

METHOD FOR REMOVING SOLID CATALYST

BACKGROUND OF THE INVENTION

Field of the Invention

5 [0001]

The present invention relates to a method of removing a solid catalyst after use from a fixed-bed multitubular reactor which includes a reaction tube filled with the solid catalyst.

10

Description of Related Art

[0002]

As a reactor that is used upon performing a contact gas-phase reaction in the presence of a solid catalyst, for example, a fixed-bed multitubular reactor is known which includes a reaction tube filled with the solid catalyst, such as a shell-and-tube type fixed-bed multitubular reactor. The shell-and-tube type reactor is a reactor having a structure in which a plurality of tubes (reaction tubes) is contained within a shell (a body).

20 [0003]

In such a reactor, the solid catalyst is filled in the tubes (the reaction tubes) to perform the reaction process, and during an exchange time of the catalyst, removing of the used solid catalyst from the reaction tube and filling of a new solid catalyst is repeatedly performed.

25 For that reason, when the solid catalyst is sampled, there is a problem in that a

disintegrated catalyst or a granular catalyst comes into contact with a tube inner surface and is gradually attached to the tube inner surface, thereby making the inner diameter of the tube thin. When the tube inner diameter becomes thin, a substantial decline in the catalyst filling amount, an increase in pressure loss or the like is caused, whereby the scheduled operation period of time is not reached or the designed reaction cannot be performed.

As means of solving such a problem, Patent Document 1 suggests a method of discharging the solid catalyst, then washing the tube inner surface with water and then drying the same and making the tube inner surface uniform.

10 [0004]

Furthermore, Patent Document 2 suggests a method in which, since when moisture condenses on the tube inner surface upon performing the catalyst exchange operation in the atmosphere, there is a concern that rust may be generated due to the moisture, condensation of moisture in air on the tube inner surface is prevented by supplying water into the shell (around the tube) to raise the temperature of circulating water to be higher than the air temperature by 2 to 40°C.

Prior Art Documents

Patent Documents

20 [0005]

[Patent Document 1] Japanese Laid-Open Patent Application No.

2006-159197

[Patent Document 2] Japanese Laid-Open Patent Application No. 2001-38196

25 DISCLOSURE OF INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0006]

However, since the method described in Patent Document 1 involves washing the inner portion of the tube with water whenever the catalyst is exchanged, there is an accompanying complicated operation, which undesirably leads to an increase in cost. Furthermore, there is a concern that if the drying is insufficient after washing the inner surface with water, rust will be generated on the tube inner surface, which may damage the reactor. When a plurality of tubes is included, confirming the respective dried states and washed states is extremely complicated and is not realistic.

In the method described in Patent Document 2, although the moisture condensation on the tube inner surface can be prevented, the attachment of the catalyst powder cannot be prevented, whereby the tube inner diameter may become thin. Furthermore, in a high temperature state, since there is a need to supply water with a higher temperature to the inner portion of the shell, there is undesirably a great burden on a worker.

[0007]

The present invention was made in view of the above circumstances, and an object thereof is to provide a method of removing a solid catalyst that can suppress the attachment of the catalyst powder onto a reaction tube inner surface even when the washing operation is not performed whenever the solid catalyst is sampled from the reaction tube of the fixed-bed multitubular reactor.

MEANS TO SOLVE THE PROBLEMS

[0008]

As means for solving the problem, the present invention includes the aspects as

below.

[0009]

[1] A method of removing a solid catalyst after use from a fixed-bed multitubular reactor which includes a reaction tube filled with a solid catalyst, the
 5 method comprising: a removing process of removing the solid catalyst within the reaction tube in the state of maintaining the temperature of a gaseous atmosphere within the reaction tube in the range of 15°C to 28°C, and the relative humidity in the range of 40 % to 60 %.

[0010]

10 [2] A method of removing a solid catalyst after use from a fixed-bed multitubular reactor which includes a reaction tube filled with a solid catalyst, the method comprising: a process of adjusting the temperature of an atmosphere gas within the reaction tube to the range of 15°C to 28°C, and the relative humidity to the range of 40 % to 60 % during a removing operation of the solid catalyst.

15 [0011]

[3] The method of removing the solid catalyst described in [1], wherein the temperature of the gaseous atmosphere within the reaction tube is adjusted to the range of 15 °C to 28 °C, and the relative humidity is adjusted to the range of 40% to 60%, by supplying a temperature and humidity controlling gas, in which the temperature is
 20 adjusted to the range of 15 °C to 28 °C and the relative humidity is adjusted to the range of 40 to 60 %, into the reaction tube in the removing process.

[0012]

[4] The method of removing the solid catalyst described in any one of [1] to [3], wherein, as a part of the temperature and humidity controlling gas, a low humidity gas is

used which is obtained by heating gas cooled to be equal to or less than 0 °C to 15 °C to 28 °C.

[0013]

[5] The method of removing the solid catalyst described in any one of [1] to [4],
5 wherein the solid catalyst is a composite metal oxide catalyst that contains molybdenum, bismuth, and iron which are used in a gas-phase catalytic reaction of propylene, isobutylene or tert-butanol.

[0014]

[6] The method of removing the solid catalyst described in any one of [1] to [4],
10 wherein the solid catalyst is a heteropolyacid (salt) catalyst that contains molybdenum and phosphorous which are used in a gas-phase catalytic reaction of methacrolein.

