Kinetics and Catalysis, Vol. 43, No. 6, 2002, pp. 826–829. Translated from Kinetika i Kataliz, Vol. 43, No. 6, 2002, pp. 888–892.
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Dehydroamination of Methylcyclohexanols

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Received March 1, 2002

Abstract—The catalytic dehydroamination of 2-, 3-, and 4-methylcyclohexanols on Pd- and Ni-containing heterogeneous systems in the presence of ammonia was studied. The main reaction products were *ortho*-, *meta*-, and *para*-toluidines; 2,2'-, 3,3'-, and 4,4'-dimethyldiphenylamines were formed as by-products. The effects of the chemical composition of catalysts and reaction conditions on the yields of desired products were found.

INTRODUCTION

Presently, processes that occur on the surfaces of various catalytic systems and combine a number of reactions are of strong theoretical and practical interest. In a number of cases, the use of highly selective catalysts makes it possible either to avoid multistage procedures for the synthesis of desired products or to eliminate stages that result in great amounts of waste that is difficult to utilize [1].

Catalytic dehydrogenation reactions of various alicyclic systems are widely used for the production of aromatic hydrocarbons, including compounds containing functional groups [2–7]. At the same time, reactions in which amination processes are coupled with alicyclic ring dehydrogenation have been almost not studied. In the subsequent text, we used the term dehydroamination to denote the amination reactions of alicyclic oxygen-containing compounds (alcohols and ketones) coupled with dehydrogenation processes on heterogeneous catalysts [8–11].

Other reactions can occur on the introduction of an aminating agent (ammonia or an amine) into the reaction system. It is difficult to couple two reactions—dehydrogenation and amination—at the surface of a catalyst. In this case, the catalyst is of crucial importance.

The aim of this work was to study the effects of catalyst composition and reaction conditions on the yields of desired products in the dehydroamination of cyclohexanols substituted at the alicyclic ring. The reactions were performed on Ni- and Pd-containing catalysts supported on SiO_2 and Al_2O_3.

EXPERIMENTAL

Preparation of 2–10% Pd/Al_2O_3 catalysts. Palladium catalysts were prepared by the impregnation of commercial A 1 γ-Al_2O_3 with 5% $PdCl_2$ solutions in a 10% hydrochloric acid solution. The aluminum oxide precalcined at 400°C in air was impregnated with a solution of the required concentration for 2 h. The solution was evaporated in an air bath with continuous stirring. The catalyst was dried at 120°C for 4 h and calcined in a muffle furnace at 400°C for 4 h.

Preparation of a 15% Ni + 6% Cu + 1.5% Cr + 3% Na_2SO_4/SiO_2 catalyst. Silica gel ShSM (GOST 3956-54) was used as a catalyst support; it had the following characteristics: $V_s = 0.36$ cm^3/g, $S = 580$ m^2/g, and $d = 16$ Å. To prepare the catalyst, the silica gel was precalcined in air at 400°C for 4 h. The support was impregnated with metal salts as described below. A weighed portion (74.0 g) of $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in 80 ml of distilled water. The support (74.5 g) was gradually introduced into the nickel nitrate solution with continuous stirring. The duration of the impregnation at room temperature was 0.5 h. After the impregnation, the solution was evaporated and the sample was dried in air at 120°C for 6 h.

Copper acetate $Cu(CH_3COO)_2 \cdot H_2O$, 18.75 g was dissolved in 200 ml of distilled water on heating (90°C), and the sample after supporting nickel nitrate was impregnated with the obtained solution with stirring for 0.5 h. The sample was dried at 120°C with stirring for 6 h.

CrO_3 (2.9 g) was dissolved in 70 ml of distilled water, and the sample prepared at the previous stages was impregnated with the resulting solution. The duration and temperature conditions of drying were the same as in the preceding stage.

Na_2SO_4 (3 g) was dissolved in 70 ml of distilled water, and the catalyst sample was impregnated with the resulting solution for 0.5 h. After evaporating the solution and drying, the catalyst was calcined in air at 400°C for 4 h. The composition of the finished catalyst (~100 g) was as follows (wt %): 15% Ni + 6% Cu + 1.5% Cr + 3% Na_2SO_4/SiO_2. Catalysts with other quantitative compositions were prepared by analogous procedures.

The preparation procedure for a 15% Ni + 6% Cu + 1.5% Cr + 3% Na_2SO_4/Al_2O_3 catalyst was similar to that described above; however, A 1 aluminum oxide was used as a support. Catalysts of different compositions supported on SiO_2 and Al_2O_3 were prepared by a common procedure; the nickel contents of these catalysts varied from 5 to 20 wt %.

