

Boron Trifluoride Complex Compound for Polymerization of Trioxane ✓**Background of the Invention****1. Field of the Invention**

The present invention relates to a boron trifluoride complex compound. More particularly, it relates to a boron trifluoride complex catalyst showing excellent operation stability during homopolymerization of trioxane or copolymerization of trioxane and a cyclic ether.

2. Description of Related Art

Boron trifluoride has been widely used as a catalyst for various reactions such as polymerization, alkylation, condensation, rearrangement and cyclization reactions.

Boron trifluoride is a colorless incombustible gas under the conditions of room temperature and normal pressure, and it is used in a form of a gas or a complex compound with an organic compound such as methyl alcohol, ethyl alcohol, phenol, acetic acid, diethyl ether, n-dipropyl ether and n-dibutyl ether.

Heretofore, the physical properties of the complex compounds have been investigated from an academic viewpoint. For example, there have been carried out researches concerning the chemical shift in fluorine-19 and isotopic equilibrium in the boron trifluoride complex compound (Zh. Fiz. Khim. (1974), 48(4)) and the infrared radiation spectra of vapor mixture from a solution which has various ranges of the ratio of ethyl ether to boron trifluoride (Zh. Fiz. Khim. (1967), 41(11), 2772-6). However, these researches were carried out from the view point of the physical properties. Accordingly, these publications neither teach to use the complex compound of boron trifluoride with the organic compound as a catalyst, nor disclose

any effects of the compound for catalytic activities.

When the boron trifluoride complex compound is applied to various reactions, it is well known that a complex compound diluted with an organic solvent inert to boron trifluoride is often used. As the inert organic solvents, there are known aliphatic hydrocarbons such as pentane, hexane, heptane and cyclohexane, aromatic hydrocarbons such as benzene and toluene, and the like.

Since 1950's, the boron trifluoride complex compound and the diluted complex compound have been used as a polymerization catalyst for the homopolymerization of trioxane and the copolymerization of trioxane with cyclic ethers. For example, U.S. Patent No. 2,989,510 and No. 2,989,506 disclose a method employing boron trifluoride-n-dibutyl ether as a catalyst for polymerization of trioxane. U.S. Patent No. 3,027,352 discloses a method employing boron trifluoride-diethyl ether as a catalyst for copolymerization of trioxane and ethylene oxide. U.S. Patent No. 5,144,005 recently issued describes a complex compound which has equimolar proportions of boron trifluoride and n-dibutyl ether, diluted with cyclohexane, for use as a polymerization catalyst for the copolymerization of trioxane and dioxolane.

When the conventional boron trifluoride complex compound of boron trifluoride with an organic compound capable of forming the complex compound therewith, especially the complex compound of boron trifluoride with ethers, is employed as a catalyst for polymerization of trioxane after dilution with an organic solvent inert to boron trifluoride, there has occurred problems such that the operation becomes unstable due to unstable polymerization behavior and that polymerization yield changes due to the unstable operation. However, no effective solution for these problems has been proposed, and it has been difficult to continue the polymerization

Summary of the Invention

The present inventors have made extensive and intensive studies to solve the above problems. As a result, they have found that the stability of a polymerization operation is markedly enhanced by employing a complex compound solution which has a specific molar ratio of boron trifluoride to an organic compound capable of forming a complex compound therewith, and accomplished the present invention.

Accordingly, the present invention relates to a solution containing a boron trifluoride complex compound, which solution comprises (a) a boron trifluoride complex compound of boron trifluoride with an organic compound and (b) a free organic compound which is an organic compound not forming a complex compound with boron trifluoride though capable of doing so; in which solution, boron trifluoride is contained at an amount of 0.98 mole or less based on one mole of the total amount of said organic compound contained therein. In other words, the boron trifluoride complex compound solution contains 0.98 mole or less of boron trifluoride based on one mole of the total amount of said organic compound capable of forming complex compounds contained in the solution.

Further, the present invention relates to a method of polymerization or copolymerization of trioxane using the boron trifluoride complex compound solution of this invention as a catalyst.

