



Dehydrogenation of dicyclohexylamine in gaseous phase over a nickel catalyst: effect of reaction parameters

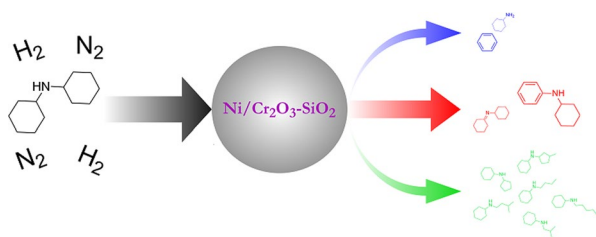
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Abstract

This work deals with a study of the effect of reaction temperature and partial pressure of hydrogen on the product selectivity of the gas-phase dehydrogenation of dicyclohexylamine. Laboratory experiments of dicyclohexylamine dehydrogenation were performed in a glass tubular flow-through reactor with the use of commercial supported nickel $\text{Ni}/\text{Cr}_2\text{O}_3\text{-SiO}_2$ catalyst. The systematic variation in reaction temperature (433–463 K) and partial pressure of hydrogen, i.e. the molar ratio of dicyclohexylamine to H_2 and N_2 (1:0:30–1:15:0), was used to investigate the dehydrogenation of dicyclohexylamine from the perspective of the formation of products. It was confirmed that the major products of dicyclohexylamine dehydrogenation are imine *N*-cyclohexylidencyclohexanamine and aromatic amine *N*-phenylcyclohexylamine, while the latter is the dominant product. The sequential hydrogenolysis reaction of *N*-phenylcyclohexylamine was observed to result in the formation of cyclohexylamine and benzene. Furthermore, a significant increase in the concentration of the other six products was observed. The mass spectrometry detection identified these products as *N*-butylcyclohexanamine, *N*-pentylcyclohexanamine, *N*-isopentylcyclohexanamine, *N*-(2-methylbutyl)cyclohexanamine, *N*-cyclopentylcyclohexanamine, and *N*-(3-methylcyclopentyl)cyclohexanamine. The reaction results in the formation of two dehydrogenation products, which are accompanied by other subsequent reactions, such as hydrogenolysis, isomerization, and cyclization.

Graphical abstract



Keyword Dicyclohexylamine · Dehydrogenation · Hydrogenolysis · Isomerization · Cyclization

Introduction

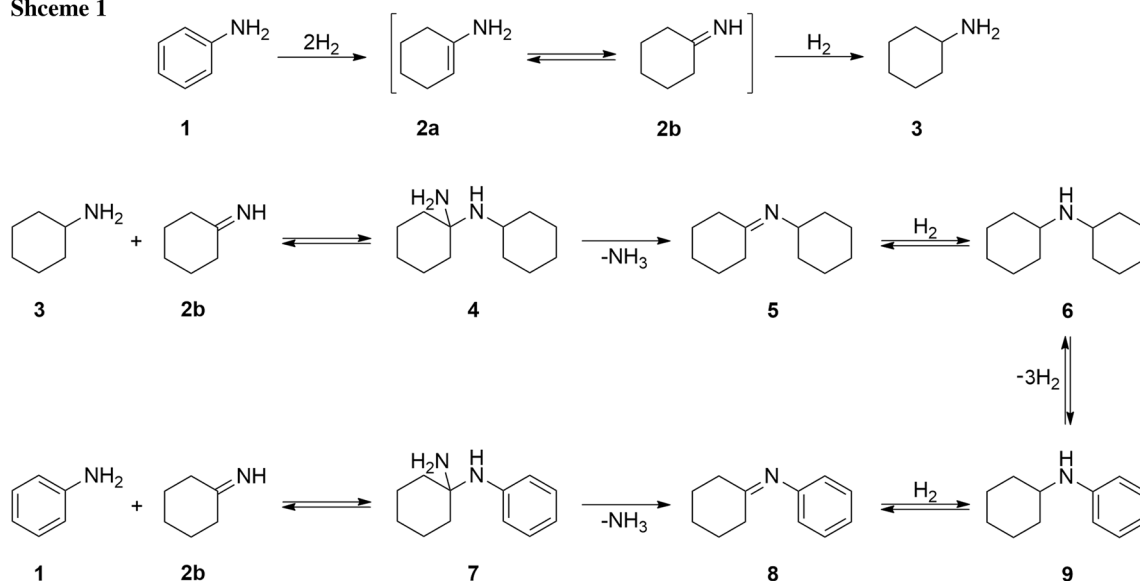
The present study examines the behavior of dicyclohexylamine over a nickel catalyst in the gaseous phase under reaction conditions of 433–463 K and a high molar excess

