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METHOD OF ACTIVATING CATALYTIC ALLOYS

Shin-Ichi Taira, Nagoya, and Akio Kuroda, Kanagawa-ken, Japan, assignors to Toyo Rayon Kabushiki Kaisha, Tokyo, Japan, a corporation of Japan

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ABSTRACT OF THE DISCLOSURE

A method of activating Raney alloys to form new Raney type catalysts by treating Raney alloys with water in the presence of either aluminas, amines, non-N-substituted lactams, N-substituted lactams, oximes, N-substituted acid amides or urea derivatives.

This invention relates to the activation of Raney alloys for obtaining improved Raney type catalysts having excellent activities and durability. More particularly, the invention relates to a method for the activation of Raney alloys, as well as the various modifications thereof, wherein Raney alloys are treated with water in the presence of either aluminas, amines, lactams, oximes, N-substituted acid amides or urea derivatives.

It is well known that Raney catalysts can be prepared by treating an alloy of aluminum with a metal active for catalystic hydrogenation such as nickel, cobalt, iron or copper, i.e. a so-called Raney alloy, with an aqueous solution of a sufficient concentration of a strong inorganic alkali, say, caustic soda to elute the aluminum from the alloy. When a Raney catalyst is prepared in large quantities on a commercial scale by this method, great care must be taken due to the heat and large amount of hydrogen gas which are violently generated from the reaction of aluminum in the alloy with said aqueous solution of a strong inorganic alkali. In addition, there is also the disadvantage that specially designed equipment must be used. Furthermore, the resultant Raney catalyst is deactivated or ignites spontaneously when it comes into contact with air or becomes dry in air, and hence great caution is required in its handling. Consequently, this catalyst is usually stored in water or alcohols. However, a decline in its catalytic activity takes place during its storage, and it has a poor durability when used for hydrogenation. Further its regeneration is difficult. Thus, the usual Raney catalyst, prepared by the elution of a major part of the aluminum in the alloy with an aqueous solution of a strong inorganic alkali, had many difficulties in commercial preparation and use because of its high cost, poor durability and delicacy in handling.

In addition, there has also been known a method which comprises treating the Raney alloy with an aqueous solution in which sodium hydroxide is contained in less than its stoichiometric quantity. Also there is known a method wherein the alloy is activated by water, steam or an aqueous solution containing a substance such as cane sugar, salt or sodium carbonate, which plays a role in raising the boiling point of water (U.S. Pat. 1,915,473). Thus a bulky catalyst containing alumina is obtained. However, for preparing a highly active catalyst by these methods, there is such inconvenience that a very long time is required for sufficient activation of the alloy.

We have found that certain substances, i.e., aluminas, amines, lactams, oximes, N-substituted acid amides and urea derivatives all have the effect of promoting the activation of the Raney alloys with water and hence improved Raney type catalysts are provided. Specifically, it has been found that when the Raney alloys are treated even at a low temperature in a relatively short time with water in

the presence of one or more of the aforesaid substances it is possible to provide new Raney type catalysts which have excellent activity, durability, selectivity, and ease in handling and regeneration. According to the present invention, it is possible to activate the Raney alloys without causing the violent evolution of heat and hydrogen gas as in the prior art, but with controlled evolution. The products thus obtained are improved Raney type catalysts containing alumina which results from the aluminum in the alloy. It is believed that the catalysts have a unique structure judging from the fact that their activities and durabilities are higher than those of any conventional Raney type catalysts.

More specifically, this invention relates to a method of activating Raney alloys which comprises treating a Raney alloy with water in the presence of at least one substance selected from the group consisting of aluminas, amines, non-N-substituted lactams, N-substituted lactams having at least one hydrogen atom on the carbon atom adjacent to the CO group, oximes, N-substituted acid amides having at least one hydrogen atom on either the carbon atom adjacent to the CO of the amide group or the nitrogen atom of the amide group, and urea derivatives in which each of the two nitrogen atoms of the urea group has one hydrogen atom or in which one of the two nitrogen atoms has one hydrogen atom while the other nitrogen atom has no hydrogen atom.

The Raney alloy to be used in this invention may be any of the alloys consisting of aluminum and metals active for catalytic hydrogenation such as iron, nickel, cobalt or copper. In other words, it may be any of the alloys which are usually known as Raney alloys. Usually, the commercially available alloys are used, i.e. alloys consisting of aluminum and either iron, cobalt, nickel or copper, and preferably those in which the weight ratio of aluminum to these metals is 7:3–1:1 and whose particle size is smaller than 50 mesh. Further, mixtures of the Raney alloys may also be used. Also conveniently used are the alloys which contain a third component, for example, such as boron, titanium, chromium, manganese, molybdenum, zirconium, lead, tin and tungsten.

The above-mentioned several substances which are to be present in treating the Raney alloys with water according to this invention are described below in details. The term "promoter," as herein used, denotes the above-mentioned substances.

Many types of structurally different aluminas are known. While they are usually represented by the formulas Al_2O_3, $Al_2O_3 \cdot H_2O$ or $Al_2O_3 \cdot 3H_2O$, there are many other types of aluminas whose composition cannot be expressed by a simple chemical formula. All of these, however, can be effectively used in this invention as a promoter, $Al_2O_3 \cdot 3H_2O$ being particularly preferred. For instance, the well-known hydrargillite (gibbsite) and bayerite are expressed by the formula, $Al_2O_3 \cdot 3H_2O$. The substance expressed by the formula $Al(OH)_3$ and generally referred to as aluminum hydroxide can also be used as the promoter because $Al(OH)_3$ or aluminum hydroxide is a substance consisting presumably of water and alumina or aluminum oxide and it is to be understood that aluminas, as used herein and the appended claims, comprehends this substance also. It is also to be understood that the use of aluminum or such compounds as form aluminas under activating conditions, for example, the inorganic aluminum compounds such as sodium aluminate, alum, aluminum sulfate and aluminum nitrate and the organic aluminum compounds such as aluminum ethoxide and aluminum isopropoxide is also comprehended by this invention.

Any amine can be used as a promoter in this invention. The amines, as herein used, denote the organic bases con-

taining the nitrogen atom. Namely, the compounds having the general formula



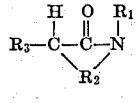
wherein R_1, R_2 and R_3 respectively represent an organic radical or hydrogen atom, with the proviso that these three members are not hydrogen atoms at the same time, are within the scope of the invention. In other words, the amines used in this invention are classified as primary, secondary and tertiary amines and basic compounds containing imino group and, preferably, they are aliphatic amines, aromatic amines, alicyclic amines, heterocyclic amines, amidines and iminourea derivatives. Specific examples of conveniently usable amines are given below, but it is to be understood that the amines usable are not limited to those given.

The primary amines include, for example, methylamine, ethylamine, n-propylamine, n-butylamine, laurylamine, oleylamine, stearylamine, benzylamine, aniline, o-, m- and p-phenylenediamine, cyclohexylamine, bornylamine, allylamine, ethanolamine, 4-aminopyridine, 4-aminoquinoline, ethylenediamine, bis-aminomethylcyclobutane, 2-methylpentamethylenediamine, hexamethylenediamine, trimethyl hexamethylenediamine, decamethylenediamine, dodecamethylenediamine and o-, m- and p-xylylenediamine. The secondary amines include such as dimethylamine, diethylamine, dihexylamine, allylmethylamine, benzylmethylamine, diallylamine, trimethyleneimine, pyrrolidine, piperidine and hexamethyleneimine. The tertiary amines include trimethylamine, triethylamine, dimethylethylamine, benzyldiethylamine, pyridine, N-ethylpiperidine, N-methylpyrrolidine, 2,4,6-trimethylpyridine, 8-hydroxyquinoline and 5-methoxyacridine. The amidines include such as formamidine, acetamidine, propionamidine, lauramidine, stearamidine. The iminourea derivatives include such as guanidine, phenylguanidine, creatine, creatinine and arginine.

