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## CATALYST USEFULL FOR PRODUCING METHACRYLIC ACID

### BACKGROUND OF THE INVENTION

### FIELD OF THE INVENTION

5       The present invention relates to a catalyst which can be employed for producing methacrylic acid from methacrolein, isobutyl aldehyde, isobutene, isobutyric acid or the like in a gas-phase catalytic oxidation.

### 10       DESCRIPTION OF THE RELATED ART

A catalyst consisting of a heteropolyacid or a salt thereof is known to be useful as a catalyst which is employed for producing methacrylic acid by a gas phase catalytic oxidation of methacrolein or the like, and has  
15       widely been reported with regard to its composition, structure, physical properties and the like as well as production methods thereof. For example, Japanese Patent Publication (JP-B) No. H6(1994)-79666 discloses a catalyst with a pore distribution in which 10 % or more  
20       of pores have a pore diameter of from 1  $\mu\text{m}$  to 10  $\mu\text{m}$  and 10 % or more of pores have a pore diameter of from 0.1  $\mu\text{m}$  to 1  $\mu\text{m}$  based on the total volume of the entire pores. Also, JP-B-H3(1991)-26101 discloses a method for

producing a catalyst which includes the steps of suspending or dissolving starting materials for the catalyst in water and adding an ammonium source and a nitrate source so that the ammonium source and the nitrate source are contained in amounts of from 7 moles to 15 moles and of from 0.1 moles to 4.0 moles, respectively, based on 12 molybdenum atoms immediately after mixing of the entire constituents. Moreover, JP-B-H2(1990)-15255 discloses a method in which a catalyst involving ammonia or ammonium group is heated at a rate of from 10 °C/hour to 100 °C/hour up to a calcination temperature of from 300 °C to 500 °C during a process of the preparation for the catalyst.

However, any of these conventional catalysts is not satisfactory in terms of the reaction efficiency when utilized in a production of methacrylic acid, especially with regard to selectivity to methacrylic acid.

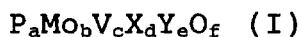
#### SUMMARY OF THE INVENTION

One of objectives of the present invention is to provide a catalyst capable of producing methacrylic acid at a higher selectivity.

The inventors of the present invention have researched

in a solid phase transfer reaction from a Dawson-type heteropolyacid salt into a Keggin-type heteropolyacid salt using a heating diffusion-reflection infrared absorption spectroscopy. As a result, the present  
5 inventors have found that a Keggin-type hetero-polyacid salt having a lots of micropores and high crystallinity may be excellent as a catalyst for the methacrylic acid production, and such a Keggin-type hetero-polyacid salt may be obtained by a method in which the transfer reaction  
10 is conducted in the presence of ammonium nitrate, preferably in a larger amount of the ammonium nitrate in order to faster the transfer reaction. Based on the findings, the present invention has been accomplished.

The present invention provides a catalyst comprising  
15 a Keggin-type heteropolyacid salt which is represented by Formula (I):



wherein P, Mo, V and O represent phosphorus, molybdenum, vanadium and oxygen, respectively; X represents at least  
20 one element selected from potassium, rubidium, cesium and thallium; Y represents at least one element selected from copper, arsenic, antimony, boron, silver, bismuth, iron, cobalt, lanthanum and cerium; a, b, c, d, e and

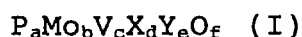
f represent the atomic ratios of P, Mo, V, X, Y and O, respectively; and when b equals to 12, then a, c, d and e represent, independently from one another, numerical values exceeding 0 and not more than 3; and f is defined  
 5 based on the oxidation condition of the elements other than oxygen and also on the atomic ratios thereof;

the catalyst having a pore distribution, obtained by a mercury porosimetry method, in which a total pore volume of pores having a radius of 0.05  $\mu\text{m}$  or less is about 0.01  
 10  $\text{cm}^3/\text{g}$  or less and a total volume of pores having a radius exceeding 0.05  $\mu\text{m}$  is about 0.2  $\text{cm}^3/\text{g}$  or more.

