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Liquid-phase hydroamination of cyclohexanone

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Activity and selectivity of supported Ni, Pt, and Pd catalysts were studied in the liquid-phase reductive amination of cyclohexanone at temperatures ranging from 100 to 150 °C. The catalyst 20% Ni/SiO_2 is most active and selective providing a maximum yield of cyclohexylamine. The influence of the reaction conditions on the parameters of the catalytic process was studied. A detailed analysis of the reaction products was carried out using ^{13}C NMR spectroscopy and gas chromatography coupled with mass spectrometry (GC-MS). This made it possible to refine the reaction mechanism and to identify a new by-product earlier unknown in the literature.

Key words: amination, reductive amination, cyclohexanone, cyclohexylamine.

The annual worldwide demand for cyclohexylamine stands at several thousands tonnes[1] and, hence, it is an important product of modern large-scale chemistry. The main methods for its production are the hydrogenation of aniline and reductive amination (hydroamination) of cyclohexanone.[1—4]

Carbonyl compounds are hydroaminated by ammonia and hydrogen in the presence of hydrogenation catalysts, among which the catalysts based on nickel and platinum group metals are used most frequently.[4] This reaction was first carried out in the liquid phase at room temperature and atmospheric pressure on the nickel and copper catalysts.[5] Higher yields of amines were obtained by using Raney nickel at elevated hydrogen pressure (20—150 atm) and 40—150 °C (see Ref. 6). Further investigations showed that this reaction can be carried out in the liquid or gas phase in the presence of massive metal and supported heterogeneous hydrogenation catalysts based on transition metals Ni, Co, and Fe or platinum group metals.[3,4,7—9]

The synthesis of primary amines is complicated by the formation of secondary and tertiary amines. The product distribution can depend on the catalyst nature, the ratio of a carbonyl compound and ammonia, and other reaction conditions. For instance, the liquid-phase hydroamination of cyclohexanone by ammonia in the presence of the nickel catalysts leads to predominant formation of cyclohexylamine, whereas secondary amine is the major product in the case of the platinum catalysts.[4,7,10,11] The nickel catalysts are considered to be most available and efficient for cyclohexylamine production.[4,7]

According to the commonly accepted mechanism of ketone hydroamination,[2,4,7,8,12,13] at the first non-catalytic step ammonia reacts with ketone to form intermediate primary imine, which is further hydrogenated on the catalyst to form primary amine. In turn, the primary amine can react with ketone to form secondary imine, whose hydrogenation gives secondary amine. Such side reactions as the hydrogenation of ketone and its aldol condensation can also occur during hydroamination.[7,8]

It is of certain interest to use in this reaction supported catalysts having a more developed surface (compared to bulky catalysts) but containing a smaller amount of metal. The purpose of this work is to study the activity and selectivity of a series of supported catalysts based on Ni, Pt, and Pd in the liquid-phase hydroamination of cyclohexanone and to reveal specific features of the reaction mechanism.

Experimental

The study was carried out in the presence of the following supported catalysts: 3% Pt/SiO_2, 3% Ni/SiO_2, 4% Pd/Al_2O_3, and 20% Ni/SiO_2.

Catalyst 3% Pt/SiO_2 was prepared by the adsorption impregnation of SiO_2 (S_{sp} = 300 $m^2 g^{-1}$, V_{pore} = 1.1 $cm^3 g^{-1}$) with an aqueous-ammonia solution of H_2PtCl_6 for 20 h. Catalyst 4% Pd/Al_2O_3 was prepared by the impregnation to incipient wetness of γ-Al_2O_3 (S_{sp} = 250 $m^2 g^{-1}$, V_{pore} = 0.4 $cm^3 g^{-1}$) with a solution of $Pd(NO_3)_2$. After preparation the catalysts were dried for 12 h at room temperature and then for 12 h at 110 °C, after which they were calcined in an air flow for 4 h at 300 °C. Catalysts 3% Ni/SiO_2 and 20% Ni/SiO_2 were prepared using the coprecipitation method by the consecutive impregnation of SiO_2 with solutions of nickel nitrate and ammonium carbonate, storing the suspension formed for 1 h at 80 °C. After drying, the catalysts were calcined in an air flow for 2 h at 200 °C. Then the Ni and Pd catalysts were reduced for 2 h in an H_2 flow at 450 and 300 °C, respectively.

