United States Patent Office 2,849,478 Patented Aug. 26, 1958

2,849,478

PREPARATION OF NITRILES

Geoffrey Zubay, Cambridge, Mass., and Carl E. Johnson, Griffith, and Thomas D. Nevitt, Valparaiso, Ind., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

No Drawing. Application December 18, 1956
Serial No. 628,973

4 Claims. (Cl. 260—465.1)

This invention relates to the preparation of nitriles, and in particular it concerns the preparation of nitriles by the dehydrogenation of amines.

Amines have been dehydrogenated to produce nitriles in prior art operations, but such operations have generally been beset with difficulties. Conversion of the amine to the nitrile has generally been incomplete. A considerable portion of the amine is also converted to undesired byproducts such as ammonia, secondary amines and tertiary amines. To attain more complete conversion of the amine it has been necessary to recycle unconverted amine to the reaction zone. It has also been proposed to add hydrogen acceptors to the reaction zone to take up evolved hydrogen and thus attain more complete conversion of the amine. It has also been suggested that ammonia be added to the reaction zone for the purpose of suppressing formation of ammonia, secondary-, and tertiary amines. Prior art techniques have also frequently used high pressures, e. g. on the order of 3,000 p. s. i. g. in the reaction zone. This enormously increased the expense of the operation.

An object of this invention is to provide a process for converting amines in an essentially quantitative manner to nitriles. A further object is to provide a process for converting amines to nitriles without the formation of undesired byproducts such as ammonia, secondary amines and tertiary amines. A further object of this invention is to provide an efficient and economic process for converting amines to nitriles which does not require the use of high pressures in the reaction zone. Other objects and advantages of the present invention will be more fully understood from the detailed description thereof.

We have discovered that amines having the general formula RCH_2NH_2, in which R is a hydrocarbon radical having from 1 to 15 carbon atoms, can be dehydrogenated essentially quantitatively to the corresponding nitrile by contacting the amine with an alumina supported catalyst containing about 1 to 10 weight percent of an alkali metal oxide, and about 10 to 50 weight percent of chromium oxide. A temperature between 425 and 550° C. with a space velocity of at least 2 liquid volumes of amine/hour/volume of catalyst is employed in carrying out the reaction. Quantitative conversion to the nitrile can be obtained when the reaction zone is at substantially atmospheric pressures. By employing the defined catalyst under the specified conditions of operation, the formation of ammonia, secondary-, and tertiary amines is completely eliminated.

Suitable amines which may be converted to nitriles by the process of this invention are those amines which have the general formula RCH_2NH_2, R being a straight, branched, or cyclic hydrocarbon radical having from 1 to 15 carbon atoms. For example, the hydrocarbon radical R may be a methyl, ethyl, n-propyl, n-butyl, isobutyl, n-amyl, n-hexyl, isohexyl, n-octyl, isooctyl, n-decyl, n-undecyl, n-tridecyl, n-pentadecyl, phenyl, tolyl, xylyl, benzyl, or other alkylated aromatic radicals, cyclohexyl, methylcyclohexyl, ethylcyclohexyl, tertiary butylcyclohexyl, or other similar hydrocarbon radical. These amines which are used as feed stock in the process of this invention are primary amines.

The catalyst which is used is one containing between about 1 and 10 weight percent of an alkali metal oxide, between about 5 and 50 weight percent of chromium oxide with the remainder being essentially alumina. Preferred ranges of catalyst composition are about 2 to 6 weight percent of alkali metal oxide and about 15 to 40 weight percent of chromium oxide. Of the various alkali metal oxides, sodium oxide or potassium oxide are highly satisfactory. The presence of alkali metal oxide in the catalyst composition greatly increases the conversion of the amine to the nitrile under the reaction conditions employed in the process of this invention and results in elimination of the undesired byproducts of ammonia, secondary amines and tertiary amines. The catalyst may be prepared by conventional catalyst preparation techniques known to the art. A preferred method of preparing the catalyst consists of impregnating the chromium oxide-alumina catalyst (which is available as a hydroforming catalyst for petroleum naphthas in refinery operations and which can be prepared according to techniques such as are described in U. S. 2,290,033) with an aqueous solution of a water soluble potassium or sodium compound. If desired it may be incorporated during an earlier stage of the manufacture of the chromium oxide-alumina composition. For example, the catalyst can be prepared by dissolving nitrates of aluminum and chromium in water, introducing ammonia into the solution, washing the precipitate formed, followed by drying and calcining, thereafter impregnating the chromium oxide-alumina composition with an aqueous solution of the alkali metal oxide compound, e. g. KOH, followed by drying and recalcining. The catalyst may be employed in any of the various physical forms such as pellets, granules, powder, etc. Minor amounts of impurities or added ingredients may also be contained therein.