The present invention also provides a method for producing the above-described catalyst as well as a method for producing methacrylic acid using the catalyst.

#### 15 DESCRIPTION OF THE INVENTION

A catalyst in the present invention may comprise a Keggin-type heteropolyacid salt which is represented by Formula (I):



wherein P, Mo, V and O represent phosphorus, molybdenum, vanadium and oxygen, respectively; X represents at least one element selected from potassium, rubidium, cesium

and thallium; Y represents at least one element selected from copper, arsenic, antimony, boron, silver, bismuth, iron, cobalt, lanthanum and cerium; a, b, c, d, e and f represent the atomic ratios of P, Mo, V, X, Y and O, respectively; when b equals to 12, then a, c, d and e represent, independently from one another, numerical values exceeding 0 and not more than 3; and f is defined based on the oxidation condition of the elements other than oxygen and also on the atomic ratios thereof.

Among such Keggin-type heteropolyacid salts, one in which cesium is essential as an X element or copper is essential as a Y element is preferred, respectively. The Keggin-type heteropolyacid salt in which both copper and arsenic or both copper and antimony are essential, respectively, is more preferred.

The catalyst in the present invention has a pore distribution, obtained by a mercury porosimetry method, in which a total pore volume of pores having a radius of 0.05  $\mu\text{m}$  or less is about 0.01  $\text{cm}^3/\text{g}$  or less; and also having a total volume of pores having a radius exceeding 0.05  $\mu\text{m}$  (or having a radius exceeding 0.05  $\mu\text{m}$  and less than 200  $\mu\text{m}$ ) is about 0.2  $\text{cm}^3/\text{g}$  or more. When a catalyst having a pore distribution in which the total pore volume

of pores having a radius of 0.05  $\mu\text{m}$  or less is more than about 0.01  $\text{cm}^3/\text{g}$  is used in production of methacrylic acid, selectivity to methacrylic acid may be insufficient. Also, when a catalyst having a pore distribution in which the total volume of pores having a radius exceeding 0.05  $\mu\text{m}$  is about less than 0.2  $\text{cm}^3/\text{g}$  is used in production of methacrylic acid, conversion of a starting material such as methacrolein may be insufficient. The total volume of pores having a radius exceeding 0.05  $\mu\text{m}$  may be about 0.4  $\text{m}^3/\text{g}$  or less.

The catalyst in the present invention may be used as a molded article thereof which may be in a columnar or cylindrical shape having a diameter of from about 3 mm to about 10 mm and a length of from about 3 mm to about 10 mm or in a sphere shape having a diameter of from about 3 mm to about 10 mm. The catalyst preferably has a falling strength of 97 % or higher, the strength being measured below. Measurement of falling strength:

Onto a JIS standard sieve which has a mesh size of 2.36 mm, a pipe having a inner diameter of 30 mm and a length of 5000 mm is placed as standing vertically. About 30 g of a catalyst to be measured is allowed to fall down from the top of the pipe and then the amount of the catalyst

remaining on the sieve is measured. The rate (% by weight) of the remaining amount of the catalyst to the amount of the catalyst allowed to fall down is regarded to be a falling strength of the catalyst.

5       The falling strength in the above-described range may contribute to suppress pulverization or disintegration of the catalyst during shipping or packing into a reaction container.

10       The catalyst described above may be produced by a method in which a molded article of a Dawson-type heteropolyacid containing ammonium nitrate is prepared and is calcined while controlling the ammonium nitrate content in the molded article and/or the calcination condition so that a transfer reaction from the Dawson-type heteropolyacid  
15       salt to a Keggin-type heteropolyacid salt occurs in the presence of ammonium nitrate. The amount of ammonium nitrate contained in the molded article is preferably about 10 % by weight or more, and is more preferably about  
20       15 % by weight or more. In view of the strength of the resulting catalyst, the amount of ammonium nitrate contained in the molded article is preferably about 40 % by weight or less.

