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(54) Title: PREPARATION OF XYLYLENDIAMINE USING IMIDAZOLE AS A SOLVENT

(57) Abstract: The present invention relates to a preparation method of xylylenediamine using imidazoles as a solvent, more partic-
ularly to a preparation of xylylenediamine by the hydrogenation of phthalonitrile under ammonia atmosphere, wherein an imidazole,
which is chemically stable and highly soluble in phthalonitrile, is used as a reaction solvent to significantly reduce the amount of
ammonia and obtain high-purity xylylenediamine under mild reaction conditions with high yield.

Description

PREPARATION OF XYLYLENDIAMINE USING IMIDAZOLE AS A SOLVENT

[1]

Technical Field

[2]

[3] The present invention relates to a preparation method of xylylenediamine using an imidazole as a solvent, more particularly to a preparation of xylylenediamine by hydrogenation of phthalonitrile in the presence of ammonia, wherein an imidazole, which is chemically stable and dissolves phthalonitrile significantly, is used as a reaction solvent to significantly reduce the amount of ammonia and obtain high-purity xylylenediamine under mild reaction conditions with high yield.

[4]

Background Art

[5]

[6] Xylylenediamine is a useful compound as a source of polyamide resins and curing agents and as an intermediate material for isocyanate resins.

[7] In general, xylylenediamine is prepared by the hydrogenation of phthalonitrile in the presence of a catalyst containing nickel and/or cobalt. However, this method has the problem, producing a lot of impurities, due to partial reduction, polymerization, etc.

[8] Thus, various methods have been proposed for more effective hydrogenation of phthalonitrile.

[9] U.K. Patent No. 1,149,251 discloses a method using ammonia and a solvent selected from aromatic hydrocarbons, aliphatic alcohols, aliphatic hydrocarbons, dimethylformamide, dioxane, etc. In this method, the reaction is performed at a temperature of 60-130 ° C and a pressure of 1000-5000 psig in order to maintain the ammonia in the liquid phase. However, some of the solvents and ammonia existed in the gas phase are shown to reduce the effect of ammonia and result in generation of various byproducts.

[10] U.K. Patent No. 852,972 discloses a process for the production of xylylenediamines by the hydrogenation of phthalonitrile in the presence of a cobalt-based catalyst. However, this method requires a high reaction pressure of more than 4000 psig.

[11] The following techniques have been proposed to solve these problems.

[12] U.S. Patent No. 4,482,741 attains a yield of 94 % under relatively mild conditions

of 1000 psig and 95 ° C using a cobalt-based catalyst and a xylylenediamine as a reaction solvent.

[13] U.S. Patent Publication No. 2002-0,177,735 A1 attains a yield of 80 % or higher using mesitylene as a solvent in the presence of nickel- and/or cobalt-based catalysts.

[14] U.S. Patent No. 6,476,269 B2, European Patent No. 1,193,244 A2, etc. have proposed the process for preparing *m*-xylylenediamine (MXDA) of Mitsubishi Gas Chemical (MGC) of Japan, which is industrially used at present.

[15] The process of MGC comprises five steps: ammoxidation, trapping, hydrogenation, separation-extraction and recovery. Of them, the trapping and hydrogenation steps will be described below.

[16] The gas produced by ammoxidation contains unreacted *m*-xylene, ammonia, N₂, O₂, etc., as well as isophthalonitrile (IPN), the target product. Also, it contains byproducts such as CO, CO₂, HCN, H₂O, aromatic amides, aromatic carboxylic acids. Thus, a process for selectively separating IPN from the gas produced through ammoxidation is essential.

[17] In general, IPN is separated by the solidification being cooling the reaction products and then by melting the solidified IPN. However, this method appears to have a side reaction (polymerization) because IPN has to be melted at high temperature, which lowers the purity of IPN and causes accumulation of polymers inside the reaction apparatus.

