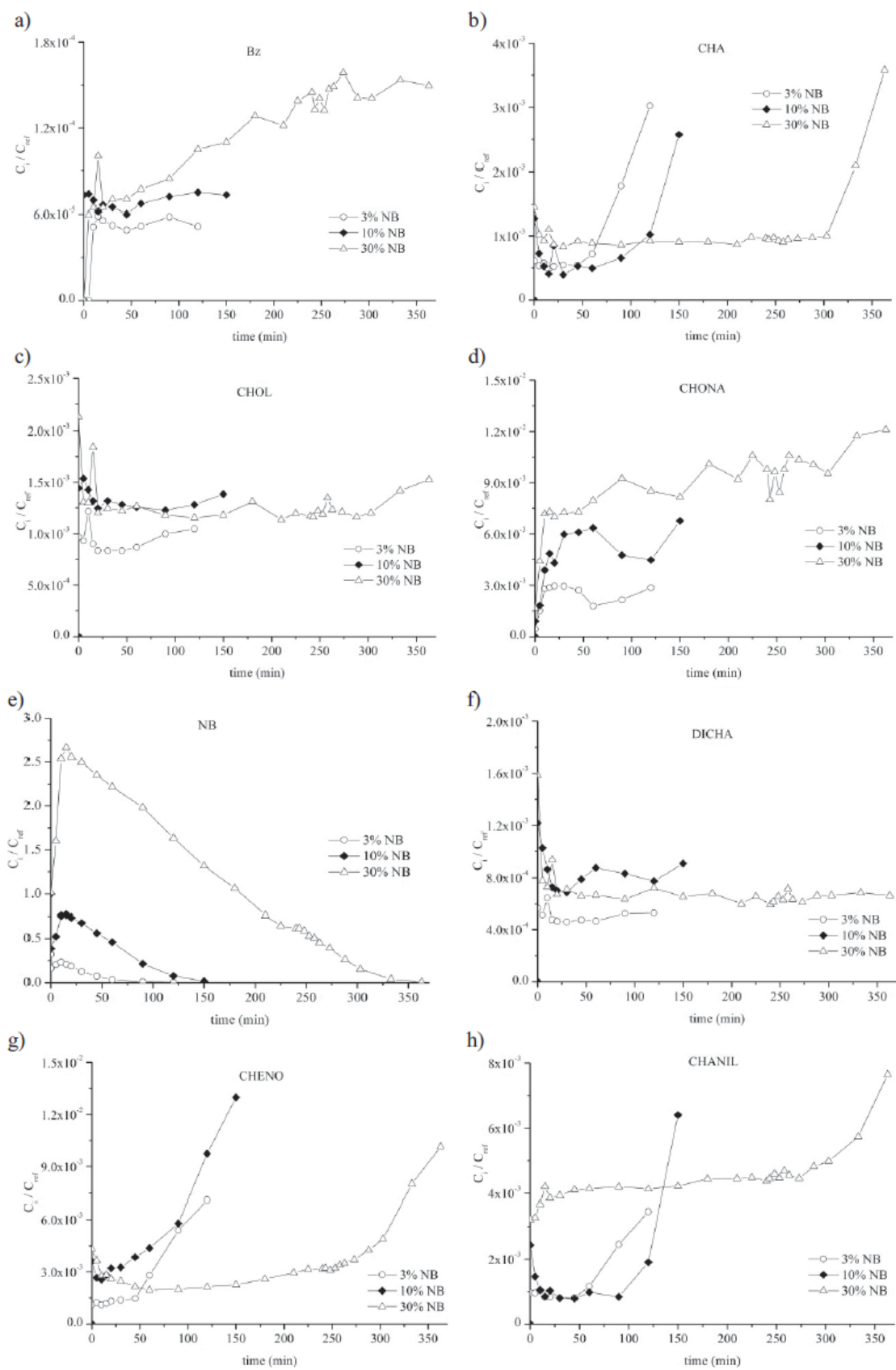


Figure 2. Influence of initial nitrobenzene concentration in the formation of secondary products and NB consumption vs. time; runs B4, B7, and B11.