      The molded article of the Dawson-type heteropolyacid

described above may be prepared by mixing starting materials with each other in water, drying the resulting aqueous slurry to obtain a dried solid and then molding the dried solid. The starting materials may be compounds  
5 containing respective elements in the resulting catalyst to be aimed. The starting materials may be oxoacids, oxoacid salts, oxides, nitrates, carbonates, hydroxides and halides of respective elements, which are employed in a ratio which giving a desired atomic ratio in the  
10 catalyst. Examples of the starting materials include a phosphorus-containing compound such as phosphoric acid and a phosphate, a molybdenum-containing compound such as molybdic acid, a molybdate, molybdenum oxide and molybdenum chloride, and a vanadium-containing compound  
15 such as vanadic acid, a vanadate, vanadium oxide and vanadium chloride. An X element-containing compound may be an oxide, nitrate, carbonate, hydroxide, halide or the like. A Y element-containing compound may be an oxoacid, oxoacid salt, nitrate, carbonate, hydroxide,  
20 halide or the like. Any of the compounds described above may be employed in such amounts that the respective elements in Formula (I) other than oxygen fulfill the respective ratios shown by a, b, c, d and e in Formula

(I).

In order to allow the molded article to have the ammonium nitrate content within the preferable range, i.e., the content of from about 10 % by weight to about 40 % by weight, an ammonium nitrate and/or a ammonium nitrate-generating compound (such as nitric acid, ammonia, nitrate compounds and ammonium salt compounds) may be added, if necessary, to an aqueous slurry of the starting materials as being prepared and/or to a dried solid thereof upon molding, provided that the amount of ammonium nitrate (which may be attributable to an ammonium source or nitrate source in the starting materials) is taken into account.

In the preparation of the molded article of the Dawson-type heteropolyacid described above, an aqueous slurry of the starting materials is adjusted preferably at a pH of from about 2 to about 8 and is prepared preferably without using organic materials. After drying, the resulting dried solid (obtained from the aqueous slurry) may be molded preferably after adding an inorganic fiber (in an amount of from about 1 part by weight to about 10 parts by weight) and water (in an amount of from about 5 parts by weight to about 30 parts by weight) and, if necessary, ammonium nitrate (in an amount of from about

5 parts by weight to about 40 parts by weight), all based on 100 parts by weight of the dried solid. Upon molding, the presence of a large amount of ammonium nitrate allows the molding process to be conducted smoothly even in the absence of an alcohol- or cellulose-based organic binder (lubricant) as a molding aid. Such an absence of the organic binder also serves to prevent the reaction between ammonium nitrate and the organic binder upon calcining. In a method for producing the catalyst in the present invention, an inorganic fiber such as a ceramic fiber or glass fiber may be employed as a reinforcing agent, whereby obtaining a catalyst having a sufficient strength without using an expensive whisker or carbon fiber.

The temperature at which the molded article described above is calcined may finally be elevated to a temperature in the range of from about 350 °C to about 500 °C. If the temperature is gradually elevated while supplying a relatively large amount of a gas such as air and an inert gas, the transfer reaction from a Dawson-type heteropolyacid salt to a Keggin-type heteropolyacid salt can not be effected in the presence of ammonium nitrate, which is undesirable. This is because, in such a gradual elevation of temperature, ammonium nitrate tends to be

eliminated from the calcining system as gases of ammonia and nitric acid (which results from the dissociation equilibrium of the ammonium nitrate) before the temperature reaches a temperature at which the transfer  
5 reaction occurs (i.e., a temperature in a the range of from about 180°C to about 240°C). It is preferred that the temperature is elevated as rapidly as about 15°C/hour at least up to about 180°C. During the calcination, the gas (for example, air, an inert gas such as nitrogen or  
10 the like) may be supplied in a volume which is 500 times or less per hour, preferably 200 times or less per hour, as much as the volume of the molded article. When the temperature is in the range of from about 180°C to about 240°C, it is preferred that the volume of the gas to be  
15 supplied is controlled so as to be about 500 times or less per hour, more preferably 200 times or less per hour, as much as the volume of the molded article and that the gas is circulated in the calcining system, while adjusting the circulating gas volume at a volume which is about  
20 1000 times or more per hour, preferably about 2000 times or more per hour, as much as the volume of the molded article. In such, an operation for supplying the gas, the heat (which may be generated as a result of the

decomposition of ammonium nitrate) tends to be released rapidly, which is desirable in view of safety.