of hydrogenation gas during which the equilibrium reaction of hydrogenation/dehydrogenation plays an important role. For example, such reaction conditions are used in the industrial production of dicyclohexylamine by gas-phase hydrogenation of aniline or disproportionation of cyclohexylamine over a nickel catalyst [1]. During the hydrogenation of aniline or the disproportionation of cyclohexylamine towards a main product, dicyclohexylamine, undesirable side products are formed from the dehydrogenation of dicyclohexylamine [1]. Dicyclohexylamine is an industrially important chemical, which purity is crucial. The purpose of this research

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Scheme 1



is to determine the effects of reaction conditions (similar to those used in the industrial production of dicyclohexylamine by hydrogenation of aniline or disproportionation of cyclohexylamine) on the subsequent dehydrogenation of dicyclohexylamine, as well as the resulting side reactions.

Due to their high reactivity, amines are important intermediates used for the production of various industrial chemicals and are applied in the areas of medicine, biology, materials, and the environment [2, 3]. Amines are used for the synthesis of agrochemicals, drugs, dyes, pesticides, detergents, lubricants, polymers, and inhibitors that are effective to prevent corrosion due to the adsorption of polar amino group on metal surface [3–5]. One of the most effective organic corrosion inhibitors, i.e. volatile corrosion inhibitors, is dicyclohexylamine and its salts, as well as benzotriazole [6]. Dicyclohexylamine (DCHA) is also used for the production of rubber vulcanization accelerators, textiles, varnishes and metalworking fluids [7, 8]. DCHA is mainly produced by catalytic hydrogenation of aniline over metal catalysts, primarily supported nickel catalysts [9]. The reaction scheme of the hydrogenation of aniline to DCHA can be simplified as follows (see Scheme 1): hydrogenation of aniline (1) to intermediates cyclohex-1-en-1-amine (2a) and cyclohexylideneimine (2b) which are subsequently hydrogenated to cyclohexylamine (CHA, 3). The condensation reaction of intermediate 2b with cyclohexylamine leads to the formation of *N*-cyclohexylcyclohexane-1,1-diamine (4) followed by its hydrogenolysis to *N*-cyclohexylidenecyclohexanamine (5) and hydrogenation to dicyclohexylamine (6). There is also a condensation reaction between aniline and intermediate 2b leading to formation of *N*-phenylcyclohexane-1,1-diamine (7) followed by its hydrogenolysis to

N-cyclohexylidenecyclohexanamine (8) and hydrogenation to *N*-phenylcyclohexylamine (9) [10]. The use of nickel catalysts for the hydrogenation of aniline results in the formation of an equilibrium mixture of CHA (33 wt.%) and DCHA (67 wt.%). It is the result of the subsequent equilibrium disproportionation (condensation) reaction of cyclohexylamine [1]. Other species introduced in Scheme 1 are undesirable side products of the hydrogenation of aniline. The alternative routes for obtaining DCHA as a raw material include the hydrogenation of nitrobenzene over a Pd/C catalyst, the amination of cyclohexanone in a stream of hydrogen over supported nickel catalysts (support: kieselguhr, γ -Al₂O₃, pumice or silica gel) or the hydrogenation of a mixture of aniline and phenol over Pd catalysts [11–13]. Other than the catalytic hydrogenation of aniline, DCHA is now produced by the catalytic disproportionation of cyclohexylamine in a stream of hydrogenation gas over a nickel catalyst at the temperature of 433–473 K [14]. In our previous work, we examined the temperature dependence (433–463 K) of the equilibrium constants of the simultaneous reactions of disproportionation of CHA to the DCHA process. In Scheme 1, it is shown that DCHA undergoes dehydrogenation to *N*-cyclohexylidenecyclohexanamine (NCCCHA) and *N*-phenylcyclohexylamine (NPCHA). The main product of the above-mentioned disproportionation reaction, the DCHA, has been found to undergo dehydrogenation to the aromatic product NPCHA [1].