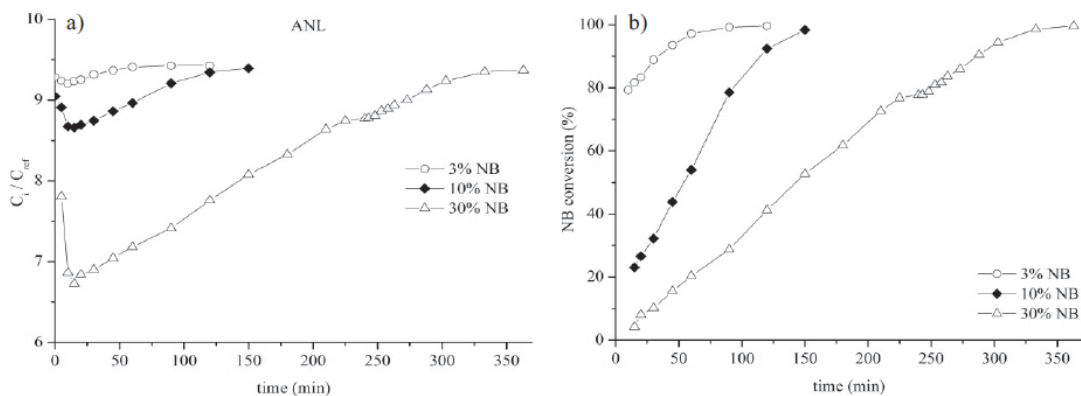


Figure 3. Influence of initial NB concentration in the (a) ANL formation and (b) NB conversion vs. time; runs B4, B7 and B11.

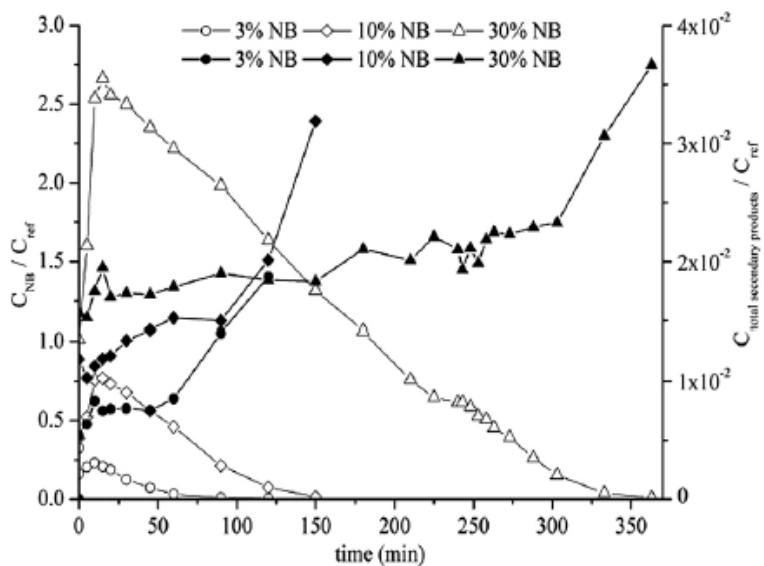


Figure 4. Comparison between total formation of secondary products (closed symbols) and NB consumption (open symbols) as a function of reaction time for different initial NB concentrations; runs B4, B7, and B11.