After completing the transfer reaction as described above, the ammonium nitrate may be removed by, for example, increasing the amount of the gas supply. The obtained molded article may be further calcined at a temperature higher than the above-described temperature, whereby obtaining a catalyst comprising a Keggin-type heteropolyacid salt in the present invention. The calcination may be conducted in air at a temperature of from about 350°C to about 400°C, or may be conducted in an inert gas such as nitrogen at a temperature of from about 400 °C to about 500°C. After the calcination in an inert gas, a further calcining is preferably conducted in air at a temperature of from about 400°C or lower, since the catalyst obtained after the calcination in an inert gas may be in a hyper-reduced state. As a result of the calcination described above, oxygen (O) as a chemical constituent of a catalyst becomes present in the catalyst in an amount which is defined based on the oxidation condition of the elements in the catalyst other than oxygen and also on the atomic ratios of the elements.

Using a catalyst comprising a Keggin-type

heteropolyacid salt in the present invention, methacrylic acid can be produced at a high selectivity in a gas phase catalytic oxidation of a raw material such as methacrolein, isobutyl aldehyde, isobutane or isobutyric acid in the presence of a molecular oxygen. The production of methacrylic acid may be carried out by packing the catalyst in the present invention in an immobilized bed multiple tube reactor and supplying a starting-material gas containing a raw material and an oxygen into the reactor.

For example, when methacrolein is utilized as a raw material, the reaction may be conducted at a methacrolein concentration in the starting-material gas of about 1 % by volume to about 10 % by volume in the presence of oxygen in a molar amount of about 1 by mole to about 5 mole based on the methacrolein under the pressure of from about 0.1 MPa to about 0.3 MPa at a space velocity of from about 500 h<sup>-1</sup> to about 5000 h<sup>-1</sup> at a reaction temperature of from about 250 °C to about 350°C. When isobutane is utilized as a raw material, the reaction may be conducted at an isobutane concentration in the starting-material gas of about 15 % by volume to about 70 % by volume in the presence of oxygen in an amount of about 5 % by volume to about 50 % by volume under a pressure of from 0.1 MPa

to about 1 MPa at a space velocity of from about 500 h<sup>-1</sup>  
to about 5000 h<sup>-1</sup> at a reaction temperature of from about  
250°C to about 350°C.

According to the present invention, a catalyst having  
5 an excellent strength and being capable of producing  
methacrylic acid at a high selectivity is provided.

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,  
10 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. 2001-196171 filed on June 28, 2001, indicating  
15 specification, claims and summary, is incorporated herein  
by reference in their entirety.

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

20

#### EXAMPLES

The present invention is further described in the following  
examples which are not intended to restrict the present

invention. The definition of a falling strength is as described above.

#### Example 1

5 Into 4800 g of an ion exchange water, were added 450 g of 85 % by weight ortho-phosphoric acid, 130 g of copper (II) phosphate trihydrate, 819 g of cesium nitrate and 284 g of a 60 % by weight aqueous solution of arsenic acid, which were then dissolved with stirring at 40°C to obtain an aqueous solution (Solution A). On the other hand, 6990 g of an ion  
10 exchange water was charged in a 20L stainless steel vessel equipped with a jacket and a stirrer having a max blend fin, which was kept at 40°C. Into the vessel, was added 6356 g of ammonium molybdate tetrahydrate, which was then dissolved with stirring to obtain an aqueous solution (Solution B).  
15 Into Solution B, was added the entire amount of Solution A over a period of 2 minutes with stirring at 120 rpm, to precipitate solids so as to obtain a slurry thereof. After that, 137 g of vanadium pentaoxide was added into the slurry. A steam was passed through the jacket of the vessel with  
20 stirring at 120°C for 8 hours. The pH of the resulting slurry was 7.