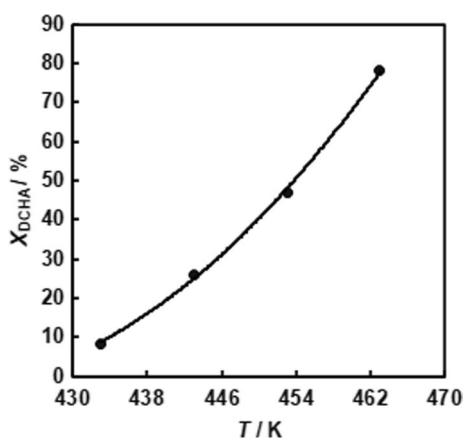


Fig. 1 The effect of reaction temperature on the conversion of DCHA

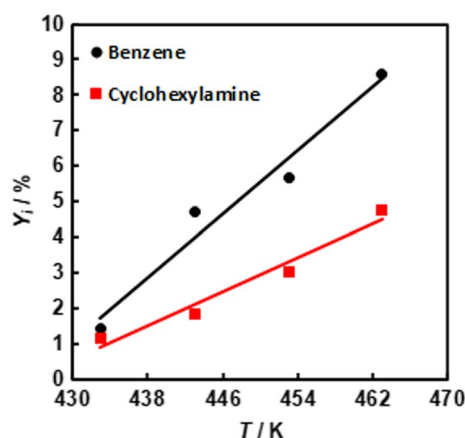


Fig. 3 Benzene and cyclohexylamine reaction yield as a function of reaction temperature

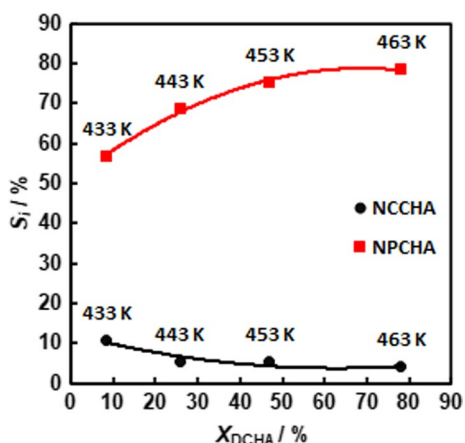


Fig. 2 Relationship between NCCHA and NPCHA reaction selectivity and conversion of DCHA where reaction temperature was varied

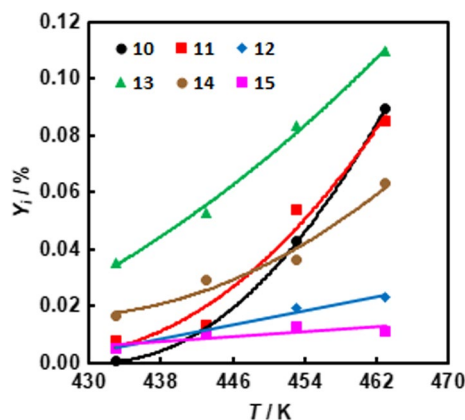


Fig. 4 Reaction yield of more other six products formed during DCHA dehydrogenation as functions of reaction temperature

Results and discussion

The effect of reaction temperature on the reaction selectivity and yield of DCHA dehydrogenation

A variation in the reaction temperature of 433–463 K was carried out at a molar ratio of DCHA/H₂/N₂ of 1:0:30 and feed of DCHA of 15 g h⁻¹. Results are shown in Figs. 1, 2, 3, 4. The temperature-induced enhancement of the selectivity of NPCHA (S_{NPCHA}) compared to the selectivity of NCCHA (S_{NCCHA}) was attributed to a significant difference in the reaction enthalpy of both dehydrogenation reactions of DCHA (diff. of 109.3 kJ mol⁻¹) [1]. The observed increase in yield (Y_i) of both benzene (ca. 8.6% at 463 K) and cyclohexylamine (ca. 4.7% at 463 K) is due to the hydrogenolysis (by hydrogen released in the dehydrogenation of DCHA) of C–C and C–N bonds of NPCHA.

