

Preparation Method for 2-mercaptobenzothiazole

Technical Field

The disclosure relates to the field of organic synthesis, and particularly to a preparation method for 2-mercaptobenzothiazole.

Background

2-mercaptobenzothiazole (also called as an accelerator M or an accelerator MBT and further called as quick heating powder) is a general-purpose rubber vulcanization accelerator. It has the characteristics of fast vulcanization acceleration action, low vulcanization flatness, no early vulcanization during mixing and the like, and is widely applied to the rubber processing industry.

There are many synthesis methods for the accelerator M, and according to adopted raw materials, may be divided into an o-nitrochlorobenzene method, an aniline method, a mixed nitrobenzene and aniline method, a nitrobenzene method, a nitroso-benzene method and the like. The o-nitrochlorobenzene method, the aniline method and the mixed nitrobenzene and aniline method are usually adopted more. However, when the o-nitrochlorobenzene method is adopted for producing the accelerator M, cost of raw materials is high, and a production process is complex, so that it is unsuitable for industrial application. The mixed nitrobenzene and aniline method is low in production cost, and may reduce H_2S produced by reaction by 1/3 of the aniline method, but it has the problems of difficulties in control of the reaction and high requirements on material of reactor, so that the method is adopted less in China at present. Therefore, the aniline method for synthesizing the accelerator M is a method generally adopted by each auxiliary producer.

The aniline method for producing the accelerator M has the characteristics of stable raw material sources, low difficulties in operation and low requirements on the material of reactor. However, it still has the shortcomings of relatively low purity of a product, high tar yield, relatively low yield and the like.

Summary

The disclosure is intended to provide a preparation method for 2-mercaptobenzothiazole, so as to solve the problems of relatively low purity of a

product, high tar yield and relatively low yield when an accelerator M is produced by an aniline method in prior art.

In order to achieve the purpose, according to an aspect of the disclosure, a preparation method for 2-mercaptobenzothiazole is provided, which includes that: an aniline method is adopted to perform reaction in the presence of a catalyst to prepare the 2-mercaptobenzothiazole, the catalyst comprising sulfonic acid type imidazolium ionic liquid.

Furthermore, the sulfonic acid type imidazolium ionic liquid is [TSVM]HSO₄ and/or [MPS]₂HSO₄.

Furthermore, the catalyst further includes a carrier for supporting the sulfonic acid type imidazolium ionic liquid.

Furthermore, the carrier is selected from one or more of a group formed by an activated alumina, cordierite honeycomb ceramics, mercaptoalkyl-functionalised silica gel, an ion exchange resin and a HZSM molecular sieve (Hydrogen type Zeolite Sieve of Molecular porosity molecular sieve).

Furthermore, a weight ratio of the sulfonic acid type imidazolium ionic liquid and the carrier is (0.1~20):100.

Furthermore, a reaction temperature of the reaction is 200~280°C, reaction pressure is 3.0~8.0MPa, and reaction time is 2~12h.

Furthermore, the reaction temperature of the reaction is 240~250°C, the reaction pressure is 4.5~5.5MPa, and the reaction time is 4~6h.

Furthermore, in the aniline method, an aniline, a carbon disulfide and a sulfur are taken as reaction raw materials, a molar ratio of the aniline, the carbon disulfide and the sulfur is 1:(1.0~1.3):(1.1~2), and a weight ratio of the aniline and the sulfonic acid type imidazolium ionic liquid is 100:(1~5).

Furthermore, the molar ratio of the aniline, the carbon disulfide and the sulfur is 1:(1.0~1.1):(1.2~1.5), and the weight ratio of the aniline and the sulfonic acid type imidazolium ionic liquid is 100:(1~2).

Furthermore, the 2-mercaptobenzothiazole is prepared by adopting an intermittent or continuous production process.

In the preparation method provided by the disclosure, the aniline method is adopted to prepare the 2-mercaptobenzothiazole with a catalytic action of the sulfonic acid type imidazolium ionic liquid. The sulfonic acid type imidazolium ionic liquid is a

type of acidic functionalized ionic liquid, and has the advantages of both a solid acid and a liquid acid. In the disclosure, the sulfonic acid type imidazolium ionic liquid is adopted as an active ingredient of the catalyst, and may remarkably improve a conversion rate of the reaction raw materials and increase a yield of the 2-mercaptobenzothiazole. Meanwhile, due to the characteristics of high catalytic activity, no volatilization, low corrosion, high thermal stability and the like of the 2-mercaptobenzothiazole, the preparation method provided by the disclosure also has the comprehensive advantages of simple process, low cost, low tar yield, high environment friendliness and the like.

