

METHOD FOR REACTIVATING CATALYST
FOR PRODUCTION OF METHACRYLIC ACID

FIELD OF THE INVENTION

5 The present invention relates to a method for reactivating a heteropolyacid catalyst which is used when methacrylic acid is produced by subjecting methacrolein to a gaseous phase catalytic oxidation reaction.

10 BACKGROUND OF THE INVENTION

Heretofore, as one of the methods for producing methacrylic acid, a method is known in which methacrolein is subjected to a gaseous phase catalytic oxidation reaction using a heteropolyacid catalyst. In this reaction, the activity
15 of the catalyst usually falls gradually with the passage of reaction time. Therefore, in order to prolong the life of the catalyst, it has been investigated that the catalyst activity is recovered through a reactivation method. For example, in Japanese Patent Application Laid-Open No. (JP-A-)
20 58-156351 discloses a method of heat treating a catalyst comprising a free phosphomolybdic acid or free phosphovanadomolybdic acid and having been used in the above-mentioned reaction to reduce its activity, under a flow of a gas containing at least 10% by volume of water vapor at

a temperature of from 70 °C to 240 °C. Moreover, JP-A-6-7685 discloses a method of heat treating a catalyst comprising phosphorus, molybdenum and vanadium and having been used in the above-mentioned reaction to reduce its activity, under
5 a flow of a gas containing at least 0.1 % by volume of molecular oxygen at a temperature of from 300 °C to 410 °C.

However, these conventional methods can not necessarily exhibit satisfactory effects of recovering the catalyst activity and, in some cases, a reactivated catalyst with a
10 desired activity can not be obtained.

SUMMARY OF THE INVENTION

One of the objects of the present invention is to provide a method of reactivating a catalyst for production of
15 methacrylic acid, the method being superior in activity of reactivated catalysts to the conventional methods.

After a diligent investigation, the present inventors have found that the above object can be achieved by heat treating a catalyst used in the above-mentioned reaction, under a
20 specific conditions of combination of molecular-oxygen and water-vapor concentrations in a flow of gas and a temperature range for the reactivation, thereby the present inventors have accomplished the present invention.

Namely, the present invention provides a method for

reactivating a heteropolyacid catalyst which contains phosphorus, molybdenum and vanadium and which may have been used in a gaseous phase catalytic oxidation reaction of methacrolein to produce methacrylic acid, the method
5 comprising the step of treating the catalyst with heat at a temperature of from 290 °C to 400 °C under a flow of a gas containing at least 3 % by volume of molecular oxygen and at least 3 % by volume of water vapor.

10 DESCRIPTION OF THE INVENTION

A catalyst which is reactivated in the present invention is a heteropolyacid catalyst comprising phosphorus, molybdenum and vanadium. The catalyst may be used in the production of methacrylic acid conducted by a gaseous phase
15 catalytic oxidation reaction of methacrolein. The catalyst may comprise a free heteropolyacid or may comprise a salt of heteropolyacid. With respect to the composition, physical properties and preparation method of a heteropolyacid catalyst for production of methacrylic acid, many reports have been
20 made (see, for example, JP-A-59-12758, JP-A-60-239439, JP-A-5-96172, JP-A-8-10621 and JP-A-11-226411). A catalyst which is reactivated in the present invention can be obtained in accordance with the methods disclosed in the reports, while the methods should not be construed as a limitation upon the

scope of the present invention.

The gaseous phase catalytic oxidation reaction of methacrolein using the heteropolyacid catalyst may be performed by supplying a raw material gas, i.e., methacrolein together with molecular oxygen or water vapor, to a fixed-bed reactor packed with the catalyst. In the industrial production thereof, a multitubular-type reactor may be used as the reactor. The raw material gas may contain a methacrolein in an amount of from 1% by volume to 10 % by volume, molecular oxygen in an amount of from 3 % by volume to 20 % by volume, water vapor in an amount of from 5 % by volume to 30% by volume, an inert gas such as nitrogen and carbon dioxide and the like. Air may be used as a source of molecular oxygen, and steam may be used as a source of water vapor. Regarding reaction conditions, the supply rate of a raw material gas may be from 500 to 5000 h⁻¹ in terms of space velocity (standard state basis; ditto below), i.e., supply rate (L/h) of the raw material gas per 1 L of the catalyst, and the reaction temperature may be from 250 to 350 °C. A reaction product gas containing the obtained methacrylic acid may be subjected to a separation and purification operation after being condensed or being separated from water contained therein. The unreacted methacrolein which is recovered can be recycled as a raw material. The exhaust gas can be recycled as a source of the

above-mentioned inert gas, after, if needed, it is burned.