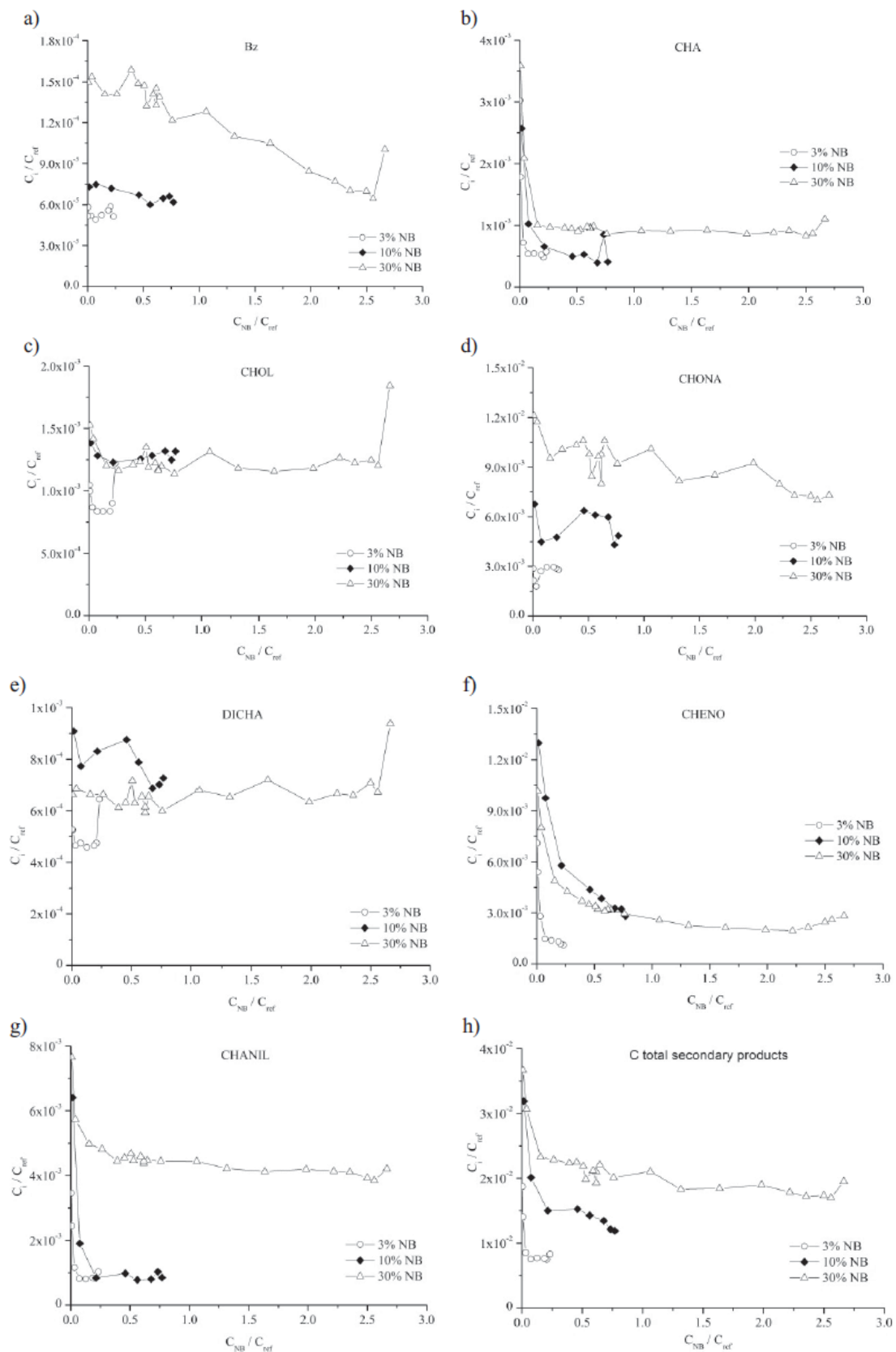


Figure 5. Influence of NB initial concentration in the formation of secondary products; runs B4, B7, and B11.