Detailed Description of the Embodiments

It is important to note that embodiments in the application and characteristics in the embodiments may be combined without conflicts. The disclosure will be described below in combination with the embodiments in detail.

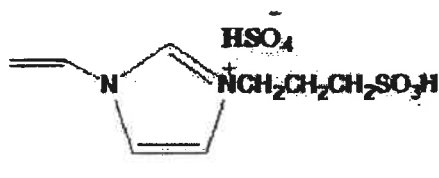
As described in the Background, when 2-mercaptobenzothiazole is produced by a prior aniline method, there exist the problems of relatively low purity of a product, high tar yield and relatively low yield. In order to solve the problems, the inventor of the disclosure provides a preparation method for 2-mercaptobenzothiazole. An aniline method is adopted to perform reaction in the presence of a catalyst to prepare the 2-mercaptobenzothiazole, and the catalyst includes sulfonic acid type imidazolium ionic liquid.

In the preparation method provided by the disclosure, the aniline method is adopted to prepare the 2-mercaptobenzothiazole under a catalytic action of the sulfonic acid type imidazolium ionic liquid. The sulfonic acid type imidazolium ionic liquid is a type of acidic functionalized ionic liquid, and has the advantages of both a solid acid and a liquid acid. In the disclosure, the sulfonic acid type imidazolium ionic liquid is adopted as an active ingredient of the catalyst, and may remarkably improve a conversion rate of the reaction raw materials and increase a yield and a purity of the 2-mercaptobenzothiazole. Meanwhile, due to the characteristics of high catalytic activity, no volatilization, low corrosion, high thermal stability and the like of the 2-mercaptobenzothiazole, the preparation method provided by the disclosure also has the comprehensive advantages of simple process, low cost, low tar yield, high environment friendliness and the like.

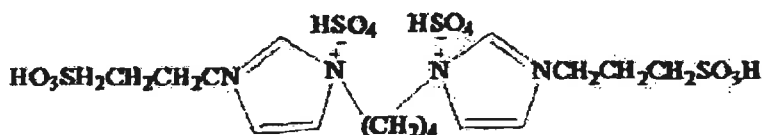
In the preparation method provided by the disclosure, as long as the sulfonic

acid type imidazolium ionic liquid is adopted to catalyze the reaction between aniline, carbon disulfide and sulfur as the active ingredient, a reaction process may be endowed with the advantages of high yield, low cost, environment friendliness and the like. In a preferred embodiment, the sulfonic acid type imidazolium ionic liquid is [TSVM]HSO₄ and/or [MPS]₂HSO₄.

Wherein, a structure of the [TSVM]HSO₄ ionic liquid is as follows:



a structure of the [MPS]₂HSO₄ ionic liquid is as follows:



Both of the two types of sulfonic acid type imidazolium ionic liquid have relatively high catalytic activity, and are relatively low in cost and extensive in source, and using them as the active ingredient of the catalyst may further increase the yield of the 2-mercaptobenzothiazole, reduce emissions of waste gas, waste water and sold waste and reduce production cost.

In the preparation method of the disclosure, the sulfonic acid type imidazolium ionic liquid may be directly adopted to catalytically prepare the 2-mercaptobenzothiazole as a catalyst, that is, non-supported sulfonic acid type imidazolium ionic liquid may be directly added into a reaction system for catalytic reaction. In a preferred embodiment, a supported sulfonic acid type imidazolium ionic liquid is adopted as a catalyst, that is, the catalyst further includes a carrier for supporting the sulfonic acid type imidazolium ionic liquid. The supported sulfonic acid type imidazolium ionic liquid catalyst not only is applied to catalytic reaction in an ordinary intermittent reaction kettle or kettle type continuous reactor, but also may be mounted in a fixed tower to realize continuous production by continuous input and output of reaction raw materials, and has the advantages of relatively high yield, relatively low energy consumption, relatively low production cost and the like.

According to the abovementioned instruction of the disclosure, those skilled in the art may select a concrete carrier of the supported sulfonic acid type imidazolium

ionic liquid catalyst. In a preferred embodiment, the carrier includes, but not limited to, one or more of an active alumina, a cordierite honeycomb ceramics, a mercaptoalkyl-functionalised silica gel, an ion exchange resin and an HZSM molecular sieve. All of these carriers have the advantages of stable physical properties, large specific surface area and relatively better bonding action with the sulfonic acid type imidazolium ionic liquid. In addition, these carriers are also relatively low in cost.