The slurry was transferred into a vat, which was then placed in a drier at 120°C to allow water in the slurry to be evaporated

off, whereby obtaining a dried solid. The dried solid was analyzed by an X-ray diffraction and an infrared absorption spectroscopy, and was identified as a Dawson-type heteropolyacid salt. The ammonium nitrate content in the  
5 dried solid was 4.5 % by weight.

Into 100 parts by weight of the dried solid, was added 4 parts by weight of a silica-alumina-based ceramic fiber (manufactured by TOSHIBA MONOFLUX; 400SL), 8 parts by weight of ammonium nitrate and 14.7 parts by weight of an ion exchange  
10 water, to obtain a mixture thereof. The mixture was kneaded to obtain a paste thereof. The paste was extruded using a mold to obtain a molded article having a diameter of 5 mm and a length of 6 mm, which was then dried. The ammonium nitrate content in the resulting molded article was 11 %  
15 by weight. The extrusion was conducted smoothly. The 15 parts by weight of the paste remained inside the extruder based on 100 parts by weight of the paste which had been supplied into the extruder.

The molded article ( $100\text{ cm}^3$ ) was packed in a cylinder,  
20 through which air was passed at 8 L/h while heating to  $250^\circ\text{C}$ . In this calcination step, the temperature was raised at  $80^\circ\text{C/h}$  up to  $200^\circ\text{C}$ , and was then raised stepwise from  $200^\circ\text{C}$  to  $250^\circ\text{C}$  over 10 hours. Subsequently, the article was calcined in

a nitrogen flow at 435°C for 3 hours, and was then further calcined in an air flow at 390°C for 3 hours, whereby obtaining a catalyst. The composition of the obtained catalyst was represented by  $P_{1.5}Mo_{12}V_{0.5}Cs_{1.4}Cu_{0.3}As_{0.4}$  with oxygen (O) being present in the amount corresponding thereto. The catalyst was analyzed in a pore distribution by a mercury porosimetry. As a result, the catalyst had a total pore volume of entire pores of 0.25 cm<sup>3</sup>/g, in which a total volume of pores having a radius of 0.05 μm or less was 0.01 cm<sup>3</sup>/g or less. The falling strength was 98.8 %.

The above-obtained catalyst (9 ml) was packed in a glass tube reactor having a inner diameter of 15 mm. Into the tube reactor, a starting-material gas having a composition of 4 % by volume of methacrolein, 12 % by volume of oxygen, 16 % by volume of water vapor and nitrogen as the balance was passed at the space velocity (in terms of normal state) of 670 hr<sup>-1</sup>, and the temperature therein was raised to 290°C, so as to conduct the oxidation of the methacrolein. As a result, the conversion of methacrolein was 87.1 % and the selectivity to methacrylic acid was 84.7 %. In varying the oxidation temperature from 270°C to 310°C, the relationship between the conversion of methacrolein and the selectivity to methacrylic acid was further investigated. As a result,

when the conversion of methacrolein was 80%, the selectivity to methacrylic acid was 85.3 %.