At higher temperatures, the formation of benzene predominated, which could be caused by subsequent hydrogenolysis and dehydrogenation of cyclohexylamine. Figure 4 demonstrates that dehydrogenation of DCHA leads to the formation of six more reaction products. The concentrations of these products are minor (ca. <0.12 mol% at 463 K) compared to both dehydrogenation products NCCHA and especially NPCHA.

The effect of partial pressure of hydrogen on the reaction selectivity and yield of DCHA dehydrogenation

A variation in the partial pressure of hydrogen, i.e. the molar ratio of DCHA/H₂/N₂ of 1:0:30–1:15:0, was carried out at a reaction temperature of 443 K and feed of DCHA of 15 g h⁻¹. The results are presented in Figs. 5, 6, 7, 8. The partial pressure of hydrogen was calculated from the molar ratio of the initial

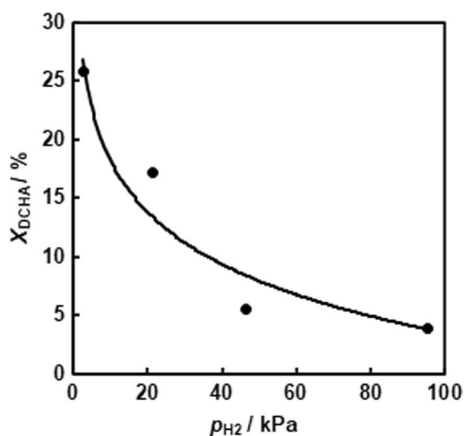


Fig. 5 The effect of partial pressure of hydrogen on the conversion of DCHA

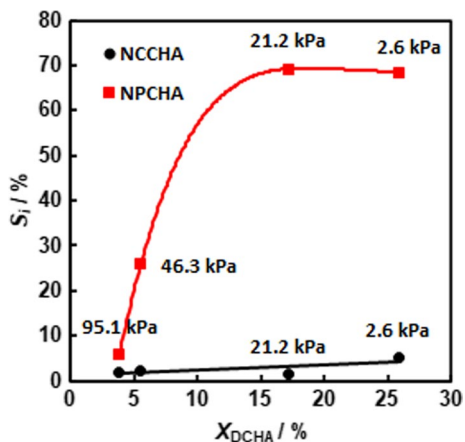


Fig. 6 Relationship between NCCHA and NPCHA reaction selectivity and conversion of DCHA where the partial pressure of hydrogen was varied

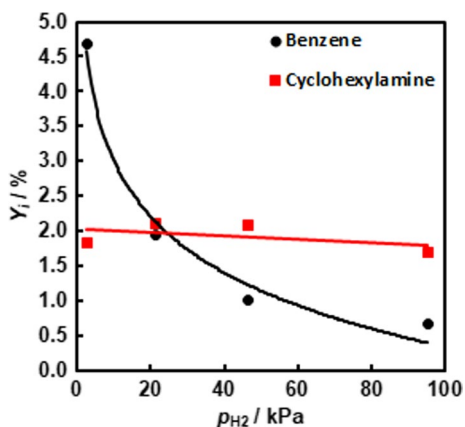


Fig. 7 Benzene and cyclohexylamine reaction yield as a function of partial pressure of hydrogen