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Cyclohexanone (**1**) was hydroaminated in a 25-cm^3 high-pressure steel reactor (Parr) according to the following procedure. A catalyst (0.01—0.2 g) was loaded into the reactor. Prior to the reaction, the Ni and Pd catalysts were subjected to an additional reductive treatment in the reactor at 250 °C and 50 atm for 2 h. After the end of reduction, the reactor was evacuated with a fore pump and a solution containing cyclohexanone (**1**) (0.02 mol) and a solvent (10 mL) was pumped into the reactor. This procedure excludes contact of the reduced catalyst and air oxygen. Catalyst 2% Pt/SiO$_2$ was used without the additional treatment in the reactor. After solutions were loaded, the reactor was evacuated for 30 s and ammonia (0.06 mol) was fed with stirring (300 rpm). Then the reactor was fed with hydrogen (0.04 mol) to the pressure about 50 atm. The reactor was heated with a rate of 6 °C min^{-1} to 100—150 °C and stored for a specified time. After the end of experiment, the reactor was cooled to room temperature and the pressure was slowly dropped. The resultant solution was separated from the catalyst and analyzed by gas chromatography (GC) on a Kristall 2000 chromatograph using a capillary column (diameter 0.2 mm, length 50 m, phase SE-50) and a flame-ionization detector. An analysis was carried out in the temperature-programmed regime from 50 to 250 °C with a rate of 3 °C min^{-1}. The temperature of the injection port was 270 °C. Calibration solutions of the corresponding compounds were used for the identification of the major products and determination of their concentration. The data obtained were used to calculate the conversion of cyclohexanone (**1**) and selectivity of formation of the reaction products.

The structures of products were additionally refined by ^{13}C NMR spectroscopy (Bruker AVANCE-400, working frequency 100.61 MHz) and GC-MS (Varian Saturn 2000). ^{13}C NMR spectra were recorded at room temperature. The procedure of recording inverse-gated decoupling (IGATED) spectra with long delays between pulses (30—60 s) for complete ^{13}C nuclei relaxation was used for quantitative measurements. The concentrations of the products calculated from the GC and NMR data showed good correspondence within 5 rel.%.

Results and Discussion

Identification of products and the reaction mechanism. Several experiments at 150 °C in the presence of catalyst 3% Pt/SiO$_2$ were carried out for the reliable identification of products of reductive amination of cyclohexanone.

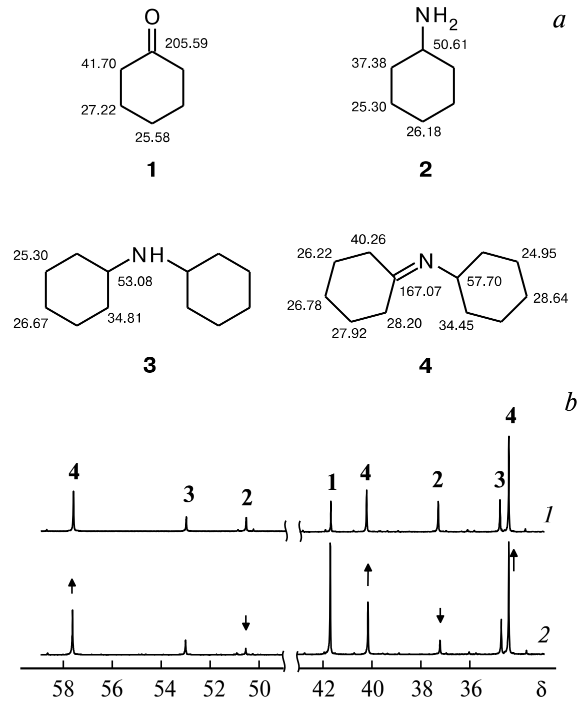


Fig. 1. *a*. Chemical shifts of carbon atoms in the ^{13}C NMR spectra for compounds **1**—**4**. *b*. The ^{13}C NMR spectra of the reaction mixtures after cyclohexanone conversion in the presence of 3% Pt/SiO2 (*1*) and after the addition of cyclohexanone (*2*).