Compounds which can be converted to amines under activating conditions of the Raney alloys can also be used in this invention instead of the aforementioned amines. Hence, this embodiment is also included in the scope of this invention. The compounds which can be converted to amines, for example by hydrogenation, are nitro compounds, nitroso compounds, hydroxylamino compounds, azo compounds, azoxy compounds, hydrazo compounds, nitriles, isonitriles and Schiff's bases.

The non-N-substituted lactams to be used in this invention may be any cyclic amides whose amide group does not have a substituent on their nitrogen atom. Specific examples are gamma-butyrolactam, delta-valerolactam, epsilon-caprolactam, zeta-enantholactam, eta-caprylolactam, lambdi-laurolactam and the like.

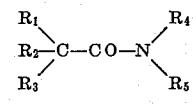
The N-substituted lactams, having at least one hydrogen atom on the carbon atom adjacent to the CO group, are represented by the general formula



wherein R_1 and R_2 are organic radicals and R_3 is either a hydrogen atom or an organic radical. Specific examples of conveniently usable N-substituted lactams are the following: N-methyl-gamma butyrolactam, N-isopropyl-gamma - butyrolactam, N - methyl - delta - valerolactam, N-methyl-epsilon caprolactam, N-ethyl-epsilon-caprolactam and N-methyl-3-methyl-deltavalerolactam.

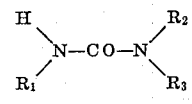
The oximes are classified into aldoxime and ketoxime, but both can be equivalently used in this invention. As specific examples, acetaldoxime, n-butylaldoxime, benzaldoxime, acetophenoneoxime, benzophenoneoxime and cyclohexanoneoxime can be mentioned.

The N-substituted acid amides, having at least one hydrogen atom on either the carbon atom adjacent to the CO of the amide group or the nitrogen atom of the amide group, are represented by the general formula



wherein R_5 is an organic radical and R_1, R_2, R_3 and R_4 respectively represent a hydrogen atom or an organic radical, with the proviso that at least one of them is a hydrogen atom. The conveniently available N-substituted acid amides are, for example, the followings: N-methylacetamide, N,N-dimethylacetamide, N-methylpropionamide, N,N-dimethylpropionamide, N-hydroxymethyl isobutyramide, N-methyl phenylacetamide and N,N-dimethyl phenylacetamide.

The urea derivatives, in which each of the two nitrogen atoms of the urea group has one hydrogen atom or in which one of the two nitrogen atoms has one hydrogen atom while the other nitrogen atom has no hydrogen atom, are represented by the general formula



wherein R_1 and R_2 are organic radicals and R_3 is either a hydrogen atom or an organic radical. As specific examples, N,N'-dimethylurea, N,N'-diethylurea, N,N,N'-trimethylurea and N,N,N'-triethylurea can be mentioned.

The hereinabove described substances can be used alone or together. Since their use in an excessively small amount does not produce the desired results, they are usually used in an amount of at least 1/20 by weight of the Raney alloy. The amount of the promoter applied depends on the kind of promoter, the amount of water to be used and the treating temperature. Generally speaking, when promoter is applied greater than one-half, particularly about twice, the weight of the Raney alloy, the activation is promoted effectively. When aluminas are applied as a promoter, much less quantity of them is enough for promotion than those of the other promoters.

In case of applying the promoters, water-soluble ones are preferably chosen except for aluminas. However, those which are insoluble or hardly soluble in water are also applicable. In this case, desirable results are frequently brought about by using suitable solvents which dissolve the promoters and are also miscible with water. Such solvents usually employed are, for example, methanol, ethanol, isopropanol, dioxane, tetrahydrofuran and dimethylformamide.

The water is used in an amount which is essentially sufficient for reacting equivalently with the aluminum contained in the alloy, but usually an amount more than twice the equivalent is desirable. When it is desired to erode the alloy slightly or when there is a special reason, the amount of water can suitably be reduced.

One of the features of this invention is that the effective activation of the Raney alloys can be attained under mild conditions of relatively low temperatures and then the degree of erosion of the alloys can be controlled at will. Specifically, the desired end can be attained at a temperature not lower than 0° C. For shortening the time of activation, usually a temperature higher than 10° C. is preferred. Although elevated temperature up to 350° C. can be applied, the preferred temperature is one not exceeding 150° C. from the consideration of the fact that there are slight decreases in the activities of the catalysts prepared at higher temperatures.

The activation can be carried out under atmospheric or higher pressure in the presence of air, nitrogen or hydrogen gases.

It was found that the time required for the activation could be shortened still further by the use of a small amount of an alkaline substance together with the aforesaid specific promoters. The alkaline substances are the following: alkali metal hydroxide, alkaline earth metal hydroxide, alkali metal or alkaline earth metal salts of inorganic or organic weak acids, e.g., carbonates, phosphates, borates, acetates, propionates and phenoxides, alkali metal alcoholates, quaternary ammonium hydroxides, hydrazine hydrate and ammonium hydroxide. As the application of a large quantity of such alkaline substance as alkali metal hydroxides, alkaline earth metal hydroxides, alkali metal alcoholates, quaternary ammonium hydroxides or hydrazine hydrate causes the violent evolution of heat and hydrogen gas and then many profitable features of the present invention are lost, the applicable amount of the alkaline substance should be under 1/5 equivalent to the aluminum contained in the Raney alloy.

As the operating conditions to activate the Raney alloys according to this invention is mild and hence special equipment for the operation are not required, there is the advantage that the operation can be done in the reactor in which the hydrogenation reaction is to be carried out. In this case, it is, of course, possible to adopt a mode wherein the organic compound to be hydrogenated, and, if necessary, hydrogen gas are present together in the reactor. Thus, the activation of the Raney alloy and the hydrogenation of the organic compound can be carried out at the same time. When the organic compound is one which can be converted to an amine by hydrogenation, the aforesaid reactioins can be carried out merely in the presence of Raney alloy, water, hydrogen gas and the said organic compound. In such a case the amine formed from the said organic compound plays a role of the promoter and still better results are obtained by adding a small amount of the previously noted alkaline substances or catalytically active substances for hydrogenation, e.g. the Raney type catalyst obtained by this invention, Raney nickel, Raney cobalt, nickel boride, palladium on carbon or platinum oxide. In contrast with the conventional process, in which hydrogenation had to be carried out by charging the reactor with the delicate Raney catalyst which had been prepared independently, these embodiments of this invention have great commercial advantages. Hydrogenolysis, reductive alkylation and other reactions can also be carried out in like manner as mentioned above.

The improved Raney type catalysts obtained by this invention are, as previously noted, not only very active and durable but also nonpyrophoric and are not deactivated even when they are dried in air. And after having been used as catalysts for hydrogenations, they can either be used for successive hydrogenations or be stored in slurry or frozen form. Alternatively, they can be dried in air and stored in this state and, as required, be reused for hydrogenations. On the other hand, when their activities are decreased by repeated uses they can be readily regenerated by applying one or more of the following ways: treating with water, treating with water after being admixed with aluminum or a fresh Raney alloy, or treating with an aqueous alkaline solution. Further, the Raney type catalysts obtained by the invention are also excellent in selectivities. For instance, hydrogenation of nitriles with the conventional Raney catalysts results in forming relatively large amounts of secondary amines and other by-products, whereas desired primary amines are formed selectively and in excellent yields with the catalysts of this invention.

The fact that the invention can provide the improved Raney type catalysts having the many characteristics above noted is another important feature of this invention.