Methacrolein used as the above-mentioned raw material can be produced suitably by subjecting isobutylene or t-butyl alcohol to a gaseous phase catalytic oxidation reaction using an oxide catalyst containing molybdenum, bismuth and iron. Methacrylic acid can be produced through two-stage gaseous phase catalytic oxidation reactions comprising such a gaseous phase catalytic oxidation reaction of isobutylene or t-butyl alcohol as a first-stage reaction and as the second-stage reaction, the aforementioned gaseous phase catalytic oxidation reaction using the resulting methacrolein as a raw material. The first-stage reaction may be performed by supplying isobutylene or t-butyl alcohol together with molecular oxygen to a fixed bed reactor filled with a catalyst. In industrial production, a multitubular type reactor is used as the reactor. The raw material gas for the first-stage reaction may contain a isobutylene or t-butyl alcohol in an amount of from 2 to 10% by volume, molecular oxygen in an amount of from 3 to 20% by volume, water vapor in an amount of from 0 to 30% by volume, an inert gas such as nitrogen and carbon dioxide and the like. Air can be used as a source of molecular oxygen and steam can be used as a source of water vapor. It is possible to use, as a source of the inert gas, the exhaust gas recovered from the second-stage reaction after, if needed,

being burned. Regarding conditions of the first-stage reaction, the supply rate of a raw material gas may be from 500 to 5000 h⁻¹ in terms of space velocity, and the reaction temperature may be from 300 to 400 °C. The mode in which the methacrolein obtained in the first-stage reaction is subjected to the second-stage reaction is classified roughly into two types; the first is a separation mode in which the first-stage reaction product gas is subjected to a separation operation to obtain a methacrolein with a relatively high purity, which is then subjected to the second-stage reaction, and the second is a directly-combined mode in which the first-stage reaction product gas containing methacrolein is directly subjected to the second-stage reaction without being subjected to a separation operation [see, for example, "Petrochemical process" (edited by The Japan Petroleum Institute, published by Kodansha Scientific, Ltd., 2001), pages 174-175].

When methacrolein is subjected to a gaseous phase catalytic oxidation reaction in the presence of a heteropolyacid catalyst in the manner mentioned above, in usual, a by-product sticks firmly to a catalyst or a catalyst thermally deteriorates with a passage of reaction time and, as a result, the activity of the catalyst falls gradually. In the present invention, the reactivation of a catalyst is performed by heat treating a catalyst used in the above-mentioned reaction under

a flow of a gas containing molecular oxygen and water vapor, respectively, in concentrations not lower than specific values in a specific temperature range.

In the above-mentioned gas for the heat treatment of
5 the catalyst, the concentration of molecular oxygen may be at least 3% by volume, and is preferably 10% by volume or more. When the molecular oxygen concentration is too low, the activity of a reactivated catalyst may be unsatisfactory. The upper limit of the molecular oxygen concentration is not
10 particularly restricted. However, the molecular oxygen concentration may be up to about 20% by volume since it is convenient to use an air as a source of molecular oxygen.

Moreover, in the above-mentioned gas for the heat
treatment of the catalyst, the concentration of water vapor
15 may be at least 3% by volume, and is preferably 8% by volume or more. When the water vapor concentration is too low, the activity of a reactivated catalyst may be unsatisfactory. On the other hand, the activity of a reactivated catalyst tends to increase with increase of the water vapor concentration.
20 However, it also tends to reach almost a level of saturation of the activity when the water vapor concentration exceeds 30% by volume. Therefore, the upper limit of the water vapor concentration may be up to 30% by volume. As a source of water vapor, steam can be used.

The flow rate of the above-mentioned gas may be from 10 to 2000 h⁻¹, and is preferably from 100 to 1000 h⁻¹, in terms of space velocity. The above-mentioned gas for the heat treatment of the catalyst can contain, other than the molecular oxygen and the water vapor, an inert gas such as nitrogen and carbon dioxide. The gas for the reactivation may be free of methacrolein.

The temperature in the above-mentioned heat treatment may be 290 °C or higher, and is preferably 320 °C or higher, whereas the temperature may be 400 °C or lower, and is preferably 370 °C or lower. Not only when the temperature is too low, but also when it is too high, the resulting treated catalyst may have an insufficient activity. The period of time for the above-mentioned heat treatment depends on other conditions, and may be from 0.5 to 20 hours.