[18] As an alternative, IPN may be trapped using water. However, this method is disadvantageous in that a lot of slurry is formed and a large amount of energy is consumed. In addition, such byproducts as formamide and ammonium formate may be formed from the reaction with water. To solve these problems, a method contacting the ammoxidation product directly with a trapping solvent to selectively dissolve IPN was proposed. As a trapping solvent, it is preferable to use one having a boiling point higher than that of *m*-xylene, the source material, dissolving IPN well and having no functional group capable of participating in the following hydrogenation step. As such a trapping solvent, a trimethylbenzene isomer mixture comprising 1,3,5-trimethylbenzene (mesitylene) and 1,2,4-trimethylbenzene (pseudocumene) is proposed. However, this solvent has a relatively low solubility to IPN, and thus a large amount of solvent is needed to trap IPN.

[19] In the production process of MXDA by hydrogenation of IPN, the reaction is generally carried out in the presence of large amount of ammonia and a relatively high pressure condition to prevent side reactions. The reaction conditions should be improved to reduce operation cost.

[20]

Disclosure

[21]

[22] The present inventors have tried to solve the problems caused by byproduct formation, excessive use of ammonia and solvent, and high reaction pressure, etc in a preparation of xylylenediamine. In doing so, they have found that xylylenediamine can be prepared in good yield under mild reaction conditions using imidazole, which has better polarity and higher boiling point than conventional solvents, as reaction solvent in the hydrogenation of phthalonitrile in the presence of ammonia and a catalyst. In addition, the solvent dissolves phthalonitrile better and significantly reduces the amount of ammonia used.

[23] Thus, in an aspect of the present invention, there is provided a method of preparing xylylenediamine in good yield under mild reaction conditions using a specific organic compound as a reaction solvent.

[24]

Best Mode

[25]

[26] The present invention relates to a preparation method of xylylenediamine by the hydrogenation of phthalonitrile in the presence of a catalyst, ammonia and a reaction solvent, wherein imidazoles are used as a reaction solvent.

[27] Hereunder is given a more detailed description of the present invention.

[28] The present invention relates to a preparation method of xylylenediamine by the hydrogenation of phthalonitrile in the presence of an imidazole as a reaction solvent, nickel or cobalt based catalysts and ammonia.

[29] In general, selection of the solvent is very important in a continuous process treating phthalonitrile as source material because the solvent directly affects the performance of the hydrogenation process. If the solvent does not dissolve phthalonitrile well, a large amount of solvent should be used in the continuous process, and inevitably, unwanted problems arise therefrom. Also, side reactions such as polymerization or decomposition of amine groups may occur during the hydrogenation to give polymers, methylbenzylamine or xylene. As such, not only the catalyst but also the reaction solvent becomes a very important factor in the hydrogenation.

[30] 2-methoxyethanol, which is typically used as a solvent in hydrogenation, is not suitable for the hydrogenation of phthalonitrile since it cannot dissolve phthalonitrile well. Common solvents like ethyl acetate, ethylene glycol, isopropyl alcohol, methanol, toluene, etc. are restricted in use for the same reason.

[31] Whereas acetone has a relatively good dissolving ability, it is restricted in use because impurities such as propyl alcohol or ketimines are produced by side reactions.

[32] In other words, the ability to dissolve phthalonitrile is an important factor in selecting the solvent used in the hydrogenation of phthalonitrile.