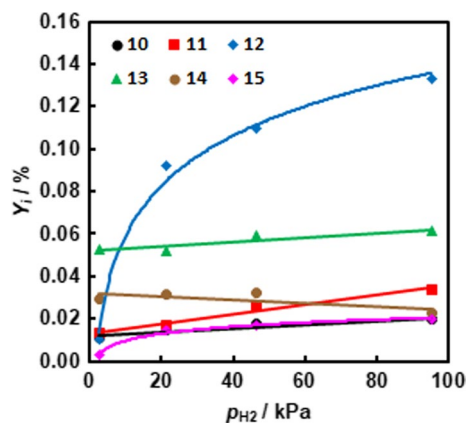


Fig. 8 Reaction yield of more other six products formed during DCHA dehydrogenation as functions of partial pressure of hydrogen

gaseous mixture DCHA-H₂-N₂ and by mass balance based on the fractional conversion of DCHA to NCCHA and NPCHA, i.e. H₂ formed by DCHA dehydrogenation. The partial pressure of hydrogen is decreasing, which has a significant impact on the conversion of DCHA (X_{DCHA}). This shift in thermodynamic equilibrium is due to the increase in the driving force for dehydrogenation reactions, primarily the dehydrogenation of DCHA to NPCHA [15]. The increase in S_{NPCHA} compared to S_{NCCHA} was caused by a change in the stoichiometric number, so dehydrogenation of DCHA to the aromatic product NPCHA is more affected by the change in the partial pressure of hydrogen. When the partial pressure of hydrogen is lowered, the yield of benzene increases (ca. 4.7% at 2.6 kPa) compared to the yield of cyclohexylamine, which is constant in the range of studied partial pressure of H₂ (ca. 1.7–1.8% at 2.6–95.1 kPa). The formation of benzene is affected by the change of partial pressure of hydrogen due to the hydrogenation/dehydrogenation equilibrium, compared to the formation of cyclohexylamine, i.e. hydrogenolysis of C-N bond, which is essentially affected by reaction temperature [16]. Another reason is that hydrogenolysis of the C-N bond is not a reversible reaction, which means that the formation of cyclohexylamine is unaffected by the change in partial pressure of hydrogen. With the exception of product **12**, the partial pressure of hydrogen does not enhance the yield of the other six detected products. It is impossible to exclude that the formation of product **12** is more stable at higher partial pressures of H₂. In contrast to the concentration of NCCHA and especially NPCHA, concentrations of these products are minor (ca. 0.14 mol%).

Identification of other products formed during the DCHA dehydrogenation

The reaction mixtures of the DCHA dehydrogenation were analyzed using GC-FID and GC-MS methods. The GC-FID chromatogram presented in Fig. 9 reveals the presence

of six side products of DCHA dehydrogenation, as well as NCCHA and the main product NPCHA. The MS spectra for the other six products are provided in the Supplementary material of this article. The products were identified as *N*-butylcyclohexanamine (**10**), *N*-pentylcyclohexanamine (**11**), *N*-isopentylcyclohexanamine (**12**), *N*-(2-methylbutyl)cyclohexanamine (**13**), *N*-cyclopentylcyclohexanamine (**14**), and *N*-(3-methylcyclopentyl)cyclohexanamine (**15**).

Both *N*-butylcyclohexanamine and *N*-pentylcyclohexanamine are formed by hydrogenolysis of the C–N bond of the one cyclohexane ring of DCHA. The formed *N*-hexylcyclohexanamine is further transformed into products **10** and **11** by C–C hydrogenolysis of the linear hexyl group. Using a nickel catalyst with acid support (Cr₂O₃-SiO₂) led to the isomerization reaction of both abovementioned *N*-alkylcyclohexanamines, respectively of *N*-pentylcyclohexanamine to *N*-isopentylcyclohexanamine and *N*-(2-methylbutyl)cyclohexanamine. The published kinetic study of the hydrogenolytic cleavage of the C–C bond of cyclohexane over Ir/Al₂O₃ catalysts describes an identical phenomenon [17]. Due to the primary hydrogenolysis, the cyclohexane ring is transformed into linear hexane which undergoes an isomerization reaction giving rise to 2-methylpentane and 3-methylpentane and also secondary hydrogenolysis of hexane leading to the formation of butane, propane, and ethane [17]. It cannot be ruled out that the formation of *N*-cyclopentylcyclohexanamine is the result of the cyclization reaction of *N*-pentylcyclohexanamine. The cyclization of *n*-pentane to cyclopentane over Pt-Au catalysts has been described in the published literature [18]. The last identified side product, *N*-(3-methylcyclopentyl)cyclohexanamine is presumably formed by the C–N cleavage (hydrogenolysis) of one of the cyclohexane rings of the DCHA molecule and subsequent isomerization reaction of the linear hexyl group. The hydroisomerization reaction of *n*-hexane is already active at a temperature of 150 °C and over catalysts with acid active sites, such as zeolites [19]. The above-discussed reactions are demonstrated in Scheme 2.