The following examples are given to illustrate this invention, but they are not limited to the present invention in any manner, since it is obvious that many variations embraced by the above descriptions of the invention are possible.

Although the general procedures of practising this invention are described below by the instances of hydrogenation reaction, the illustrated methods can be suitably practised in like manner when being applied to the other reactions.

GENERAL PROCEDURES

(1) Preparation of catalyst (activation of Raney alloy)

Procedure A.—A Raney alloy, water and a promoter or promoters and, if necessary, a suitable solvent and/or a small amount of hydrogenation catalyst and/or a small amount of an alkaline substance are placed in a vessel. The mixture is stirred for a required time at a prescribed temperature. At this time, if the hydrogen gas generated is collected in a gas burette in a suitable manner during the course of the reaction, the progress of the activation can be checked. The resultant catalyst is transferred to a hydrogenation reactor immediately or, if necessary, after washing with water or a suitable solvent.

Procedure B.—A Raney alloy, water and a promoter or promoters and, if necessary, a suitable solvent and/or a small amount of a hydrogenation catalyst and/or a small amount of an alkaline substance are placed in a pressure vessel. After replacing the air in the vessel by hydrogen or nitrogen gas, the mixture is stirred for a required time at a prescribed temperature. The resultant catalyst is similarly treated as in Procedure A. After preparation of the catalyst, the vessel used for the activation in Procedure A or B can, of course, be utilized as a reactor of successive hydrogenation without transferring the catalyst.

(2) Hydrogenation

Procedure C (hydrogenation under ordinary or low pressure).—The catalyst prepared by either Procedure A or B and the organic compound to be hydrogenated and, if necessary, a suitable solvent and/or an additive which acts favorably for the hydrogenation (e.g. an alkaline substance in case of the hydrogenation of carbonyl compounds and phenols, and liquid NH_3 in case of nitriles) are placed in an airtight vessel connected with a gas burette to measure the amount of hydrogen gas absorbed. After replacing the air in the vessel thoroughly by hydrogen gas, the contents of the vessel are vigorously stirred at a prescribed temperature until the hydrogen uptake ceases.

Procedure D (hydrogenation under high pressure).—The catalyst prepared by either Procedure A or B and the organic compound to be hydrogenated and, if necessary, a suitable solvent and/or an additive such as described in Procedure C are placed in an autoclave. After replacing the air in the autoclave thoroughly by hydrogen gas of the prescribed pressure, hydrogenation is carried out at the prescribed temperature until no further decrease in the hydrogen pressure is observed.

(3) The simultaneous hydrogenation with preparation of the catalyst

Procedure E.—A Raney alloy, water, the organic compound to be hydrogenated and a promoter or promoters and, if necessary, a suitable solvent and/or a small amount of a hydrogenation catalyst and/or an additive are placed in the vessel as described in Procedure C. The subsequent operation is carried out as in Procedure C, but caution must be taken as evolution of hydrogen gas occurs within the reactor.

Procedure F.—A Raney alloy, water, the organic compound to be hydrogenated and a promoter or promoters and, if necessary, a suitable solvent and/or a small amount

of a hydrogenation catalyst and/or an additive are placed in the vessel equipped with an efficient reflux condenser and the contents are stirred at the prescribed temperature until the evolution of hydrogen gas ceases. In this case, if the amount of hydrogen generated by the reaction between water and the aluminum contained in the alloy is insufficient for completion of the hydrogenation, a hydrogen source such as aluminum grain is required to be present together.

Procedure G.—A Raney alloy, water, the organic compound to be hydrogenated and a promoter or promoters and, if necessary, a suitable solvent and/or a small amount of a hydrogenation catalyst and/or an additive are placed in an autoclave. The subsequent operation is carried out as described in Procedure D.

In Procedures E, F and G, if the organic compound to be hydrogenated is one which can be converted to an amine by hydrogenation, a promoter is not necessarily needed.

(4) Treatment of the reaction products

After completion of the hydrogenation, the catalyst was separated from the reaction mixture and then the reaction products were treated by suitable means according to the cases. In some cases, the reaction products were analyzed by means of gas chromatography. The figures indicated in the "Yield" column of Table II and III by the notation "G.C." are one determined by this means.

EXAMPLE 1

Examples of preparing the catalysts are shown in Table I. The catalyst of No. 14 was used in the Experiment No. 14 of Example 2 after being washed with water and dried in air.

EXAMPLE 2

Examples of hydrogenations carried out with the catalysts prepared in Example 1 are shown in Table II. In the Experiments Nos. 40, 45 and 46, the mole ratio between hexamethylenediamine and hexamethyleneimine in the reaction products were determined by gas chromatography. The amounts of distillation residues, after distilling off these compounds from the reaction products, were 2.1% (Experiment No. 40), 1.3% (Experiment No. 45) and 2.7% (Experiment No. 46) of the weights of starting materials respectively.

EXAMPLE 3

Examples in which hydrogenations were effected simultaneously with the preparations of the catalysts are shown in Table III. In Experiments Nos. 16 and 29 the amounts of residues, after distilling off hexamethyleneimine and hexamethylenediamine from the reaction products, were 2.6% (Experiment No. 16) and 7.1% (Experiment No. 29) of the weights of starting materials respectively.

EXAMPLE 4

After removing the resultant methyl isobutyrate by decantation in Experiment No. 4, Table II, 120 g. of methyl methacrylate was charged in the reactor. The successive hydrogenations were repeated 15 times under identical conditions as in Experiment No. 4 (the reaction temperature spontaneously rose to about 80° C.), and decrease in the catalytic activity was not found. Further, after completion of the last hydrogenation, the catalyst was washed with ethanol, water and then was dried in air. Methyl methacrylate was again hydrogenated with this catalyst under identical conditions as in Experiment No. 4. The result was about the same as that of Experiment No. 4.

EXAMPLE 5

The recovered catalyst of Experiment No. 43, Table II was washed with ethanol, water and then was dried in air at room temperature. After placing this catalyst, 25 g. of resorcinol, 50 ml. of water and 10 g. of sodium hydroxide in an autoclave, hydrogenation was carried out under initial hydrogen pressure of 80 kg./cm.² and at 100–110° C. for 6½ hours. After filtering off the catalyst, the filtrate was acidified with hydrochloric acid and cooled to 0° C. The precipitated crystal was recrystallized from benzene. The yield of dihydroresorcinol (M.P. 103–4° C.) was 87% of the theoretical.

EXAMPLE 6

The recovered catalyst of Experiment No. 45, Table II, was washed with water and then with ethanol to remove the water. With this catalyst, epsilon-aminocapronitrile was successively hydrogenated under identical conditions as in Experiment No. 45. The results are shown in Table IV.

TABLE IV

Batch number	Reaction time, min.	Analysis of reaction products, G.C. Hexamethylenediamine, mol percent	Hexamethyleneimine, mol percent	Residue after distillation, percent based on starting material
1	20	99.31	0.69	1.2
4	40	99.08	0.92	1.8
9	70	98.16	1.84	2.1
15	120	98.02	1.98	2.6

EXAMPLE 7

The recovered catalyst of Experiment No. 62, Table III, was dried in air at 80° C. This catalyst was charged in an autoclave with 50 g. of adiponitrile and 100 ml. of liquid ammonia. Hydrogenation was carried out under initial hydrogen pressure of 150 kg./cm.² at 120–122° C. for 25 minutes. The yield of hexamethylenediamine was 97.1% of the theoretical. Again with this catalyst, adiponitrile was successively hydrogenated 7 times under identical conditions. A decrease in activity of the catalyst was hardly found and the yields of hexamethylenediamine were 96.8–97.4% of the theoretical throughout the experiments.