The GC and GC-MS analyses of the liquid phase after the reaction show three major products (Table 1): primary amine, cyclohexylamine (**2**, m/z = 99); secondary amine, dicyclohexylamine (**3**, m/z = 181); and secondary imine, *N*-cyclohexylidenecyclohexylamine (**4**, m/z = 179). The ^{13}C NMR spectrum of the reaction mixture exhibits signals indicating the presence of compounds **1**—**4** (Fig. 1 and Table 1, entry *1*).

To reveal whether secondary imine **4** is the final reaction product or not, a small amount of cyclohexanone (0.005 mol) was added to the reaction mixture at room temperature. As can be seen from the ^{13}C NMR spectra

Table 1. Hydroamination of cyclohexanone (**1**) in the presence of 3% Pt/SiO$_2$^{a}

Entry	Catalyst amount/g	t/h	Conversion of **1** X (%)	Composition of products^b (mol.%)				Selectivity (mol.%)		
				2	3	4	5^c	2	3	6
1	0.05	1	23.4	24.5	5.6	66.1	3.8	90.6	5.6	3.8
2	0.05	3	58.3	22.1	15.7	58.8	3.5	80.9	15.7	3.4
3	0.05	6	73.0	20.6	26.5	51.7	1.2	72.3	26.5	1.2
4	0.20	4	100.0	63.5	36.2	0.0	0.3	63.5	36.2	0.3

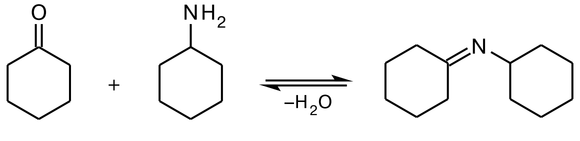
[a] Reaction conditions: **1** (0.03 mol), NH$_3$ (0.06 mol), H$_2$ (0.04 mol), decane (10 mL) as solvent, 150 °C.

[b] According to the gas chromatography data.

[c] Three products with M = 177.

(see Fig. 1, *b*), after the addition of **1** the intensity of signals of cyclohexylamine **2** decreases and that of secondary imine **4** increased, while the intensity of signals of dicyclohexylamine **3** remained unchanged. This indicates that **4** is formed by the non-catalytic reaction of cyclohexanone (**1**) with cyclohexylamine (**2**) even at room temperature (Scheme 1).

Scheme 1



1 **2** **4**

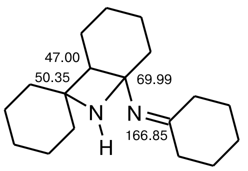
An additional experiment with pure reactants **1** and **2** confirmed that the reaction occurs under normal conditions and its equilibrium shifts to the right as the temperature decreases.

It is evident that secondary imine **4** is not the final reaction product but is formed on cooling of the reaction mixture (see Scheme 1). Indeed, imine **4** is observed by analysis only in products of incomplete ketone conversion (see Table 1, entries *1—3*) when cyclohexanone (**1**) and cyclohexylamine (**2**) are simultaneously present in the solution. Only primary and secondary amines are the products of complete ketone conversion (see Table 1, entry *4*).

According to the common hydroamination mechanism,[2,4,7,8,12] the catalytic hydrogenation of secondary imine affords secondary amine. Thus, under the reaction conditions, secondary imine **4** is but an intermediate. Therefore, for the calculation of the conversion of ketone and selectivity for final products (see Table 1), the concentrations of **1** and **2** determined by GC analysis were amplified by the value of concentration of **4** according to the reaction stoichiometry (see Scheme 1).