In the supported catalyst, those skilled in the art may select a proportional relationship between the catalytic active ingredient and the carrier. In a preferred embodiment, a weight ratio of the sulfonic acid type imidazolium ionic liquid and the carrier is (0.1~20):100. A relationship between using amounts of the two is set within the abovementioned range, so that the active ingredient of the catalyst may be dispersed on the carrier more uniformly, and relatively high catalytic activity is achieved. Meanwhile, cost may also be reduced, and difficulties in reaction operations may be reduced.

In a preferred embodiment, a reaction temperature of the reaction in a preparation process is 200~280°C, reaction pressure is 3.0~8.0MPa, and reaction time is 2~12h. In the preparation method provided by the disclosure, the sulfonic acid type imidazolium ionic liquid is adopted as the catalytic active ingredient, so that difficulties in operations for the 2-mercaptobenzothiazole may be reduced, and reaction conditions may be milder. The temperature, the pressure and the time conditions are favorable for increasing a reaction rate, simultaneously reducing occurrence of side reaction and endowing the reaction with a relatively high rate and yield. More preferably, the reaction temperature of the reaction is 240~250°C, the reaction pressure is 4.5~5.5MPa, and the reaction time is 4~6h.

In the preparation method provided by the disclosure, those skilled in the art may select a relationship between using amounts of each raw material. In a preferred embodiment, in the aniline method, an aniline, a carbon disulfide and a sulfur are taken as reaction raw materials, a molar ratio of the aniline, the carbon disulfide and the sulfur is 1:(1.0~1.3):(1.1~2), and a weight ratio of the aniline and the sulfonic acid type imidazolium ionic liquid is 100:(1~5). Setting the ratio of the using amounts of each raw material within the range is favorable for further increasing the conversion rate of the reaction and simultaneously achieving a higher reaction speed and a

higher target product yield. In addition, controlling the using amount of the catalyst within the abovementioned range is also favorable for reducing the cost and making the whole reaction more applicable to industrial large-scale application. More preferably, the molar ratio of the aniline, the carbon disulfide and the sulfur is 1:(1.0~1.1):(1.2~1.5), and the weight ratio of the aniline and the sulfonic acid type imidazolium ionic liquid is 100:(1~2).

The preparation method provided by the disclosure is applied to any production mode. In a preferred embodiment, the 2-mercaptobenzothiazole is prepared by adopting an intermittent or continuous production process. Intermittent refers to an intermittent kettle type catalytic reaction manner, and continuous refers to a continuous tower type reaction manner (for example, a fixed bed reaction manner or a trickle bed reaction manner).

The disclosure will further be described below in combination with examples in detail, and these embodiments should not be understood to limit the scope of protection of the disclosure.

Example 1

93 grams of an aniline, 76 grams of a carbon disulfide and 38.4 grams of a sulfur (a molar ratio of the three is 1:1:1.2) were added into a pressure reactor, and 1.86 grams of a non-supported sulfonic acid type imidazolium ionic liquid [TSVM]HSO₄ (a weight ratio between the aniline and it is 100:2) was added into a system. A reaction temperature was controlled to be 250°C, a reaction pressure was controlled to be 4.5MPa, and after 6h reaction, a crude product melt was obtained.

The crude product melt was pressed into a crystallizer containing a toluene solvent, discharged hydrogen sulfide was absorbed and treated with alkali liquor, and after the melt was crystalized, washing, filtering and drying were performed to obtain a 2-mercaptobenzothiazole product, wherein the product has a purity 98% or more and a yield of 90%.

Examples 2 to 7

A preparation method was the same as example 1, and differences were in the reaction temperatures, the reaction pressure and the reaction time, and process conditions and product results of each example are shown in the following table.

	Reaction temperature	Reaction pressure	Reaction time (h)	Product purity	Product yield

	(°C)	(MPa)		(%)	(%)
Example 2	240	5.5	6	98	92
Example 3	240	4.0	4	97.5	92
Example 4	200	8.0	12	97	84
Example 5	200	8.0	14	97.2	83
Example 6	280	3.0	2	95.4	84
Example 7	300	10.0	2	96.3	83

Examples 8 to 13

A preparation method was the same as embodiment 1, and differences were in the molar ratios of each raw material, and raw material relationships and product results of each example are shown in the following table.

