ACTIVITY AND SELECTIVITY OF COBALT, NICKEL AND COPPER CATALYSTS FOR HYDROGENATION OF LAURONITRILE

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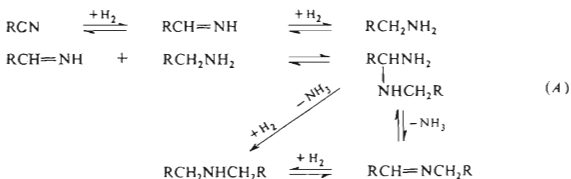
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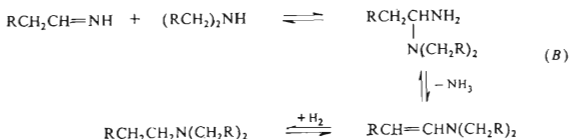*Prague Institute of Chemical Technology, 166 28 Prague 6*

Cobalt and nickel metal powders possessing various specific surface areas were prepared by decomposition of their salts under hydrogen. The activity of the metals for hydrogenation of lauronitrile was found to be proportional to their specific surface areas. Oxide carriers do not affect the specific activity of the metals. The relative specific activities of the metals are in the ratio Ni : Co : Cu = 20 : 10 : 1. Pure nickel affords 2·3 times more secondary amine than cobalt; on copper catalyst, secondary amine is formed predominantly.

Hydrogenation of nitriles can result in formation of primary, secondary, and tertiary amines. The chemism of their formation is straightforward and has been elucidated a long time ago, by Braun, Blessing, and Zobel[1] for the first time in a complex fashion. The pathway given by the authors, modified by Greenfield[2], is

$$RCN \quad \overset{+H_2}{\rightleftharpoons} \quad RCH{=}NH \quad \overset{+H_2}{\rightleftharpoons} \quad RCH_2NH_2$$

$$RCH{=}NH \quad + \quad RCH_2NH_2 \quad \rightleftharpoons \quad \overset{\displaystyle RCHNH_2}{\underset{\displaystyle NHCH_2R}{|}}$$

$$RCH_2NHCH_2R \quad \overset{+H_2}{\rightleftharpoons} \quad RCH{=}NCH_2R \tag{A}$$

The formation of secondary amine *via* imine is more likely than hydrogenolysis of the diamino derivative. Imine cannot be intermediate in the formation of tertiary amine, and enamine has been claimed[2,3] to be the precursor of the latter:

$$RCH_2CH{=}NH \quad + \quad (RCH_2)_2NH \quad \rightleftharpoons \quad \overset{\displaystyle RCH_2CHNH_2}{\underset{\displaystyle N(CH_2R)_2}{|}}$$

$$RCH_2CH_2N(CH_2R)_2 \quad \overset{+H_2}{\rightleftharpoons} \quad RCH{=}CHN(CH_2R)_2 \tag{B}$$

The participation of enamine in the formation of tertiary amine can account for some anomalies in the effects of the nitrile structure and of the catalyst type on the selectivity of hydrogenation of nitriles.

The rate of the nitrile hydrogenation and the composition of the product are affected primarily by the type of the catalyst used. For synthesis of primary amines, cobalt and nickel catalysts are preferred. Copper and rhodium catalysts afford predominantly secondary amines, tertiary amines can be prepared on palladium catalysts.

Most works dealing with hydrogenation of nitriles in the presence of nickel and cobalt catalysts are patents. The results of the various works are difficult to compare, as the experimental conditions frequently have not been defined unambiguously and the substrates and catalysts used were not pure substances. It is worth mentioning that addition of titanium or cobalt to Raney's nickel suppresses the formation of secondatry amine[4]; the admixtures are supposed to lower the relative sorption of amine with respect to nitrile as compared with the untreated catalyst. We have found[5] that the specific activity (per 1 m^2 surface of the metal) is approximately the same for cobalt and nickel; this result should be, however, looked upon as approximate, with regard to the small number of experimental data obtained.