According to chromatographic analysis data, the final reaction mixture contains additional three products in a minor concentration. The GC-MS data show that they have the same molecular weight (*M* = 177) and, obviously, are isomers of the same compound (compound **5**, see Table 1 and Scheme 2). However, the ^{13}C NMR analysis of the solutions at room temperature does not detect these products. In this case, only one by-product, which we named the adduct (compound **6**) is observed along with major products **2—4**. It is most likely that products **5** are formed due to the decomposition and subsequent isomerization of adduct **6** in the injection port of the chromatograph at 270 °C.

To reveal the mechanism of formation of adduct **6**, we carried out the reaction without a catalyst at 100 °C for 1 h at the same reactant load as in the catalytic reaction (0.03 mole of cyclohexanone (**1**), 0.06 mole of NH_3, 0.04 mole of H_2). In this case, the conversion of **1** was 4% and adduct **6** was the single reaction product. The structure of earlier unknown compound **6** was elucidated by ^{13}C NMR spectroscopy of the reaction mixture obtained.

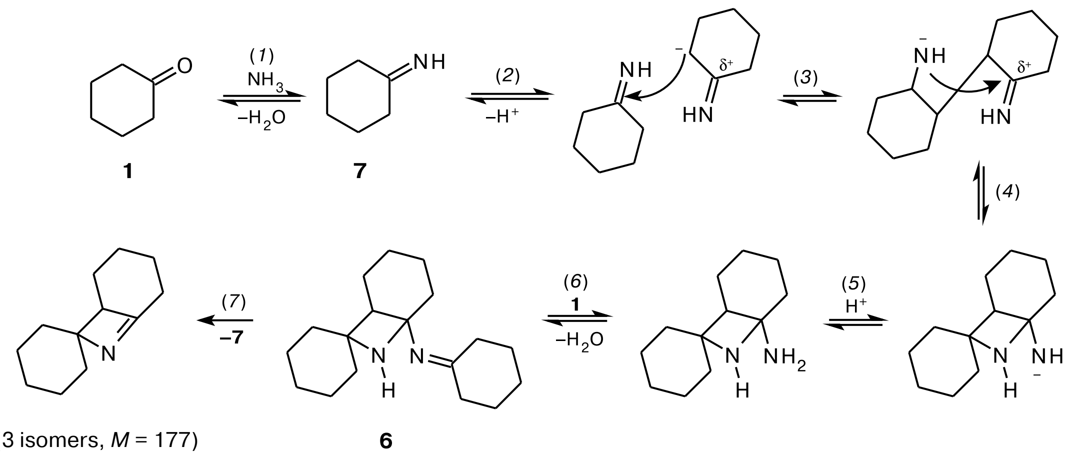


6

$\delta_C(CH_2)$		$\delta_C(CH_2)$	
21.70	29.22	26.61	36.69
22.03	29.47	26.79	40.81
22.87	35.81	26.84	42.84
23.00	38.95		

The obtained results suggest that adduct **6** is formed *via* the non-catalytic route from cyclohexanone **1** and

