Patents

Preparation method of diethylene glycol monomethyl ether

Abstract

The application discloses a preparation method of diethylene glycol monomethyl ether, which comprises the step of carrying out contact reaction on a raw material containing diethylene glycol and methanol and an acid catalyst under an inactive atmosphere condition to obtain the diethylene glycol monomethyl ether. The method overcomes the defects of an organic synthesis method using alkali and a methylating agent in the prior art, adopts a catalytic synthesis method, and carries out catalytic etherification reaction on diethylene glycol and methanol, thereby providing a green synthesis route for preparing the diethylene glycol monomethyl ether compound, which reduces the environmental pollution, reduces the production cost, does not need the processes of sodium salt generated by post-treatment and the like.

Classifications

C07C41/09 Preparation of ethers by dehydration of compounds containing hydroxy groups

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Current Assignee : Dalian Institute of Chemical Physics of CAS

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Info: Patent citations (2), Non-patent citations (1) , Cited by (2), Legal events, Similar documents, Priority and Related Applications

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Claims (10)

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1. A preparation method of diethylene glycol monomethyl ether is characterized in that a raw material containing diethylene glycol and methanol is in contact reaction with an acid catalyst under the condition of inactive atmosphere to obtain the diethylene glycol monomethyl ether.

2. The production method according to claim 1, wherein the acid catalyst is at least one selected from a heteropoly acid catalyst and a solid acid catalyst.

3. The production method according to claim 2, wherein the heteropolyacid catalyst is at least one member selected from the group consisting of phosphotungstic acid, phosphomolybdic acid, silicotungstic acid and silicomolybdic acid.

4. The method of claim 2, wherein the solid acid catalyst is at least one selected from Amberlyst-15, H-beta, and H-ZSM-5.

5. The method according to claim 1, wherein the molar ratio of diethylene glycol to methanol is 1:1 to 20.

6. The method according to claim 1, wherein the molar ratio of diethylene glycol to methanol is 1: 4.

7. The preparation method according to claim 1, wherein the acid catalyst is present in the raw material in an amount of 0.5 to 20% by mass.

8. The process according to claim 1, wherein the etherification reaction conditions are as follows: the reaction temperature is 100-250 °C, and the reaction time is 2-10 h.

9. The process according to claim 1, wherein the etherification reaction conditions are as follows: the reaction temperature is 110-220 °C, and the reaction time is 2-6 h.

10. The method according to claim 1, wherein the inert gas atmosphere is at least one selected from the group consisting of nitrogen, helium, and argon.

Description

Preparation method of diethylene glycol monomethyl ether

Technical Field

The application relates to a preparation method of diethylene glycol monomethyl ether, belonging to the field of chemical materials.

Background

Diethylene glycol monomethyl ether contains an alcohol ether structure, is an excellent high-boiling point solvent, can dissolve organic molecules, synthetic polymers and natural macromolecules, and has certain water solubility, so that the diethylene glycol monomethyl ether is widely used as a solvent for dyes, synthetic resins, nitrocellulose, cellulose acetate, oils and the like, and is also used as a high-boiling point solvent in printing ink, paint and the like, and is also used as a cleaning agent, a plasticizer, an extracting agent and the like.

At present, the method for synthesizing diethylene glycol monomethyl ether mainly adopts a co-product generated by ethylene oxide and methanol under the catalysis of BF 3-diethyl ether. The process uses ethylene oxide, so that potential safety hazards of easy explosion exist; in addition, the product is abundant and purification is difficult.

Diethylene glycol is an important byproduct in the synthesis of ethylene glycol by the reaction of ethylene oxide and water in petrochemic
significance for the utilization of the ethylene glycol. At present, the reports of preparing diglyme by using diglycol as a raw material are le
adopted to react with sodium hydroxide and chloromethane to prepare diethylene glycol mono (di) methyl ether (CN 92108541.9); also, re
improved Williamson synthesis method, which uses diethylene glycol as a raw material and dimethyl sulfate as a methylating agent to pr
monomethyl ether (CN 91108228.X) under the action of a basic catalyst. The above methods are all organic synthesis methods, using a l
agent and a large amount of alkali, and simultaneously generating a large amount of byproducts such as sodium salt and the like. Therefo
environment-friendly and green process for synthesizing diethylene glycol monomethyl ether is needed.

Disclosure of Invention

According to one aspect of the application, a method for preparing diethylene glycol monomethyl ether is provided, which overcomes the defects of an organic synthesis method using alkali and a methylating agent in the prior art, adopts a catalytic synthesis method, and carries out catalytic etherification reaction on diethylene glycol and methanol, thereby providing a green synthesis route for preparing diethylene glycol monomethyl ether compounds, which reduces environmental pollution, reduces production cost, does not need processes such as post-treatment of generated sodium salt and the like.