EXAMPLE 8

The nickel catalyst prepared under the same conditions of Experiment No. 36, Table I, was washed with water and then wtih methanol. The catalyst was placed in an autoclave with 200 g. of methyl methacrylate, and the hydrogenation was carried out under initial hydrogen pressure of 50 kg./cm.². The reaction was over in 5 minutes and the temperature spontaneously rose from 22° C. to 90° C. After separating the resultant methyl isobutyrate from the catalyst, methyl methacrylate was successively hydrogenated 23 times under the same conditions described above. The activity of the catalyst was gradually decreased and the time required for completion of the hydrogenation became 65 minutes at the end. The recovered catalyst was washed briefly with methanol and then it was stirred in 60 ml. of water for 2 hours at 85–90° C. Then the catalyst was washed with methanol and again used for the hydrogenation of methyl methacrylate under the same conditions. The regenerated catalyst was so active that the reaction was finished in 6 minutes, and the temperature of the autoclave rose spontaneously from 24° C. to 87° C. The yield of methyl isobutyrate (B.P. 93° C.) was about theoretical.

EXAMPLE 9

4 g. of Raney alloy (Co:Al=1:1), 8 g. of hexamethylenediamine and 35 ml. of water were placed in a vessel equipped with a reflux condenser, following which the mixture was stirred for 70 minutes at 50–70° C. The resulting catalyst was washed with water and then water was removed as much as possible from the catalyst. The catalyst was placed in an autoclave with 60 g. of epsilon-aminocapronitrile, 5 ml. of water and 0.3 g. of sodium hydroxide. The hydrogenation was carried out under initial hydrogen pressure of 100 kg./cm.² at 100–105° C. for 30 minutes. The yield of hexamethylenediamine was

97.6% of the theoretical. When the catalyst was repeatedly used for 18 times without any treatment, its selectivity declined and the yield of hexamethylenediamine decreased to 89.4% of the theoretical. To the mixture of the catalyst and a part of the reaction products 1 g. of aluminum grain and 50 ml. of water were added and the admixture was stirred for 30 minutes at 24–26° C. The regenerated catalyst was washed with water and then water was removed as much as possible from the catalyst. With this catalyst, epsilon-aminocapronitrile was hydrogenated under the same conditions mentioned above. The yield of hexamethylenediamine was 97.8% of the theoretical and the fact was owing to the perfect revival of the catalyst in selectivity.

TABLE I

[Example 1—Preparation of the catalyst]

Catalyst No.	Procedure	Raney alloy: Composition	Raney alloy: Weight (g.)	Promoter (g.)	Water (ml.)	Solvent (ml.)	Additive (g.)	Reaction temperature, ° C.	Reaction time (min.)
1	A	Ni:Al=1:1	5	Al_2O_3 (2)	100			80–85	200
2	B	Cu:Al=1:1	4	Al_2O_3 (3)	60			100	120
3	B	Ni:Al=1:1	6	$Al_2O_3 \cdot H_2O$, (3)	50			60–70	180
4	A	Ni:Al=4:6	10	$Al_2O_3 \cdot 3H_2O$, (5)	100			80	120
5	B	Ni:Al=1:1	2.5	$Al_2O_3 \cdot 3H_2O$, (5)	50			120	90
6	B	Ni:Al=1:1	20	$Al_2O_3 \cdot 3H_2O$, (1)	100			70–75	310
7	A	Co:Al=1:1	10	Sodium aluminate, (0.8).	40			50	70
8	B	Ni:Al=1:1	3	Aluminum ethoxide, (4).	50			90	100
9	A	Ni:Al=1:1	5	Al, (0.5)	50		Sodium borate, (0.6)	45–50	80
10	A	Ni:Al=1:1	20	$Al_2O_3 \cdot 3H_2O$, (1)	50		NaOH, (0.4)	5–7	60
11	A	Ni:Al=1:1	2	n-Butylamine, (7.3)	50			60	90
12	B	Ni:Al=4:6	10	Cyclohexylamine, (10)	200			100	60
13	B	Fe: Al=45:55	4	p-Toluidine, (12)	100			100	150
14	B	Co:Al=45:55	10	Hexamethylene diamine, (20).	100			80	60
15	B	Co:Al=45:55	10	Decamethylene diamine, (20).	100			80	60
16	A	Ni:Al=1:1	4	Piperidine, (7.5)	80			50–55	160
17	A	Ni:Al=1:1	2	Diethylamine, (5)	50			60–65	120
18	A	Cu:Al=4:6	2	Triethylamine, (10)	50			45–50	100
19	B	Ni:Al=1:1	2	Pyridine, (10)	100			80–85	100
20	A	Ni:Al=4:6	5	Creatinine, (1)	30			15–20	90
21	B	Ni:Al=1:1	4	Phenylhydroxylamine, (10)..	70	BuOH, 30		70–80	110
22	B	Ni:Al=1:1	4	Azobenzene, (14)	30	EtOH, 50		95–100	120
23	A	Co:Al=1:1	5	Adiponitrile, (15)	10		Raney Co, (0.5)	50–55	70
24	A	Ni:Al=1:1	2	Diethylamine, (5)	50		NaOH, (0.1)	27–30	75
25	B	Ni:Al=4:6	10	Cyclohexylamine, (10)	100		Tetramethylammonium hydroxide, (0.2).	50	60
26	B	Co:Al=1:1	5	Hemxaethylene, diamine, (20). $Al_2O_3 \cdot 3H_2O$,(5).	100			60	60
27	A	Ni:Al=1:1	6	8-hydroxyquinoline, (15). Al_2O_3, (3)	70			50–57	70
28	A	Ni:Al=1:1	2.5	n-Butylamine, (7.5) $Al_2O_3 \cdot 3H_2O$, (1)	50		NaOH, (0.1)	20	70
29	A	Cu:Al=4:6	3	Cyclohexylamine, (10). $Al_2O_3 \cdot 3H_2O$, (5)	50		K_2CO_3, (0.1)	30	90
30	A	Ni:Al=1:1	2	Pyridine, (7) $Al_2O_3 \cdot 3H_2O$, (5)	25		NaOH, (0.2)	30	90
31	A	Ni:Al=1:1	5	γ-Butyrolactam, (30)	70			80	150
32	A	Co:Al=1:1	10	δ-Valerolactam, (80)	25			70	200
33	A	Ni:Al=4:6	3	ε-Caprolactam, (50)	30			100	130
34	A	Ni:Al=1:1	4	λ-Laurolactam, (10)	15	BuOH, (30)		75	140
35	A	Ni:Al=1:1	3	γ-Butyrolactam, (30)	15		NaOH, (0.2)	23–32	70
36	A	Ni:Al=4:6	10	δ-Valerolactam, (50)	50		$Ba(OH)_2$, (0.2)	20–30	100
37	A	Ni:Al=1:1	4	ε-Caprolactam, (70)	35		NaOH, (0.1)	21–28	70
38	A	Co:Al=1:1	10	ε-Caprolactam, (70)	30		NaOH, (0.5)	24–35	50
39	A	Co:Al=45:55	11.1	η-Caprololactam, (50)	30		KOH, (0.1)	20–32	90
40	A	Ni:Al=1:1	20	γ-Butyrolactam, (50)	30		2% ethyltrimethyl ammonium hydroxide aq., (10).	22–26	110
41	A	Ni:Mo:Al=45:5:50	5	δ-Valerolactam, (50) λ-Laurolactam, (10)	15		10% tetramethyl ammonium hydroxide aq., (2).	15–23	70
42	A	Ni:Al=1:1	4	ε-Caprolactam, (10) $Al_2O_3 \cdot 3H_2O$, (2)	40			45–50	90
43	A	Co:Al=45:55	11.1	ε-Caprolactam, (80) $Al_2O_3 \cdot 3H_2O$, (3)	30		NaOH, (0.1)	20–38	80
44	A	Co:Al=1:1	10	ε-Caprolactam, (50) Aluminum isopropoxide, (6).	50		Sodium isopropoxide, (2)	3–8	40
45	A	Ni:Al=4:6	4	N-Methyl-γ-butyrolactam, (20).	20			90–100	170
46	A	Co:Al=1:1	10	N-Methyl-γ-butyrolactam, (40).	20			80–83	220
47	A	Ni:Al=1:1	4	N-Ethyl-ε-caprolactam, (20).	50			75–80	170
48	A	Ni:Al=1:1	2	N-methyl-3-methyl-δ-valerolactam, (10).	30			94–100	180
49	A	Co:Al=45:55	20	N-methyl-δ-valerolactam, (20).	50		NaOH, (0.08)	40–50	150
50	A	Ni:Al=1:1	5	N-methyl-δ-valerolactam, (10). $Al_2O_3 \cdot 3H_2O$, (2)	40			55–58	120
51	A	Ni:Al=1:1	5	N-Methyl-δ-valerolactam, (70). $Al_2O_3 \cdot 3H_2O$, (1)	300		$Ba(OH)_2$, (0.14)	30–33	80