The dehydroamination of cyclohexanols was studied in a quartz reactor (20 mm i.d.) on a fixed-bed catalyst (particle size of 1.5–2.6 mm; volume of 50 cm^3). The reaction was performed at 300–400°C and a reactant space velocity of 0.3–1.2 h^{-1} in a flow of ammonia at cyclohexanol-to-ammonia molar ratios from 1 : 1 to 1 : 25.

Under optimum process conditions (temperature of 380°C, cyclohexanol space velocity of 0.25 h^{-1}, and cyclohexanol-to-ammonia molar ratio of 1 : 5), the yields of toluidines were 75–82%. The calculations were performed based on reacted methylcyclohexanol at 90–95% conversion.

The reaction products were analyzed and the course of reaction was monitored by GLC using an LKhM-8MD chromatograph (temperature programming from 90 to 210°C; column with $l = 2$ m and $d = 5$ mm packed with Chromosorb W (60–80 mesh) modified with 5% KOH and an Apieson K (12%) liquid phase) and a Chrom 5 chromatograph with a glass column ($l = 2$ m; $d = 2$ mm) packed with Chromaton N-AW-DMCS (0.16–0.20 mm) impregnated with 15% Apieson L.

RESULTS AND DISCUSSION

We used 2-, 3-, and 4-methylcyclohexanols as model compounds for studying the effects of catalyst composition and process conditions on the occurrence of coupled amination and dehydrogenation reactions. We found that in the dehydroamination of methylcyclohexanols the corresponding toluidines were main reaction products. Di(methylphenyl)amines, cresols, and minor amounts of di(methylcyclohexyl)amines were also detected in the reaction mixture. Nickel and palladium catalysts that differed in composition were tested in order to study the effect of the nature of catalysts on the dehydroamination reactions of methylcyclohexanols.

We found that, in the dehydroamination of methylcyclohexanols with ammonia in the presence of 2–10% Pd/Al_2O_3 catalysts, the dehydroxylation of cyclohexanols and the formation of hydrocarbons were observed along with the dehydroamination reaction. Toluene, benzene, and methylcyclohexane were identified among the hydrocarbons. In this case, the yield of toluidines was no higher than 25%.

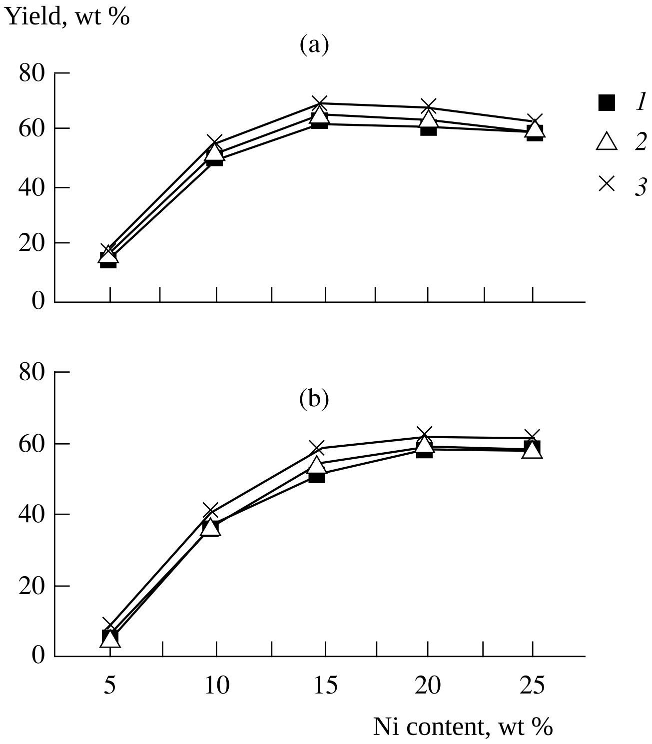
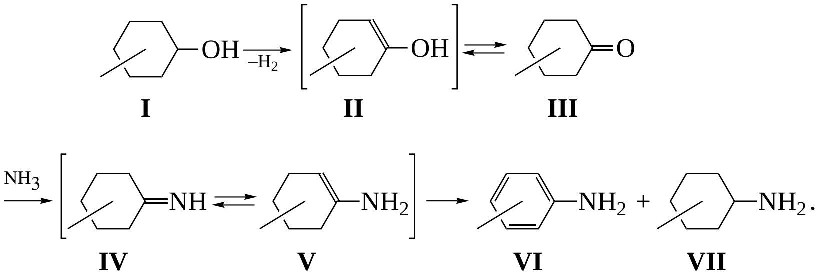


Fig. 1. Yields of (*1*) *ortho*-toluidine, (*2*) *meta*-toluidine, and (*3*) *para*-toluidine as functions of the nickel contents of (a) Ni/Al_2O_3 and (b) Ni/SiO_2 catalysts. $T = 380$°C; methylcyclohexanol : ammonia, 1 : 5; $v = 0.25$ h^{-1}.