#### Comparative Example 1

5 Into 100 parts by weight of the dried solid prepared in the same manner as in Example 1, was added 4 parts by weight of a ceramic fiber (manufactured by TOSHIBA MONOFLUX; 400SL) and 21.5 parts by weight of an ion exchange water, to obtain a mixture thereof. The mixture was kneaded to obtain a paste thereof. The paste was extruded using a mold to obtain a  
10 molded article having a diameter of 5 mm and a length of 6 mm, which was then dried. The ammonium nitrate content of the resulting molded article was 4.2 % by weight. The extrusion was not conducted smoothly. 20 Parts by weight of the paste remained inside the extruder based on 100 parts  
15 by weight of the paste which had been supplied into the extruder. The molded article was calcined in the same manner as in Example 1 except for raising the temperature to 250°C while passing air at 80 l/h, whereby obtaining a catalyst. The catalyst was analyzed in a pore distribution by a mercury  
20 porosimetry. As a result, the catalyst had a total pore volume of entire pores of 0.24 cm<sup>3</sup>/g, in which a total volume of pores having a radius of 0.05 μm or less was 0.02 cm<sup>3</sup>/g. The falling strength was 98.2 %.

Using the catalyst, methacrolein was oxidized at 290°C in the same manner as in Example 1. As a result, the conversion of methacrolein was 92.9 % and the selectivity to methacrylic acid was 78.7 %. In varying the oxidation temperature from 270°C to 310°C, the relationship between the conversion of methacrolein and the selectivity to methacrylic acid was further investigated. As a result, when the conversion of methacrolein was 80%, the selectivity to methacrylic acid was 81.2 %.

#### Example 2

Into 100 parts by weight of the dried solid prepared in the same manner as in Example 1, was added 4 parts by weight of a ceramic fiber (manufactured by TOSHIBA MONOFLUX; 400SL), 18 parts by weight of ammonium nitrate and 10 parts by weight of an ion exchange water, to obtain a mixture thereof. The mixture was kneaded to obtain a paste thereof. The paste was extruded using a mold to obtain a molded article having a diameter of 5 mm and a length of 6 mm, which was then dried. The ammonium nitrate content of the resulting molded article was 18 % by weight. The extrusion was conducted smoothly. The 9 parts by weight of the paste remained inside the extruder based on 100 parts by weight of the paste which had been supplied into the extruder. The molded article was calcined

in the same manner as in Example 1, whereby obtaining a catalyst. The catalyst was analyzed in a pore distribution by a mercury porosimetry. As a result, the catalyst had a total pore volume of entire pores of  $0.31 \text{ cm}^3/\text{g}$ , in which a total volume of pores having a radius of  $0.05 \text{ }\mu\text{m}$  or less was  $0.01 \text{ cm}^3/\text{g}$  or less. The falling strength was 98.3 %.

Using the catalyst, methacrolein was oxidized at  $290^\circ\text{C}$  in the same manner as in Example 1. As a result, the conversion of methacrolein was 81.5 % and the selectivity to methacrylic acid was 85.6 %. In varying the oxidation temperature from  $270^\circ\text{C}$  to  $310^\circ\text{C}$ , the relationship between the conversion of methacrolein and the selectivity to methacrylic acid was further investigated. As a result, when the conversion of methacrolein was 80%, the selectivity to methacrylic acid was 86 %.

### Example 3

A catalyst was produced in the same manner as in Example 2 except that, in the calcination step of the molded article, the temperature-raising rate up to  $200^\circ\text{C}$  was changed from  $80^\circ\text{C/h}$  to  $20^\circ\text{C/h}$ . The catalyst was analyzed in a pore distribution by a mercury porosimetry. As a result, the catalyst had a total pore volume of entire pores of  $0.3 \text{ cm}^3/\text{g}$ , in which a total volume of pores having a radius of  $0.05$

$\mu\text{m}$  or less was  $0.01 \text{ cm}^3/\text{g}$  or less. The falling strength was 98.7 %.

Using the catalyst, methacrolein was oxidized at  $290^\circ\text{C}$  in the same manner as in Example 1. As a result, the conversion  
5 of methacrolein was 83.3 % and the selectivity to methacrylic acid was 84.7 %. In varying the oxidation temperature from  $270^\circ\text{C}$  to  $310^\circ\text{C}$ , the relationship between the conversion of methacrolein and the selectivity to methacrylic acid was further investigated. As a result, when the conversion of  
10 methacrolein was 80%, the selectivity to methacrylic acid was 85 %.