TABLE I.—Continued

Catalyst No.	Procedure	Raney alloy Composition	Raney alloy Weight (g.)	Promoter (g.)	Water (ml.)	Solvent (ml.)	Additive (g.)	Reaction temperature, ° C.	Reaction time (min.)
52	A	Co:Al=45:55	4	Acetoxime, (25)	50			70–75	180
53	A	Ni:Al=1:1	4	Cyclohexanone oxime, (30).	20	EtOH, (40)		40–45	240
54	A	Ni:Al=1:1	4	Benzophenoneoxime, (17).	30	EtOH, (50)		38–40	290
55	A	Ni:Al=1:1	4	Benzaldoxime, (15); $Al_2O_3 \cdot 3H_2O$, (1)	20	EtOH, (40)		24	125
56	A	Ni:Al=1:1	4	N, N-di-methylacetamide, (50).	30			65–70	215
57	B	Ni:Al=4:6	5	N-methylacetamide, (20).	50			80	120
58	A	Ni:Al=1:1	4	N, N-dimethylpropionamide, (40).	60			100	160
59	A	Ni:Al=1:1	4	N, N-dimethylpropionamide, (40).	60		NaOH, (0.1)	20–23	70
60	A	Ni:Al=1:1	4	N, N-dimethylpropionamide, (40). $Al_2O_3 \cdot 3H_2O$, (3)	60			50–55	125
61	A	Co:Al=1:1	6	N-hydroxymethylisobutyramide, (10). Al_2O_3, (2)	20	i-PrOH	Conc. NH_4OH aq., (4)	60–67	100
62	A	Ni:Al=1:1	3	N, N'-dimethylurea, (10).	20			80–85	250
63	B	Ni:Al=1:1	4	N, N, N'-trimethylurea, (15).	40			90–96	180
64	A	Ni:Al=4:6	8	N, N'-dimethylurea, (20).	30		NaOH, (0.07)	48–50	95
65	A	Ni:Al=1:1	10	N, N'-dimethylurea, (15).	80		Hydrazine hydrate, (0.8)	18–26	80
66	A	Ni:Al=1:1:	6	N, N, N'-triethylurea, (9). $Al_2O_3 \cdot 3H_2O$, (0.2)	50			70–78	120
67	A	Ni:Al=1:1	4	Trimethylureau, (10). $Al_2O_3 \cdot 3H_2O$, (0.2)	40			55–60	140

TABLE II

[*Example 2*—Hydrogenation]

Ex. No.	Catalyst No.	Procedure	Sample (g.)	Solvent (ml.)	Additive (g.)	Initial press (kg./cm.²)	Reaction temperature (° C.)	Reaction time (min.)	Product	Yield (mol percent)
1	1	D	Diphenylacetylene, (25).	EtOH, (100)		30	30–35	65	Diphenylethane.	99.2
2	2	D	Acetophenone, (30).	EtOH, (40)		50	110–120	100	Methylphenylcarbinol.	94.7
3	3	D	Cinnamaldehyde, (41).	i-PrOH, (50)	1% NaOH aq., (0.5)	60	60–65	30	Hydrocinnamyl alcohol.	93.6
4	4	D	Methyl methacrylate, (120).			120	20–80	10	Methyl isobutyrate.	97.8
5	5	C	Cyclohexene, (4.1)	MeOH, (50)			20	95	Cyclohexane	99.5 G.C.
6	6	D	Naphthalene, (52).	EtOH, (100)		100	110–120	80	Tetralin	91.8
7	7	D	2-methyl glutaronitrile, (50).	Liquid NH_3, (100)		140	90–95	30	2-methyl pentamethylenediamine. 3-methyl piperidine.	87.2 10.4
8	8	C	Nitrobenzene, (5)	EtOH, (30)			25–27	25	Aniline	100 G.C.
9	9	D	Phenol, (20)	EtOH, (100)	NaOH, (0.5)	80	90–100	60	Cyclohexanol	95.1
10	10	D	Naphthalene, (52)	EtOH, (100)		100	110–118	65	Tetralin	93.6
11	11	C	Cyclohexene, (4.1).	MeOH, (50)			20	90	Cyclohexane	99.6 G.C.
12	12	D	Methyl methacrylate, (120).			100	25–70	25	Methyl isobutyrate.	98.8
13	13	D	2-butyne-1, 4-diol, (43).	EtOH, (80)		75	105–110	450	2-butene-1, 4-diol.	91.7
14	14	D	Adiponitrile, (100).	Liquid NH_3, (100)		100	120	80	Hexamethylene diamine.	95.4
15	15	D	Sebaconitrile, (100).	Liquid NH_3, (100)		110	115–120	170	Decamethylene diamine.	94.8
16	16	C	p-Nitrotoluene, (3.65).	MeOH, (50)	H_2O, (1)		21–26	34	p-Toluidine	98.7
17	17	C	Cyclohexene, (4.1).	MeOH, (50)			18	65	Cyclohexane	99.3 G.C.
18	18	D	Benzophenone, (13).	EtOH, (60)	1% NaOH aq., (0.5)	70	120–125	25	Benzhydrol	96.8
19	19	C	Ethyl cinnamate, (7.1).	EtOH, (40)			25	12	Ethyl hydrocinnamate.	100 G.C.
20	20	D	Benzophenone, (25).	EtOH, (100)	1% NaOH aq. (0.5)	60	50–55	20	Benzhydrol	98.5

TABLE II

[*Example 2*—Hydrogenation]

