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HYDROGENATION OF AROMATIC NITRILES**John B. Wilkes, Albany, Calif., assignor to California Research Corporation, San Francisco, Calif., a corporation of Delaware****No Drawing. Filed June 11, 1958, Ser. No. 741,233****5 Claims. (Cl. 260-570.9)**

This invention relates to a process for the hydrogenation of aromatic nitriles, and, more particularly, to a process for the hydrogenation of aromatic nitriles in the presence of a cobalt and nickel-containing catalyst.

At the present time the hydrogenation of adiponitrile to hexamethylenediamine is being practiced on a commercial scale. The reaction is carried out at relatively low temperatures and high pressures over a metallic cobalt hydrogenation catalyst. It has been found, however, that when attempts are made to hydrogenate aromatic nitriles at essentially the same reaction conditions and in the presence of the same type of cobalt catalyst, undesirable side reaction products are produced resulting in comparatively poor yields of the desired aromatic amines. Thus, in the hydrogenation of, for example, isophthalonitrile to metaxylylenediamine, considerable quantities of the undesirable 3-methylbenzylamine are produced by hydrogenolysis at relatively moderate hydrogenation conditions.

It has now been found that aromatic nitriles can be hydrogenated to produce the corresponding amines in high yields with a minimum amount of undesirable side reactions by employing a hydrogenation catalyst containing cobalt and over 10 percent by weight of nickel, based upon the total weight of the cobalt and nickel present. It has been discovered that the presence of nickel in the hydrogenation catalysts considerably suppresses the formation of undesirable reaction products, thus leading to high purity amine products.

According to the present process, at least one aromatic nitrile containing at least one cyano radical all directly attached to the aromatic nucleus and attached to non-adjacent carbon atoms of the aromatic nucleus, is contacted with hydrogen and ammonia at a temperature of from about 100° to 400° F. and at a superatmospheric pressure in the presence of a nickel and cobalt catalyst wherein the weight ratio of the nickel to the cobalt in said catalyst is in the range of from 1:9 to 15:1. The resulting reaction product is comprised essentially of the amine or amines corresponding to the aromatic nitrile or nitriles present in the initial feed.

As noted above, the aromatic nitriles comprising the feed of subject process are aromatic mono and polynitriles wherein all cyano radicals are directly attached to the aromatic nucleus, and in the case of polynitriles, directly attached to nonadjacent carbon atoms of the aromatic nucleus. Although polynitriles having cyano radicals attached to adjacent carbon atoms of the aromatic nucleus, such as ortho aromatic dinitriles, can be hydrogenated by the present process, yields of the corresponding polyamine are generally so low and side reactions so prevalent that the reaction is completely unattractive from a practical point of view. Illustrative of the basic or unsubstituted compounds contemplated within the scope of the aromatic nitriles are such compounds as benzonitrile, isophthalonitrile, terephthalonitrile, 1,3,5-

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tricyanobenzene as well as the polynuclear analogs thereof.

In addition to the cyano radicals, the aromatic nitriles of the feed may have additional substituents, such as alkyl (methyl, ethyl, propyl, butyl, etc.), amide, ester groups and the like. In such compounds, the main requirement is that they are relatively inert during hydrogenation under the conditions of the present process. Examples of such compounds are the isomeric tolunitriles, cyanoethylbenzenes, dicyanotoluenes, and dimethylterephthalonitrile. In these compounds having comparatively inert groups in addition to the cyano radical or radicals, the groups can be attached to the carbon atoms of the aromatic nucleus either in an adjacent or non-adjacent manner. Thus, in the case of polynitriles, the additional groups can even be attached between two meta-substituted cyano groups.

The aromatic nitriles comprising the feed can be present either alone or in mixture or in the presence of hydrocarbons. Preferred feeds are isophthalonitrile, terephthalonitrile and mixtures thereof. More preferable still is a feed stock containing isophthalonitrile and/or terephthalonitrile having associated therewith a solvent for the nitrile. Examples of especially desirable solvents are aromatic hydrocarbons, particularly the isomeric xylenes, dioxane, and aliphatic alcohols. On a weight ratio basis, the solvent is preferably present in an amount wherein the solvent to nitrile ratio of the feed is in the range of from about 1:1 to about 10:1.

The hydrogenation reaction temperature can vary from about 100° to about 400° F., with a preferred range of from about 200° to 325° F. Similarly, initial pressures can vary from just sufficient to maintain the ammonia in liquid phase up to a pressure of 5000 p.s.i.g. and higher, a generally preferred pressure range being from about 2500 to 3500 p.s.i.g. The space rate can vary over the range of from about 0.05 to 0.3 pound of nitrile per pound of catalyst per hour. The amount of hydrogen employed can vary over a range of from about 2 to 10 or more mols of hydrogen per mol of nitrile.