- [33] In addition, the solvent should have a boiling point higher than the temperature at which the hydrogenation is performed. Generally, ammonia is added during hydrogenation to prevent side reactions such as deamination. For the ammonia to offer the desirable effect, it should remain in the liquid phase. That is, if the boiling point of the solvent is not higher than the reaction temperature, the effect of the ammonia addition decreases.
- [34] In the present invention, imidazoles are used as a solvent to improve the ability to dissolve phthalonitrile and the effect provided by ammonia. More particularly, the N-alkylimidazoles to be used in the present invention has an alkyl group which is substituted with C₀-C₆ alkyl. The imidazoles are advantageous in that, as an aprotic solvent, they are slightly basic with pKa of 7.3-7.8, have a high melting point of 180-260 ° C and do not participate in the hydrogenation.
- [35] Slightly basic imidazoles are superior in dissolving phthalonitrile (hereunder referred to as 'PN') to conventional solvents, but it cannot completely dissolve PN if it is used in 1.25 weight equivalence of PN or less. As a result, production yield of xylylenediamine (hereunder referred to as 'XDA') decreases and reaction does not proceed well because part of PN remains in solid state. In contrast, if it is used in 20 weight equivalence or more, productivity decreases because of increasing amount of solvent used and cost of production facilities. In addition, the energy consumption increases to remove XDA from the solvent. Therefore, the imidazole is preferably used in the amount of from 1.25 to 20 weight equivalence of PN.
- [36] In an embodiment of the present invention, the reaction is performed using methylimidazole, which has a basicity (pKa) of 7.4 and a boiling point of 198 ° C .
- [37] For example, preparation of *m*-xylylenediamine by the hydrogenation of isophthalonitrile using methylimidazole as a reaction solvent in the presence of ammonia and a catalyst is performed as follows. This example is not limited to methylimidazole but can be applied to the imidazoles in accordance with the present invention.
- [38] Isophthalonitrile, a source material, methylimidazole, a reaction solvent, and benzyl ether, an internal standard of gas chromatography, are fed into an autoclave, and then activated nickel-based catalyst is added. Then, isophthalonitrile is dissolved in the solvent while slowly heating and stirring the mixture. Next, ammonia is added to the reactor and hydrogen gas is fed to perform hydrogenation.
- [39] The reaction solvent is used in the amount of from 1.25 to 20 g, preferably 2.5-10 g, per 1 g of the source material.
- [40] Further, the ammonia is used in the volume of from 0.25 to 4 cc, preferably 0.75-2 cc, per 1 g of the source material. If less than 0.25 cc of ammonia is used, various byproducts are formed. In contrast, if over 4 cc is used, production cost increases.
- [41] The reaction temperature is maintained at 50-200 ° C , preferably 90-150 ° C , and

the reaction pressure is maintained at 500-1500 psig, preferably 600-1200 psig. If the reaction temperature is below 50 ° C , conversion of isophthalonitrile (hereunder referred to as 'IPN') and yield of *m*-xylylenediamine (hereunder referred to as 'MXDA') decrease rapidly. Otherwise, if it exceeds 200 ° C , byproducts are produced by side reactions. If the reaction pressure is below 500 psig, the conversion of IPN and yield of MXDA decrease because of low hydrogen concentration. In contrast, if it exceeds 1500 psig, facility cost and energy consumption increase.

[42] During the reaction, sample is taken from the reaction mixture for analysis and the reaction is carried out until no product composition change was observed. The reaction sample is analyzed by gas chromatography, etc.

[43] As described above, the present invention enables a preparation of high-purity xylylenediamine in good yield with significantly reduced amount of ammonia by the hydrogenation of phthalonitrile using specific organic compounds as a reaction solvent.

[44] Hereinafter, the present invention is described in further detail through examples. However, the following examples are only for the understanding of the present invention and they should not be construed as limiting the scope of the present invention.

[45]

[46] **Example 1: Effect of reaction temperature**

[47] Into a 100 mL autoclave (Parr Instrument Company, Moline) were added 4.0 g of isophthalonitrile (Aldrich), 40 g of methylimidazole (Aldrich), a solvent, 3.0 g of activated nickel catalyst (Nickel alpha, Degussa) and 0.5 g of benzyl ether (Aldrich), an internal standard. The mixture was stirred and heated for about 30 min and the reaction temperature was maintained constantly at 50-200 ° C .

[48] Then, 7 cc of ammonia (industrial liquid ammonia) was added to the autoclave and hydrogen pressure was increased to 1000 psig. The reaction was completed about 5 hours after the hydrogenation began and obtained *m*-xylylenediamine (MXDA).

[49]

Table 1

Reactants				Reaction condition		Product
IPN (g)	Solvent (g)	Catalyst (g)	NH ₃ (cc)	Temperature (°C)	Pressure (psig)	Yield (%)
4	40	3	7	60	1000	80
				70		85
				90		87
				110		94
				130		99
				150		93

[50] As seen in Table 1, yield of MXDA increased with the reaction temperature increased to 130 ° C . However, the yield decreased a bit at 150 ° C .