Ex. No.	Catalyst No.	Procedure	Sample (g.)	Solvent (ml.)	Additive (g.)	Initial press (kg./cm.²)	Reaction temperature (° C.)	Reaction time (min.)	Product	Yield (mol percent)
21	21	D	Aniline, (50)	Cyclohexane, (50)		90	190–205	370	Cyclohexylamine. Dicyclohexylamine. Aniline	53.7 21.6 19.2
22	22	D	m-Nitroacetophenone, (17).	EtOH, (100)		65	80–90	120	m-Aminoacetophenone.	97.2
23	23	D	ε-Aminocapronitrile, (50).	Liquid NH_3, (50)		75	110–120	50	Hexamethylenediamine.	95.2
24	24	C	Cyclohexene, (4.1).	MeOH, (50)			20	40	Cyclohexane	100 G.C.
25	25	D	Methyl methacrylate, (120).			100	80–70	15	Methyl isobutyrate.	98.1
26	26	D	Adiponitrile, (50)	Liquid NH_3, (70)		120	120	50	Hexamethylene diamine.	97.6
27	27	D	Quinoline, (20)	EtOH, (60)		140	60–64	130	1,2,3,4-tetrahydroquinoline.	96.7
28	28	C	Cyclohexene, (4.1)	MeOH, (50)			20	35	Cyclohexane	100 G.C.
29	29	D	Benzophenone, (12.7).	EtOH, (60)		50	110	20	Benzhydrol	98.3
30	30	D	Methyl methacrylate, (30).			1 0	30–80	2	Methyl-isobutyrate.	97.7
31	31	D	Benzene, (30)			80	100–140	180	Cyclohexane	91
32	32	D	Benzil, (35)	EtOH, (150)	10% NaOH aq., (0.5)	100	60–65	60	Hydrobenzoin	92.3
33	33	D	Styrene, (200)			100	50	30	Ethylbenzene	97.4
34	33	C	Cyclohexanone-oxime, (2).	EtOH, (40)	1% NaOH aq., (1)		21	200	Cyclohexylamine.	87
35	34	D	Furfural, (32)	EtOH, (70)		70	130–150	220	Tetrahydrofurfuryl alcohol.	83.6
36	35	D	t,t,c-Cyclododecatriene, (50).	MeOH, (150)		100	40–45	75	Cyclododecane	98 G.C.
37	36	D	Cyclohexanone, (100).	EtOH, (50)	1% NaOH aq., (1)	50	60–70	45	Cyclohexanol	96.7
38	37	C	Diphenylacetylene, (15).	i-PrOH, (100)			20–25	60	Diphenylethane	98.8
39	37	D	Benzhydrol, (18)	EtOH, (50)		60	130–150	85	Diphenylmethane.	86
40	38	D	Adiponitrile. (100),	Liquie NH_3, (100)		80	120	50	Hexamethylenediamine. Hexamethyleneimene.	98.77 G.C 1.23 G.C.
41	39	D	Sebaconitrile, (80)	Liquid NH_3, (120)		70	120–122	50	Decamethylene diamine.	98.2
42	40	D	Valeronitrile, (80)	Liquid NH_3, (50)		120	125–127	30	Pentylamine	97.8
43	41	D	p-Nitrosodimethylaniline, (15).	EtOH, (80)		120	25	25	p-Aminodimethylaniline.	95.3
44	42	C	m-Dinitrobenzene, (4.6).	EtOH, (50)			20–31	35	m-Phenylenediamine.	97.4
45	43	D	ε-Aminocapronitrile, (100).	Liquid NH_3, (100)		80	118–122	20	Hexamethylenediamine. Hexamethyleneimine.	99.26 G.C. 0.74 G.C.
46	44	D	Adiponitrile, (100)	Liquid NH_3, (100)		120	118–122	45	Hexamethylenediamine. Hexamethyleneimine.	98.14 G.C. 1.86 G.C.
47	45	D	Cinnamaldehyde, (26).	EtOH, (70)	1% NaOH aq., (1)	45	50–60	35	Hydrocinnamyl alcohol.	94.3
48	46	D	ε-Aminocapronitrile, (100).	Liquid NH_3, (150)		90	120–125	25	Hexamethylenediamine.	97.2
49	45	C	Cyclohexanone-oxime, (4).	EtOH, (25)			26	230	Cyclohexylamine.	87
50	47	D	3-nitro-4-methyl acetophenone, (34).	EtOH, (100)		80	95–100	35	3-amino-4-methylacetophenone.	93.2
51	48	D	Oleic acid, (45)	EtOH, (200)		70	80–87	75	Stearic acid	97.6
52	49	D	Adiponitrile, (100)	Liquid NH_3, (200)		130	110–115	60	Hexamethylene diamine.	96.8
53	50	C	Styrne, (13)	MeOH, (40)			26–32	40	Ethylbenzene	99.8 G.C.
54	51	D	Naphthalene, (25).	EtOH, (40)		70	120–130	110	Tetralin	92
55	52	D	Cyclohexanone-oxime, (55).	i-PrOH, (80)		50	70–80	80	Cyclohexylamine.	93.6
56	53	D	Acetophenone, (30).	EtOH, (100)	1% NaOH aq., (2)	70	60–65	30	Methylphenylcarbinol.	97.2
57	54	C	Cyclohexene, (4.1)	MeOH, (50)			25	45	Cyclohexane	99.8 G.C
58	55	D	Benzaldehyde, (46).	MeOH, (100)	1% NaOH aq., (1)	50	54–57	50	Benzyl alcohol	91.3
59	56	D	Hydroquinone, (50).	EtOH, (100)	5% NaOH aq., (1)	60	100–130	120	Cyclohexaen-1,4 diol.	98.9
60	57	D	Methyl methacrylate, (30).			80	21–53	6	Methyl isobutyrate.	98.1
61	58	D	Mesityloxide, (45)	MeOH, (50)	1% NaOH aq., (1)	75	60–65	140	Methyl isobutylcarbinol.	95.2
62	59	D	Mesityloxide, (45)	MeOH, (50)	1% NaOH aq., (1)	75	60–65	80	Methyl isobutylcarbinol.	96.1
63	60	D	Mesityloxide, (45)	MeOH, (50)	1% NaOH aq., (1)	75	60–65	110	Methyl isobutylcarbinol.	94.7
64	61	D	1,2-dicyano cyclobutane, (20).	Liquid NH_3, (50)		90	105–110	25	1,2-diaminomethyl cyclobutane.	84.5
65	62	D	Propargyl alcohol, (56).			130	40–50	30	Propanol	95.4
66	63	C	p-Nitrotoluene, (4.8)	MeOH, (30)	H_2O, (0.5)		27–30	45	p-Toluidnie	97.3
67	64	D	Styrene, (100)			85	30–66	25	Ethylbenzene	96.5
68	65	D	Phenol, (130)	EtOH, (150)	NaOH, (1)	140	105–110	75	Cyclohexanol	97.4
69	66	D	Proplophenone, (87)	EtOH, (100)	1% NaOH aq., (2)	65	70–80	110	Ethylphenyl	89.6
70	67	D	Benzophenone-oxime, (19.7).	EtOH, (80)		54	78–81	55	Benzhydrylamine.	94.2

TABLE III

[*Example 3*—The simultaneous hydrogenation with preparation of the catalyst]