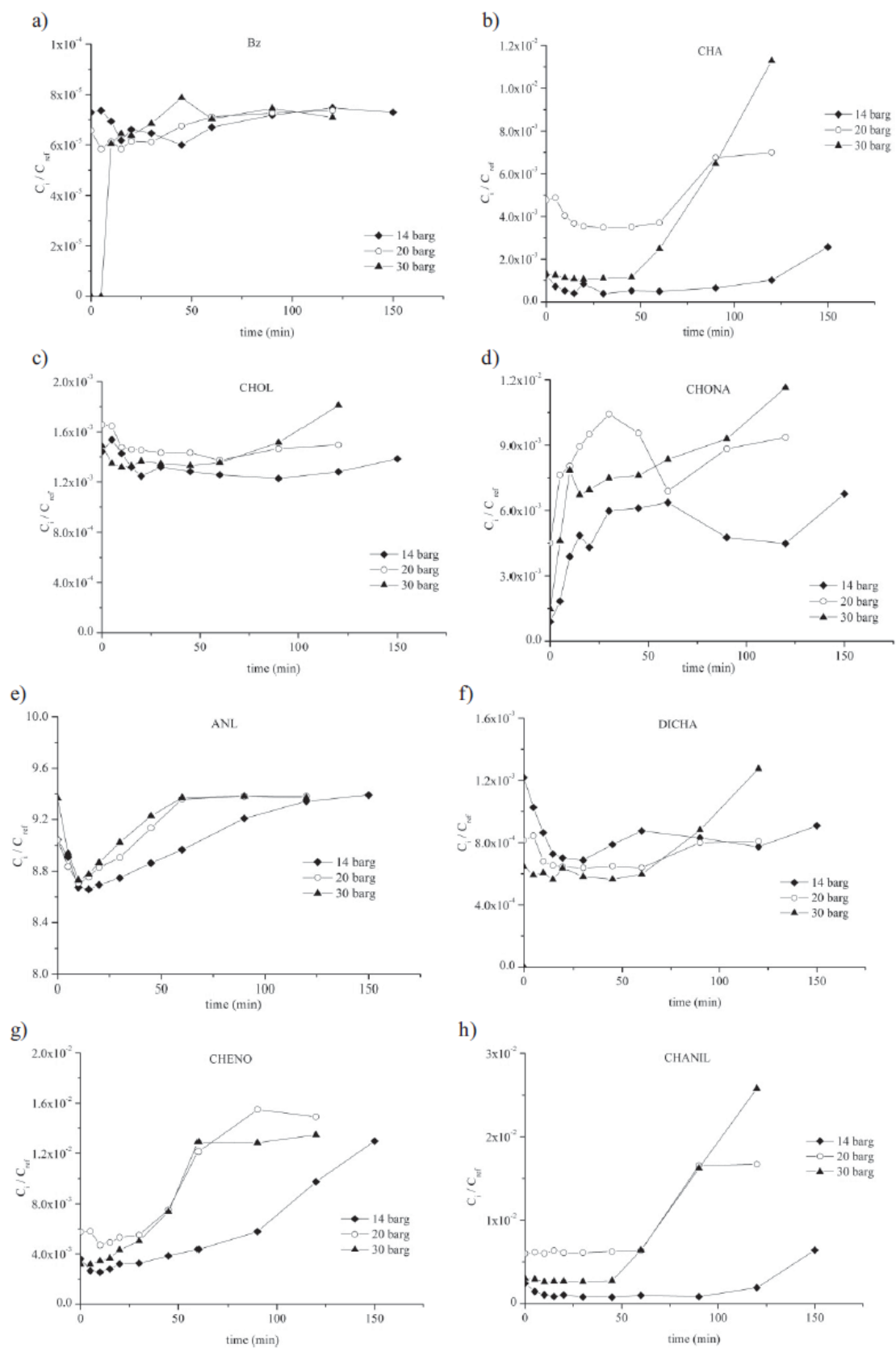


Figure 6. Influence of reaction pressure in the formation of secondary products and ANL vs. time; runs B2, B3, and B4.