The catalyst employed in the subject process is one containing both nickel and cobalt wherein the weight ratio of nickel to cobalt lies in the range of from about 1:9 to 15:1, and preferably, from about 1:4 to 4:1. Both the cobalt and the nickel must be in the form of the metal since it has been found that catalysts containing the oxides or sulfides of these metals require operating temperatures that are too high to give even reasonable yields of the desired amine and/or polyamine. It is much preferred that the catalyst be of the unsupported type since supported cobalt-nickel catalysts give rise to considerably lower hydrogenation rates. Various promoters such as silica, thoria, and the like, can also be present if desired. The catalyst can be made by pelleting a mixture of nickel and cobalt oxides, sintering at a temperature of from about 1200° to 1800° F., and thereafter reducing with hydrogen at a temperature of from about 700° to 900° F. The metal oxides can be technical grade or obtained from the thermal decomposition of carbonates, nitrates, sulfates or the like. In the case of high nickel-content catalysts, sintering temperatures can even be higher than the noted ranges.

The present process is preferably conducted in continuous, fixed bed operation, i.e., the aromatic nitrile,

hydrogen, ammonia and solvent are continuously passed through a reaction vessel containing a fixed bed of catalyst. Since the reaction is exothermic, and since the ratio of ammonia to nitrile in the feed bears directly on the product yield (see below), it is preferred that the ammonia (within rather specific limitations discussed below) and/or the hydrogen be employed in excess to aid in maintaining the reaction temperature within the range of from about 100° to 400° F. However, it must be understood that the present process can be conducted by batch, fluid bed or like manner.

As noted hereinbefore, the use of conventional cobalt catalysts in the hydrogenation of, for example, meta and para aromatic dinitriles, leads to hydrogenolysis of the desired diamine with the result that undesirable side reaction products are produced. Thus, in the hydrogenation of isophthalonitrile to metaxylylenediamine, 3-methyl-benzylamine is produced, presumably from the reaction of metaxylylenediamine with hydrogen on the catalyst surface to give a methyl group and ammonia. To show the effect of nickel in reducing this hydrogenolysis, two different hydrogenations of isophthalonitrile were made under identical conditions, the difference being that Run 1 used a catalyst of cobalt and Run 2 used a nickel-cobalt catalyst having a metals weight ratio of 1:1. Both catalysts were made from technical grade oxides. The finely divided oxide or oxides were mixed in the indicated proportions, pelleted with a lubricant, sintered at about 1600° F. and reduced with hydrogen at about 750° to 900° F. In both hydrogenations (conducted in an autoclave), the pressure was 3000 p.s.i.g., the temperature was 325° F., the reaction time was 3 hours, and the weight ratio of isophthalonitrile:paraxylene:ammonia was 26:42:32. The results of Runs 1 and 2 are shown in Table I below. The term MXDA refers to the compound metaxylylenediamine.

TABLE I

Run No.	Products, distribution percent		
	3-methyl-benzylamine	MXDA	Polymer
1.....	23.0	66.2	10.8
2.....	1.8	92.7	5.7

From the above table, it can be seen that under identical hydrogenation conditions that the process employing the nickel-cobalt catalyst produced considerably less 3-methylbenzylamine than the process using a straight cobalt catalyst. The amount of polymer produced is also only about one-half as much. The polymer is apparently a byproduct of hydrogenolysis or may also be formed by independent reactions of metaxylylenediamine, isophthalonitrile, or intermediate hydrogenation products and appears as a heavy bottoms fraction upon product distillation.

For optimum yields upon hydrogenation, it has been found that the ratio of nickel to cobalt in the catalyst has a direct relationship to the minimum required ratio of ammonia to nitrile in the feed. Thus, it has been found that, as the nickel-cobalt ratio of the catalyst increases, the ratio of ammonia to nitrile of the feed should also increase in order to maintain high yields of the diamine. The results of numerous hydrogenations showing both the effectiveness of the process of the present invention and the effect of the ammonia to nitrile with varying nickel to cobalt ratios in the catalyst are summarized in Table II below. In all of the runs, the finely divided oxides were mixed in the indicated proportions, pelleted with a lubricant, sintered at about 1600° F. and reduced with hydrogen at about 750° to 900° F. In all of the runs indicated, isophthalonitrile, paraxylene and ammonia (in the proportions shown on the table) were passed into an autoclave charged with the catalyst. The

autoclave was heated to 250° F., hydrogen was added to a pressure of 3200 p.s.i.g., the mixture was agitated and hydrogenation was conducted by repressuring with hydrogen when the pressure dropped to 2800 p.s.i.g. All products were analyzed by distillation. The letters MXDA and IPN appearing in the table represent metaxylylenediamine and isophthalonitrile, respectively.