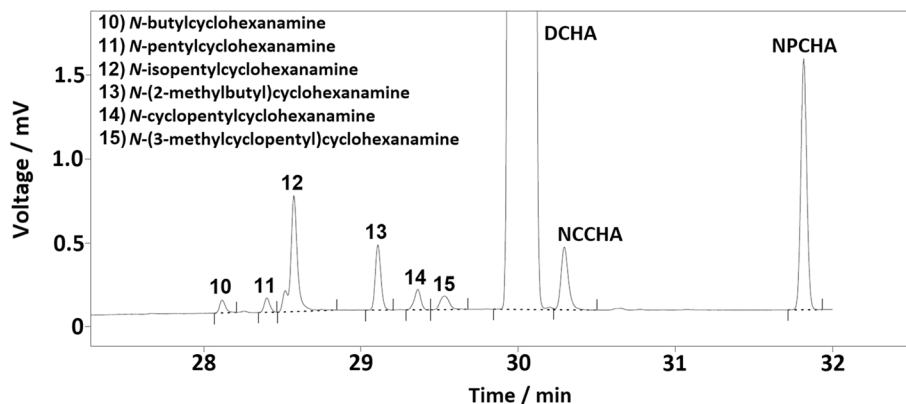
Conclusion

The dehydrogenation of dicyclohexylamine over a commercial Ni/Cr₂O₃-SiO₂ catalyst was investigated at a reaction temperature of 433–463 K and partial pressure of hydrogen of 2.6–95.1 kPa. The formation of the aromatic dehydrogenation product *N*-phenylcyclohexylamine is more dependent on the reaction temperature and partial pressure of hydrogen than the other dehydrogenation product *N*-cyclohexylidene-cyclohexanamine. The increasing reaction temperature and decreasing partial pressure of hydrogen are also factors that influence the formation of benzene. During the dehydrogenation process, dicyclohexylamine undergoes hydrogenolysis and isomerization reactions, which lead to the formation of other products. However, the concentration of these side products in the reaction mixture is less than 0.14 mol%. In conclusion, the industrial production of highly pure dicyclohexylamine by gas-phase hydrogenation of aniline or disproportionation of cyclohexylamine over a nickel catalyst is appropriate to carry out at the reaction temperature of 433 K and the high molar ratio of hydrogen to the organic reactant. The reaction conditions described here are suitable for suppressing consecutive dehydrogenation reactions of the produced dicyclohexylamine and for inhibiting other side reactions of the dicyclohexylamine.