The process is carried out by introducing heated amine into the dehydrogenation reaction zone and maintaining the temperature therein at least at about 425° C. and usually at not more than about 550° C. The amine feed is introduced into the reaction zone at a liquid hourly space velocity of at least 2 liquid volumes of amine/hour/volume of catalyst. As the reaction temperature is increased, the space velocity may be increased so that at temperatures in the neighborhood of 500° C. a space velocity in the vicinity of about 10–15 may be used. While superatmospheric pressures, e. g. 1,000 p. s. i. g. or thereabout can be used, we have discovered that when employing our catalyst it is possible to obtain essentially quantitative conversion of the amine to its corresponding nitrile when using substantially atmospheric pressures in the reaction zone. Since essentially quantitative conversion to the nitrile is obtained when practising our invention, recovery of the nitrile is a simple operation. The products from the reaction zone are cooled and the liquid nitrile is recovered in a form usually suitable for immediate sale. The gas produced during the dehydrogenation reaction is essentially pure hydrogen uncontaminated with ammonia. If one desires to produce an unsaturated nitrile, this can be effected by maintaining the end portion of the catalyst mass at a temperature in the neighborhood of 600–650° C. whereupon the nitrile passing through this higher temperature zone is dehydrogenated to its corresponding unsaturated nitrile, e. g. acrylonitrile being produced from n-propyl nitrile.

A number of experiments were performed which illustrate the results and advantages obtained by the practice of this invention. The experiments were carried out using as a reactor a one-half inch glass tube containing about 25 cc. of catalyst above which was placed three

inches of glass beads which function as a preheat section. The amine was metered into the reactor by means of a positive displacement pump, vaporized in the preheat section in which it reached the operating temperature, and then passed down flow through the bed of catalyst. A commercial catalyst containing approximately 18 weight percent Cr_2O_3 with the remainder being H41 Alcoa alumina was used in run 1. This same catalyst was impregnated with a concentrated solution of potassium nitrate, then dried, and calcined at about 1,000° F. for one hour to effect decomposition of potassium nitrate to potassium oxide. This catalyst then contained approximately 4 percent potassium oxide, 18 percent chormium oxide, the remainder being alumina. Substantially atmospheric pressures were used in the reaction zone. The reaction products were removed from the bottom of the reactor and passed through a wet ice condenser from which the normally liquid reaction products (amines, nitriles, etc.) were recovered. The remaining gases were then passed through a Dry Ice condenser in which ammonia was liquefied. The amount of unconverted amine, nitrile and byproduct higher molecular weight secondary amines, tertiary amines, etc. were determined by gas chromatography. In the experiments performed, n-hexylamine was dehydrogenated to n-hexylnitrile. In all of the experiments, a space velocity of 1.8 liquid volumes of amine/hour/volume of catalyst was used. Temperatures between about 410 and 450° C. were used in the various runs. The results obtained in these runs are shown in Table I which follows:

Table I

Run No.	Catalyst	Temp., ° C.	Liquefiable products, weight percent			
			n-Hexyl amine	n-Hexyl nitrile	Waste products	
					Sec-amines etc.	NH_3
1	Cr_2O_3-Al_2O_3	410	28	32	37	3
2	K_2O-Cr_2O_3-Al_2O_3	410	21	50	26	3
3	K_2O-Cr_2O_3-Al_2O_3	430	Trace	95–98	0	0
4	K_2O-Cr_2O_3-Al_2O_3	450	Trace	95–98	0	0

It is readily seen from the above data that the extent of conversion and the minimizing of wasteful byproducts is unexpectedly greater when using the alkalized catalyst than when using the non-alkalized catalyst. It is evident from runs 3 and 4 that by employing the catalyst and reaction conditions of this invention, one can convert the amine to the nitrile in an essentially quantitative manner without formation of waste byproducts such as ammonia, secondary amines and tertiary amines, etc. The gas produced is free of ammonia and is thus essentially pure hydrogen.

Thus having described our invention what is claimed is:

1. A process for the preparation of nitriles which comprises contacting an amine having the general formula RCH_2NH_2, in which R is a hydrocarbon radical having from 1 to 15 carbon atoms, with a catalyst comprised essentially of about 1 to 10 weight percent of alkali metal oxide, about 10 to 50 weight percent of chromium oxide and the remainder essentially alumina at a temperature between 425° C. and 550° C. at a space velocity of at least 2 liquid volumes of amine/hour/volume of catalyst, and recovering nitriles from the reaction products.

2. The process of claim 1 in which the contacting is effected under substantially atmospheric pressures.

3. The process of claim 2 in which the amine is n-propylamine.

4. The process of claim 2 in which the amine is n-hexylamine.

References Cited in the file of this patent

UNITED STATES PATENTS

2,271,751	Visser et al.	Feb. 3, 1942
2,388,218	Olin	Oct. 30, 1945
2,731,488	Thompson	Jan. 17, 1956