[0015]

[7] A fixed-bed multitubular reactor including:
a plurality of reaction tubes in which a solid catalyst is filled;
15 a reactor main body that houses the plurality of reaction tubes;
an upper cover; and
a lower cover,
wherein the upper cover has a reaction gas outlet through which a reaction
product is discharged, and
20 the lower cover has a reaction gas inlet through which a raw material gas is
supplied, or
the upper cover has a reaction gas inlet through which a raw material gas is
supplied, and
the lower cover has a reaction gas outlet through which a reaction product is
25 discharged,

the reactor main body has a heating medium inlet through which a heating medium for heating or cooling the plurality of reaction tubes is introduced into a shell side within the reactor main body, and

means for supplying a temperature and humidity controlling gas, in which the temperature is adjusted to the range of 15 °C to 28 °C and the relative humidity is adjusted to the range of 40 % to 60 %, into the reaction tube during a removing operation of the solid catalyst after use in the reaction tubes.

Effects of the Invention

[0016]

According to the method of removing the solid catalyst of the present invention, even if the washing operation is not performed whenever the solid catalyst is sampled from the reaction tube of the fixed-bed multitubular reactor, it is possible to suppress the attachment of the catalyst powder onto the reaction tube inner surface.

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BRIEF DESCRIPTION OF THE DRAWINGS

[0017]

FIG. 1 is a schematic diagram that shows an example of a fixed-bed multitubular reactor.

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EMBODIMENTS OF THE INVENTION

[0018]

A fixed-bed multitubular reactor in the present invention may include a reaction tube filled with the solid catalyst, and a known fixed-bed multitubular reactor can be suitably applied.

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FIG. 1 is a schematic diagram that shows an example of a shell-and-tube type fixed-bed multitubular reactor, but the present invention is not limited thereto.

A reactor 10 of this example is schematically constituted by a reactor main body 10a that houses reaction tubes 12 of a plurality of lines, an upper cover 10b, and a lower cover 10c.

The solid catalyst 11 is filled in the respective reaction tubes 12, a gas-phase catalytic reaction is performed while passing a gaseous raw material compound (a raw material gas) through the reaction tube 12, thereby obtaining the reaction product which is the object.

In the lower cover 10c, a reaction gas inlet 13 is provided through which the raw material or the like is supplied, and in the upper cover 10b, a reaction gas outlet 14 is provided through which the reaction product or the like is discharged. In the reactor main body 10a, a heating medium inlet 15, through which a heating medium for heating or re-heating the reaction tube 12 is introduced to the shell 10d side in the reactor main body 10a, and a heating medium outlet 16, through which the heating medium is discharged from the shell 10d side in the reactor main body 10a, are provided.

[0019]

The plurality of reaction tubes 12 are metallic tubes of substantially the same shape having an inner diameter selected from the range of about 15 to 50 nm. Herein, “substantially the same shape” means that an outer diameter, a thickness and a length of the reaction tube are within the range of a design error. In addition, the permitted design error is generally within $\pm 2.5\%$, and, preferably, within $\pm 0.5\%$.

The reaction tube 12 may have a coil shape, but a straight tube of a straight shape is generally used. The straight tube may be any one of a horizontal arrangement or a vertical arrangement but generally has a longitudinal shape that is placed in a

vertical direction to pass the raw material compound in the vertical direction.

[0020]

The kind, the shape, the property and the state of the solid catalyst are not particularly limited. The solid catalyst may be a molding catalyst or a supporting
5 catalyst. The molding catalyst may have any shape such as a circular shape, columnar shape, a cylindrical shape, and a star shape, and may be molded by any means such as a tablet presser, an extruder, and an oscillating granulator.

Similarly, the supporting catalyst may use any carrier such as silica, alumina, silica/alumina composite, magnesia, and titanium dioxide and may have any shape such
10 as a circular shape, a columnar shape, a cylindrical shape, or a plate shape.

The present invention can be applied to the removing of any kind of solid catalyst, and is particularly suitable for a catalyst having a relatively low strength and containing oxide in which disintegration and the collapse easily occur. For example, the present invention is particularly effective for the catalyst that contains molybdenum
15 among the catalysts containing single or composite metal oxide or heteropolyacids or salts thereof. The catalyst that contains molybdenum includes, for example, a composite metal oxide catalyst (C1) that contains molybdenum, bismuth, and iron, and a heteropolyacid (salt) catalyst (C2) that contains molybdenum and phosphorous or the like.

20 The catalyst (C1) is, for example, used in a gas-phase contact oxidation reaction of propylene, isobutylene and tert-butanol, and the catalyst (C2) is, for example, used in a gas-phase contact oxidation reaction of methacrolein.

[0021]

The method of removing the solid catalyst of the present invention has a process
25 (a removing process) of removing the solid catalyst within the reaction tube in the state

of maintaining the temperature of an atmosphere gas within the reaction tube at 15 °C to 28 °C, and the relative humidity in the range of 40 % to 60 %. A more preferable range of the gaseous atmosphere temperature within the reaction tube is 18 °C to 28 °C.

Although the temperature and the relative humidity of the gaseous atmosphere within the reaction tube in the present invention is a temperature and a relative humidity of gas passing through the reaction tube in the state in which the catalyst is filled, if it is difficult to perform the measurement in the state in which the catalyst is filled, and the temperature and the relative humidity are replaced with a temperature and a relative humidity that are measured in the lower cover 10c or the upper cover 10b which are space portions after passing through the inner portion of the reaction tube, by sending air with a controlled temperature and humidity from the reaction gas outlet 14 or the reaction gas inlet 13.