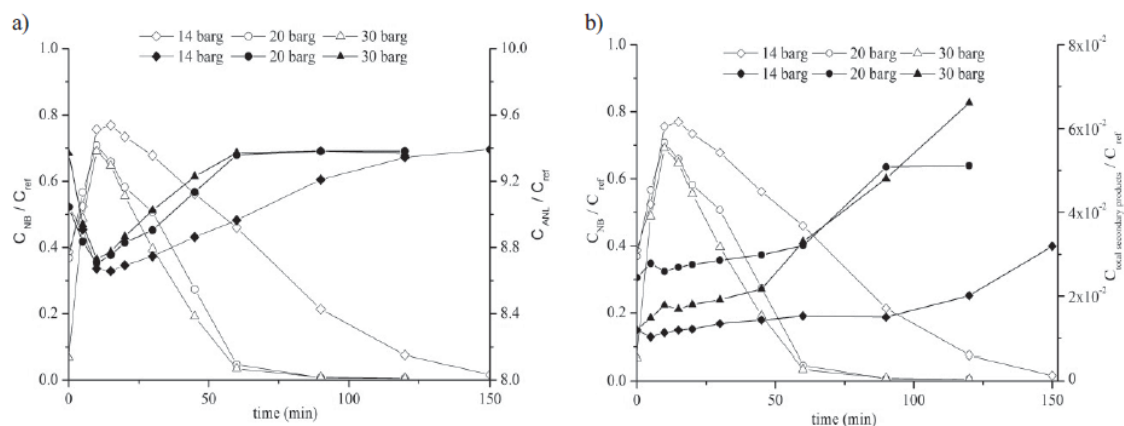
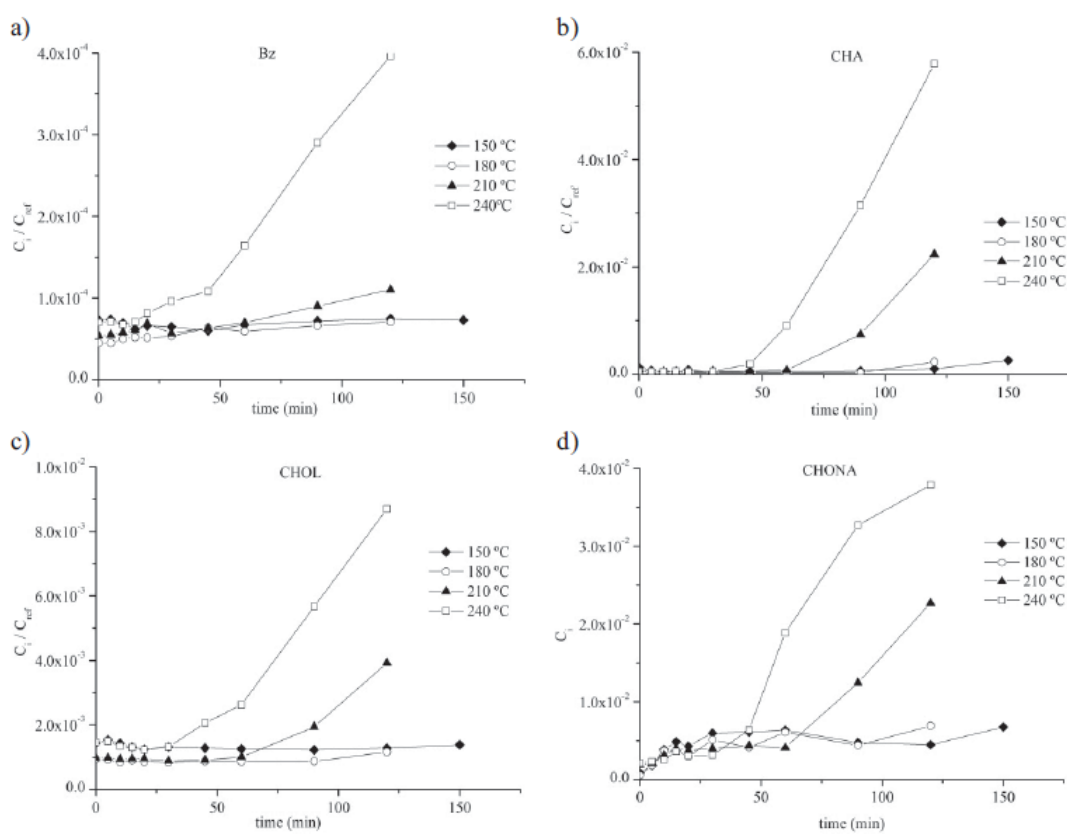


Figure 7. Comparison between (a) ANL formation and (b) total formation of secondary products (closed symbols) and NB consumption (open symbols) as a function of reaction time; runs B2, B4, and B5.