Ex. No.	Procedure	Raney alloy: Composition	Raney alloy: Weight (g.)	Promoter (g.)	Water (ml.)	Sample (g.)	Solvent (ml.)	Additive (g.)	Initial press (kg./cm.²)	Reaction temperature (° C.)	Reaction time (min.)	Products	Yield (mole percent)
1	G	Ni:Al=1:1	4	Al_2O_3, (2.5)	10	t,t,c-Cyclododecatriene, (30).	Dioxane, (25)		40	70–75	80	Cyclododecane	75.2
2	F	Ni:Al=1:1	5	$Al_2O_3 \cdot H_2O$, (1.5)	100	2-butyne-1,4-diol, (16)		Al, (10)		100	380	Butane-1,4-diol	83.7
3	G	Ni:Al=45:55 Cu:Al=1:1	4 1	$Al_2O_3 \cdot H_2O$, (2)	25	Toluene, (20)	i-PrOh, (30)		70	120–130	130	Methylcyclohexane Toluene	75.6 G.C. 24.4 G.C.
4	G	Ni:Al=1:1	4	$Al_2O_3 \cdot 3H_2O$, (1)	40	2-butyne-1,4-diol, (20)			80	85	160	Butane-1,4-diol	86
5	G	Ni:Al=45:55	10	$Al_2O_3 \cdot 3H_2O$, (3)	20	Biphenyl, (50)	i-PrOH, (40)		110	190–200	123	Bicyclohexyl Phenyl cyclohexane Biphenyl	73.6 G.C. 21.3 G.C. 5.1 GC
6	G	Cu:Al=1:1	5	$Al_2O_3 \cdot 3H_2O$, (2)	50	Benzophenone, (15)			60	105–110	70	Benzhydrol	81.4
7	G	Ni:Al=1:1	5	Aluminum isoproxide, (3).	30	Benzylidene acetone, (31)	MeOH, (50)		50	95–100	140	Methyl-β-phenylethyl carbinol.	74
8	G	Ni:Al=1:1	4	Al_2O_3, (2.5)	10	t,t,c-Cyclododecatriene, (30).	Dioxane, (25)	Na_2CO_3, (0.2)	40	70–75	80	Cyclododecane	98.1
9	G	Ni:Al=45:55 Cu:Al=1:1	4 1	$Al_2O_3 \cdot H_2O$, (2)	25	Toluene, (20)	i-PrOH, (30)	NaOH, (0.1)	70	120–130	130	Methylcyclohexane Toluene	95.2 G.C. 4.8 G.C.
10	G	Cu:Al=1:1	5	$Al_2O_3 \cdot 3H_2O$, (2)	50	Benzophenone, (15)		KOH, (0.2)	60	105–110	25	Benzhydrol	93.1
11	E	Ni:Al=4:6	12	Aluminum sulphate, (4).	100	Acetone, (20)		NaOH, (2)		27–33	260	Isopropyl alcohol	99.4 G.C.
12	G	Ni:Al=1:1	3	n-Butylamine, (15)	20	2-butyne-1,4-diol, (50)			30	20–36	60	Butane-1,4-diol	93.8
13	G	Ni:Al=1:1	6	Cyclohexylamine (90)	55	p-Cresol, (85)			130	130–135	110	4-methylcyclohexanol.	96.2
14	G	Ni:Al=45:55	4	2,4-diaminotoluene, (20).	100	2,4-dinitrotoluene, (60)			70	20–60	75	2,4-diamino toluene	95.6
15	G	Co:Al=1:1	4	Nonamethylene diamine, (15).	10	Azelonitrile, (65)			150	90–95	60	Nonamethylenediamine.	96.7
16	G	Co:Al=1:1	5	ε-Aminocapronitrile, (50).	8				75	115–125	55	Hexamethylenediamine. Hexamethyleneimine	95.4 G.C. 4.6 G.C.
17	G	Ni:Al=1:1	10	Laurylamine, (40)	20	Lauronitrile, (45)	Tetrahydrofuran (150)		140	110–117	120	Laurylamine	97.4
18	G	Ni:Al=4:6	5	Piperidine, (20)	10	Styrene, (32)	i-PrOH, (30)		45	40–50	85	Ethylbenzene	87.3
19	G	Ni:Al=4:6	6	Diethylamine, (10)	30	Ethyl cinnamate, (36)	EtOH, (100)		60	40–50	100	Ethyl hydrocinnamate.	92.6
20	G	Ni:Al=1:1	5	2,6-dimethylpyridine, (45).	10	Benzal acetophenone, (21)			50	60–65	165	1,3-diphenylpropanol-1.	88.8
21	G	Co:Al=1:1	4	Triethylamine, (50)	10	Benzonitrile, (24)			100	85–93	65	Benzylamine Dibenzylamine	94.3 5.1
22	G	Ni:Al=1:1	14	Arginine, (1.5)	50	Acetone, (200)			95	74–86	70	Isopropyl alcohol	97.2
23	G	Co:Al=1:1	10	2-methyl-4-amino-pyrimidine-5-nitrile, (30).	20		i-PrOH, (60)		70	60–65	145	2-methyl-4-amino-5-aminomethyl pyrimidine.	89.1
24	G	Ni:Al=1:1	5	4-nitroso-m-nitrotoluene, (10).	15	t,t,c,-Cyclododecatriene, (65).	i-PrOH, (70)		90	105–110	90	Cyclododecane	95.3
25	G	Ni:Al=1:1	2	2-nitro-1-butanol, (5)	10	Crotyl alcohol, (36)	EtOH, (10)		40	70–76	105	n-Butanol	92.8
26	G	Co:Al=1:1	10	Adiponitrile, (80)	20				150	107–120	155	Hexamethylenediamine	83.6
27	G	Ni:Al=1:1	5	4-nitroso-m-nitrotoluene, (10).	15	t,t,c,-Cyclododecatriene, (65).	i-PrOH, (70)	Raney Ni, (0.5)	40	50–60	65	Cyclododecane	93.4
28	G	Ni:Al=4:6	10	Nitrocyclohexane, (8)	15	β-Bromonaphthalene, (24)	Dioxane, (35)	5% Pd-C, (0.5)	100	20–25 125–130	240	Tetralin	75.4
29	G	Co:Al=45:55	5	Adiponitrile, (50)	10			Raney Co, (0.5)	140	115–120	55	Hexamethylenediamine. Hexamethyleneimine	96.2 G.C. 3.8 G.C.
30	G	Co:Al=1:1	5	2-methylglutaronitrile, (45).	10		EtOH, (20)	NaOH, (0.17)	90	100–110	80	2-methylpentamethylenediamine. 3-methylpiperidine	91.2 7.4
31	G	Co:Al=4:6	10	Isophthalonitrile, (40)	15		i-PrOH, (25)	NaOH, (0.08)	120	100–110	60	m-Xylylenediamine	86.7
32	G	Co:Al=4:6	5	Hexamethylenediamine, (40). $Al_2O_3 \cdot H_2O$, (2)	10	Adiponitrile, (40)			140	110–115	40	Hexamethylenediamine.	97.4
33	G	Ni:Al=1:1	15	Piperidine, (35) $Al_2O_3 \cdot 3H_2O$, (1)	35	Pyridine, (61)			125	180–193	180	Piperidine	92.8
34	G	Ni:Al=4:6	4	p-Nitrotoluene, (24) Al_2O_3, (4)	150				85	75–80	75	p-Toluidine	95.7