In addition, "the relative humidity" is indicated by a generally used ratio of an amount A of vapor contained in air at any temperature to the maximum amount B of vapor that can be contained at that temperature.

$$\text{Relative humidity \%} = A/B \times 100$$

[0022]

According to the findings of the inventors, when the temperature of the gaseous atmosphere within the reaction tube is within the range mentioned above, upon removing the solid catalyst, if the relative humidity of the gaseous atmosphere within the reaction tube is equal to or greater than 40 %, the catalyst is not too dried, and the catalyst being disintegrated and collapsing and being easily attached to the reaction tube is prevented. Furthermore, if the relative humidity is equal to or less than 60 %, on the contrary, the catalyst absorbs moisture and the adhesion is not increased, and it is prevented that the catalyst is easily attached to the reaction tube. Thus, by maintaining the relative

humidity in the temperature range within the range mentioned above, the drying and the moisture absorption of the solid catalyst after use is suppressed, whereby it is possible to satisfactorily suppress attachment of the catalyst powder to the reaction tube during removing.

5 Furthermore, the removing operation of the solid catalyst is normally performed in the atmosphere, but a worker generally performs the operation while wearing protection equipment such as an anti-dust suit and a protective mask as an anti-dust measure. When the temperature of the gaseous atmosphere within the reaction tube is within the range during removing of the solid catalyst, the operation is possible under the
10 operation circumstances adjusted to be within the temperature range, and heating and cooling measures are preferably easy.

[0023]

In the removing process, means for maintaining the temperature and the relative humidity of the gaseous atmosphere in the reaction tube within the range is not
15 particularly limited, but it is desirable to sample the solid catalyst while supplying a temperature and humidity controlling gas, in which the temperature and the relative humidity are adjusted to the ranges mentioned above, into the reaction tube.

The temperature and humidity controlling gas should not affect the removing solid catalyst, and although it is not particularly limited, air is preferable from the
20 viewpoint of the operation environment or the like.

[0024]

A preparation method of the temperature and humidity controlling gas is not particularly limited, but a known temperature controlling method, and humidity controlling method can be used. For example, under the condition that a vapor amount
25 of gas is constant, when the gas temperature is lowered, the relative humidity rises.

Furthermore, when performing the humidification by the known method, the relative humidity can be raised without lowering the temperature of the gas.

Meanwhile, upon raising the gas temperature under the condition that a vapor amount of gas is constant, the relative humidity is lowered. However, in order to prevent the generation of moisture condensation on the inner surface of the reaction tube, it is desirable that the temperature of the gaseous atmosphere in the reaction tube be equal to or less than the temperature of the outside of the reaction tube, and to do that, it is desirable that the relative humidity be lowered without raising the gas temperature.

For example, after gas Y having a temperature ($X^{\circ}\text{C}$) in the range of 15°C to 28°C is cooled to a temperature lower than the temperature having the relative humidity of 100 %, when heating the gas Y to $X^{\circ}\text{C}$ by a gas heater or the like, it is possible to obtain a low humidity gas having a vapor content lower than the gas Y at the same temperature $X^{\circ}\text{C}$ as that of the gas Y. When the relative humidity of the low humidity gas is lower than 40 %, it is possible to prepare a temperature and humidity controlling gas having the temperature of $X^{\circ}\text{C}$ and the relative humidity within the range of 40 % to 60% by mixing the low humidity gas with the gas Y.

Specifically, by heating the gas, which is cooled to be equal to or less than 0°C , to 15°C to 28°C , a low humidity gas having a relative humidity of about 15 % to 30 % is obtained, and it is desirable to maintain the temperature of the gaseous atmosphere within the reaction tube in the range of 15°C to 28°C and the relative humidity in the range of 40 % to 60% by the use of the low humidity gas as a part of a temperature and humidity controlling gas to be supplied to the reaction tube.

Furthermore, the low humidity gas may be prepared by the method of using a drying agent such as a silica gel used in general air drying as a method of lowering the

relative humidity without raising the temperature of a gas.

[0025]

A direction of supplying the temperature and humidity controlling gas is not particularly limited if the gas can be supplied into the reaction tube. Gas may be
5 provided from a parietal portion (the gas outlet 14 in the example of FIG. 1) of the reactor and may be supplied from a lower portion (the gas inlet 13 in the example of FIG. 1) of the reactor.

It is desirable that the temperature and the relative humidity of the gaseous atmosphere within the reactor be more uniform, and, for this reason, the temperature and
10 humidity controlling gas may be provided from a plurality of places. The flow rate of the temperature and humidity controlling gas is preferably set as small as possible within the range in which the atmosphere temperature and the relative humidity in the reactor can be maintained within the range. When gas is supplied at an excessively large flow rate, the catalyst powder is blown about, whereby the working environment may
15 deteriorate.

[0026]

A method of removing the solid catalyst from the reaction tube is not particularly limited, but known methods can be used. For example, the method includes a method of directly inserting a suction line into the reaction tube to suck up the solid
20 catalyst, a method of installing a suction line in the uppermost portion of the reaction tube and inserting a line blowing air into the reaction tube to sample air by a spout-up type, and a method of removing a plate supporting the catalyst provided in the lower portion of the reaction tube and dropping the catalyst from the bottom portion of the reaction tube to perform the removing. In addition, upon blowing air, it is desirable to
25 consider the temperature, the relative humidity or the supply amount so that the

temperature and the relative humidity of the gaseous atmosphere do not deviate greatly even locally.