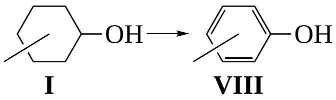
Nickel-containing catalysts that differ in composition (5–20% Ni) supported on silicon and aluminum oxides were studied. A comparison between the results of the dehydroamination of methylcyclohexanols with ammonia on these catalysts (Fig. 1) suggests that a nickel-containing catalyst supported on silica exhibited a lower activity in this reaction, and the highest yield of toluidines was observed at a nickel content of 20%, whereas the nickel content of an optimum catalyst supported on aluminum oxide was 15%.

We performed experiments with the addition of copper and chromium as modifying elements to the dehydrogenation catalysts. We found that the addition of up to 6% Cu to a catalyst improved its selectivity to aromatic amines and increased the yield of toluidines by 8–10%. The modification with chromium oxides (up to 5%) improved the stability of catalysts and the selectivity to primary aromatic amines. We also found that the addition of up to 3% Na_2SO_4 increased the catalyst service life from 50 to 100 h or longer. Thus, we experimentally found that an optimum catalyst composition is the following (wt %): Ni, 15; Cu, 6; Cr, 1.5; Na_2SO_4, 3; and the balance is alumina. In accordance with experimental data, the formation of toluidines can be described by the following scheme:



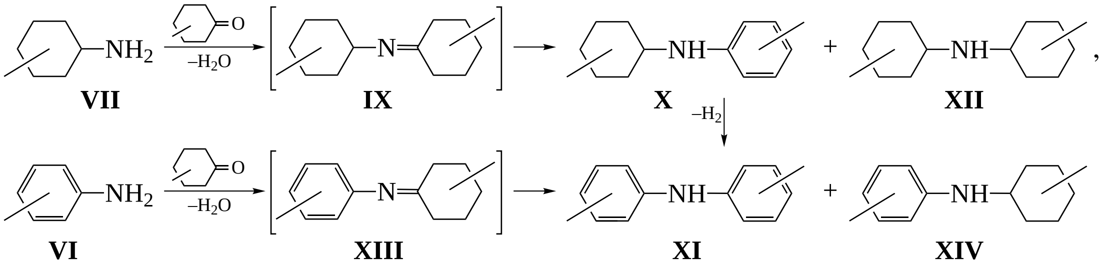
(I)

The reactions of the dehydrogenation of methylcyclohexanols to corresponding cresols



(II)

and the formation of di(methylphenyl)amines



(III)

occur simultaneously in the system.

Under the specified reaction conditions, the formation of a considerable amount of cresols **VIII** would be expected as a result of the exhaustive dehydrogenation of methylcyclohexanols **I**. However, their actual concentration in the reaction products was no higher than 3–5%. This low concentration of cresols cannot result from the direct amination of cresols to **VI**. It is well known [12–14] that the reaction of phenol amination is an acid-catalyzed process in which solid acids are used as catalysts. In our case, the use of a catalyst modified with sodium sulfate almost excludes the occurrence of the amination reaction by this mechanism. This was supported experimentally: the amination of *para*-cresol on the test catalysts almost did not occur at 350–400°C. At the same time, the addition of 4-methylcyclohexanol in small amounts (5–10%) to the parent *para*-cresol increased the conversion of *para*-cresol into the corresponding *para*-toluidine up to 45%. In this case, the reaction occurred according to a mechanism that includes the formation of imine **IV** and the catalytic redistribution of hydrogen with the formation of compounds **VI** and **VII**. In this context, the above scheme of the formation of **VI** from **I** with the participation of dehydrogenating sites of the catalyst is most probable; this scheme includes a step of imine formation. The imine mechanism suggests the participation of methylcyclohexanone **III**, which is a dehydrogenation product of **I**, in the reaction. Methylcyclohexanone readily reacts with ammonia to form imine **IV**, which is converted into methylcyclohexylamine **VII** and toluidine **VI** because of dehydrogenation and the catalytic redistribution of hydrogen. Methylcyclohexylamine is dehydrogenated to toluidine. In our opinion, diphenylamine **XI** is formed by analogous imine mechanism (III) via the interaction of methylcyclohexanone with methylcyclohexylamine or toluidine. Of the two nucleophilic agents—methylcyclohexylamine and toluidine—compound **VII** mainly participates in the reaction because its nucleophilicity is higher. Along with methylcyclohexanone **III**, imine **IV** can also participate in the formation of di(methylphenyl)amine **XI**.