The preparation method of the diethylene glycol monomethyl ether comprises the step of carrying out contact reaction on a raw material containing diethylene glycol and methanol and an acid catalyst under an inactive atmosphere condition to obtain the diethylene glycol monomethyl ether.

The invention provides a synthesis method of diethylene glycol monomethyl ether, which comprises the following reaction equation:

optionally, the acidic catalyst is selected from at least one of a heteropolyacid catalyst, a solid acid catalyst.

The catalyst provided by the application is a high-boiling-point and environment-friendly acid catalyst.

Optionally, the heteropolyacid catalyst is selected from at least one of phosphotungstic acid, phosphomolybdic acid, silicotungstic acid, silicomolybdic acid.

Optionally, the solid acid catalyst is selected from at least one of Amberlyst-15, H-beta, H-ZSM-5.

Optionally, the molar ratio of the diethylene glycol to the methanol is 1: 1-20.

Preferably, the molar ratio of diethylene glycol to methanol is 1: 4.

Optionally, the mass percentage of the acidic catalyst in the raw material is 0.5-20%.

The upper limit of the mass percentage of the acidic catalyst in the raw material is 2%, 2.5%, 5%, 10%, 20%, and the lower limit of the mass percentage of the acidic catalyst in the raw material is 0.5%, 2%, 2.5%, 5%, 10%.

Alternatively, the etherification reaction conditions are: the reaction temperature is 100-250 °C, and the reaction time is 2-10 h.

The upper limit of the reaction temperature of the etherification reaction is selected from 110 °C, 150 °C, 180 °C, 200 °C, 220 °C and 250 °C, and the lower limit of the reaction temperature of the etherification reaction is selected from 100 °C, 110 °C, 150 °C, 180 °C, 200 °C and 220 °C.

The upper limit of the reaction time of the etherification reaction is selected from 4h, 6h, 8h and 10h, and the lower limit of the reaction time of the etherification reaction is selected from 2h, 4h, 6h and 8 h.

Preferably, the etherification reaction conditions are: the reaction temperature is 110-220 °C, and the reaction time is 2-6 h.

Optionally, the inert atmosphere comprises at least one of nitrogen, helium, argon.

The beneficial effects that this application can produce include:

1) the synthesis method of diethylene glycol monomethyl ether provided by the invention utilizes diethylene glycol as a raw material, which is an important byproduct in ethylene glycol synthesis, so that the preparation of diethylene glycol monomethyl ether by catalytic conversion of diethylene glycol is a high value-added utilization of the synthesized ethylene glycol byproduct.

2) Compared with the prior art, the method for preparing the diethylene glycol monomethyl ether by adopting the catalytic synthesis method can avoid using a large amount of alkali and methylating reagent, reduce the generation of sodium salt, relieve the pressure on the environment, reduce the production cost of enterprises and be a green synthetic route.

3) The invention adopts a high-boiling point and environment-friendly catalyst, and avoids using a large amount of inorganic acid or inorganic base.

Detailed Description

The present application will be described in detail with reference to examples, but the present application is not limited to these examples.

Unless otherwise specified, the raw materials in the examples of the present application were purchased commercially, and the instruments used were those recommended by the manufacturer.

The molecular sieves used were purchased from south-opening catalyst factories, Amberlyst-15 from south-China synthetic chemical Co., Ltd.

The conversion, selectivity, in the examples of the present application were calculated as follows:

in the examples of the present application, the conversion of diethylene glycol and the selectivity of diethylene glycol monomethyl ether were calculated on a carbon mole basis:

diethylene glycol conversion = mole number of diethylene glycol carbon in the feed) - (mole number of diethylene glycol carbon in the product)]/(mole number of diethylene glycol carbon in the feed) × (100%)

The selectivity for diethylene glycol monomethyl ether is diethylene glycol monomethyl ether in moles of carbon ÷ total of carbon moles of the different organics of the product x 100%.

In the present application, an agilent gas 7890 gas chromatograph is used for gas chromatography for product analysis.

Example 1

This example provides a process for the preparation of diethylene glycol monomethyl ether. Adding 20g of diethylene glycol and methanol in a molar ratio of 1:4 and 1g of phosphotungstic acid catalyst into a 50ml high-pressure reaction kettle, stirring and mixing uniformly at room temperature, sealing the kettle, replacing air with nitrogen for 5 times, heating to 200 °C, and reacting for 2 hours under the autogenous pressure. The stirring was stopped. The reaction kettle was cooled to room temperature. Taking a proper amount of reaction liquid to neutralize with triethylamine. The neutralized reaction solution was filtered and analyzed by gas chromatography. As a result, the conversion of diethylene glycol was 68.1%, and the selectivity of diethylene glycol monomethyl ether was 60.4%.