In addition to the catalyst type, the selectivity of nitrile hydrogenation is affected also by the reaction conditions. Most of the published data concerning hydrogenation of nitriles on cobalt and nickel indicate that the content of secondary amine in the product increases with temperature[6]. In hydrogenation of nitriles derived from higher fatty acids on nickel, the formation of secondary amine dropped with increasing pressure in the range of 1—5 MPa (ref.[6]). In the reaction scheme, the hydrogenation steps are favoured by increasing hydrogen pressure, while the condensation reactions should be unaffected by the partial pressure of hydrogen. The formation of secondary amines in the production of primary amines is most frequently suppressed by addition of ammonia. The effect of reaction conditions on the hydrogenation of nitriles will be studied and related to the mechanism in forthcoming papers of this series.

In this work, we are concerned with the preparation of pure nickel and cobalt powders and measurement of their activity and selectivity for hydrogenation of lauronitrile. Metal powders possessing the specific surface area of $1-50$ m^2/g were prepared by decomposition of the oxides, formates, and oxalates in hydrogen atmosphere at various temperatures from room temperature up to 400°C. The specific activity of nickel on carriers was evaluated for a comparison too.

EXPERIMENTAL

Chemicals and Catalysts

Cobalt(II) nitrate hexahydrate *p.a.* (Lachema) containing 0·0045% Fe, 0·026% Na, 0·0048% K. Nickel nitrate hexahydrate *p.a.* (Lachema), with 0·009% Fe, 0·036% Na, and 0·0045% K. The formates and oxalates were *c.p.* chemicals (Lachema), sodium and ammonium carbonates *p.a.* (Lachema).

Catalysts: Co on silica gel, contact 45/20 (Ruhrchemie, FRG), Ni on alumina, contact 6524 (Leuna Werke, GDR), Ni on chromic oxide, contact 51-U-12 (USSR), Ni on kieselguhr, contact Cherox 3703 (Czechoslovak-Soviet Friendship Chemical Works, Záluži), Cu on silica gel, contact R 3—11 BASF (FRG), Cu on kieselguhr, contact (Usines de Melle, France).

Lauronitrile was obtained by double vacuum rectification of the so-called coconut nitrile on a column with 10 TP. The starting material contained 53% lauronitrile, 20 and 26% nitriles derived from lower and higher acids, respectively, and other components. The first rectification afforded a 95% concentrate of the desired substance, from which 99% lauronitrile was obtained on repeated rectification.

The amines as analytical standards were isolated from the reaction mixture after hydrogenation of lauronitrile. The catalyst was separated by centrifugation, and 99·9% primary amine was obtained by double vacuum rectification on a column with 10 TP. The residue from the first rectification was distilled at 0·13 kPa to give crude didodecylamine containing 5·8% primary amine; pure substance, m.p. 40·5°C, could be isolated on crystallization of the distillate from a methanol–1-butanol mixture 1 : 1.

Nickel and cobalt powders were prepared either by reduction of the oxides or by decomposition of the formates and oxalates in hydrogen stream. Co_3O_4 was prepared in two ways: Co_3O_4 I: Solution of cobalt(II) nitrate was precipitated with solution of ammonium carbonate at 60°C, the precipitate was washed on a filter, dried at 100°C, and annealed at 550°C for 8 h. The specific surface area of the oxide was 52·9 m^2/g. Co_3O_4 II: Cobalt(II) nitrate was freed from crystal water by heating and for the most part decomposed at higher temperatures. The residue was ground and annealed at 550°C for 8 h. The specific surface area of the oxide was 10·2 m^2/g. Nickel oxide was prepared analogously as Co_3O_4 I. Metal powders were obtained from the oxides and salts by decomposition in hydrogen and nitrogen stream in an electric furnace. The temperatures of decomposition were measured by means of a thermocouple located in the wall of the glass reactor in the place where the starting material was situated. In this apparatus the industrial catalysts were activated as well. After the reduction, the nitrile was poured over the pyrophoric powders and the slurry was transferred quantitatively into the hydrogenation autoclave.