#### Comparative Example 2

A catalyst was produced in the same manner as in Example 2 except that, in the calcination step of the molded article,  
15 the air-passing rate up to  $250^\circ\text{C}$  was changed from 8 L/h to 80 L/h and the temperature-raising rate up to  $200^\circ\text{C}$  was changed from  $80^\circ\text{C/h}$  to  $15.6^\circ\text{C/h}$ . The catalyst was analyzed in a pore distribution by a mercury porosimetry. As a result, the catalyst had a total pore volume of entire pores of  $0.28 \text{ cm}^3/\text{g}$ , in which a total volume of pores having a radius of  
20  $0.05 \mu\text{m}$  or less was  $0.02 \text{ cm}^3/\text{g}$ . The falling strength was 96.6 %.

Using the catalyst, methacrolein was oxidized at  $290^\circ\text{C}$

in the same manner as in Example 1. As a result, the conversion of methacrolein was 86.4 % and the selectivity to methacrylic acid was 82.2 %. In varying the oxidation temperature from 270°C to 310°C, the relationship between the conversion of methacrolein and the selectivity to methacrylic acid was further investigated. As a result, when the conversion of methacrolein was 80%, the selectivity to methacrylic acid was 82.4 %.

#### Example 4

A catalyst was produced in the same manner as in Example 2 except that the size of the molded article was changed from that having a diameter of 5 mm and a length of 6 mm to that having a diameter of 3 mm and a length of 6 mm. The catalyst was analyzed in a pore distribution by a mercury porosimetry. As a result, the catalyst had a total pore volume of entire pores of 0.31 cm<sup>3</sup>/g, in which a total volume of pores having a radius of 0.05 μm or less was 0.01 cm<sup>3</sup>/g or less. The falling strength was 99.1 %.

The above-obtained catalyst (2 ml) was packed in a glass tube reactor having a inner diameter of 15 mm. Into the tube reactor, a starting-material gas having a composition of 37 % by volume of isobutane, 37 % by volume

of oxygen, 16 % by volume of water vapor and nitrogen as the balance was passed at the space velocity (in terms of normal state) of  $2040 \text{ hr}^{-1}$ , and the pressure and the temperature were raised to 270 kPa and  $332^{\circ}\text{C}$ , respectively, so as to conduct the oxidation of the isobutene. As a result, the conversion of isobutane was 9.1 % and the selectivity to methacrylic acid was 54.5 %.

#### Example 5

Into 224 kg of an ion exchange water having a temperature of  $40^{\circ}\text{C}$ , were added 38.2 kg of cesium nitrate, 10.2 kg of copper (II) nitrate trihydrate, 24.2 kg of 85 % by weight phosphoric acid and 25.2 kg of 70 % by weight nitric acid, which were then dissolved therein to obtain a solution (Solution A). On the other hand, 297 kg of ammonium molybdate tetrahydrate was dissolved in 330 kg of an ion exchange water having a temperature of  $40^{\circ}\text{C}$ . Into the resulting solution, 8.19 kg of ammonium metavanadate was added and was suspended to obtain a suspension (Solution B). Into Solution B, was dropwise added Solution A while stirring. Further, into the resulting solution, 10.2 kg of antimony trioxide was added and was stirred in a sealed container at  $120^{\circ}\text{C}$  for 17 hours, to obtain a slurry. The pH of the slurry was 6.3.

The slurry was dried using a spray drier to obtain a dried powder. The dried powder was analyzed by an X-ray diffraction and an infrared absorption spectroscopy, and was identified as a Dawson-type heteropolyacid salt. The ammonium nitrate content in the dried powder was 12 % by weight.

Into 100 parts by weight of the dried powder, was added 4 parts by weight of a ceramic fiber (manufactured by TOSHIBA MONOFLUX; 400SL), 8 parts by weight of ammonium nitrate and 10 parts by weight of an ion exchange water, to obtain a mixture thereof. The mixture was kneaded to obtain a paste thereof. The paste was extruded to obtain a molded cylindrical article having a diameter of 5 mm and a height of 5 mm, which was then dried at 90°C. The ammonium nitrate content of the resulting molded article was 18 % by weight.