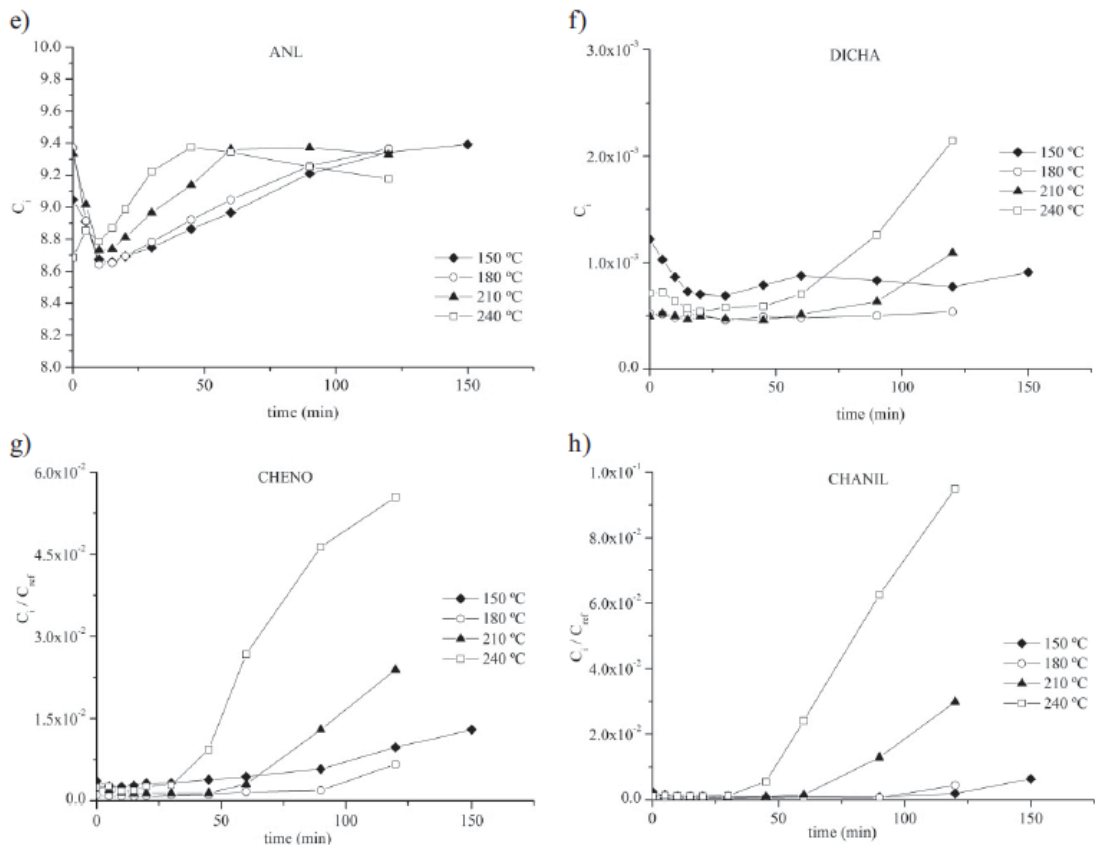


Figure 8. Influence of reaction temperature in the formation of ANL and by-products vs. reaction time; runs B4, B5, B9, and B10.

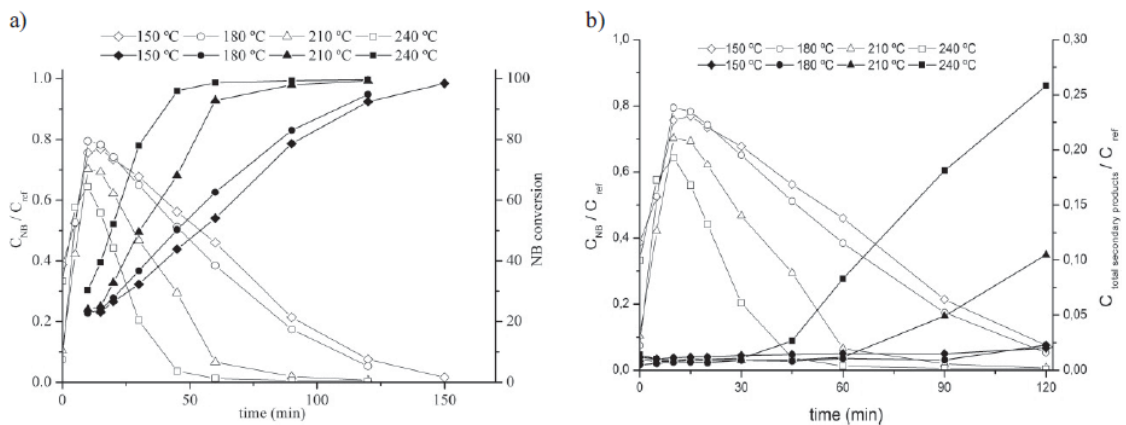


Figure 9. Comparison between (a) NB conversion and (b) total formation of secondary products (closed symbols) and NB consumption (open symbols) as a function of reaction time for different reaction temperatures; runs B4, B5, B9, and B10.