Nitrile Hydrogenation

The hydrogenations were carried out in a 150 ml Rotamag autoclave (manufactured at the Slovak Institute of Technology, Bratislava) with a rotary magnetic stirrer with two screws, maximum speed 2100 rpm. The autoclave was thermostated to within $\pm 1°C$ in an oil thermostat; the reaction temperatures reported are the bath temperatures. After activation in electric furnace, the catalyst in suspension in the nitrile was transferred into the autoclave. The closed autoclave was triply flushed with hydrogen, and at a pressure of 0·5 MPa connected with the oil thermostat heated to the desired temperature of hydrogenation, and allowed to attain the temperature for 15 min. The pressure of hydrogen was then increased and the stirring was activated. The start of stirring was regarded as the start of hydrogenation. The pressure was held constant by periodically feeding hydrogen in the range of 1 MPa, the mean value of this range being reported in the Results as the working pressure. If the pressure did not change for a time corresponding to about 10% of the total hydrogenation period, the experiment was looked upon as finished. In additional 5 min the stirring was discontinued and the thermostat disconnected, and after cooling down, the pressure in the autoclave was reduced and sample was taken for analysis. The instantaneous rate of hydrogenation was determined based on the time required for the pressure to decrease by 1 MPa. The activity of the catalyst was evaluated in terms of the reaction rate calculated from the total hydrogenation period (mmol H_2 s^{-1} g^{-1}), the specific activity was calculated per 1 m^2 of the metal surface (mmol H_2 s^{-1} m^{-2}).

Analytical Methods

The specific surface areas of the pure metals were determined by means of adsorption of nitrogen at —196°C by employing the dynamic method in the apparatus described previously[7]. The

starting substance was converted to the metal in the measuring apparatus under the same conditions as were those applied to the preparation of the metal for hydrogenation, and during the evaluation the two samples were assumed to possess the same specific surface area. In several experiments, the surface area was measured on the starting material taken in a quantity necessary for the nitrile hydrogenation, and the powder obtained was then transferred into the autoclave. The specific surface area of nickel in the supported catalysts was determined by chemisorption of oxygen as described by Bujanova and coworkers[8,9]. The method was standardized by using pure nickel with known surface area, and the value 0·021 mmol O_2 m^{-2} was obtained, which is in a good agreement with the value 0·022 mmol O_2 m^{-2} obtained in[8,9].

With nickel and cobalt as the catalysts, the reaction mixture only contained primary and secondary amine, the starting nitrile was completely hydrogenized, and no tertiary amine was formed; the latter was present when copper was used as the catalyst. The primary and secondary amines were determined by GL chromatography and by potentiometric titration. No difficulties are encountered in chromatographic separation of substances with such different molecular weights. Apiezon L (20%) on alkalized Chromaton N-AW-HMDS was employed. The measurements were carried out on a Chrom-4 apparatus equipped with a 1 m column, using flame ionization detection. The sample was dissolved in a tenfold quantity of 1-butanol; the primary amine was determined at 160°C, and on raising the temperature to 250°C within 5 min, dodecylamine eluted. The proportions of the two amines were evaluated from the peak areas, their sum being considered as 100%. Taking into account the nonlinearity of response for the secondary amine, external standards whose composition was near to that of the samples analyzed were set up from the pure amines.

For potentiometric titration, the samples were heated up to 180°C to expel CO_2 and NH_3, and after weighting, dissolved in 2-propanol. The total alkalinity was determined by titration of an aliquot with acid using glass and calomel electrodes. In the second titration, the primary amine was masked with salicylaldehyde. For the determination of the tertiary amine, the initial sample was allowed to stand for 1 h with 10 ml of acetic anhydride, diluted with acetic acid, and titrated.