The reactivation treatment of a catalyst can be performed in a manner such that the catalyst is taken out of a reactor in which the catalyst has been used, the catalyst is charged into a reactivation container prepared separately and then the catalyst is treated with heat, or alternatively, in a manner such that the catalyst is maintained in the reactor and is treated without being taken out of the reactor. However, it is preferred to perform the reactivation treatment within the reactor as in the latter mode from a viewpoint of operability

of switching between reaction and catalyst reactivation.

A catalyst to be treated in the present invention is preferably, among the aforementioned heteropolyacid catalysts, a catalyst comprising a salt of heteropolyacid, and is more preferably an acidic salt (partially neutralized salt) of heteropolyacid.

The reactivation method in the present invention can suitably be employed as a method for reactivating a catalyst for the second-stage reaction in two-stage gaseous phase catalytic oxidation reactions comprising the aforementioned gaseous phase oxidation reaction of isobutylene or t-butyl alcohol as a first-stage reaction and the gaseous phase oxidation reaction of the resulting methacrolein as a second-stage reaction. As described above, the two-stage gaseous phase oxidation reactions may include a separation mode in which a methacrolein is separated from a first-stage reaction product gas with a relatively high purity and then is subjected to the second-stage reaction, and a directly-combined mode in which the first-stage reaction product gas containing methacrolein is directly subjected to the second-stage reaction without being subjected to a separation operation. The reactivation method in the present invention can be applied to a catalyst for the second-stage reaction in any mode of those described above. Particularly,

the reactivation method in the present invention show great effects on catalyst activity recovery in the latter directly-combined mode, since in the mode almost the whole of the unreacted raw material and by-product contained in the first-stage reaction product gas is introduced into a second-stage reactor, which easily results in reducing the activity of a catalyst for the second-stage reaction.

In the above-mentioned two-stage gaseous phase catalytic oxidation reactions, not only a catalyst for the second-stage reaction but also a catalyst for the first-stage catalyst may lose its catalytic activity gradually with the passage of reaction time. Therefore, particularly in two-stage gaseous phase catalytic oxidation reactions of the directly-combined mode, it is desirable to perform reactivation of a catalyst for the first-stage reaction simultaneously with the reactivation of a catalyst for the second-stage reaction. The reactivation of a catalyst for the first-stage reaction can suitably be performed by treating the catalyst with heat under a flow of a gas containing a molecular oxygen in an amount of at least 3% by volume, preferably of from 10 to 20% by volume, at a temperature of from 360 to 450 °C, preferably at a temperature of from 360 to 400 °C. The gas used for reactivation of a catalyst for the first-stage reaction may contain water vapor, but is not

necessary. In addition to molecular oxygen or water vapor, the gas may contain an inert gas such as nitrogen or carbon dioxide.

The reactivation of a catalyst for the first-stage
5 reaction also can be performed in a manner such that the catalyst is taken out of a reactor in which the catalyst has been used, the catalyst is charged into a reactivation container prepared separately and then the catalyst is treated with heat, or alternatively, in a manner such that the catalyst is maintained
10 in the reactor and is treated without being taken out of the reactor. However, it is preferred to perform the reactivation treatment within the reactor as in the latter mode from a viewpoint of operability of switching between reaction and catalyst reactivation.

15 In two-stage gaseous phase catalytic oxidation reactions of directly-combined mode, it is possible to perform reactivation of a catalyst for the first-stage reaction together with reactivation of a catalyst for the second-stage reaction with a good operability while maintaining the
20 catalysts in reactors because it is easy to flow a gas through the first-stage reactor and the second-stage reactor in series in this order. For example, the reactivation of catalysts for the first-and-second-stage reactions may be conducted by a method in which a gas containing molecular oxygen and water

vapor in predetermined concentrations is allowed to flow through a first-stage reactor and a second-stage reactor in series, while maintaining each of the temperature of catalyst layer in each reactor at a predetermined temperature.

5 Alternatively, the reactivation of catalysts may be conducted by a method in which a gas containing molecular oxygen in a predetermined concentration is allowed to flow through a first-stage reactor and a second-stage reactor in series, while maintaining each of the temperature of catalyst layer in each
10 reactor at a predetermined temperature, and at the same time a gas containing water vapor in a predetermined concentration is added at the entrance of the second-stage reactor. By performing such a catalyst reactivation by introducing a gas containing molecular oxygen into the first-stage reactor and
15 the second-stage reactor in series, it is possible to simultaneously perform removal of a solid matter such as carbonaceous substances that may be solidified in a channel extending from the exit of the first-stage reactor to the entrance of the second-stage reactor.