Example 2

This example provides a process for the preparation of diethylene glycol monomethyl ether. Adding 20g of diethylene glycol and methanol in a molar ratio of 1:4 and 2g of silicotungstic acid catalyst into a 50ml high-pressure reaction kettle, stirring and mixing uniformly at room temperature, sealing the kettle, replacing air with nitrogen for 3 times, heating to 150 °C, and reacting for 4 hours under the autogenous pressure. The stirring was stopped. The reaction kettle was cooled to room temperature. Taking a proper amount of reaction liquid to neutralize with triethylamine. The neutralized reaction solution was filtered and analyzed by gas chromatography, and the result was that the conversion of diethylene glycol was 60% and the selectivity of diethylene glycol monomethyl ether was 72%.

Example 3

This example provides a process for the preparation of diethylene glycol monomethyl ether. 20g of diethylene glycol and methanol in a molar ratio of 1:4 and 0.5g of silicomolybdic acid catalyst are added into a 50ml high-pressure reaction kettle, stirred and mixed uniformly at room temperature, the kettle is sealed, air is replaced by nitrogen for 3 times, the temperature is increased to 180 °C, the reaction pressure is self-pressure, and the reaction lasts for 2 hours. The stirring was stopped. The reaction kettle was cooled to room temperature. Taking a proper amount of reaction liquid to neutralize with triethylamine. The neutralized reaction solution was filtered

and analyzed by gas chromatography. As a result, the conversion of diethylene glycol was 68.1%, and the selectivity of diethylene glycol monomethyl ether was 60.4%.

Example 4

This example provides a process for the preparation of diethylene glycol monomethyl ether. 20g of diethylene glycol and methanol with a molar ratio of 1:4 and 0.4g of H-beta (silicon-aluminum ratio of 40) catalyst are added into a 50ml high-pressure reaction kettle, stirred and mixed uniformly at room temperature, the kettle is sealed, air is replaced by nitrogen for 4 times, the temperature is increased to 180 °C, the reaction pressure is self-pressure, and the reaction is carried out for 8 hours. The stirring was stopped. The reaction kettle was cooled to room temperature. Taking a proper amount of reaction liquid to enter a gas chromatograph for analysis. The result was a conversion of diethylene glycol of 46% and a selectivity of diethylene glycol monomethyl ether of 75%.

Example 5

This example provides a process for the preparation of diethylene glycol monomethyl ether. 20g of diethylene glycol and methanol in a molar ratio of 1:4 and 0.4g of HZSM-5 (silicon to aluminum ratio of 25) catalyst are added into a 50ml high-pressure reaction kettle, stirred and mixed uniformly at room temperature, the kettle is sealed, air is replaced by nitrogen for 5 times, the temperature is raised to 220 °C, the reaction pressure is self-pressure, and the reaction is carried out for 4 hours. The stirring was stopped. The reaction kettle was cooled to room temperature. Taking a proper amount of reaction liquid to enter a gas chromatograph for analysis. As a result, the conversion of diethylene glycol was 42%, and the selectivity of diethylene glycol monomethyl ether was 77%.

Example 6

This example provides a process for the preparation of diethylene glycol monomethyl ether. 20g of diethylene glycol and methanol in a molar ratio of 1:2 and 1g of Amberlyst-15 catalyst are added into a 50ml high-pressure reaction kettle, the mixture is stirred and mixed evenly at room temperature, the kettle is sealed, air is replaced by nitrogen for 5 times, the temperature is increased to 180 °C, the reaction pressure is self-pressure, and the reaction lasts for 10 hours. The stirring was stopped. The reaction kettle was cooled to room temperature. Taking a proper amount of reaction liquid to enter a gas chromatograph for analysis. As a result, the conversion of diethylene glycol was 47% and the selectivity of diethylene glycol monomethyl ether was 73%.

The results show that the high-boiling-point environment-friendly catalyst for preparing diethylene glycol monomethyl ether disclosed by the invention can be used for efficiently catalyzing diethylene glycol to convert and prepare diethylene glycol monomethyl ether. The method provides a new green synthesis method of diethylene glycol monomethyl ether with industrial prospect.

Although the present application has been described with reference to a few embodiments, it should be understood that various changes, substitutions and alterations can be made herein without departing from the spirit and scope of the application as defined by the appended claims.