RESULTS AND DISCUSSION

Preparation of nickel and cobalt. The effects of the initial compound and of the conditions of decomposition on the specific surface area of cobalt are demonstrated by Table I. Cobalt powder with the mean surface area of 6—7 m^2/g can be prepared reproducibly by reduction of the oxide Co_3O_4 I (K 4, K 5, K 34). At 250—290°C the oxide requires 2 h reduction. The surface area of the metal obtained is about seven times lower than that of the starting oxide. Reduction of Co_3O_4 II, with a relatively small surface area, results in a decrease of the surface area to a third (K 6). The largest area, nearly 50 m^2/g, emerged from the decomposition of cobalt(II) formate at 250°C. The more stable oxalate requires a higher temperature for decomposition, up to 300°C; at which cobalt sinters rather rapidly; the metal powder possessed a surface area as small as 15—20 m^2/g. In another work carried out in our laboratory[10], observable sintering of cobalt has been established to proceed at temperature 270°C. Broadbent and coworkers[11] have found 300°C to be the lower temperature limit of decomposition of anhydrous cobalt(II) oxalate. In our experiments,

TABLE I
Conditions of Preparation of Cobalt Powders and Their Specific Surface Areas

| Sample | Conditions of sample preparation | | | | Specific surface area $m^2 g^{-1}$ |
	starting compound	temperature °C	period h	weight g	
K 4	Co_3O_4 I	250 285	1 1	0·2391	6·9
K 5	Co_3O_4 I	250 285	1 1	0·1761	6·9
K 34	Co_3O_4 I	250 285	1 1	0·5602	6·2[a]
K 6	Co_3O_4 II	250 285	1 1	0·5676	3·7
K 12	formate	20—300 300	1 1	0·0350	4·1
K 16	formate	250	2	0·0250	14·6
K 35	formate	20—210 150	0·5 1·5	0·4725	32·9
K 14	formate	250 250	1 1	0·0310	47·3
K 11	oxalate	285 300	1 4	0·0362	20·5[b]
K 17	oxalate	300	3	0·305	15·4
K 35	oxalate	20—210 150 300	0·5 1·5 3	0·2093	3·0[a]
K 37	oxalate	20—210 250 300	0·5 1·5 3	0·2043	3·4[a]
K 38	oxalate	20—210 250 300	0·44 1·5 3	0·1991	3·8[a]
K 39	oxalate	20—210 250 300	0·5 1·5 3	0·2098	5·2

[a] Samples activated and measured in a larger adsorption vessel; [b] calculated from two points of the adsorption isotherm, in the remaining cases from three points.

TABLE II

Conditions of Preparation of Nickel Powders and Their Specific Surface Areas

Sample[a]	Conditions of catalyst preparation				Specific surface area $m^2 g^{-1}$
	starting compound	temperature °C	period h	weight g	
N 21	oxide	20—400	1	0·4740	0·64
		400	3		
		400	3		
N 23	oxide	20—400	1	0·1938	0·60
		400	3		
		400	3		
N 18	formate	20—300	1	0·0490	2·6
		300	1		
N 19	formate	300	1	0·0515	2·0
N 36	formate	20—250	0·5	0·4020	3·7[b]
		300	1·5		
n 1	formate	20—250	0·5	0·4463	4·1[b]
		300	1·5		
n 5	formate	20—250	0·5	0·4374	3·2[b]
		300	1·5		
n 6	formate	20—250	0·5	0·7417	3·7[b]
		300	1·5		
n 7	formate	20—250	0·5	0·4319	3·4[b]
		300	1·5		
N 20	oxalate	20—300	1	0·0682	7·3
		300	2		
N 24	oxalate	20—300	1	0·0743	10·8
		300	2		
N 25	oxalate	20—300	1	0·1185	8·5
		300	2		
n 2	oxalate	20—250	0·5	0·6511	12·1[b]
		300	1·5		
n 3	oxalate	20—250	0·5	0·4774	10·9[b]
		300	1·5		
n 4	oxalate	20—250	0·5	0·4889	11·5[b]
		300	2·5		
n 8	oxalate	20—250	0·5	0·2639	10·7[b]
		300	2·5		
n 9	oxalate	20—250	0·5	0·4745	12·4[b]
		300	2·5		
n 10	oxalate	20—250	0·5	0·4071	11·3[b]
		300	2·5		