20 When the two-stage gaseous phase catalytic oxidation reactions of directly-combined mode are performed by supplying isobutylene or t-butyl alcohol to the first-stage reactor together with molecular oxygen and water vapor, it is possible to switch from reaction to catalyst reactivation smoothly by

stopping the supply of isobutylene or t-butyl alcohol after performing the reaction for a certain period of time and then, if needed, adjusting the concentrations of molecular oxygen and water vapor in the gas supplied and adjusting the
5 temperature of a catalyst layer in each reactor.

Two-stage gaseous phase catalytic oxidation reactions of directly-combined mode may be performed by gradually raising the first-stage reaction temperature and the second-stage reaction temperature, specifically the heating medium
10 temperatures of the first-stage reactor and the second-stage reactor, depending on inactivation of the catalyst due to the passage of the reaction time so as to maintain the predetermined conversions in the first-stage reaction and the second-stage reaction, respectively. Therefore, in such a method,
15 switching from reaction to catalyst reactivation treatment can be performed very smoothly by stopping the supply of isobutylene or t-butyl alcohol when the heating medium temperature of the first-stage reactor has become 360°C or higher and that of the second-stage reactor has become 290°C
20 or higher, which may be at a time when both catalysts reach the temperatures required for reactivation treatment. It is preferred to perform the operation of catalyst reactivation regularly at a frequency of from once per half a year to once per year.

In accordance with the present invention, it is possible to sufficiently recover the activity of a heteropolyacid catalyst containing phosphorus, molybdenum and vanadium which has been used in a gaseous phase catalytic oxidation reaction of methacrolein and to obtain a reactivated catalyst having an excellent activity.

The invention being thus described, it will be apparent that the same may be varied in many ways. Such variations are to be regarded as within the spirit and scope of the invention, and all such modifications as would be apparent to one skilled in the art are intended to be within the scope of the following claims.

The entire disclosure of the Japanese Patent Application No. 2002-113081 filed on April 16, 2002, indicating specification, claims and summary, are incorporated herein by reference in their entirety.

EXAMPLES

The present invention is described in more detail by reference to the following Examples, which should not be construed as a limitation upon the scope of the present invention.

Referential Example 1

(a) Preparation of catalyst

In 224 kg of ion exchange water heated to 40°C, 38.2 kg of cesium nitrate $[\text{CsNO}_3]$, 10.2 kg of copper nitrate trihydrate $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$, 24.2 kg of 85% by weight of orthophosphoric acid and 25.2 kg of 70% by weight of nitric acid were dissolved to obtain the resulting solution (liquid A). On the other hand, after 297 kg of ammonium molybdate tetrahydrate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ was dissolved in 330 kg of ion exchange water heated to 40 °C, 8.19 kg of ammonium metavanadate $[\text{NH}_4\text{VO}_3]$ was suspended therein to obtain the resulting suspension (liquid B). Liquid A was dropped into liquid B under stirring, 10.2 kg of antimony trioxide $[\text{Sb}_2\text{O}_3]$ was added thereto, and subsequently was stirred at 120 °C for 17 hours in a sealed container to obtain a slurry. The slurry was dried using a spray dryer, to obtain a catalyst precursor powder. To 100 parts by weight of the powder, 4 parts by weight of a ceramic fiber [FIBERFRAX RFC400SL, manufactured by Toshiba Monofrax Co., Ltd.], 8 parts by weight of ammonium nitrate and 10 parts by weight of ion exchange water were added, were kneaded, and then were subjected to extrusion molding to have a cylindrical form with 5 mm in diameter and 5 mm in height. After dried at a temperature of 90 °C at a humidity of 35 %RH for 3 hours, the molded article was calcined in an air flow at 220 °C for 22 hours, in an air flow at 250 °C for 1 hour, in a nitrogen flow at 435 °C for 3 hours, and subsequently

in an air flow at 390 °C for 3 hours, in this order, to obtain a catalyst. The catalyst comprised an acidic salt of heteropolyacid containing phosphorus, molybdenum, vanadium, antimony, copper and cesium in atomic ratios of 1.5, 12, 0.5, 0.5, 0.3 and 1.4, respectively.