Experimental

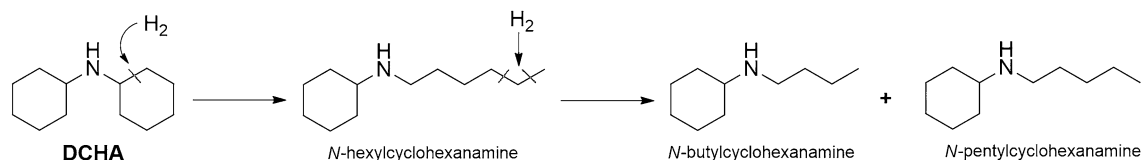
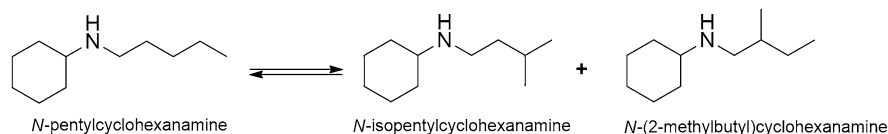
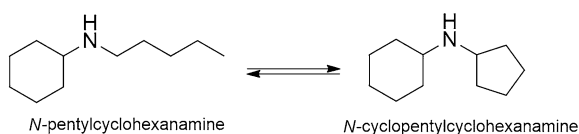
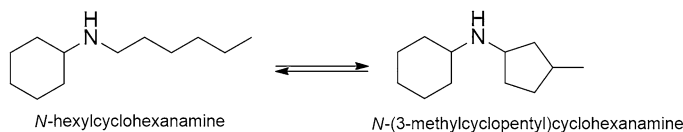
All chemicals have been acquired from commercial suppliers. Reactant DCHA (99.9%) from BorsodChem MCHZ, solvent *N,N*-dimethylformamide (99.9%) from Penta Chemicals. Gas chromatography standards: CHA (99.9%), NCCHA (> 50%) and NPCHA (> 50%) were acquired from BorsodChem MCHZ. Benzene (99.9%) was purchased from Penta Chemicals. The technical gases, electrolytic hydrogen (grade 3.0), nitrogen (grade 4.0), and helium (grade 5.5), were purchased from SIAD Czech spol. Dehydrogenation

Fig. 9 GC-FID chromatogram of the reaction mixture of DCHA dehydrogenation



Scheme 2

(1) Hydrogenolysis of C-N bond and C-C bonds

(2) Acid catalyzed (Ni/Cr₂O₃-SiO₂) isomerization reaction(3) Acid catalyzed (Ni/Cr₂O₃-SiO₂) cyclization reaction(4) Acid catalyzed (Ni/Cr₂O₃-SiO₂) cyclization-isomerization reaction

of DCHA was performed with the use of a commercial supported nickel catalyst Ni/Cr₂O₃-SiO₂ PRICAT Ni 60/15 (from Johnson Matthey Catalysts). Original cylindrical particles of the catalyst were crushed, sieved, and used a fraction of granulate of 1.2 to 3.5 mm.

Apparatus and reaction procedure

The experiments were carried out in the experimental apparatus (see Fig. 10) described in our previous work [20]. From gas cylinders (1, 3) hydrogen and nitrogen were through mass flow controllers (2, 4) fed into the gas mixer (5). Gases were additionally purified (due to a trace amount of O₂ and H₂O) in apparatus filled with copper catalyst, heated to the temperature of 403 K (6), and dried in a column filled with molecular sieve (7). By a piston pump (8), the DCHA (9) was fed into a glass tubular continuous-flow reactor (10). Reactor (of an inner diameter of 12 mm) was placed in a bath of the low-melting alloy Rose's metal (11), which was used as heat transfer. In order to eliminate premature condensation of the gaseous reaction mixture, the outlet tube of the reactor was heated by an infrared lamp (12). The outlet reaction mixture was partially condensed in a Liebig condenser (13) cooled by water (14) and absorbed at temperature -15 to -18 °C into a freeze trap filled with solvent

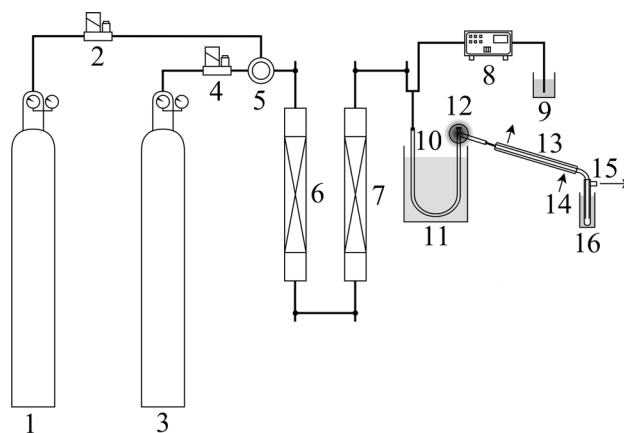


Fig. 10 Experimental apparatus for the catalytic dehydrogenation of dicyclohexylamine in gaseous phase

N,N-dimethylformamide (15) placed in a bath filled with a mixture of ethanol-dry ice (16). Waste gases (eg. H₂, N₂) were disposed of. The samples of the reaction mixture were analyzed using the gas chromatographic method.