[0027]

In the case of performing the removing operation of the solid catalyst in the atmosphere, if the temperature and the relative humidity of the atmosphere are within the range, the removing process of the present invention can be performed, but it is desirable to always supply a temperature and humidity controlling gas during a removing operation in case of a change in the weather or the like.

Furthermore, generally, the removing work period of the catalyst requires several weeks. For example, in view of the average temperature and the average humidity of a day for each month of meteorological observation in Hiroshima announced by the Japan Meteorological Agency, 2009, it is considered that the only period of time, when the temperature of the gaseous atmosphere in the reaction tube can be maintained in the range of 15 °C to 28 °C and the relative humidity thereof can be maintained in the range of 40 % to 60% even if it is not positively controlled, is April or May. However, in view of an abrupt change in weather or the like, even in this period of time, it is desirable to always supply a temperature and humidity controlling gas during the removing operation.

[0028]

According to the removing method of the solid catalyst of the present invention, it is possible to suppress the attachment of the catalyst powder onto the inner surface of the reaction tube by a simple method of suppressing the temperature and the relative humidity of the gaseous atmosphere in the reaction tube to a specific range.

Thus, even if the reaction tube is not washed whenever the catalyst is exchanged, the attachment of the catalyst powder can be suppressed, whereby the frequency of the

washing operation of the reaction tube can be reduced. Furthermore, it is possible to suppress the attachment of the catalyst powder onto the reaction tube inner surface by a simple method even in a fixed-bed multitubular reactor with several thousand reaction tubes provided thereon.

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[Embodiment]

[0029]

Hereinafter, embodiments and comparative examples of the present invention will be further specifically described, but the present invention is not limited by the examples described later.

10

[Synthesis Example 1: Manufacturing of Solid Catalyst B1]

Slurry containing a catalyst raw material was dried to prepare a powder catalyst A1 (compositional formula: $\text{Mo}_{12.0}\text{Bi}_{1.0}\text{Fe}_{1.0}\text{Co}_{3.0}\text{Zn}_{0.5}\text{Sn}_{0.5}\text{O}_x$ (x is an atom ratio of oxygen required for satisfying an atom ratio of each component) having an average particle diameter of 50 μm . 30 kg of the powder catalyst A1 was mixed with 1 kg of methyl cellulose, pure water of 15 kg was added thereto and kneaded and then was subjected to an extrusion molding in a columnar shape having an outer diameter of 5 mm and a height of 5 mm. This operation was repeated 26 times, the extrusion-molded catalyst was subjected to a hot-air drying to evaporate moisture, whereby a solid catalyst B1 of 800 kg usable in a gas-phase contact oxidation reaction of propylene, isobutylene, tert-butanol was obtained.

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[0030]

[Synthesis Example 2: Manufacturing of Solid Catalyst B2]

Slurry containing a catalyst raw material was dried to prepare a powder catalyst A2 (compositional formula: $\text{P}_{1.0}\text{Mo}_{12.0}\text{V}_{0.8}\text{Cu}_{0.1}\text{K}_{0.6}\text{Cs}_{0.5}\text{Bi}_{0.3}\text{Sb}_{0.3}\text{As}_{0.2}\text{O}_z$ (z is an atom

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ratio of oxygen required for satisfying an atom ratio of each component) having an average particle diameter of 25 μm . After 2,700 kg of the powder catalyst A2 was mixed with 84 kg of graphite powder, the mixture was subjected to a tablet compression having an outer diameter 5 mm and a height of 5 mm, whereby a solid catalyst B2 of 2,780 kg usable in a gas-phase contact oxidation reaction of methacrolein was obtained.

[0031]

[Examples 1 to 4, Comparative Examples 1 to 4]

A solid catalyst B1 (900 g) obtained in the Synthesis Example 1 was uniformly mixed with 600 g of Raschig rings manufactured of SUS 304 of a filling density of 0.82 kg/L, and the mixture was filled into the reaction tube 12 of the shell-and-tube type fixed-bed multitubular reactor 10 having the configuration shown in FIG. 1. The reactor 10 included 37 stainless steel tubes (reaction tubes 12) having an inner diameter 27 mm and a length of 6 mm.

Specifically, the solid catalyst B1 was dropped and filled into the reaction tube 12 while supplying a temperature and humidity controlling gas having a temperature of 20 °C and a relative humidity of 50 % from the lower reaction gas inlet 13 of the reactor main body 10a at a flow rate of 18,500 NL per hour. The filling amount of the solid catalyst B1 was 900 g per the reaction tube.

Next, in the state of supplying a heating medium set at 350 °C from the heat medium inlet 15 to the shell side 10d in the reactor main body 10a and heating the reaction tube 12 from the outside, by distributing air into the reaction tube 12, methyl cellulose in the solid catalyst was removed.

Next, the raw material mixture gas including isobutylene of 5 volume %, oxygen of 12 volume %, vapor of 10 volume %, and nitrogen of 73 volume % was supplied from the reaction gas inlet 13 at a flow rate of 92,500 NL per hour. After reacting the raw

material mixture gas by allowing the same to pass through a catalyst layer in the reaction tube 12 for 100 hours, the supplying of the raw material mixture gas was stopped.

Next, the heating medium of the shell side 10d in the reactor main body 10a was sampled, commercially created air for drying instruments was supplied at a flow rate of 18,500 NL per hour from the reaction gas inlet 13, and the catalyst layer was cooled to an ambient temperature.