	Molar ratio of aniline, carbon disulfide and sulfur	Weight ratio of aniline and [TSVM]HSO ₄	Product purity (%)	Product yield (%)
Example 8	1:1.1:1.5	100:2	98	90
Example 9	1:1.1:1.5	100:1	98	89
Example 10	1:1.1:1.1	100:3	97	91
Example 11	1:1.1:2	100:4	97	92
Example 12	1:1.3:2	100:5	98	90
Example 13	1:1:1	100:10	98	92

Examples 14 to 19

A preparation method was the same as example 1, and differences were in types of the catalyst, and catalyst types and product results of each example are shown in the following table.

	Catalyst				Pr oduct purity (%)	Pr oduct yield (%)
	Sulfonic acid type imidazolium ionic liquid		Carrier			
	Type	Weight (g)	Type	We ight (g)		
Example 14	[TSVM]HSO ₄	1.86	HZSM molar sieve	9.3	97	90

Example 15	[TSVM]HSO ₄	1.86	HZSM molar sieve	18.6	98	91
Example 16	[TSVM]HSO ₄	0.37	HZSM molar sieve	370	94	87
Example 17	[MPS] ₂ HSO ₄	1.86	NONE		96	91
Example 18	[MPS] ₂ HSO ₄	1.86	cordierite honeycomb ceramics	6.2	98	92
Example 19	[TSVM]HSO ₄ / [MPS] ₂ HSO ₄ (weight ratio: 1:1)	1.86	mercapto alkyl-functionalised silica gel	7.4	98	90

From the above descriptions, it can be seen that the examples of the disclosure achieve the following technical effects: the sulfonic acid type imidazolium ionic liquid is adopted as the active ingredient of the catalyst, and may remarkably improve a conversion rate of the reaction raw materials and increase a yield of the 2-mercaptobenzothiazole. Meanwhile, the preparation method provided by the disclosure also has the comprehensive advantages of simple process, low cost, low tar yield, high environment friendliness and the like.

The above is only the preferred embodiment of the disclosure and not intended to limit the disclosure. For those skilled in the art, the disclosure may have various modifications and variations. Any modifications, equivalent replacements, improvements and the like made within the spirit and principle of the disclosure shall fall within the scope of protection of the disclosure.

Claims:

1. A preparation method for 2-mercaptobenzothiazole, wherein an aniline method is adopted to perform reaction in the presence of a catalyst to prepare the 2-mercaptobenzothiazole, the catalyst comprising sulfonic acid type imidazolium ionic liquid, in the aniline method, an aniline, a carbon disulfide and a sulfur are taken as reaction raw materials.

2. The preparation method as claimed in claim 1, wherein the sulfonic acid type imidazolium ionic liquid is [TSVM]HSO₄ and/or [MPS]₂HSO₄, wherein, a structure of the [TSVM]HSO₄ ionic liquid is as follows:



; and

a structure of the [MPS]₂HSO₄ ionic liquid is as follows:



3. The preparation method as claimed in claim 1 or 2, wherein the catalyst further comprises a carrier for supporting the sulfonic acid type imidazolium ionic liquid.

4. The preparation method as claimed in claim 3, wherein the carrier is selected from one or more of a group formed by an activated alumina, a cordierite honeycomb ceramics, a mercaptoalkyl-functionalised silica gel, an ion exchange resin and a Hydrogen type Zeolite Sieve of Molecular porosity molecular sieve.

5. The preparation method as claimed in claim 4, wherein a weight ratio of the sulfonic acid type imidazolium ionic liquid and the carrier is (0.1~20):100.

6. The preparation method as claimed in claim 4 or 5, wherein a reaction temperature of the reaction is 200~280°C, reaction pressure is 3.0~8.0MPa, and reaction time is 2~12h.

7. The preparation method as claimed in claim 6, wherein the reaction temperature of the reaction is 240~250°C, the reaction pressure is 4.5~5.5MPa, and the reaction time is 4~6h.

8. The preparation method as claimed in claim 1, wherein, a molar ratio of the

aniline, the carbon disulfide and the sulfur is 1:(1.0~1.3):(1.1~2), and a weight ratio of the aniline and the sulfonic acid type imidazolium ionic liquid is 100:(1~5).

9. The preparation method as claimed in claim 8, wherein the molar ratio of the aniline, the carbon disulfide and the sulfur is 1:(1.0~1.1):(1.2~1.5), and the weight ratio of the aniline and the sulfonic acid type imidazolium ionic liquid is 100:(1~2).

10. The preparation method as claimed in claim 1, wherein the 2-mercaptobenzothiazole is prepared by adopting an intermittent or continuous production process.