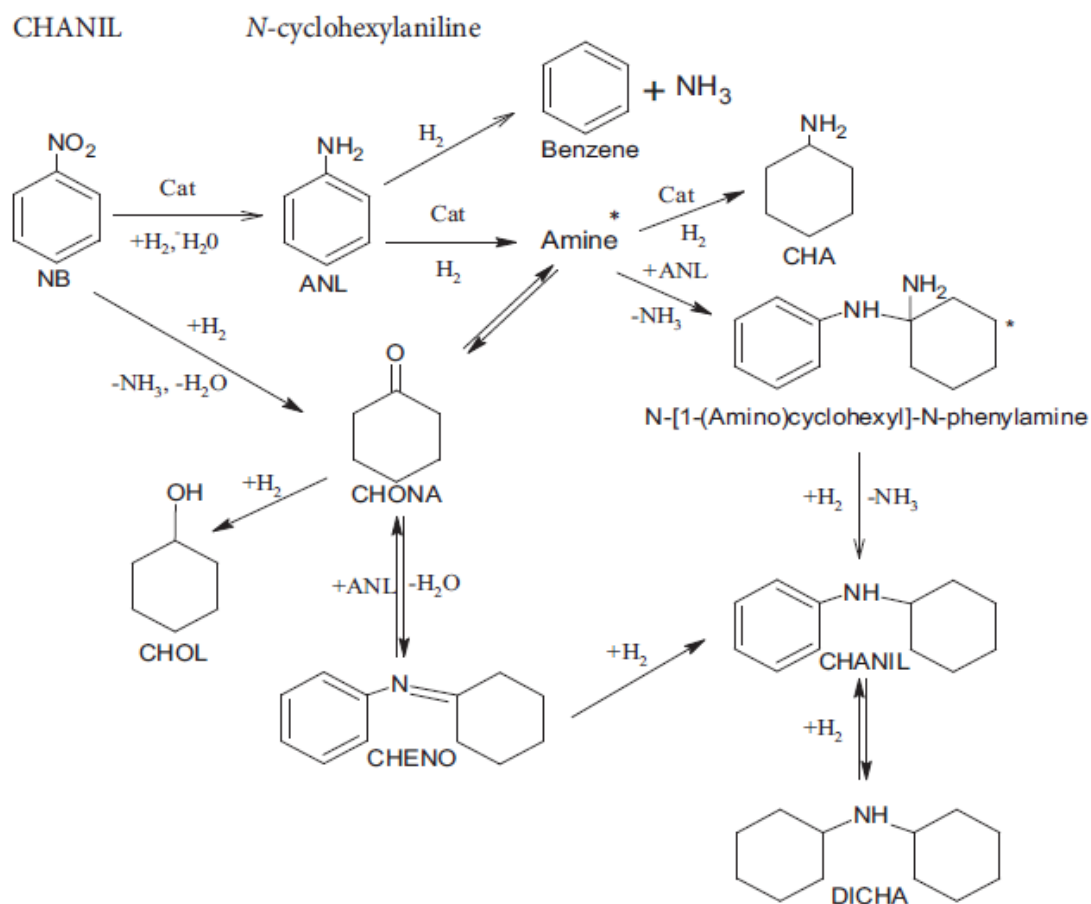


Figure 10. Reaction network proposed for formation of ANL and secondary products including Bz. *Very reactive and unstable compound.

Table 1. Main catalysts studied for NB hydrogenation.

Process type	Catalyst type	Ref.
Vapor phase	Cu-based catalysts	[9]
	Ni-based catalysts	[10, 11]
	Pd-based catalysts	[12, 13]
Liquid phase	Ni-based catalysts	[2]
	Pt-based catalysts	[14, 15]
	Pd-based catalysts	[6, 15–19]

Table 2. Initial conditions of the experiments performed.

Test	Experimental conditions
B1	150 °C, 14 barg, 10 wt % NB
B2	150 °C, 20 barg, 10 wt % NB
B3	150 °C, 30 barg, 10 wt % NB
B4	150 °C, 14 barg, 10 wt % NB
B5	240 °C, 14 barg, 10 wt % NB
B6	150 °C, 14 barg, 10 wt % NB
B7	150 °C, 14 barg, 30 wt % NB
B8	150 °C, 14 barg, 10 wt % NB
B9	180 °C, 14 barg, 10 wt % NB
B10	210 °C, 14 barg, 10 wt % NB
B11	150 °C, 14 barg, 3 wt % NB
B12	150 °C, 14 barg