Next, under the conditions of each example shown in Table 1, a temperature and humidity controlling gas was supplied at a flow rate of 18,500 NL per hour from the reaction gas outlet 14, it was confirmed that the gaseous atmosphere of the reaction gas inlet 13 was under the conditions of each example, and it was confirmed that the temperature and the humidity of the gaseous atmosphere in the reaction tube became identical to those of the supplied temperature and humidity controlling gas. The measurement results are shown in Table 1. Next, the lower cover 10c was removed. Next, the plate supporting the catalyst was removed, and the solid catalyst was dropped and sampled from the reaction tube bottom portion.

[0032]

[Evaluation Method]

A series of operations from the filling of the solid catalyst to the reaction and the removing was repeated three times by the method mentioned above, and an average filling length of the catalyst layers of 37 reaction tubes after each filling was measured.

The average filling length of the catalyst was obtained by measuring a depth of an unfilled space in the reaction tube 12 from a tube plate surface 17 over the reaction tube shown in FIG. 1 before and after the filling one at a time and averaging the difference as the average filling length.

The depth of the unfilled space can be obtained by inserting, for example, a wire

or the like and measuring the length of the wire.

Moreover, an elongation of a second average filling length relative to the average filling length obtained firstly, and an elongation of an average filling length obtained thirdly relative to an average filling length obtained secondly were obtained by a formula as below. Table 1 shows that, the greater the elongation of the average filling length, the more the solid catalyst is attached to the inner surface of the reaction tube after removing the solid catalyst. The results are shown in Table 1.

Elongation of average filling length (%) = {(current average filling length – last average filling length)/last average filling length} X 100

10 [0033]

[Table 1]

	Solid catalyst		Supply gas		Atmosphere gas in tube		Average filling length(mm)	Elongation of average filling length (%)
	Type	Filling number	Temperature (°C)	Relative humidity (%)	Temperature (°C)	Relative humidity (%)		
Embodiment 1	Synthesis example 1	1	20	50	20	50	3530	
	"	2	"	"	"	"	3532	0.06
	"	3	"	"	"	"	3533	0.03
Embodiment 2	"	1	25	58	25	58	3531	
	"	2	"	"	"	"	3533	0.06
	"	3	"	"	"	"	3534	0.03
Embodiment 3	"	1	28	60	28	60	3530	
	"	2	"	"	"	"	3533	0.08
	"	3	"	"	"	"	3534	0.03
Embodiment 4	"	1	15	40	15	40	3535	
	"	2	"	"	"	"	3538	0.08
	"	3	"	"	"	"	3541	0.08
Comparative example 1	"	1	30	50	30	50	3531	
	"	2	"	"	"	"	3541	0.28
	"	3	"	"	"	"	3550	0.25
Comparative example 2	"	1	10	40	10	40	3535	
	"	2	"	"	"	"	3542	0.20
	"	3	"	"	"	"	3555	0.37
Comparative example 3	"	1	25	70	25	70	3533	
	"	2	"	"	"	"	3542	0.25
	"	3	"	"	"	"	3555	0.37
Comparative example 4	"	1	10	30	10	30	3531	
	"	2	"	"	"	"	3540	0.25
	"	3	"	"	"	"	3556	0.45

[0034]

[Results]

As shown in Table 1, the elongation of the average filling length was suppressed to be equal to or less than 0.1 % in embodiments 1 to 4 of removing the solid catalyst
5 while supplying a temperature and humidity controlling gas having a temperature in the range of 15 °C to 28 °C and a relative humidity in the range of 40 % to 60%.

In contrast, in comparative examples 1 and 2 in which the temperature of the gaseous atmosphere in the reaction tube was outside the range of 15 °C to 28 °C, in comparative example 3 in which the relative humidity was higher than 60 %, and in
10 comparative example 4 in which the temperature was lower than 15 °C and the relative humidity was lower than 40 %, the elongation of the average filling length was equal to or greater than 0.2 %.

In addition, in each review of each embodiment and comparative example, the filling was repeated three times so that the catalyst attached to the reaction tube inner
15 surface did not affect the next review, the average filling length was acquired, after removing the catalyst, the reaction tube was washed with water, dry instrument air was supplied at a flow rate of 18,500 NL per hour and was dried, and data was acquired in the state in which attached matter did not exist in the reaction tube.

[0035]

20 [Embodiments 5 to 8, Comparative Examples 5 to 8]

A solid catalyst B2 of 3,000 g obtained in the synthesis example 2 was uniformly mixed with 400g of silica alumina balls having a filling density of 1.3 kg/L, and the mixture was filled into the reaction tube 12 of the shell-and-tube type fixed-bed multitubular reactor 10 by the same method as embodiment 1. Next, the mixture was
25 baked under the air distribution at 380 °C for 10 hours.

Next, in the state of supplying a heating medium set at 300 °C from the heat medium inlet 15 to the shell side 10d in the reactor main body 10a and heating the reaction tube 12 from the outside, the raw material mixture gas including methacrolein of 5 volume %, oxygen of 12 volume %, vapor of 15 volume %, and nitrogen of 68 5 volume % was supplied from the reaction gas inlet 13 at a flow rate of 92,500 NL per hour. After reacting the raw material mixture gas by allowing the same to pass through a catalyst layer in the reaction tube 12 for 100 hours, the supplying of the raw material was stopped.

Next, the catalyst layer was cooled to an ambient temperature by the same 10 method as embodiment 1.