Patent Citations (2)

Publication number	Priority date	Publication date	Assignee	Title
WO2004020378A2 *	2002-08-28	2004-03-11	Ferro Corporation	Method of producing glycol ethers
CN104250206A *	2013-06-28	2014-12-31	中国科学院大连化学物理研究所	Preparation method of glycol ether
Family To Family Citations				

* Cited by examiner, † Cited by third party

Non-Patent Citations (1)

Title
戚蕴石等: "杂多酸对于二甘醇和乙醇的醚化反应的催化作用",《催化学报》 *

* Cited by examiner, † Cited by third party

Cited By (2)

Publication number	Priority date	Publication date	Assignee	Title
CN114621247A *	2020-12-11	2022-06-14	中国科学院大连化学物理研究所	Method for preparing/synthesizing isosorbide methyl ether
CN115738912A *	2022-10-31	2023-03-07	厦门大学	Device and method for synthesizing triethylene glycol monomethyl ether from triethylene glycol
Family To Family Citations				

* Cited by examiner, † Cited by third party, ‡ Family to family citation

Similar Documents

Publication	Publication Date	Title
CN111233641A	2020-06-05	Preparation method of diethylene glycol monomethyl ether
CN116328825B	2024-06-25	Catalyst, preparation method thereof and method for preparing methyl 3-methoxypropionate by using catalyst to catalyze methanol and methyl acetate
CN106866331A	2017-06-20	A kind of method that cyclopentadiene or dicyclopentadiene are prepared by furfuryl alcohol
CN107602358B	2020-08-28	Method for preparing methoxy acetone by using micro-reaction device
AU2013409375B2	2017-05-25	Method for preparing polyoxymethylene dimethyl ether carbonyl compound and methyl methoxyacetate
CN108017510B	2021-02-02	Preparation method of hydroxyl pivalic aldehyde and application of hydroxyl pivalic aldehyde in preparation of neopentyl glycol
CN103012079A	2013-04-03	Method for synthesizing ethylene glycol allyl ether under catalysis of solid base catalyst
CN108503608B	2019-12-27	Preparation method of 1, 4-dimethylpiperazine
CN111001438A	2020-04-14	Catalyst for synthesizing dimethyl carbonate by ester exchange method and application thereof

Publication	Publication Date	Title
CN108129260B	2021-06-08	Synthesis method of phenyl ethylene glycol
CN100567237C	2009-12-09	The method of acetal or ketal preparing alkenyl ether by gas phase decomposing
CN111233638A	2020-06-05	Synthesis method of end-capped glycol dimethyl ether
CN110878025B	2023-02-24	Method for reducing aromatic nitro compound into aromatic amine compound
CN100387338C	2008-05-14	Ester exchange catalyst and its use
CN107827717B	2020-10-23	Preparation method of diglycerol monoalkyl ether formal
CN113880689A	2022-01-04	Preparation method of 3-methyl-1, 5-pentanediol
CN102911044B	2014-06-25	Method for preparing sec-butyl acetate via n-butene addition
CN111205172A	2020-05-29	Clean production method of 2, 4-di-tert-butylphenol
CN112707883A	2021-04-27	Preparation method of epsilon-caprolactone
CN111233635A	2020-06-05	Synthesis method of diethylene glycol monoethyl ether
US9328080B2	2016-05-03	Preparation of dihydroxyethyl piperazine
CN115745807B	2024-10-18	Method for synthesizing tetramethyl hexamethylenediamine by photocatalysis
CN117820089A	2024-04-05	Synthesis method of phenoxyethanol
CN111233636A	2020-06-05	Synthesis method of end-capped diethylene glycol ether compound
CN100386145C	2008-05-07	Solid catalyst for synthesizing propylene glycol ether and its preparing process

Priority And Related Applications

Priority Applications (1)

Application	Priority date	Filing date	Title
CN201811447867.6A	2018-11-29	2018-11-29	Preparation method of diethylene glycol monomethyl ether

Applications Claiming Priority (1)

Application	Filing date	Title
CN201811447867.6A	2018-11-29	Preparation method of diethylene glycol monomethyl ether

Legal Events

Date	Code	Title	Description
2020-06-05	PB01	Publication	
2020-06-05	PB01	Publication	
2020-06-30	SE01	Entry into force of request for substantive examination	
2020-06-30	SE01	Entry into force of request for substantive examination	
2022-11-04	RJ01	Rejection of invention patent application after publication	**Application publication date**: 20200605
2022-11-04	RJ01	Rejection of invention patent application after publication	