Detailed Description of the Invention

The boron trifluoride complex compound containing solution of the present

said organic compounds forming complex compounds with boron trifluoride and free organic compounds capable of forming complex compounds but not doing so. When the amount of boron trifluoride exceeds 0.98 mole, deposits in the form of tar appear during the polymerization and copolymerization of trioxane, so that the operation stability is deteriorated. Although the minimum amount is not particularly restricted, by use of a too small amount of boron trifluoride it is difficult to exhibit merits in economy and apparatus since a great amount of the organic compounds is required.

The organic compounds capable of forming a complex compound with boron trifluoride in the present invention include alcohols, ethers, organic acids, esters and the like. More specifically, there can be used methyl alcohol, ethyl alcohol, propyl alcohol, acetic acid, diethyl ether, n-dibutyl ether and the like as the organic compounds capable of forming a complex compound with boron trifluoride. In the present invention, the most preferable organic compound is a dialkyl ether wherein each alkyl group independently has 1 to 6 carbon atoms, specifically dimethyl ether, diethyl ether, n-dipropyl ether, n-dibutyl ether, pentyl ether and the like. These ether compounds may be used individually or in combination.

The boron trifluoride complex compound solution of the present invention is used after dilution with an organic solvent inert to boron trifluoride. Suitable inert organic solvents include aliphatic hydrocarbons such as pentane, hexane, heptane, octane and cyclohexane, aromatic hydrocarbons such as benzene and toluene, and the like. The preferred solvent includes cyclohexane, benzene and toluene. These organic solvents may be used without pretreatment, but they are preferably used after removing moisture by distillation or by absorption dehydration using zeolite and other dehydrating agents. When the boron trifluoride complex compound is diluted with

restricted.

Although the production method of the boron trifluoride complex compound solution of the present invention is not particularly restricted, the solution may be obtained, for example, by blowing a prescribed amount of boron trifluoride gas into the organic compound capable of forming a complex compound with boron trifluoride such as an ether and alcohol. Moreover, the solution may be produced by further diluting a boron trifluoride complex compound solution, which has an equimolar proportion of boron trifluoride to the organic compound, with further organic compound.

The boron trifluoride complex compound solution of the present invention obtained as described above may be used as a polymerization catalyst for trioxane without dilution. However, it is more preferable to dilute the solution with an organic solvent inert to boron trifluoride.

The polymerization of trioxane is described below.

Methods for polymerization of trioxane include homopolymerization of trioxane and copolymerization of trioxane and a cyclic ether. For example, trioxane and a comonomer are copolymerized by bulk polymerization employing a self-cleaning type reactor and the like. Suitable comonomers include cyclic ethers such as ethylene oxide, propylene oxide, 1,3-dioxolane and 1,4-butanediol formal, and the comonomer may be added in an amount of 0.01 to 20 mole % based on trioxane to carry out copolymerization. Typically, methylal and the like are added to the mixture of trioxane and comonomer as a molecular weight regulator. The polymerization temperature may be 50° to 140° C. The reaction period may be 0.5 to 60 minutes. In the polymerization reaction, the boron trifluoride complex compound solution

forming a complex compound with boron trifluoride and free organic compounds not forming complex compounds is used as a polymerization catalyst after dilution with an organic solvent inert to boron trifluoride. In general, the concentration of the polymerization catalyst is 1×10^{-6} to 1×10^{-3} mole based on 1 mole of the total monomer. However, this is not particularly critical.

Description of Preferred Embodiments

Hereinafter, the present invention is illustrated in more detail referring to Examples, which should not be construed as limiting the scope of the present invention.

The polymerization stability is evaluated as follows:

The copolymerization of trioxane and 1,3-dioxolane is continuously carried out according to the following polymerization method and polymerization behavior (operation disturbance) is evaluated.

<Polymerization Method>

A self-cleaning type twin-screw polymerization reactor (having a L/D of 8) was employed. The reactor was equipped externally with a jacket, through which a heat medium was passed, and internally with a pair of shafts corotating in the same direction. The shafts were provided with convex lens type paddles meshing each other. The corotating paddles were positioned such that the longer side of the blade of the paddle had a small clearance from the inner wall of the casing and the paddle of the other shaft. The jacket was maintained at 80° C, while trioxane, 1,3-dioxolane and methylal were continuously charged into the reactor at a rate of 2 kg/hr, 80 gr/hr and

which was diluted with cyclohexane so as to contain 1 % by weight of the boron trifluoride complex compound, was also charged to the reactor. The feed rate of the boron trifluoride complex solution was such that the concentration of the boron trifluoride was 1.2×10^{-5} mole based on 1 mole of trioxane to carry out polymerization.