Scheme 2

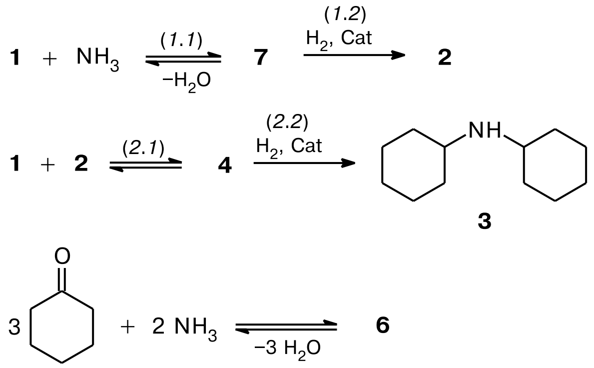


ammonia. The probable mechanism of its formation includes the following consecutive steps (Scheme 2): formation of primary imine, cyclohexylideneamine (**7**), through the interaction of cyclohexanone (**1**) with ammonia (step (*1*)); condensation of two molecules **7** with proton elimination (steps (*2*) and (*3*)); rearrangement of the product and proton addition (steps (*4*) and (*5*)); and condensation of the product with cyclohexanone to form adduct **6** (step (*6*)). The adduct undergoes thermal destruction (step (*7*)) during chromatographic analysis of the reaction mixture to give three isomers of compound **5**.

The data in Table 1 show that the content of **6** in the products decreases with the conversion of cyclohexanone **1**. This indicates that adduct **6** is consumed in the reaction, *i.e.*, the steps of its formation should be reversible (see Scheme 2).

Based on the common mechanism and the study performed, the main chemical transformations occurring upon hydroamination of cyclohexanone **1** can be presented in the simplified form by Scheme 3. This scheme includes the addition of ammonia to cyclohexanone (**1**) to form primary imine **7** (reaction (*1.1*)), catalytic hydrogenation of **7** to cyclohexylamine (**2**) (reaction (*1.2*)), interaction of cyclohexanone (**1**) with **2** to form secondary imine **4** (reaction (*2.1*)), catalytic hydrogenation of **4** to dicyclohexylamine **3** (reaction (*2.2*)), and condensation of cyclohexanone (**1**) and NH_3 to form **6** (reaction (*3*)).

Scheme 3



Cat is catalyst

Primary imine **7** was not observed by analysis of the reaction mixtures, which indicates its instability. According to the literature data,[4,7,8] secondary imine can be formed not only by the interaction of ketone with primary amine but also by the addition of primary amine to primary imine followed by the elimination of an NH_3 molecule. In an ammonia excess, the probability of this route is low. Secondary amine can interact with ketone to yield tertiary amine; however, this product is not formed under the conditions used.

Effect of the catalyst nature. The data on the effect of the catalyst nature on the selectivity of the reaction at the complete cyclohexanone conversion are presented in Table 2. The reaction was carried out for a fairy long time (3 h) using a larger amount of the catalyst (0.2 g). Note that in the case of the catalyst 3% Ni/SiO_2, which exhibited the lowest activity, the reaction time was elongated to 6 h (see Table 2, entry *1*) to achieve the complete conversion.

In the presence of the both nickel catalysts, the major reaction product is cyclohexylamine **2**, whose selectivity of formation exceeds 99%. In the case of 4% Pd/Al_2O_3 and 3% Pt/SiO_2, the selectivity for **2** is lower (80.8 and 64.5%, respectively) due to the additional formation of a considerable amount of secondary amine **3**. This result agrees with the previous studies, which showed that primary amines were the major products of hydroamination of carbonyl compounds in the presence of the nickel-containing catalysts.[4,7]

The data on the catalyst activity at a moderate conversion of cyclohexanone are listed in Table 3. The moderate cyclohexanone conversion is achieved due to a decrease in the amount of the catalyst used (0.01 g) and the reaction time (1 h). Under these conditions, the catalysts 20% Ni/SiO_2, 4% Pd/Al_2O_3, and 3% Pt/SiO_2 showed similar levels of conversion (X) and, correspondingly, activity. The selectivity for primary amine in the presence of 20% Ni/SiO_2 (98.4%, see Table 3) is close to that observed at the full conversion (see Table 2). A considerable amount of secondary amine is formed on the catalysts 4% Pd/Al_2O_3 and 3% Pt/SiO_2 under the conditions of both moderate and full conversion.

In the case of 3% Ni/SiO_2 and loading a fivefold larger amount of the catalyst (0.05 g), the conversion of cyclohexanone (**1**) is only 15.8%. Thus, this catalyst is approximately an order of magnitude less active than 20% Ni/SiO_2 (X = 29.1%), which is evidently due to the lower content of active metal.