[51]

[52] **Example 2: Effect of amount of ammonia**

[53] MXDA was prepared in the same manner as in Example 1, except that the amount of ammonia varied from 0 to 7 cc, as shown in Table 2 below. The yield of MXDA depending on the amount of ammonia is also given in Table 2.

[54]

Table 2

Reactants				Reaction condition		Product
IPN (g)	Solvent (g)	Catalyst (g)	NH ₃ (cc)	Temperature (°C)	Pressure (psig)	Yield (%)
4	40	3	0	130	1000	40
			1			71
			3			88
			5			98
			7			99

[55] As seen in Table 2, yield of MXDA increased as the addition amount of ammonia increased.

[56]

[57] **Example 3: Effect of amount of solvent**

[58] MXDA was prepared in the same manner as in Example 1, except that the amount of ammonia was varied from 5 to 40 g, as shown in Table 3 below. Yield of MXDA depending on the amount of solvent is also given in Table 3.

[59]

Table 3

Reactants				Reaction condition		Product
IPN (g)	Solvent (g)	Catalyst (g)	NH ₃ (cc)	Temperature (°C)	Pressure (psig)	Yield (%)
4	40	3	7	130	1000	99
	20					98
	10					98
	5					30

[60] As seen in Table 3, yield of MXDA was irrelevant of the addition of the amount of the solvent. However, when too little solvent was added (1.25 g of solvent per 1 g of IPN), IPN was not dissolved sufficiently, thus resulting in the yield of MXDA to only about 30 %.

[61]

[62] **Example 4: Effect of reaction pressure**

[63] MXDA was prepared in the same manner as in Example 1, except that the amount of hydrogen varied from 600 to 1200 psig, as shown in Table 4 below. Yield of MXDA depending on the reaction pressure is also given in Table 4.

[64]

Table 4

Reactants				Reaction condition		Product
IPN (g)	Solvent (g)	Catalyst (g)	NH ₃ (cc)	Temperature (°C)	Pressure (psig)	Yield (%)
4	40	3	7	130	1200	99
					1000	99
					800	98
					600	90

[65] As seen in Table 4, yield of MXDA increased as the reaction pressure increased.

[66]

[67] **Comparative Example 1: Comparison with conventional solvents**

[68] MXDA was prepared in the same manner as in Example 1, except that 40 g of benzyl ether (Aldrich, 99 %), mesitylene (Aldrich, 98 %), etc. were used as a reaction

solvent.

- [69] When benzyl ether was used, the yield of MXDA was 60 %, and when mesitylene was used, it was below 80 %. Thus, it was confirmed that the yield of MXDA was significantly lower than when methylimidazole was used as a solvent in accordance with the present invention.

[70]

Industrial Applicability

[71]

- [72] The present invention provides a preparation process of xylylenediamine by the hydrogenation of phthalonitrile in the presence of ammonia using specific imidazoles as a reaction solvent. As apparent from the above description, the reaction solvent used in the present invention is chemically more stable, dissolves phthalonitrile better and offers higher xylylenediamine yield than conventional reaction solvents. Also, since it offers good production yield with low amount of ammonia and at low reaction pressure. Thus, the present invention is advantageous both from the points of economics and efficiency.

[73]

While the present invention has been described in detail with reference to the preferred embodiments, those skilled in the art will appreciate that various modifications and substitutions can be made thereto without departing from the spirit and scope of the present invention as set forth in the appended claims.

Claims

- [1] A method of preparing xylylenediamine by mixing phthalonitrile with a catalyst, a reaction solvent and ammonia, and performing hydrogenation, wherein said reaction solvent is an imidazole.
- [2] The method of claim 1, wherein said imidazole is N-alkylimidazole wherein its alkyl group is C₀-C₆ alkyl.
- [3] The method of claim 1, wherein said imidazole is used in the amount of from 1.25 to 20 g per 1 g of phthalonitrile.
- [4] The method of claim 1, wherein said ammonia is used in the volume of from 0.25 to 4 cc per 1 g of phthalonitrile.
- [5] The method of claim 1, wherein said hydrogenation is performed at a temperature range of from 50 to 200 ° C .
- [6] The method of claim 1, wherein said hydrogenation is performed at a pressure range of from 500 to 1500 psig.