(b) Activity test of catalyst prepared

A glass microreactor with an inner diameter of 15mm was filled with 9 g of the above-obtained catalyst. A raw material gas comprising 4% by volume of methacrolein, 12% by volume of molecular oxygen and 17% by volume of water vapor, which had been prepared by mixing methacrolein, air, steam and nitrogen, was supplied into the glass microreactor at a space velocity of 670 h⁻¹, and an activity test was performed at an oven temperature (which is a temperature of a furnace for heating the microreactor; ditto below) of 280 °C. At the time when one hour lapsed since the reaction had started, the conversion of methacrolein was 96%, and the selectivity to methacrylic acid was 78%.

20 Referential Example 2

(a) Reaction using catalyst

A steel reaction tube with an inner diameter of 25 mm was filled with 1300 ml of a molded catalyst comprising an oxide containing molybdenum, bismuth, iron, cobalt and cesium

in atomic ratios of 12, 1, 2.5, 7.5 and 0.6, respectively, which was used as a first-stage reactor. A steel reaction tube with an inner diameter of 30 mm was filled with 1800 ml of the catalyst which had been prepared in the same manner as in Referential Example 1 (a), which was used as a second-stage reactor. A raw material gas comprising 5% by volume of isobutylene, 12% by volume of molecular oxygen and 7.5% by volume of water vapor which had been prepared by mixing isobutylene, air, steam and nitrogen was supplied to the first-stage reactor at a space velocity of 1200 h^{-1} to obtain the resulting first-stage reaction product gas, which was then mixed with air and nitrogen to be a gas comprising 3.2% by volume of methacrolein, 8.5% by volume of molecular oxygen and 11% by volume of water vapor, the resulting gas then being supplied to the second-stage reactor at a space velocity of 1000 h^{-1} , to conduct two-stage gaseous phase catalytic oxidation reactions. During this operation, the heating medium temperature of the first-stage reactor and that of the second-stage reactor, respectively, were controlled so that the conversion of isobutylene in the first-stage reaction became about 99% and the conversion of methacrolein in the second-stage reaction became 72% or more. Thus, the heating medium temperature of the second-stage reactor at the start of the reaction was set to 275°C , and that at the time when

3000 hours lapsed since the reaction had started was set to 293 °C. The reaction was stopped at this time, and the catalyst was taken out of the second-stage reactor. The catalyst which had been placed at the portion of about 1/3 inside from the entrance of the reactor was sampled. This sample was utilized as a used catalyst in the following Examples.

(b) Activity test of used catalyst

An activity test of the used catalyst obtained above was performed in the same manner as in Referential Example 1(b). The methacrolein conversion was 21%. The used catalyst had a total carbon amount of 0.6% by weight, whereas the catalyst prepared in Referential Example 1 (a) had a total carbon amount of 0.0%.

Example 1

After the activity test of the used catalyst was performed in Referential Example 2 (b), the used catalyst was treated with heat at an oven temperature of 350 °C for 15 hours, while supplying a gas containing 12% by volume of molecular oxygen and 18% by volume of water vapor, which had been prepared by mixing air, steam and nitrogen, at a space velocity of 500 h⁻¹ to the microreactor in which the used catalyst was left filled. Subsequently, the catalyst after the heat treatment was subjected to an activity test in the same manner as in

Referential Example 1 (b). The conversion of methacrolein was 91%. The catalyst after the heat treatment had a total carbon amount of 0.0%.

5 Examples 2 to 14 and Comparative Examples 1 to 4

The used catalyst prepared in Referential Example 2 (a) was filled into a glass microreactor with an inner diameter of 15 mm, into which a gas containing molecular oxygen and water vapor with the concentrations shown in Table 1, which
 10 had been prepared by mixing air, steam and nitrogen, was then supplied at a space velocity of 500 h^{-1} , and then heat treatment was performed at an oven temperature shown in Table 1 for a period of time shown in Table 1. Subsequently, an activity test of the catalyst after the heat treatment was performed
 15 in the same manner as in Referential Example 1 (b). The result (conversion of methacrolein) is shown in Table 1.