TABLE III.—Continued

Ex. No.	Procedure	Raney alloy: Composition	Raney alloy: Weight (g.)	Promoter (g.)	Water (ml.)	Sample (g.)	Solvent (ml.)	Additive (g.)	Initial press (kg./cm.²)	Reaction temperature (° C.)	Reaction time (min.)	Products	Yield (mole percent)
35	G	Ni:Al=1:1	4	Cyclohexanoneoxime, (35). Al_2O_3-H_2O, (1.5)	15		MeOH, (65)		100	55-65	65	Cyclohexylamine	76.8
36	G	Ni*Al=4:6	5	2,4-dinitrotoluene, 14.5 $Al_2O_3 \cdot 3H_2O$, (5)	200				55	60-75	100	2,4-diaminotoluene	83
37	F	Ni*Al=1:1	4	Hydrazobenzene, (18) $Al_2O_3 \cdot 3H_2O$, (2)	50			Al, (4)		100	330	Aniline	81
38	G	Ni*Al=45:55	3	P-nitrosodimethylaniline, (28) $Al_2O_3 \cdot 3H_2O$, (3)	20		EtOH, (30)		30	75-80	95	P-aminodimethylaniline.	92.5
39	G	Co*Al=1:1	14	ε-Aminocapronitrile, (100) $Al_2O_3 \cdot 3H_2O$, (0.3)	10			LiOH, (0.1)	80	98-105	35	Hexamethylenediamine.	97.5
40	F	Ni*Al=4:6	4	γ-butyrolactam, (15)	50	Benzophenone, (3.7)		Al, (1)		100	120	Benzhydrol	73
41	G	Ni*Al=1:1	4	γ-valerolactam, (50)	15	Nitrobenzene, (25)			75	50-65	90	Aniline	93
42	G	Ni*Al=45:55	5	ε-caprolactam, (100)	25	Furfural, (38)			70	110-140	240	Tetrahydrofurfuryl alcohol.	83.5
43	G	Co*Al=1:1	4	γ-butyrolactam, (30) λ-laurolactam, (5)	15	Benzonitrile, (20)			80	90-95	75	Benzylamine	86
44	G	Co*Al=45:55	10	ε-Caprolactam, (40)	30	ε-Amino-capronitrile, (50)			70	110-120	50	Hexamethyl enediamine	92.6
45	G	Ni*Al=45:55 Cu*Al=1:1	4 1	ε-Caprolactam, (60) $Al_2O_3 \cdot H_2O$, (2)	25	Toluene, (20)	i-PrOH, (30)		70	120-130	85	Methylcyclohexane Toluene	90.3 G.C. 9.7 G.C.
46	G	Co*Al=4:6	5	γ-Butyrolactam, (30) $Al_2O_3 \cdot H_2O$, (2)	10	Adiponitrile, (40)			140	110-115	65	Hexamethylenediamine.	91.3
47	G	Ni*Al=1:1	5	γ-Butyrolactam, (80)	20	Mesityloxide, (100)		NaOH, (0.15)	120	60-70	70	Methylisobutylcarbinol.	93
48	G	Ni*Al=45:55	3	δ-Valerolactam, (60)	10	Toluene, (28)		10% tetraethylammonium hydroxide (2)	75	140-155	85	Methylcyclohexane	90
49	F	Co*Al=1:1	10	ε-Caprolactam, (80) $Al_2O_3 \cdot 3H_2O$, (1)	70	2-butyne-1,4-diol, (20)		KOH, (0.1) Al, (10)		25-30	200	Butane-1,4-diol	88
50	G	Co*Al=1:1	10	ε-Caprolactam, (40) $Al_2O_3 \cdot 3H_2O$, (2)	30	Adiponitrile, (100)		$Co(OH)_2$, (0.1)	150	120-125	45	Hexamethylenediamine.	94.3
51	G	Ni*Al=1:1	2	N-methyl-γ-butyrolactam, (50).	30	2-butynediol, (21.5)			100	100	95	Butane-1,4-diol	92
52	G	Ni*Al=1:1	4	N-methyl-δ-valerolactam, (35).	25	Benzophenone, (25)			60	65-70	45	Benzhydrol	94.6
53	G	Ni:Al=4:6	5	N-methyl-δ-valerolactam, (100).	20	Cyclohexanone, (50)		NaOH, (0.1)	70	24	155	Cyclohexanol	87
54	G	Co:Al=1:1	15	N-methyl-γ-butyrolactam, (80).	40	Adiponitrile, (100)		NaOH, (0.1)	110	90-100	70	Hexamethylenediamine.	94.8
55	G	Ni:Al=1:1	3	N-methyl-γ-butyrolactam, (50). $Al_2O_3 \cdot 3H_2O$, (3)	15	p-Nitrotoluene, (15)			120	60	80	p-Toluidine	74
56	G	Ni:Al=1:1	4	N-methyl-γ-butyrolactam, (80). $Al_2O_3 \cdot 3H_2O$, (1.5)	10	1,5-Cyclooctadiene, (30)			25	65-70	125	Cyclooctane	96.8
57	G	Ni:Al=1:1	8	N-methyl-ε-caprolactam, (55). Al_2O_3, (1)	18	Terephthalonitrile, (28)		Hydrazine hydrate, (0.5).	100	95-104	65	p-Xylylenediamine	87.6
58	G	Ni:Al=1:1	4	Benzophenoneoxime, (15).	20	Styrene, (45)	Dioxane, (40)		70	50-55	230	Ethylbenzene	92.3
59	G	Ni:Al=1:1 Cu:Al=1:1	3 2	Cyclohexanoneoxime, (45).	20	Benzylideneaniline, (30)	EtOH, (20)		80	50-60	200	Benzylaniline Cyclohexylamine	90.8 87.2

TABLE III.—Continued

Ex. No.	Procedure	Raney alloy Composition	Raney alloy Weight (g.)	Promoter (g.)	Water (ml.)	Sample (g.)	Solvent (ml.)	Additive (g.)	Initial press (kg./cm.²)	Reaction temperature (° C.)	Reaction time (min.)	Products	Yield (mole percent)
60	G	Ni:Al=4:6	3	N,N-dimethylacetamide, (20).	15	Benzalacetophenone, (20)			80	140–145	120	1,3-diphenylpropanol-1.	80.1 G.C.
												1,3-diphenylpropane	19.9 G.C.
61	G	Ni:Al=1:1	2	N-methylacetamide, (25).	40	Diphenylacetylene, (18)	EtOH, (40)		50	80–87	170	Diphenylethane	86.3
62	G	Co:Al=1:1	5	N,N-dimethylacetamide, (30).	20	Adiponitrile, (50)			130	110–115	75	Hexamethylenediamine.	87.8
63	G	Ni:Al=4:6	3	N,N-dimethylacetamide, (20).	15	Benzalacetophenone, (20)		NaOH, (0.08)	80	140–145	120	1,3-diphenylpropanol-1.	20.4 G.C.
												1,3-diphenylpropane	79.6 G.C.
64	G	Ni:Al=4:6	3	N,N-dimethylacetamide, (20).	15	Benzalacetophenone, (20)			80	140–145	120	1,3-diphenylpropanol-1.	35.6 G.C.
												1,3-diphenylpropane	64.4 G.C
65	G	Ni:Al=1:1	4	$Al_2O_3 \cdot 3H_2O$, (5). N,N'-dimethylurea, (20).	50	Vanillin, (18)	EtOH, (40)		65	84–91	175	Vanillylalcohol	87.3
66	G	Ni:Al=1:1	8	Trimethyleneurea, (10).	80	Acrylamide, (36)			30	85–94	185	Propionamide	92.8
67	G	Ni:Al=4:6	5	N,N,N'-trimethylurea, (12).	100	Resorcinol, (55)		Sodium isopropoxide, (0.4).	100	55–62	345	Dihydroresorcinol	91.3

[1] Hours.

We claim:

1. A method of activating Raney allows which comprises reacting at a temperature within the range of 0°–350° C. a Raney alloy with water containing at least one substance, in an amount of at least 5% by weight based on the weight of said Raney alloy, selected from the group consisting of aluminas, non-N-substituted lactams of the formula

wherein R is an alkylene group, N-substituted lactams of the formula

wherein R_2 is an alkylene group and R_1 and R_3 are alkyl, oximes of the formula

wherein each R is individually selected from the group consisting of hydrogen and a hydrocarbyl group, N-substituted acid amides of the formula

wherein R_1, R_2, R_3, R_4 and R_5 are each selected from the group consisting of hydrogen and hydrocarbyl, at least one of R_1, R_2, R_3, R_4 and R_5 being hydrogen, and urea derivatives of the formula

wherein R_3 is hydrogen or an alkyl group and R_1 and R_2 are alkyl, said water containing 0–½ equivalent amount of an alkali metal hydroxide based on the aluminum content of the alloy.

2. The method according to claim 1 wherein said reaction is effected at a temperature ranging from 10° to 150° C.

3. The method according to claim 1 wherein said reaction is effected in the co-presence of a solvent of said substance.

4. The method according to claim 1 wherein said reaction is effected in the co-presence of the copound to be hydrogenated and hydrogen.

5. The method according to claim 4 wherein said reaction is effected in the co-presence of a solvent of said compound to be hydrogenated.

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PATRICK P. GARVIN, Primary Examiner

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