TABLE II

Run No.	Catalyst	Rate, g. IPN/cc. cat./hr.	Weight ratios IPN:xylylene: NH ₃	Mol percent, MXDA yield
3.....	75% Co-25% Ni.....	2.0	27:47:26	92.2
4.....	75% Co-25% Ni.....	1.6	10:69:21	94.7
5.....	75% Co-25% Ni.....	1.9	19:39:42	95.6
6.....	50% Co-50% Ni.....	3.0	26:46:28	92.4
7.....	50% Co-50% Ni.....	1.9	20:41:39	94.0
8.....	25% Co-75% Ni.....	2.3	28:46:26	84.8
9.....	25% Co-75% Ni.....	1.2	18:38:44	90.6
10.....	25% Co-75% Ni.....	0.76	10:41:49	93.9

From the results summarized in the above table, it can be seen that high yields of metaxylylenediamine were realized by employing nickel-cobalt catalysts over relatively wide variances in nickel-cobalt weight ratios. These data also show the desirability of increasing the ratio of ammonia to dinitrile in the feed as the nickel content of the catalyst increases. Thus, in Runs 3, 4 and 5, wherein a catalyst having a Ni:Co weight ratio of 1:3 was employed, it can be seen that metaxylylenediamine yields increase as the ammonia-isophthalonitrile ratio increases from approximately 1:1 (Run 3) to slightly over 2:1 (Runs 4 and 5). The same type of result is shown by Runs 6 and 7 where the Ni:Co ratio is 1:1 and the yield increases from 92.4 to 94.0 as the NH₃:IPN ratio increases from about 1:1 to 2:1. The effect of this latter ratio with increasing nickel content of the catalyst is shown in an even more pronounced manner by the results of Runs 8, 9 and 10 where the catalyst employed in the hydrogenation reaction had a nickel to cobalt weight ratio of 3:1. It can be seen that at an approximate 1:1 NH₃:IPN ratio, the metaxylylenediamine yield was only 84.8 (Run 8); at a feed ratio of about 2.5:1 the yield increased to 90.6 and at an NH₃:IPN ratio of about 5:1, the yield increased to a high 93.9.

The hydrogenation reaction of the present invention is conducted at a temperature of from about 100° to 400° F., and preferably from about 200° to 325° F. At temperatures below about 150° F., the reaction rate is too slow to be commercially attractive. At temperatures above about 350° F., undesirable hydrogenolysis of the amine product begins to occur and reaches appreciable amounts above 400° F. Although this reaction is particularly prevalent with cobalt catalysts even under moderate conditions (as shown in Table I), it also occurs to a lesser degree with nickel-cobalt catalysts at temperatures above about 350° F. This effect is shown by the hydrogenation runs summarized in Table III. All catalysts were made and the conditions the same as the hydrogenation operations described in Table II except where specific conditions are here described or shown in Table III. The catalysts used in the runs indicated in Table III all had nickel to cobalt weight ratios of 1:1 and ammonia to isophthalonitrile weight ratios of 1:1 and the reactions were conducted under a pressure of 3000 p.s.i.g.

TABLE III

Run No.	Temp., ° F.	Recovery, percent	Products, yields as percent of products		
			3-methyl-benzylamine	MXDA	Polymer
11.....	250	95.7	0	92.4	7.6
12.....	325	99.3	0.9	89.3	9.8
13.....	400	84.7	14.5	60.8	24.7

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From the results of the runs shown in Table III, it can be seen that both hydrogenolysis and polymer formation begin to occur in relatively appreciable quantity at 400° F. It is apparent that a preferred reaction temperature range lies from about 200° to 325° F. However, in a continuous fixed bed operation, the hydrogenolysis and polymer formation will be somewhat less than the autoclave runs shown in Table III inasmuch as reactant-catalyst contact times will be much shorter.

The hydrogenation process of the present invention is primarily directed to the hydrogenation of aromatic nitriles inasmuch as it has been found that nickel-cobalt catalysts are not as effective in hydrogenating aliphatic nitriles as cobalt catalysts. Thus, it was found that in the hydrogenation of adiponitrile, catalysts of high nickel content gave low yields of hexamethylenediamine even when using high ammonia to nitrile feed ratios. This was in distinct contrast to the above-described high yields of, for example, metaxylylenediamine obtained from isophthalonitrile with the same catalyst and similar reaction conditions.

I claim:

1. A process for reducing a mononuclear aromatic nitrile to an amine, wherein said aromatic nitrile has at least one cyano group directly attached to the aromatic nucleus in other than ortho relationship to other cyano groups so attached and is otherwise unsubstituted, which comprises reacting said nitrile with hydrogen and ammonia at a temperature of from about 100° to 400° F.

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under superatmospheric pressure in the presence of a cobalt-nickel metal catalyst, wherein the weight ratio of nickel to cobalt of said catalyst lies in the range from about 1:9 to 15:1.

2. The process of claim 1 wherein the weight ratio of ammonia to nitrile is maintained in the range of about 1:1 to 10:1.

3. The process according to claim 1 wherein said nitrile is dissolved in an organic solvent selected from the group consisting of aromatic hydrocarbons, dioxane, and aliphatic alcohols, and wherein the ratio of solvent to nitrile is in the range of from about 1:1 to about 10:1.

4. The process according to claim 1 wherein the temperature is from about 200° to 325° F.

5. The process according to claim 2 wherein said aromatic nitrile is isophthalonitrile.

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