Table 1

	Molecular Oxygen (%) by volume)	Water Vapor (% by volume)	Oven Temperature (°C)	Time (h)	Conversion (%)
Example 2	12	9	290	15	45
Example 3	12	9	310	15	58
Example 4	12	9	330	15	73
Example 5	12	9	350	15	87
Example 6	12	9	370	15	93
Example 7	12	9	390	15	86
Comparative Example 1	12	9	410	15	31
Comparative Example 2	21	0	330	15	43
Comparative Example 3	20	2.5	330	15	64
Example 8	19	9	330	15	73

Example 9	17	18	330	15	80
Example 10	15	30	330	15	82
Example 11	10	50	330	15	82
Comparative Example 4	0	18	330	15	46
Example 12	12	18	350	2	90
Example 13	12	18	350	15	91
Example 14	12	18	350	60	89

Example 15

Two-stage gaseous phase catalytic oxidation reactions were performed again in the same manner as in Referential Example 2 (a). At the time when 72 hours lapsed since the reaction had started, the heating medium temperature of the first-stage reactor and that of the second-stage reactor were set to 348°C and 275 °C, respectively, and at the time when 6000 hours lapsed since the reaction had started, the heating medium temperature of the first-stage reactor and that of the second-stage reactor were set to 362 °C and 294 °C, respectively. At this time, the conversion of isobutylene in the first-stage reaction was 99.0%, and the conversion of methacrolein in the second-stage reaction was 73.2%.

The reaction was stopped temporarily at this stage, and reactivations of the catalyst for the first-stage reaction and of the catalyst for the second-stage reaction were performed. Specifically, a gas containing 14% by volume of molecular oxygen and 18% by volume of water vapor prepared by mixing air, steam and nitrogen was flown through the

first-stage reactor and the second-stage reactor in series so that the space velocity thereof became 690 h^{-1} in the first-stage reactor and 500 h^{-1} in the second-stage reactor. Subsequently, the heating medium temperatures of the first-stage reactor and of the second-stage reactor were raised slowly to 370°C and 350°C , respectively, and were maintained for 10 hours.

Then, the heating medium temperatures of the first-stage reactor and of the second-stage reactor were set to 350°C and 288°C , respectively, and the two-stage gaseous phase catalytic oxidation reactions were resumed under the same conditions as those of Referential Example 2. At the time when 2200 hours had lapsed since the resumption of the reaction, the heating medium temperatures of the first-stage reactor and of the second-stage reactor were set to 354°C and 289°C , respectively. At this stage, the isobutylene conversion in the first-stage reaction was 99.2 % and the methacrolein conversion in the second-stage reaction was 80.3 %.

Example 16

After performing the two-stage gaseous phase catalytic oxidation reactions in Referential Example 2 (a), the catalyst in the first-stage reactor was left as it was, and the catalyst in the second-stage reactor was changed to a fresh catalyst prepared in Referential Example 1 (a). Then, the two-stage

gaseous phase catalytic oxidation reactions were performed again under the same conditions as those of Referential Example 2. At the time when 4000 hours had lapsed since the resumption of the reaction, the heating medium temperature of the first-stage reactor and of the second-stage reactor were set to 363 °C and 292 °C, respectively. At this stage, the isobutylene conversion in the first-stage reaction was 98.9 % and the methacrolein conversion in the second-stage reaction was 72.6 %.

10. At this stage, only the supply of isobutylene was stopped, and the heating medium temperatures of the first-stage reactor and of the second-stage reactor were maintained at 363 °C and 292 °C, respectively, for 2 hours.

After that, the supply of isobutylene was resumed so that the reaction was started. At the time when 20 hours had lapsed since the resumption of the reaction, the isobutylene conversion of the first-stage reaction was 99.7 % and the methacrolein conversion of the second-stage reaction was 85.8 %.

What is claimed is:

1. A method for reactivating a heteropolyacid catalyst which contains phosphorus, molybdenum and vanadium and which has been used in a gaseous phase catalytic oxidation reaction of methacrolein to produce methacrylic acid, the method comprising the step of treating the catalyst with heat at a temperature of from 290 °C to 400 °C under a flow of a gas containing at least 3 % by volume of molecular oxygen and at least 3% by volume of water vapor.
2. A reactivation method according to claim 1, wherein the catalyst to be treated with heat is a catalyst which has been used in a second-stage gaseous phase catalytic oxidation reaction in two-stage reactions comprising a first-stage gaseous phase catalytic oxidation reaction of at least one compound selected from isobutylene and t-butyl alcohol in the presence of an oxide catalyst containing molybdenum, bismuth and iron to obtain a reaction product gas containing methacrolein and said second-stage gaseous phase catalytic oxidation reaction of the first-stage reaction product gas in the presence of a heteropolyacid catalyst containing phosphorus, molybdenum and vanadium.
3. The reactivation method according to claim 1 or 2, the method further comprising the step of treating the catalyst which has been used in the first-stage reaction with

heat at a temperature of from 360 °C to 450 °C under a flow of a gas containing at least 3 % by volume of molecular oxygen.