[a] N Samples measured by means of physical adsorption of nitrogen, n samples measured also by means of chemisorption of oxygen; [b] samples activated and measured in a larger adsorption vessel.

oxalate did not decompose at 250°C. The surface area and degree of decomposition depend, naturally on the mutual relation between the temperature and the period of decomposition and moreover the weight of the batch seems to have played a role in our arrangement too. The reproducibility of the specific surface areas of cobalt prepared from the formate or oxalate was rather poor.

In decomposing nickel compounds, we failed to obtain the metal with so high a dispersion (Table II) as that reported by Broadbent coworkers[12], who were able to obtain nickel with surface areas of 100 and 50 m²/g by heating the oxalate at 300°C in nitrogen stream for 6 h or at 380°C for 70 min, respectively.

Comparing the data of Tables I and II, we find that in the case of decomposition of oxalates, the nickel powder obtained possesses a larger specific surface area than the cobalt powder, whereas in the case of the formates, the reverse is true.

Evaluation of the catalyst activity. The effect of the speed of stirring in the autoclave on the reaction rate was examined for hydrogenation of lauronitrile and for hydrogenation of nitrobenzene. The rate of hydrogen uptake during the hydrogenation of nitrobenzene exceeded that for the fastest hydrogenation of lauronitrile.

TABLE III

Effect of Dispersion of Cobalt on the Lauronitrile Hydrogenation Rate
  Temperature 160°C, pressure 4·4 MPa, lauronitrile amount 0·228 mol.

Catalyst	Metal weight g	Specific surface area $m^2 g^{-1}$	Period s	Reaction rate		Sec-amine % mol
				$mmol\ s^{-1}\ g^{-1}$	$mmol\ s^{-1}\ m^{-2}$	
K 37, K 38 K 39	0·613	4·1[a]	13 500	0·055	0·014	11·0
K 34	0·560	6·2[a]	13 300	0·061	0·010	11·0
K 35	0·472	32·9[a]	5 000	0·200	0·006	11·4
K 17	2·400	15·4	1 320	0·145	0·009	7·7
K 4	3·000	6·9	2 200	0·069	0·010	11·0
K 6	4·000	3·7	2 040	0·056	0·015	11·0
K 4	1·000	6·9	6 600	0·069	0·010	11·5
K 12	1·000	4·1	14 100	0·032	0·008	12·9
K 16	2·000	14·6	1 590	0·144	0·010	12·5
Average					*0·0102*	*11·11*

[a] Surface area and activity measured on the same catalyst sample.

In both cases, the hydrogenation rates were independent of the stirring intensity if the stirring speed exceeded 1 000 rpm. The nitrile hydrogenation experiments were carried out applying the speed of 1 700 rpm, hence securely in the kinetic region. The kinetics of lauronitrile hydrogenation on nickel and on cobalt differ considerably (Fig. 1). The question arises as to which quantity should be used to characterize the metal activity. In view of the complex shape of the kinetic curve for the nitrile hydrogenation on cobalt, the activity was expressed as the average rate of hydrogen uptake calculated from the entire hydrogenation period. An inaccurate determination of the hydrogenation end point, however, reduces the accuracy of the value obtained, and taking into account also the poor reproducibility of metal preparation, we can see that the activity and selectivity of the metals can only be compared if a higher number of experiments have been carried out.