Examples 1 to 6

Boron trifluoride complex compounds were prepared by blowing a prescribed molar quantity of boron trifluoride gas into 1 mole of each one of the ether compounds, n-diethyl ether and n-dibutyl ether. The inert organic solvent employed for dilution of the boron trifluoride complex compound was prepared by dehydrating a high quality reagent with zeolite so as to contain 10 ppm or less of water. Using the thus-prepared solution as a polymerization catalyst, polymerization was carried out according to the above-described polymerization method. The results are shown in Table 1.

Table 1 shows that excellent polymerization stability is exhibited when the boron trifluoride complex compound solution comprising boron trifluoride complex compounds containing 0.98 mole or less of boron trifluoride (based on 1 mole of the total amount of said organic compounds capable of forming a complex compound with boron trifluoride and free organic compounds not forming complex compounds) is used as a polymerization catalyst.

Comparative Examples 1 and 2

Boron trifluoride complex compounds were prepared according to the same method as in Example 1 and subjected to polymerization to evaluate polymerization

Table 1 shows that polymerization stability deteriorates when the boron trifluoride complex compound solution used as a polymerization catalyst comprises boron trifluoride complex compounds containing more than 0.98 mole of boron trifluoride (based on 1 mole of the total amount of said organic compounds capable of forming a complex compound with boron trifluoride and free organic compounds not forming complex compounds).

Polymerization stability during the polymerization or copolymerization of trioxane is achieved only by using the boron trifluoride complex compound solution of the present invention, which comprises boron trifluoride complex compounds containing 0.98 mole or less of boron trifluoride, based on 1 mole of the total amount of said organic compounds capable of forming a complex compound with boron trifluoride and free organic compounds not forming complex compounds, as a polymerization catalyst.

The present invention avoids the problems such as disturbance of polymerization behavior and unstable operation and, at the same time, achieves continuous stable polymerization operation without changing polymerization yield.

Table 1

	Molar Ratio of Boron Trifluoride to Organic Compound	Type of Organic Compound	Type of Inert Organic Solvent for Dilution	Polymerization Stability	
				Disturbance of Operation	Pollution in Pipe
Ex. 1	0.98	dibutyl ether	cyclohexane	Not caused after 2000 hr.	None
Ex. 2	0.95	"	"	"	"
Ex. 3	0.75	"	"	"	"
Ex. 4	0.50	"	"	"	"
Ex. 5	0.25	"	benzene	"	"
Ex. 6	0.95	diethyl ether	cyclohexane	"	"
Comp. Ex. 1	0.99	dibutyl ether	cyclohexane	Caused after 850 hr.	Slightly Observed
Comp. Ex. 2	1.00	"	benzene	Caused after 700 hr.	Observed

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Claims

1. A solution containing a boron trifluoride complex compound for homo or co-polymerization of trioxane, which solution comprises (a) a boron trifluoride complex which is a complex of boron trifluoride with an organic compound and (b) free organic compound, which is an organic compound not forming a complex compound with boron trifluoride though capable of doing so; in which solution, boron trifluoride is contained at an amount of 0.98 mole or less based on one mole of the total amount of said organic compound contained therein.
2. The boron trifluoride complex compound containing solution according to claim 1, wherein boron trifluoride is contained at an amount of 0.98 to 0.01 mole based on one mole of the total amount of said organic compound contained in the solution.
3. The boron trifluoride complex compound containing solution according to claim 1 or 2, wherein the organic compound is a dialkyl ether compound in which each alkyl group is independently a group having 1 to 6 carbon atoms.
4. The boron trifluoride complex compound containing solution according to any one of claims 1 to 3, wherein the amount of boron trifluoride is 0.90 to 0.10 mole relative to one mole of said organic compound.
5. The boron trifluoride complex compound containing solution according to any one of claims 1 to 4, which is diluted with an organic solvent inert to boron trifluoride.
6. A method of polymerizing trioxane, comprising homopolymerizing trioxane or copolymerizing trioxane and a cyclic ether in the presence of a catalyst which is the boron trifluoride complex compound containing solution claimed in any one of claims 1 to 5.