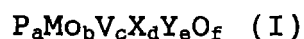
The molded article (36 L) was packed in a stainless steel cylinder having an inner diameter of 30 cm, through which air was supplied and was passed at 2.5 m<sup>3</sup>/h while heating to 250°C with circulating and passing an exhausted gas at 80 m<sup>3</sup>/h. In this calcination step, the temperature was raised at 50°C/h up to 220°C, and then was kept at 220°C for 10 hours, and was raised from 220°C to 250°C

over 2 hours. Subsequently, the molded article was calcined in a nitrogen flow at  $15 \text{ m}^3/\text{h}$  at  $435^\circ\text{C}$  for 3 hours, and then was further calcined in an air flow at  $390^\circ\text{C}$  for 3 hours, whereby obtaining a catalyst. The composition of the obtained catalyst was represented by  $\text{P}_{1.5}\text{Mo}_{12}\text{V}_{0.6}\text{Cs}_{1.4}\text{Cu}_{0.3}\text{Sb}_{0.5}$  with oxygen (O) being present in the amount corresponding thereto. The catalyst was analyzed in a pore distribution by a mercury porosimetry. As a result, the catalyst had a total pore volume of entire pores of  $0.26 \text{ cm}^3/\text{g}$ , in which a total volume of pores having a radius of  $0.05 \mu\text{m}$  or less was  $0.01 \text{ cm}^3/\text{g}$  or less. The falling strength was 99.2 %.

Using the catalyst, methacrolein was oxidized at  $290^\circ\text{C}$  in the same manner as in Example 1. As a result, the conversion of methacrolein was 86.2 % and the selectivity to methacrylic acid was 84.4 %. In varying the oxidation temperature from  $270^\circ\text{C}$  to  $310^\circ\text{C}$ , the relationship between the conversion of methacrolein and the selectivity to methacrylic acid was further investigated. As a result, when the conversion of methacrolein was 80%, the selectivity to methacrylic acid was 85.8 %.

What is claimed is:

1. A catalyst comprising a Keggin-type heteropolyacid salt which is represented by Formula (I):



5        wherein P, Mo, V and O represent phosphorus, molybdenum, vanadium and oxygen, respectively; X represents at least one element selected from potassium, rubidium, cesium and thallium; Y represents at least one element selected from copper, arsenic, antimony, boron, silver, bismuth,  
10        iron, cobalt, lanthanum and cerium; a, b, c, d, e and f represent the atomic ratios of P, Mo, V, X, Y and O, respectively; when b equals to 12, then a, c, d and e represent, independently from one another, numerical values exceeding 0 and not more than 3; and f is defined  
15        based on the oxidation condition of the elements other than oxygen and also on the atomic ratios thereof;

         the catalyst having a pore distribution, obtained by a mercury porosimetry method, in which a total pore volume of pores having a radius of 0.05  $\mu\text{m}$  or less is about 0.01  
20         $\text{cm}^3/\text{g}$  or less and a total volume of pores having a radius exceeding 0.05  $\mu\text{m}$  is about 0.2  $\text{cm}^3/\text{g}$  or more.

2. A method for producing a catalyst according to claim 1, the method comprising the step of calcining a

molded article of the Dawson-type heteropolyacid salt containing ammonium nitrate so that a transfer reaction from the Dawson-type heteropolyacid salt into a Keggin-type heteropolyacid salt occurs in the presence  
5 of ammonium nitrate.

3. A method according to claim 2, wherein the ammonium nitrate content in the molded article of the Dawson-type heteropolyacid salt is 10 % by weight or more.

4. A method for producing methacrylic acid, wherein  
10 methacrolein, isobutyl aldehyde, isobutane or isobutyric acid are subjected to a gas phase catalytic oxidation in the presence of a catalyst according to claim 1.