The results show that on all catalysts the reaction proceeds *via* the common mechanism (see Scheme 3) to form

Table 2. Effect of the catalyst nature on the selectivity of hydroamination at the complete conversion of cyclohexanone (**1**)[a]

Entry	Catalyst	Selectivity (mol.%)		
		2	**3**	**6**
1	3% Ni/SiO_2[b]	99.2	0.2	0.6
2	20% Ni/SiO_2	99.7	0.2	0.1
3	4% Pd/Al_2O_3	80.8	19.0	0.2
4	3% Pt/SiO_2	64.5	35.2	0.3

[a] Reaction conditions: **1** (0.02 mol), NH_3 (0.06 mol), H_2 (0.04 mol), THF (10 mL) as solvent, catalyst amount 0.2 g, 150 °C, 3 h.

[b] The reaction time was 6 h.

Table 3. Activity of the catalysts in the hydroamination of cyclohexanone (**1**)[a]

Entry	Catalyst	Conversion of **1**, *X* (%)	Selectivity (mol.%)		
			2	**3**	**6**
1	3% Ni/SiO_2[b]	15.8	95.7	0.3	4.0
2	20% Ni/SiO_2	29.1	98.4	0.4	1.2
3	4% Pd/Al_2O_3	18.6	70.9	26.9	2.2
4	3% Pt/SiO_2	27.0	85.1	13.3	1.6

[a] Reaction conditions: **1** (0.02 mol), NH_3 (0.06 mol), H_2 (0.04 mol), THF (10 mL) as solvent, catalyst weight 0.01 g, 150 °C, 1 h.

[b] The catalyst amount was 0.05 g.

the same products, whose ratio depends on the catalyst nature and reaction conditions.

Catalyst 20% Ni/SiO_2 is one of the most active in the series studied. In addition, regardless of conversion, in the presence of this catalyst cyclohexanone (**1**) almost exclusively transforms into cyclohexylamine (**2**), whereas dicyclohexylamine (**3**) and adduct **6** are formed in trace amounts. Therefore, the influence of the reaction conditions on the parameters of the process was studied on this catalyst.

Solvent effect. The results of cyclohexanone hydroamination in various solvents at 150 °C in the presence of the catalyst 20% Ni/SiO_2, which were obtained at moderate ketone conversion, are presented in Table 4. It is seen that the solvent nature affects the reaction parameters. In nonpolar solvents (benzene, cyclohexane, and decane) the selectivity for primary amine is 95.2—97.5% at the cyclohexanone conversion 23.8—25.6%. The lower selectivity in decane is due to the formation of a comparatively large amount of adduct **6** (4.5%). The reason for such an effect of decane is unclear, because all these solvents are similar in nature (see Table 4).

In polar solvents, in THF, and especially in 1,4-dioxane, the conversion is higher (29.1 and 40.8%, respectively) than that in nonpolar solvents. In these solvents the selectivity for primary amine is also higher (98.4—98.8%). Presumably, this is due to a higher solubility of ammonia in polar solvents compared to nonpolar solvents. As the NH_3 concentration in the liquid phase increases, the rate of reaction (*1.2*) (see Scheme 3) should increase because the shift of equilibrium of stage (*1.1*) toward the formation of imine **7**. An increase in the NH_3 concentration should also suppress the formation of dicyclohexylamine (**3**), since it favors the predominant interaction of cyclohexanone (**1**) with ammonia (reaction (*1.1*)) rather than with cyclohexylamine (**2**) (reaction (*2.1*)).