The dehydrogenation of DCHA was carried out at the reaction temperature range of 433–463 K, atmospheric pressure, molar ratio of DCHA/H₂/N₂ of 1:0:30–1:15:0 and feed of DCHA of 15 g h⁻¹ over 27.5 g of Ni/

Cr₂O₃-SiO₂ catalyst (1.2–3.5 mm). The selected reaction conditions for the dehydrogenation of DCHA were similar to those for the hydrogenation of aniline or disproportionation of CHA [1]. The granulate of nickel catalyst, 1.2–3.5 mm, was chosen based on our previous experience with a similar reaction system [1]. Since Rose's metal was used as a heat transfer medium and the reactor had a relatively narrow inner diameter (12 mm), it was assumed that the conditions would be isothermal. Therefore, it was only monitored the temperature profile of the heat transfer medium.

Analytical

The gas chromatographic method was used to analyze chemical and reaction mixture samples using a Shimadzu GC-2010 chromatograph with a flame ionization detector (GC-FID): non-polar column ZB-1 (60 m × 0.25 mm × 1 μm). The column temperature regime was set as follows: initial temperature 55 °C for 9 min, heating with the first temperature ramp of 10 °C per min up to the temperature of 80 °C for 7 min, heating with the second temperature ramp of 15 °C per min up to the final temperature of 210 °C. Both the injector and the detector were heated to 250 °C. The main products of DCHA dehydrogenation, namely NCCHA and NPCHA, were identified using chromatographic standards. The structures of side products of DCHA dehydrogenation were independently identified by gas chromatography using a mass spectrometric detector (EI 70 eV) using a Thermo GC-MS DSQ II chromatograph with column HP5 (30 m × 0.25 mm × 0.25 mm). The temperature regime was identical to that of the above-described GC-FID method.

N-Butylcyclohexanamine (10) MS: $m/z = 30, 41, 56, 112, 155$ (Ref. [21]).

N-Pentylcyclohexanamine (11) MS: $m/z = 28, 44, 56, 70, 126$.

N-Isopentylcyclohexanamine (12) MS: $m/z = 30, 41, 56, 70, 112, 126$.

N-(2-Methylbutyl)cyclohexanamine (13) MS: $m/z = 29, 41, 44, 55, 126$.

N-Cyclopentylcyclohexanamine (14) MS: $m/z = 28, 41, 56, 68, 82, 124$ (Ref. [22]).

N-(3-Methylcyclopentyl)cyclohexanamine (15) MS: $m/z = 28, 41, 56, 68, 82, 138$.

Data processing

The obtained chromatographic data, i.e. area units (area%) were converted to mass fractions (wt.%) and subsequently to molar fractions (mol%). The reactions are discussed in this work in terms of conversion of DCHA (X_{DCHA}), reaction (percentage) selectivity (S_i), and reaction (percentage) yield (Y_i) as follows :

$$X_{\text{DCHA}} = \left(\frac{x_{\text{DCHA,in}} - x_{\text{DCHA,out}}}{x_{\text{DCHA,in}}} \right) \cdot 100 \quad (1)$$

$$S_i = \left(\frac{x_{i,\text{out}}}{x_{\text{DCHA,in}} - x_{\text{DCHA,out}}} \right) \cdot 100 \quad (2)$$

$$Y_i = \left(\frac{x_{i,\text{out}}}{x_{\text{DCHA,in}}} \right) \cdot 100, \quad (3)$$

where x_{DCHA} is the molar fraction of DCHA, and x_i molar fraction of specie i . The partial pressure of hydrogen (p_{H_2}) is defined as follows:

$$p_{\text{H}_2} = x_{\text{H}_2} \cdot p \quad (4)$$

where x_{H_2} is the molar fraction of hydrogen in the gaseous reaction mixture and p is the total pressure of the gaseous reaction mixture (atmospheric pressure).

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s00706-023-03086-z>.

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Data availability On reasonable request, the corresponding author (Roman Valeš) will provide experimental data supporting the findings of this work.

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