Next, besides the conditions shown in Table 2, the dropping removing of the solid catalyst was performed similarly to embodiment 1, and the measurement and the evaluation were performed in the same manner as embodiment 1. The result is shown in Table 2.

15 [0036]

[Table 2]

	Solid catalyst		Supply gas		Atmosphere gas in tube		Average filling length (mm)	Elongation of average filling length (%)
	Type	Filling number	Temperature (°C)	Relative humidity (%)	Temperature (°C)	Relative humidity (%)		
Embodiment 5	Synthesis example 2	1	20	50	20	50	4935	
	"	2	"	"	"	"	4943	0.16
	"	3	"	"	"	"	4955	0.24
Embodiment 6	"	1	25	58	25	58	4940	
	"	2	"	"	"	"	4951	0.22
	"	3	"	"	"	"	4963	0.24
Embodiment 7	"	1	28	60	28	60	4931	
	"	2	"	"	"	"	4948	0.34
	"	3	"	"	"	"	4963	0.30
Embodiment 8	"	1	15	40	15	40	4942	
	"	2	"	"	"	"	4958	0.32
	"	3	"	"	"	"	4975	0.34
Comparative example 5	"	1	30	50	30	50	4932	
	"	2	"	"	"	"	4981	0.99
	"	3	"	"	"	"	5034	1.06
Comparative example 6	"	1	10	40	10	40	4944	
	"	2	"	"	"	"	4985	0.83
	"	3	"	"	"	"	5025	0.80
Comparative example 7	"	1	18	30	18	30	4942	
	"	2	"	"	"	"	4982	0.81
	"	3	"	"	"	"	5025	0.86
Comparative example 8	"	1	30	70	30	70	4941	
	"	2	"	"	"	"	4991	1.01
	"	3	"	"	"	"	5053	1.24

[0037]

[Result]

As shown in Table 2, the elongation of the average filling length was suppressed to be equal to or less than 0.4 % in embodiments 5 to 8 of removing the solid catalyst while supplying a temperature and humidity controlling gas having a temperature in the range of 15 °C to 28 °C and a relative humidity in the range of 40 % to 60%.

In contrast to this, in comparative examples 5 and 6 in which the temperature of the gaseous atmosphere in the reaction tube was out of the range of 15 °C to 28 °C, in comparative example 7 in which the relative humidity was lower than 40 %, and in comparative example 8 in which the temperature was greater than 28 °C and the relative humidity was greater than 70 %, the elongation of the average filling length was high and equal to or greater than 0.8 %, and the attachment of the catalyst powder was considerably progressed.

In addition, in each review of each embodiment and comparative example, the filling was repeated three times so that the attached catalyst did not affect the next review, the average filling length was acquired, after removing the catalyst, the reaction tube was washed with water, dry instrument air was supplied at a flow rate of 18,500 NL per hour and was dried, and data was acquired in the state in which attached matter did not exist in the reaction tube.

[0038]

[Synthesis Example 3: Manufacturing of Solid Catalyst B3]

The same preparation method, kneading method, and molding method as those of synthesis example 1 were repeated thirty times, the extrusion-molded catalyst was subjected to a hot-air drying to evaporate moisture, whereby a solid catalyst B3 of 900 kg usable in a gas-phase contact oxidation reaction of propylene, isobutylene, tert-butanol

was obtained.

[0039]

[Synthesis Example 4: Manufacturing of Solid Catalyst B4]

After 2,000 kg of the powder catalyst A2 obtained by the same preparation
5 method of synthesis example 2 was mixed with 240 kg of graphite powder, the mixture
was subjected to a tablet compression in a columnar shape having an outer diameter 5
mm and a height of 5 mm, whereby a solid catalyst B4 of 2,240 kg usable in a gas-phase
contact oxidation reaction of methacrolein was obtained.

[0040]

10 [Examples 9 to 10, Comparative Examples 9 to 10]

A solid catalyst B3 (900 kg) obtained in the synthesis example 3 was uniformly
mixed with 600 kg of Raschig rings similarly to embodiment 1 to obtain a mixture D1 of
1,500 kg of the solid catalyst and the Raschig rings. The mixture D1 was filled by the
same method as embodiment 1 until the mixture D1 was filled into the reaction tube 12
15 of the shell-and-tube type fixed-bed multitubular reactor 10 similarly to embodiment 1.
Next, methyl cellulose in the solid catalyst was removed by the same method as
embodiment 1.

Next, in the state in which the heating medium set at 320 °C is supplied from the
heat medium inlet 15 to the shell side 10d in the reactor main body 10a to overheat the
20 reaction tube 12 from the outside, the raw material mixture gas having the same
composition as embodiment 1 was supplied from the reaction gas inlet 13. After
reacting the raw material mixture gas by allowing the same to pass through a catalyst
layer in the reaction tube 12 and analyzing a reaction rate of isobutylene over 100 hours,
the supplying of the raw material mixture gas was stopped.

25 In addition, the reaction rate of isobutylene is defined as below

Reaction rate of isobutylene (%) = (B/A) X 100

Herein, A is a mole number of the supplied isobutylene, and B is a mole number of a reacted isobutylene. The reaction result is shown in Table 3.

Next, the heating medium was sampled in the same manner as embodiment 1,
5 air for drying instruments obtained commercially was supplied under the same conditions as in embodiment 1, and the catalyst layer was cooled to an ambient temperature.

Next, under the conditions of each example shown in Table 3, a temperature and humidity controlling gas was supplied at the same flow rate as embodiment 1, it was confirmed that the gaseous atmosphere of the reaction gas inlet 13 was under the
10 conditions of each example, and D1 was dropped and sampled by the same method as embodiment 1.