Specific activity of cobalt and nickel. Tables III and IV present the results of measurements of the hydrogenation rates on the metal powders with different specific surface areas. There is a considerable error even in the average values, but it can be claimed that in the conditions applied the surface of nickel metal is twice as active for the lauronitrile hydrogenation as the surface of cobalt; 2·3 times more secondary

TABLE IV

Effect of Dispersion of Nickel on the Lauronitrile Hydrogenation Rate
Temperature 160°C, pressure 4·4 MPa, lauronitrile amount 0·228 mol.

Catalyst	Metal weight g	Specific surface area $m^2 g^{-1}$	Period s	Reaction rate		Sec-amine % mol
				$mmol\ s^{-1}\ g^{-1}$	$mmol\ s^{-1}\ m^{-2}$	
n 1	0·850	3·4[a]	7 200	0·075	0·022	21·1
n 5, n 6, n 7	1·285	3·4[a]	6 000	0·059	0·018	28·2
n 8, n 9, n 10	1·116	11·6[a]	2 250	0·182	0·016	28·2
N 20	0·240	7·3	10 800	0·176	0·024	25·6
N 18	2·000	2·6	3 480	0·066	0·025	29·2
N 19	2·000	2·0	6 000	0·038	0·020	22·0
N 21	3·013	0·6	12 000	0·014	0·021	26·9
N 19	2·000	2·0	4 920	0·035	0·018	22·0
Average					*0·0208*	*25·4*

[a] Surface area and activity measured on the same catalyst sample.

amine was formed on the former than on the latter. No relation could be traced between the reaction period (which is inversely proportional to the product of the weight and the specific surface area of the catalyst) and the content of secondary amine in the hydrogenation product, which indicates that the condensation of imine with amine takes place entirely or predominantly on the metal surface rather than in the liquid bulk. The different ability of nickel and of cobalt for the formation

TABLE V

Activity and Selectivity of Industrial Catalysts
Temperature 160°C, pressure 4·4 MPa, nitrile amount 0·228 mol.

Catalyst	Metal content % wt.	Catalyst weight g	Specific surface area $m^2 g^{-1}$	Period s	Reaction rate		Sec-amine % mol
					$mmol\ s^{-1}\ g^{-1}$	$mmol\ s^{-1}\ m^{-2}$	
Co-silica gel	43·8	2·5	—	780	0·234	—	10·0
Ni-kieselguhr	50·6	2·0	53·5	420	0·543	0·020	20·1
Ni-Cr_2O_3	40·1	1·0	16·9	3 600	0·127	0·019	19·0
Ni-Cr_2O_3	40·1	1·0	16·9	2 500	0·183	0·026	22·4
Ni-alumina	48·8	1·0	63·9	820	0·56	0·018	21·5
Raney's Ni	67·3	0·7	54·1	4 800	0·136	0·018	15·8
Cu-kieselguhr	43·0	4·0	9·9	23 600	0·005	0·001	77·0[a]
Cu-silica gel	33·0	4·0	37·0	9 700	0·012	0·001	84·0

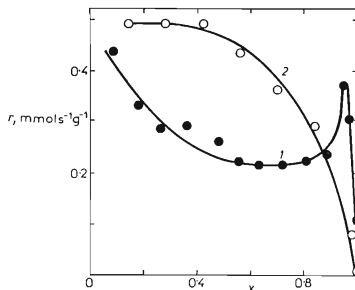[a] The product contained 10% nonreacted nitrile.

FIG. 1

Dependence of the Hydrogenation Rate on the Lauronitrile Conversion
1 On cobalt, 2 on Ni–Al_2O_3.

of secondary amine may be caused either by the different activity of the metal surfaces for the reaction of primary amine with imine, or by the different relative sorption of the reacting components. This problem will be dealt with in the forthcoming paper of this series.