The above reaction scheme was also indirectly supported by an increase in the yield of *para*-toluidine (88%) with a simultaneous decrease in the yield of *para*-cresol in the dehydroamination of 4-methylcyclohexanone, as compared with the dehydroamination of 4-methylcyclohexanol (83%). The reaction temperature was 390°C.

Table 1. Yields of *ortho*-toluidine (**VIa**), *meta*-toluidine (**VIb**), *para*-toluidine (**VIc**), 2,2'-dimethyldiphenylamine (**XIa**), 3,3'-dimethyldiphenylamine (**XIb**), and 4,4'-dimethyldiphenylamine (**XIc**) at different temperatures

T, °C	Yield, wt %					
	VIa	**VIb**	**VIc**	**XIa**	**XIb**	**XIc**
360	67	75	76	5	6	7
370	72	78	80	4	6	6
380	75	80	82	3	5	5
390	74	79	83	4	5	4
400	70	75	80	6	8	7

Note: Catalyst, 15% Ni + 6% Cu + 1.5% Cr + 3% Na_2SO_4/Al_2O_3; methylcyclohexanol : ammonia, 1 : 5; $v = 0.25$ h^{-1}.

Table 2. Yields of *ortho*-toluidine (**VIa**), *meta*-toluidine (**VIb**), *para*-toluidine (**VIc**), 2,2'-dimethyldiphenylamine (**XIa**), 3,3'-dimethyldiphenylamine (**XIb**), and 4,4'-dimethyldiphenylamine (**XIc**) at different molar ratios **I** : NH_3

I : NH_3	Yield, wt %					
	VIa	**VIb**	**VIc**	**XIa**	**XIb**	**XIc**
1 : 1	57	64	68	10	18	21
1 : 3	70	74	75	5	9	10
1 : 5	75	80	82	3	5	5
1 : 10	77	81	83	2	3	3
1 : 25	80	86	87	1	2	2

Note: Catalyst, 15% Ni + 6% Cu + 1.5% Cr + 3% Na_2SO_4/Al_2O_3; *T* = 380°C; $v = 0.25$ h^{-1}.

Table 3. Yields of *ortho*-toluidine (**VIa**), *meta*-toluidine (**VIb**), *para*-toluidine (**VIc**), 2,2'-dimethyldiphenylamine (**XIa**), 3,3'-dimethyldiphenylamine (**XIb**), and 4,4'-dimethyldiphenylamine (**XIc**) at different cyclohexanol space velocities

ν, h^{-1}	Yield, wt %					
	VIa	**VIb**	**VIc**	**XIa**	**XIb**	**XIc**
0.1	71	74	75	5	7	9
0.2	74	80	81	4	6	6
0.25	75	80	82	3	5	5
0.3	72	77	80	3	6	5
0.4	67	72	73	4	7	7

Note: Catalyst, 15% Ni + 6% Cu + 1.5% Cr + 3% Na_2SO_4/Al_2O_3; *T* = 380°C; methylcyclohexanol : ammonia, 1 : 5.

Tables 1–3 summarize the yields of toluidines **VI** and dimethyldiphenylamines **XI** depending on temperature, the molar ratio between methylcyclohexanol and ammonia, and the space velocity of the methylcyclohexanol.

The position of an alkyl substituent at the cyclohexane ring noticeably affects the reactivity of cyclohexanols and, consequently, the yield of toluidines. A comparison between the yields of *ortho*-, *meta*-, and *para*-toluidines and the yields of 2,2'-, 3,3'-, and 4,4'-dimethyldiphenylamines indicates that the lowest yield of amines was found in the dehydroamination of 2-methylcyclohexanol, whereas the effects of methyl groups at the 3- and 4-positions of the cyclohexane ring were not so significant.

Thus, we experimentally found that the dehydroamination of alkylcyclohexanols with ammonia affords aromatic amines containing an alkyl (methyl in the case under consideration) substituent at the aromatic ring in good yields.

ACKNOWLEDGMENTS

This work was supported by the Belarussian Republican Foundation for Basic Research (grant no. X99-092).

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