[0041]

[Evaluation Method]

A series of operations from the filling of the solid catalyst to the reaction and the
15 removing was repeated three times by the method mentioned above, and the D1 filling weight, the D1 filling reduction amount, and the reaction result of each time were measured.

The D1 filling weight was obtained by subtracting the remaining D1 weight after the filling from the last remaining D1 weight to calculate the D1 weights filled into
20 37 reaction tubes.

D1 filling weight = the last remaining D1 weight - the remaining D1 weight after the filling

Moreover, the first D1 filling weight, the second D1 filling weight, and the third D1 filling weight were calculated.

25 The D1 filling reduction amount was calculated by subtracting the current D1

filling weight from the last D1 filling weight.

[0042]

[Table 3]

	Solid catalyst		Supply gas		Atmosphere gas in tube		D1 filling weight (g)	D1 filling reduction amount (g)	Isobutylene Reaction rate (%)
	Type	Filling number	Temperature (°C)	Relative humidity (%)	Temperature (°C)	Relative humidity (%)			
Embodiment 9	Synthesis example 3	1	15	40	15	40	94255		95.7
	"	2	"	"	"	"	94211	44	95.7
	"	3	"	"	"	"	94183	28	95.7
Embodiment 10	"	1	28	60	28	60	94279		95.8
	"	2	"	"	"	"	94240	39	95.7
	"	3	"	"	"	"	94180	60	95.7
Comparative example 9	"	1	30	50	30	50	94285		95.8
	"	2	"	"	"	"	94030	255	95.5
	"	3	"	"	"	"	93790	240	95.2
Comparative example 10	"	1	10	30	10	30	94276		95.8
	"	2	"	"	"	"	93955	321	95.4
	"	3	"	"	"	"	93608	347	95.0

[0043]

[Result]

As shown in Table 3, the filling reduction amount was suppressed to be equal to or less than 60 g in embodiments 9 and 10 of removing the solid catalyst while supplying
5 a temperature and humidity controlling gas having a temperature in the range of 15 °C to 28 °C and a relative humidity in the range of 40 % to 60%, and a decline in reaction rate was also suppressed to be equal to or less than 0.1 %.

In contrast to this, in comparative examples 9 and 10 in which the temperature and the humidity of the gaseous atmosphere in the reaction tube were outside the range,
10 the filling reduction amount was equal to or greater than 240 g, and the decline in reaction rate was also equal to or greater than 0.3 %.

[0044]

[Examples 11 and 12, Comparative Examples 11 and 12]

A solid catalyst B4 (2,240 kg) obtained in the synthesis example 4 was
15 uniformly mixed with 268 kg of silica alumina ball similarly to embodiment 5 to obtain a mixture D2 of 2,508 kg of solid catalyst and the silica alumina balls. The mixture D1 was filled by the same method as embodiment 1 until the mixture D2 was filled into the reaction tube 12 of the shell-and-tube type fixed-bed multitubular reactor 10 similarly to embodiment 1. Next, the mixture was baked at 380 °C for 10 hours under the air
20 distribution.

Next, in the state in which the heating medium set at 300 °C is supplied from the heat medium inlet 15 to the shell side 10d in the reactor main body 10a to overheat the reaction tube 12 from the outside, the raw material mixture gas having the same composition and amount as those of embodiment 5 was supplied from the reaction gas
25 inlet 13. After reacting the raw material mixture gas by allowing the same to pass

through a catalyst layer in the reaction tube 12 and analyzing a reaction rate of methacrolein over 100 hours, the supplying of the raw material mixture gas was stopped.

In addition, the reaction rate of methacrolein is defined as below.

$$\text{Reaction rate of methacrolein (\%)} = (\text{DIC}) \times 100$$

5 Herein, C is a mole number of the supplied methacrolein, and D is a mole number of the reacted methacrolein. The reaction result is shown in Table 4.

Next, similar to embodiment 1, the heat medium was sampled, the dry instrument air was supplied under the same condition as embodiment 1, and the catalyst layer was cooled to the atmosphere temperature.

10 Next, under the conditions of each example shown in Table 4, a temperature and humidity controlling gas was supplied at the same flow rate as embodiment 1, it was confirmed that the gaseous atmosphere of the reaction gas inlet 13 was under the conditions of each example, and D2 was dropped and sampled by the same method as embodiment 1.

15 [0045]

[Evaluation Method]

A series of operations from the filling of the solid catalyst to the reaction and the removing was repeated three times by the method mentioned above, and the D2 filling weight, the D2 filling reduction amount, and the reaction result of each time were
20 measured.

The D2 filling weight was obtained by subtracting the remaining D2 weight after the filling from the last remaining D2 weight to calculate the D2 weights filled into
37 reaction tubes.

D2 filling weight = the last remaining D2 weight - the remaining D2 weight
25 after the filling

Moreover, the first D2 filling weight, the second D2 filling weight, and the third D2 filling weight were calculated.

The D2 filling reduction amount was calculated by subtracting the current D2 filling weight from the last D2 filling weight.