Activity of carrier catalysts. A carrier can not only increase the degree of dispersion of the metal, but it can also influence the course of the catalytic reaction. The results of hydrogenation of lauronitrile on industrial nickel catalysts (Table V) indicate that the catalysis is nonspecific, as the carrier does not affect the rate of the process in question. The average specific activity of nickel in four industrial catalysts including Raney's nickel is 0·0202 mmol H_2 s^{-1} m^{-2}, that of pure nickel is 0·0208

TABLE VI

Effect of Admixtures on the Lauronitrile Hydrogenation Rate and Selectivity
  Pressure 4·4 MPa, 2 g Co, 0·228 mol nitrile.

Catalyst	Admixture[a]	Temperature °C	Period s	Reaction rate mol s^{-1} g^{-1}	Sec-amine % mol
Co_3O_4 I	0	160	1 860	0·123	12·1
	5% Na_2CO_3	160	2 880	0·079	8·7
	50% Al_2O_3	160	1 680	0·136	16·8
Co_3O_4 II	0	180	1 800	0·127	14·4
	3% Na_2CO_3	180	2 220	0·103	10·8

[a] Per cent values with respect to Co.

TABLE VII

Effect of Temperature on the Rate of Lauronitrile Hydrogenation on Cobalt
  Pressure 4·4 MPa, nitrile amount 0·228 mol.

Temperature °C	Reaction rate[a] mmol s^{-1} m^{-2}	Sec-amine[a] % mol	Number of experiments
150	0·0075	11·1	2
160	0·0102	11·1	11
170	0·0220	12·8	1
180	0·0288	14·4	6

[a] Average values.

mmol H_2 s^{-1} m^{-2}. We failed to determine the specific surface area of cobalt in the carrier catalysts. The specific surface area of copper in carrier catalysts was determined in one of our other unpublished works by decomposition of N_2O. We failed to prepare pure copper possessing a sufficient activity (large specific surface area), and the specific activity was only evaluated based on experiments with the carrier catalysts, assuming that the carriers do not affect the reaction rate. The ratio of the lauronitrile hydrogenation rates on the metals in question at 160°C was 20 : 10 : 1 for nickel, cobalt, and copper, respectively.

Contrary to expectations, acidic nature carriers such as kieselguhr, alumina, or chromic oxide do not bring about a rise in the content of secondary amine in the product; its average value is 20·75%, which is even lower than that one on pure nickel (25·4%). An appreciably higher selectivity as compared with pure nickel is exhibited by Raney's nickel; it approaches that of cobalt. In this case, the residual sodium hydroxide in the catalyst may play a role. Freindlin and Sladkova[13] have found that in hydrogenation of adiponitrile on cobalt catalysts, carriers such as silica gel or alumina promote to an extent the formation of secondary amine. Adding sodium carbonate to butyronitrile, Greenfield[2] depressed the content of secondary amine in the product on nickel on kieselguhr down to less than a half; the reaction rate dropped considerably. An addition of sodium carbonate during hydrogenation of stearonitrile in the presence of cobalt lowered the formation of secondary amine to two thirds of the initial value[5]. The results given in Table VI confirm that sodium carbonate improves somewhat the selectivity for primary amine, with a decrease in the hydrogenation rate. On copper catalysts, secondary amine is formed in an approximately 85% yield, the remaining part is constituted by primary amine (4%) and tertiary amine (11%). According to the patent of Amour Co.[14], cupric-chromic catalyst affords nearly pure secondary amine, the C=C double bonds in unsaturated acids nitriles remaining intact.

Effect of temperature on the hydrogenation rate and selectivity. The results of hydrogenation of lauronitrile at various temperatures are summarized in Table VII, the various experimental data for a temperature level being averaged. Linear regression of all the data afforded the apparent activation energy of lauronitrile hydrogenation on cobalt, 84 kJ mol^{-1}. This is a rather high value for a hydrogenation reaction, which may be due to the chemisorption enthalpies of the reacting components being included. The selectivity of formation of primary amine decreases slightly with increasing temperature.

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