Table 4. Solvent effect on the hydroamination of cyclohexanone (**1**) in the presence of 20% Ni/SiO_2*

Entry	Solvent	Conversion of **1**, *X* (%)	Selectivity (mol.%)		
			2	**3**	**6**
1	Benzene	23.8	97.5	0.6	1.9
2	Cyclohexane	24.0	97.4	0.5	2.1
3	Decane	25.6	95.2	0.3	4.5
4	THF	29.1	98.4	0.4	1.2
5	1,4-Dioxane	40.8	98.8	0.5	0.7

* Reaction conditions: **1** (0.02 mol), NH_3 (0.06 mol), H_2 (0.04 mol), solvent (10 mL), catalyst amount 0.01 g, 150 °C, 1 h.

The highest values of conversion of **1** and selectivity of formation of **2** are achieved in 1,4-dioxane. A molecule of 1,4-dioxane contains one oxygen atom more than a THF molecule, which probably facilitates more efficient coordination interaction of NH_3 molecules with solvent molecules.

Effect of the temperature and the ammonia : cyclohexanone ratio. The data on the temperature effect on the reaction parameters in THF in the presence of catalyst 20% Ni/SiO_2 are given in Table 5. As the temperature increases from 100 to 150 °C, the conversion of cyclohexanone **1** increases from 20.4 to 71.7%. In all cases, the selectivity for primary amine exceeds 99%.

The data on the effect of the ratio NH_3 : **1** on the reaction parameters at 125 °C (Table 6) indicate that with a decrease in an ammonia excess from 10 : 1 to 3 : 1 the cyclohexanone conversion increases from 31.7 to 46.3%, the selectivity for primary amine **2** remains at a level of 99.2—99.5%, and the fraction of dicyclohexylamine **4** in the products increases slightly. The fraction of adduct **6** decreases from 0.8 to 0.3%, which agrees with the mechanism of its formation (see Scheme 2), because an increase in the amount of NH_3 should shift the equilibrium to the formation of adduct **6**.

As the ratio NH_3 : **1** further decreases to the stoichiometric value (1 : 1), the conversion remains nearly unchanged but the selectivity for primary amine decreases to 97.5% due to an increase in the fraction of dicyclohexylamine **3** to 2.2%. According to the reaction mechanism (see Scheme 3), a decrease in the amount of NH_3 should

Table 5. Temperature effect on the hydroamination of cyclohexanone (**1**) in the presence of 20% Ni/SiO_2*

Entry	Temperature/°C	Conversion of **1**, *X* (%)	Selectivity (mol.%)		
			2	**3**	**6**
1	100	20.4	99.1	0.0	0.9
2	125	38.6	99.5	0.1	0.4
3	150	71.7	99.7	0.1	0.2

* Reaction conditions: **1** (0.01 mol), NH_3 (0.06 mol), H_2 (0.04 mol), THF (10 mL) as solvent, catalyst amount 0.01 g; the reaction time was 1 h.

Table 6. Effect of the ammonia amount on the hydroamination of cyclohexanone (**1**) in the presence of 20% Ni/SiO_2*

Entry	Amount of NH_3 /mol	NH_3 : **1**	Conversion of **1**, *X* (%)	Selectivity (mol.%)		
				2	**3**	**6**
1	0.10	10 : 1	31.7	99.2	0.0	0.8
2	0.06	6 : 1	38.6	99.5	0.1	0.4
3	0.03	3 : 1	46.3	99.5	0.2	0.3
4	0.01	1 : 1	46.6	97.5	2.2	0.3

* Reaction conditions: **1** (0.01 mol), H_2 (0.04 mol), THF (10 mL) as solvent, catalyst amount 0.01 g, 125 °C, 1 h.

increase, in fact, the contribution of step (*2.1*) leading to the formation of imine **4**, whose hydrogenation gives dicyclohexylamine (**3**). The decrease in the conversion with an increase in the ammonia amount can be due to a decrease in the rate of hydrogenation step (*2.2*) because of the competitive adsorption of NH_3 and primary amine on the catalyst surface.

Thus, the results obtained in this work show that a two- to threefold excess of ammonia is sufficient to provide the maximum yield of primary amine in a wide range of hydroamination conditions.

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