5

[0046]

[Table 4]

	Solid catalyst		Supply gas		Atmosphere gas in tube		D1 filling weight (g)	D1 filling reduction amount (g)	Methacrolein Reaction rate (%)
	Type	Filling number	Temperature (°C)	Relative humidity (%)	Temperature (°C)	Relative humidity (%)			
Embodiment 11	Synthesis example 4	1	15	40	15	40	152815		85.4
	"	2	"	"	"	"	152512	303	85.2
	"	3	"	"	"	"	152204	308	85.1
Embodiment 12	"	1	28	60	28	60	152801		85.4
	"	2	"	"	"	"	152231	570	85.2
	"	3	"	"	"	"	151794	437	85.0
Comparative example 11	"	1	30	70	30	70	152817		85.4
	"	2	"	"	"	"	151048	1769	84.4
	"	3	"	"	"	"	149195	1853	83.4
Comparative example 12	"	1	18	30	18	30	152825		85.4
	"	2	"	"	"	"	151498	1327	84.7
	"	3	"	"	"	"	150110	1388	83.9

[0047]

[Result]

As shown in Table 4, the filling reduction amount was suppressed to be equal to or less than 600 g in embodiments 11 and 12 of removing the solid catalyst while
5 supplying a temperature and humidity controlling gas having a temperature in the range of 15 °C to 28 °C and a relative humidity in the range of 40 % to 60%, and a decline in reaction rate was also suppressed to be equal to or less than 0.2 %.

In contrast to this, in comparative examples 11 and 12 in which the temperature and the humidity of the gaseous atmosphere in the reaction tube were outside the range,
10 the filling reduction amount was equal to or greater than 1,300 g, and the decline in reaction rate was also equal to or greater than 0.7 %.

In addition, in each review of each embodiment and comparative example, the filling was repeated three times so that the catalyst attached to the reaction tube inner surface did not affect the next review, the average filling length was acquired, after
15 removing the catalyst, the reaction tube was washed with water, dry instrument air was supplied at a flow rate of 18,500 NL per hour and was dried, and data was acquired in the state in which attached matter did not exist in the reaction tube.

INDUSTRIAL APPLICABILITY

20 [0048]

Since the method of removing the solid catalyst of the present invention can suppress the attachment of the catalyst powder onto the reaction tube inner surface even if the washing operation is not performed whenever the solid catalyst is sampled from the reaction tube of the fixed-bed multitubular reactor, the method can be very suitably used
25 as the removing method of the solid catalyst.

BRIEF DESCRIPTION OF THE REFERENCE SYMBOLS

[0049]

10: reactor

5 10a: reactor main body

10b: upper cover

10c: lower cover

10d: shell side in a reactor main body

11: solid catalyst

10 12: reaction tube

13: reaction gas inlet

14: reaction gas outlet

15: heating medium inlet

16: heating medium outlet

15

What is claimed is:

1. A method for removing a solid catalyst after use from a fixed-bed multitubular reactor which includes a reaction tube filled with a solid catalyst, the method comprising:
a removing process of removing the solid catalyst within the reaction tube, in the
5 state of maintaining a temperature of an atmosphere gas in the reaction tube in the range of 15°C to 28°C, and the relative humidity in the range of 40 % to 60 %.

2. A method for removing a solid catalyst after use from a fixed-bed multitubular reactor which includes a reaction tube filled with a solid catalyst, the method comprising:
10 a process of adjusting the temperature of an atmosphere gas within the reaction tube to the range of 15°C to 28°C, and the relative humidity to the range of 40 % to 60 % during a removing operation of the solid catalyst.

3. The method for removing the solid catalyst according to Claim 2,
15 wherein the temperature of the gaseous atmosphere within the reaction tube is adjusted to the range of 15 °C to 28 °C, and the relative humidity is adjusted to the range of 40% to 60%, by supplying a temperature and humidity controlling gas, in which the temperature is adjusted to the range of 15 °C to 28 °C and the relative humidity is adjusted to the range of 40 to 60 %, into the reaction tube in the removing process.

20 4. The method for removing the solid catalyst according to Claims 3,
wherein, as a part of the temperature and humidity controlling gas, a low humidity gas is used which is obtained by heating a gas cooled to be equal to or less than 0 °C to 15 °C to 28 °C.

5. The method for removing the solid catalyst according to any one of Claims 1 to 4,
wherein the solid catalyst is a composite metal oxide catalyst that contains
molybdenum, bismuth, and iron which are used in a gas-phase catalytic reaction of
5 propylene, isobutylene or tert-butanol.
6. The method for removing the solid catalyst according to any one of Claims 1 to 4,
wherein the solid catalyst is a heteropolyacid (salt) catalyst that contains
molybdenum and phosphorous which are used in a gas-phase catalytic reaction of
10 methacrolein.
7. A fixed-bed multitubular reactor comprising:
a plurality of reaction tubes in which a solid catalyst is filled;
a reactor main body that houses the plurality of reaction tubes;
15 an upper cover; and
a lower cover,
wherein the upper cover has a reaction gas outlet through which a reaction
product is discharged, and
the lower cover has a reaction gas inlet through which a raw material gas is
20 supplied, or
the upper cover has a reaction gas inlet through which a raw material gas is
supplied, and
the lower cover has a reaction gas outlet through which a reaction product is
discharged,
25 the reactor main body has a heating medium inlet through which a heating

medium for heating or cooling the plurality of reaction tubes is introduced into a shell side in the reactor main body, and a heating medium outlet through which the heating medium is discharged from the shell side in the reactor main body,

means for supplying a temperature and humidity controlling gas, which supplies

- 5 a gas having a temperature of 15 °C to 28 °C and a relative humidity of 40 % to 60 % into the reaction tube during a removing operation of the solid catalyst after use in the reaction tubes.